Chapter 1
Introduction

This chapter gives a brief overview of the different facets of multiferroics, explaining the origin of multiferroicity and magnetoelectric coupling, their possible technological applications and the challenges involved. It also introduces the relevance and important aspects concerning the rare earth chromites, with a particular focus on pure and Fe - substituted YCrO$_3$ systems, which are selected for the present investigation. The objectives of the present investigation are outlined. The major characterization techniques used have also been summarized.
Functional electronic and magnetic materials form an important part of modern technology. Miniaturization of the electronic devices, which basically depends on silicon, has reached its limit. This led to increased interest in combining electronic and magnetic properties into multifunctional materials, so that a single device component can perform more than one task. There exist very few materials which exhibit multiple functional properties; one such class of materials is called the multiferroics, materials which display simultaneously ferromagnetic and ferroelectric polarizations and a coupling between them. This coupling effect can be exploited for the construction of novel spintronic devices, such as tunnelling magnetoresistance (TMR) sensors, spin valves with functionality that is tunable by an electric field and multi-state memories, in which data are written electrically and read magnetically [1, 2]. In the last few years, the field of multiferroic materials has seen a new surge of interest, both because of tremendous fundamental and technological interest [3-5].

Driven by the desire to achieve new functionalities, researchers have undertaken a concerted effort to identify and understand the complexities of multiferroic materials. Unlike the natural multiferroics having weak magnetoelectric coupling, the newly developed multiferroic composites yield giant magnetoelectric coupling response near to room temperature, enabling them ready for wider technological applications [6, 7]. The ultimate goal for device functionality would be a single phase multiferroic, with strong coupling between ferroelectric and ferromagnetic order parameters, making for simple control over the magnetic nature of the material with an applied electric field at room temperature. In this thesis, focus has been given to single-phase multiferroics, which are simultaneously ferromagnetic and ferroelectric in the same phase.
1.1 Ferroics

In the most general terms, a ferroic is a material which exhibits either ferroelectric or ferromagnetic or ferroelastic ordering [8]. Another proposed ordering mechanism is ferrotoroidicity, which exhibits arrangement of magnetic vortices in an ordered manner, called toroidization. The word ferroics is derived from “ferrum”, the Latin word for iron, which is the oldest known ferroic material.

Ferroic materials exhibit a large change in the properties of the materials across a critical temperature. The critical temperature, in general, is also accompanied with a symmetry breaking. Another important feature of ferroic materials is the presence of a well defined hysteresis loop, when the material is switched electrically, magnetically or mechanically. Ferroic materials are being used in many technological applications, such as electronics, data storage, sensing, communications and medicine.

1.1.1 Ferromagnets

Ferromagnetism is the oldest of the ferroic properties known to science. The element, Fe is ferromagnetic at room temperature (as also are Co and Ni). Metallic meteorites consist mostly of pure iron. Thus, at least one ferroic material, iron, existed on earth millions of years before the emergence of homo sapiens. Around 600 BC, magnetism was observed in loadstone or magnetite by its power to attract iron [9]. It has been claimed that sometimes before 2500 BC, Chinese used magnetic compass. Socrates mentioned that magnetite was used to induce iron to get the attractive power (magnetism). Thus, permanent and induced magnetism were human's earliest scientific discoveries. The science behind operation of magnetic compass enlightened only after the realization of the fact that the earth itself was a huge magnet
by Gilbert. Later, Coulomb's investigations in 16th century form the starting point in the research to understand magnetism.

The magnetic effects, except diamagnetism, observed in inorganic materials are due to the presence of unpaired electrons. Thus, magnetism is mainly observed in compounds having transition metals and lanthanides due to the presence of unpaired $d$ and $f$ electrons respectively. Magnetism can arise from either the orbital component of the angular momentum or the spin component (if there are unequal numbers of up and down spin electrons) or both. The random orientations of unpaired electrons on different atoms lead the material to be paramagnetic. Parallel alignment of these unpaired electrons makes the material ferromagnetic. If they align in antiparallel, then the material becomes antiferromagnetic. The unequal magnetic moment of the spins in antiparallel alignment will lead to ferrimagnetic behaviour. The term “weak ferromagnetism” is used to describe antiferromagnets with a small canting of the spins away from antiparallel alignment. This results in a small net magnetization, usually at low temperature. Among the different magnetic behaviours, materials having ferromagnetism are widely used in application.

Indeed, there is a strong driving force for electrons to align their spins parallel (creating unequal numbers of up and down spin electrons); this is the quantum-mechanical exchange energy. One can develop an intuition for why exchange coupling is such a strong driving force using simple electrostatic arguments: if two electrons in an atom have antiparallel spins, then they are allowed to share the same atomic or molecular orbital. As a result, they will overlap spatially, thus increasing the electrostatic Coulomb repulsion. On the other hand, if they have parallel spins, then they must occupy different orbitals and so, will have less unfavourable Coulomb
repulsion. Thus, the orientation of the spins affects the spatial part of the wave function and this in turn, determines the electrostatic Coulomb interaction between the electrons.

Ferromagnetic materials have domains in their structure. In each domain, all the spins are aligned parallel and different domains have different spin orientations. At sufficiently high field, all the domains have parallel spin oriented along the magnetic field and the direction can be switched by switching the field in opposite direction. Thus, by varying the magnetic field, ferromagnetic materials will show a hysteresis loop. Materials with low coercivity (the magnitude of the reversal field required to achieve demagnetization) are referred as soft magnets, while the materials with high coercivity are termed as hard magnets.

There are two phenomenological theories of ferromagnetism that have been successful in explaining many of the properties of ferromagnets: the Curie-Weiss localized moment theory, which arose from the study of magnetic insulators and the Stoner band theory of ferromagnetism in metals [10, 11]. In the localized moment picture, local magnetic moments exist on the ions in the solid at all temperatures; below the Curie temperature (T_C) the moments align to give a ferromagnetic state and above the Curie temperature they are disordered by thermal energy and there is no net magnetization. Such behaviour is analogous to the order-disorder description of ferroelectrics, in which the constituent ions are always off-centered, but only below the Curie temperature do the directions of off-centering align cooperatively to give a net electric polarization. In the band theory, there are equal numbers of up and down spin electrons above the Curie temperature and hence, no magnetic moment. Below T_C, the up and down spin bands are unequally populated by electrons, leading to a net magnetic moment. Here, the analogy is to
the displacive model of ferroelectricity, in which the Curie
temperature is coincident with off-centering of the ions.

Most of the ferromagnetic materials known are metallic and there
are considerable numbers of insulating ferromagnetic compounds
also. The ferromagnetism observed in those insulating compounds is
explained on the basis of superexchange interaction, which is due to
the overlap of the localized orbitals of the magnetic electrons with
those of intermediate ligands. Even though superexchange interaction
has been explained earlier, a considerably more satisfactory system of
semi-empirical rules was developed over a period of years by
Goodenough and Kanamori [12, 13]. These rules have the important
features of the occupation of various $d$ levels, as dictated by ligand
field theory. They are related to the prescriptions of Anderson’s work
about the sign of superexchange [14]. According to Goodenough-
Kanamori-Anderson rules, a 180° superexchange (the magnetic ion-
ligand-magnetic ion angle is 180°) of two magnetic ions with partially
filled $d$ shells is strongly antiferromagnetic, whereas a 90°
superexchange interaction is ferromagnetic and much weaker [13, 15,
16].

Ferromagnets are very important in industry and modern
technology and are the basis for many electrical and
electromechanical devices such as electromagnets, electric motors,
generators, transformers and magnetic storage, such as tape recorders
and hard disks.

1.1.2 Ferroelectrics

The term “ferroelectric” was first used by Erwin Schrodinger in 1912,
although the history of ferroelectricity (or what was earlier called
Seignette- electricity) can be said to have started around 1665, when
Elie Seignette of La Rochelle, France created “Sel polychreste”, later
known as Rochelle salt. However, it was not until 1920 that Joseph Valasek demonstrated that the direction of spontaneous polarization of Rochelle salt (sodium potassium tartrate tetrahydrate, NaKC$_4$H$_4$O$_6$.4H$_2$O) could be reversed by the application of an electric field [17-19]. He also observed hysteretic behaviour between 255 K and 297 K, as well as very large dielectric and piezoelectric coefficients. Later, several compounds were identified as ferroelectrics [20]. However, it took many years to unveil its importance in technological applications, especially in memory devices [21].

A ferroelectric material possesses a reversible spontaneous polarization over a certain temperature range. There is a critical temperature called Curie temperature, which marks the transition from the ordered to the disordered phase. At this temperature, the dielectric constant may reach values three to four orders of magnitude higher than that in the disordered phase. The order-disorder phase transition involves the displacement of atoms, so that crystals or crystallites exhibiting ferroelectric phenomena must be centrosymmetric. This implies that a phase transition will induce a mechanical strain, tending to change not only the volume and the shape of the material body, but also the optical refractive index. Thus, ferroelectric materials exhibit not only ferroelectric phenomena, but also piezoelectric, pyroelectric and electro-optic effects, which can be used for many technological applications. In general, ferroelectric materials also have electrically induced polarizations, but these are negligibly small compared to spontaneous polarization. Like ferromagnetics, ferroelectrics exhibit a hysteresis loop. It is quite natural that the hysteresis loop becomes gradually diminished at $T > T_c$, eventually degenerating to a straight line at $T$ much larger than $T_c$, when the ferroelectric behaviour disappears completely. However,
some ferroelectric materials can be driven from the paraelectric state to a ferroelectric state at $T > T_C$ by applying a large electric field.

Ferroelectrics differ from ferromagnetic in their fundamental mechanisms. The absence of inversion symmetry and the polar nature of ferroelectric crystals cause a spontaneous polarization along one or more crystal axes. Thus, the symmetry plays a key role in these materials. In other words, the ferroelectric crystals are characterized by having polarization vectors that can be oriented in two diametrically opposite directions by applying an external electric field.

The symmetry of the crystals is governed by their lattice structure. Though, there are thousands of crystals in nature, they all can be grouped together into 230 space groups based on the symmetry elements. The space groups in three dimensions are made from combinations of 32 crystallographic point groups with 14 Bravais lattices, which belong to one of 7 crystal systems. The 32 point groups can be further classified into (a) crystals having center of symmetry and (b) crystals which do not possess center of symmetry. Crystals with center of symmetry (labelled as centrosymmetric) include 11 point groups and they do not show polarity. The remaining 21 point groups do not have center of symmetry (i.e. non-centrosymmetric). All non-centrosymmetric point groups, except the point group 432, show piezoelectric effect along the unique directional axes. A crystal having no center of symmetry possesses one or more crystallographically unique directional axes. Space groups lacking an inversion center (non-centrosymmetric) are further divided into polar and chiral types. A chiral space group is one without any rotoinversion symmetry elements. Rotoinversion (also called an `inversion axis`) is rotation followed by inversion; for example, a mirror reflection corresponds to a two-fold rotoinversion.
Chiral space groups must therefore only contain (purely) rotational and translational symmetry. These arise from the crystal point groups 1, 2, 3, 4, 6, 222, 422, 622, 32, 23 and 432. Chiral molecules, such as proteins crystallize in chiral space groups. The term ‘polar’ is often used for those space groups, which are neither centrosymmetric nor chiral. However, the term ‘polar’ is more correctly used for any space group containing a unique anisotropic axis. These occur in point groups 1, 2, 3, 4, 6, m, mm2, 3m, 4mm and 6mm. Thus, some chiral space groups are also polar. Out of the twenty point groups which show the piezoelectric effect, ten polar point groups have only one unique direction axis and such crystals show spontaneous polarization. Thus, considering symmetry restrictions, all ferroelectric materials are pyroelectric, however not all pyroelectric materials are ferroelectric. Since all pyroelectric materials are piezoelectric, this means ferroelectric materials are inherently piezoelectric.

A colossal increase in the research on ferroelectric materials came in 1950s, leading to the widespread use of barium titanate (BaTiO₃) based ceramics in capacitor applications and piezoelectric transducer devices [20]. Since then, many other ferroelectric materials including lead titanate (PbTiO₃), lead zirconate titanate (PbZr₁₋ₓTiₓO₃), lead lanthanum zirconate titanate (Pb₁₋ₓLaₓZr₁₋ₙTiₙO₃) and relaxor ferroelectrics, like lead magnesium niobate (PbMg₁₋ₓNbₓO₃) have been developed and utilized for several applications. Later, many new applications have emerged with the development of ceramic processing and thin film technology. Ferroelectrics are key materials in microelectronics. Their excellent dielectric properties make them viable candidate for electronic components, such as tunable capacitors, non volatile memories, piezoelectric materials for medical ultrasound imaging and actuators and electro-optic materials for data storage and displays.
1.1.3 Ferroelastics

The word “ferroelasticity” has had a number of connotations, all similar and yet, not quite the same. It was used in physical metallurgy in the early 1950s by F. C. Frank for describing the rubber-like (martensitic) behaviour of Au$_{1.05}$Cd$_{0.95}$ and InTl alloys [22]. In physics, in the pre-1969 period, ferroelastic strains were associated primarily with ferroelectricity, through electrostriction. Magnetostriction also leads to strain in ferromagnetic materials, but the effect is usually much smaller than that of electrostriction. Thus, before Aizu gave a formal definition of ferroelasticity as a property, which can exist on its own, physicists’ perception was that it occurs predominantly as an adjunct to ferroelectricity and ferromagnetism [23, 24].

Ferroelastic materials display a spontaneous deformation that is stable and can be switched hysteretically by an applied stress. Ferroelasticity is the mechanical or elastic analogue of ferromagnetism and ferroelectricity. When stress is applied to a ferroelastic material, a phase change will occur in the material from one phase to an equally stable phase, either of different crystal structure (e.g. cubic to tetragonal) or of different orientation (a ‘twin’ phase). This stress-induced phase change results in a spontaneous strain in the material. Like ferromagnetic and ferroelectrics, ferroelastics exhibit a hysteresis loop.

The shape memory effect and superelasticity are manifestations of ferroelasticity [8]. Nitinol (nickel titanium), a common ferroelastic alloy, can display either superelasticity or the shape-memory effect at room temperature, depending on the nickel/titanium ratio. The shape-memory effect exhibited by several ferroelastic alloys find a number of applications, such as actuators in smart structures,
electrical and mechanical connectors and a heat engine exploiting the shape change on thermal cycling [25].

1.2 Multiferroics

The field of research that described in this thesis has a tortuous taxonomy and typically involves terms, such as “multiferroic” and “magnetoelectric”, whose overlap is incomplete (Figure 1.1).

![Figure 1.1](image.png)

**Figure 1.1** The relationship between multiferroic and magnetoelectric materials [26]. Ferromagnets (ferroelectrics) form a subset of magnetically (electrically) polarizable materials, such as paramagnets and antiferromagnets (paraelectrics and antiferroelectrics). The intersection (red hatching) represents materials that are multiferroic. Magnetoelectric coupling (blue hatching) is an independent phenomenon that can, but need not; arise in any of the materials that are both magnetically and electrically polarizable. In practice, it is likely to arise in all such materials, either directly or via strain.

The term “multiferroics” was first coined by H. Schmid in 1994 [27]. His definition referred to multiferroics as single phase materials, which simultaneously possess two or more primary ferroic properties. Ferromagnetism, ferroelectricity, ferroelasticity and ferrotoroidicity form the four basic primary ferroic order parameters and ferrotoroidicity is still being under debate. In the most general terms, multiferroics are materials in which ferromagnetism, ferroelectricity and ferroelasticity occur in the same phase. This
implies that they possess spontaneous magnetization, which can be reoriented by an applied magnetic field, a spontaneous polarization, which can be reoriented by an applied electric field and a spontaneous deformation, which can be reoriented by an applied stress.

![Figure 1.2 Phase control in ferroics and multiferroics](image)

Figure 1.2 Phase control in ferroics and multiferroics [28]. The electric field $E$, magnetic field $H$ and stress $\sigma$ control the electric polarization $P$, magnetization $M$ and strain $\varepsilon$, respectively. In a magnetoelectric multiferroic, a magnetic field may control $P$ or an electric field may control $M$ (green arrows).

The relation between multiferroic and primary ferroics are shown in Figure 1.2. For primary ferroic materials, an order parameter only appears below a certain critical symmetry transformation temperature and domain states can only be switched by a field that is conjoint to the order parameter. In contrast, the Curie temperature of a multiferroic material is dependent on multiple ordering fields (magnetic field, electric field or stress). Accordingly, their domain states can be switched by more than one field type. For example, magnetoelectric (ME) materials are characterized by the switching of an electric polarization upon applying a magnetic or electric field and vice versa.
Recently, the definition of multiferroics has been expanded to include materials, which exhibit any type of long range magnetic ordering, spontaneous electric polarization and/or ferroelasticity. It is, however, customary to exclude ferroelasticity and only consider magnetic and ferroelectric characteristics. Many researchers in the field consider materials as multiferroics, only if they exhibit coupling between the order parameters. This functionality offers an extra degree of freedom in device design. Such materials have all the potential applications of both their parent ferroelectric and ferromagnetic materials. In addition, a whole range of new applications can be envisaged. Specific device applications which have been suggested for such materials, include multiple state memory elements, electric field controlled ferromagnetic resonance devices and transducers with magnetically modulated piezoelectricity [29]. Aside from the potential applications, the fundamental physics of multiferroic materials is rich and fascinating [30, 31].

The study of the coupling between magnetic and electric (dipole) degrees of freedom was initiated already long ago under the name “magnetoelectric effect” [32, 33]. This big field, is closely related to the new development and also relies heavily on symmetry considerations [34]. The magnetoelectric effect in its most general definition delineates the coupling between electric and magnetic fields in matter. The magnetoelectric response is the appearance of an electric polarization, $P$ upon applying a magnetic field, $H$ (i.e., the direct ME effect, designated as ME$_H$ effect: $P = \alpha H$) and/or the appearance of a magnetization, $M$ upon applying an electric field, $E$ (i.e., the converse ME effect, or ME$_E$: $M = \alpha E$). $\alpha$ corresponds to the induction of polarization by a magnetic field or of magnetization by an electric field, which is designated as the linear magnetoelectric effect. Magnetoelectric coupling describes the influence of a magnetic
(electric) field on the polarization (magnetization) of a material and vice versa. Magnetoelectric multiferroics are simultaneously ferromagnetic (or at least show some kind of magnetic ordering) and ferroelectric in the same phase, with coupling between the two orders. Magnetoelectric coupling can exist independent of the nature of the magnetic and electrical order parameters and can for example occur in paramagnetic ferroelectrics [35]. It is an independent phenomenon, which may not necessarily arise in materials that are both magnetically and electrically polarizable. Magnetoelectric coupling may arise directly between the two order parameters or indirectly via strain. From an application standpoint, the real interest in multiferroic materials lies in the possibility of strong magnetoelectric coupling and the possibility to create new functionalities in materials.

It is generally difficult to find single-phase materials that are magnetic as well as ferroelectric [36]. Most ferroelectrics are transition metal oxides, in which transition ions have empty $d$ shells. These positively charged ions like to form molecules with one (or several) of the neighboring negative oxygen ions. This collective shift of cations and anions inside a periodic crystal induces bulk electric polarization. The mechanism of the covalent bonding (electronic pairing) in such molecules is the virtual hopping of electrons from the filled oxygen shell to the empty $d$ shell of a transition metal ion. Magnetism, on the contrary, requires transition metal ions with partially filled $d$ shells, as the spins of electrons occupying completely filled shells add to zero and do not participate in magnetic ordering. The exchange interaction between uncompensated spins of different ions, giving rise to long range magnetic ordering, also results from the virtual hopping of electrons between the ions. In this respect, the two mechanisms are not so dissimilar, but the difference in filling of the $d$ shells required
for ferroelectricity and magnetism makes these two ordered states mutually exclusive. Consequently, an additional electronic or structural driving force must be present for ferromagnetism and ferroelectricity to occur simultaneously.

When considering the microscopic conditions for the coexistence of magnetism and ferroelectricity, one has to note that, whereas the microscopic nature of magnetic ordering is in principle the same in most strong magnets – it is an exchange interaction of predominantly localized magnetic moments, this is not the case with ferroelectricity. There exist many different mechanisms of ferroelectric ordering and different types of ferroelectrics. In contrast to magnetism, real microscopic mechanisms of ferroelectricity are in many cases not well understood. Therefore, when discussing multiferroic systems, the main problem lies in the ferroelectric part of the story. This recognition has prompted a search for alternative ferroelectric mechanisms that are compatible with the occurrence of magnetic ordering. As a result, previously unknown multiferroic materials have been discovered and thus, the notion that multiferroics are rare has changed. Several new ideas and concepts have emerged in the last few years, typical of them being magnetic ferroelectricity induced by frustrated magnetism, lone pair effect, charge-ordering and local non-centrosymmetry [37].

We now know many systems in which magnetism and ferroelectricity coexist and many more will probably be discovered in near future. The search for materials that would be good magnetoelectric materials began in earnest in the late 1950s in Leningrad in the group of Smolenskii at the Ioffe Institute [38]. They showed some of the mixed perovskites were weakly ferromagnetic and ferroelectric, a typical example being \((1-x)\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3-\text{xPb(Mg}_{1/2}\text{W}_{1/2})\text{O}_3\). In this case, \(\text{Mg}^{2+}\) and \(\text{W}^{6+}\) ions were diamagnetic...
and caused ferroelectricity, whereas d^5 Fe^{3+} ions are responsible for the magnetic ordering. As a result of the dilution of the magnetic ions, these materials have rather low Curie or Neel temperatures. Compounds, such as boracites (Ni_{3}B_{7}O_{13}I, Cr_{3}B_{7}O_{13}Cl) [39], fluorides (BaMF_{4}, M = Mn, Fe, Co, Ni) [40, 41], magnetite Fe_{3}O_{4} [42], (Y/Yb)MnO_{3} [43], BiFeO_{3} [44] and BiMnO_{3} [45] were identified to be multiferroic in the following decades. Even though the field is known from 1960, a huge leap in the multiferroic research occurred only after 2000. A confluence of three factors explains the current high level of interest in magnetoelectrics and multiferroics. First, in 2000, Hill (now Spaldin) discussed the conditions required for ferroelectricity and ferromagnetism to be compatible in oxides and declared them to be rarely met [36]. Her paper in effect issued a grand materials development challenge that was taken up because empirically there are indeed few multiferroic materials, whatever the microscopic reasons are. Second, the experimental machinery for the synthesis and study of various contenders was already in place when this happened. Third, the relentless drive towards ever better technology is aided by the study of novel materials.

The ferromagnetic spinel CdCr_{2}S_{4} exhibits relaxor ferroelectricity below 135 K [46]. YMnO_{3} is antiferromagnetic below the Neél temperature (T_{N}) 80 K and ferroelectric below the Curie temperature (T_{CE}) 914 K [47]. In this material, ferroelectricity is associated with the tilting of MnO_{5} trigonal bipyramids. Another oxide with similar properties is BiFeO_{3} (T_{N} = 670 K, T_{CE} = 1110 K), which exhibits both magnetic and strong ferroelectric properties at room temperature [48]. The ferroelectricity arises from the stereochemical activity of the Bi lone pair [49]. In past few years, intensive studies have been conducted on this material in an attempt to understand its multiferroic mechanism and to apply it in device applications [50].
BiMnO$_3$ is shown to be simultaneously ferromagnetic and ferroelectric ($T_C = 450$ K, $T_{CE} = 105$ K) [51]. While BiFeO$_3$ and BiMnO$_3$ are proper ferroelectrics, TbMnO$_3$ which is an improper ferroelectric shows interesting features, wherein spiral magnetic ordering is the source of ferroelectricity [52]. One of the new ideas is that charge-ordered and orbital ordered perovskites could exhibit ferroelectric magnetism due to coupling between magnetic and charge ordering [53]. Beside single phase oxide materials, several two-phase systems have been shown to exhibit magnetoelectric coupling, typical examples being BaTiO$_3$ - CoFe$_2$O$_4$ [54], Tb$_x$Dy$_{1-x}$Fe$_2$ - Pb(Zr,Ti)O$_3$ (PZT) [37] and La$_{0.7}$Sr$_{0.3}$MnO$_3$ - PZT [55].

The fundamentally interesting multiferroic materials are those that could give rise to new technologies in which the low power and high speed of field-effect electronics are combined with the permanence and routability of voltage-controlled ferromagnetism [26, 7]. The most desirable situation would be to discover a truly multiferroic (single-phase) material, one that is ferromagnetic and ferroelectric at room temperature and exhibits coupling between these two order parameters. Despite a concerted effort by a wide number of researchers, the search for intrinsic multiferroics that are simultaneously both magnetic and ferroelectric at room temperature remains a difficult one, which hinders their applications. In the materials that do have both of these order parameters, one is usually much weaker and appears at much lower temperatures than the other [4]. Thus, the properties of the few compounds that simultaneously exhibit these phenomena [56, 57] are insignificant in comparison with those of useful ferroelectrics or ferromagnets, because their spontaneous polarizations or magnetizations are smaller by a factor of 1,000 or more. Thus, it is essential to search for new candidate multiferroics.
1.3 Classification of multiferroics

Multiferroics can be grouped in various ways according to different characteristics. One method is to classify the materials according to the mechanism that drives the ferroelectricity: proper and improper ferroelectrics (Table 1.1) [64].

<table>
<thead>
<tr>
<th>Mechanism of inversion symmetry breaking</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proper</td>
<td>Covalent bonding between 3d&lt;sup&gt;0&lt;/sup&gt; transition metal (Ti) and oxygen</td>
</tr>
<tr>
<td></td>
<td>Polarization of 6s&lt;sup&gt;2&lt;/sup&gt; lone pair of Bi or Pb</td>
</tr>
<tr>
<td></td>
<td>BiMnO&lt;sub&gt;3&lt;/sub&gt;, BiFeO&lt;sub&gt;3&lt;/sub&gt;, Pb(Fe&lt;sub&gt;2/3&lt;/sub&gt;W&lt;sub&gt;1/3&lt;/sub&gt;)O&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>Improper</td>
<td>Structural transition “Geometric ferroelectrics”</td>
</tr>
<tr>
<td></td>
<td>“Electronic ferroelectrics”</td>
</tr>
<tr>
<td></td>
<td>Charge ordering “Electronic ferroelectrics”</td>
</tr>
<tr>
<td></td>
<td>Magnetic ordering “Magnetic ferroelectrics”</td>
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<tr>
<td></td>
<td>Orthorhombic RMnO&lt;sub&gt;3&lt;/sub&gt;, RMn&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;, CoCr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>Hexagonal RMnO&lt;sub&gt;3&lt;/sub&gt;, LuFe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
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<tr>
<td></td>
<td>K&lt;sub&gt;2&lt;/sub&gt;SeO&lt;sub&gt;4&lt;/sub&gt;, Cs&lt;sub&gt;2&lt;/sub&gt;CdI&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
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</table>

Another method of classifying different multiferroics is to group them according to the origin of the magnetic and ferroelectric ordering: type-I and type-II [59]. Within a type-I multiferroic, the two order parameters have different sources. Some coupling exists but the ferroelectric ordering temperature is generally higher than the magnetic one and the spontaneous polarization, P is often rather large (of order 10⁻¹⁰⁻¹⁰⁰ μC/cm²). Type-II multiferroics, generally centrosymmetric and magnetic, is the relatively recently discovered materials [60, 61]. Ferroelectricity within a type-II multiferroic occurs as a result of magnetic ordering. Strong coupling is expected between the two parameters as ferroelectricity sets in at the same temperature as magnetic ordering and is driven by it. However, the polarization in
these materials is usually much smaller (~ $10^{-2}$ $\mu$C/cm$^2$) [62]. Many
groups are also investigating composite multiferroics that consist of
known magnets and ferroelectrics in the form of multilayers and self-
organized nanostructures [7].

1.3.1 Proper ferroelectrics

In a proper ferroelectric, polarization is a primary effect when
inducing ferroelectricity; driven by hydridization and strong
covalency or other purely structural effects. For example, the
collective shift of anions and cations within a periodic lattice will give
rise to a spontaneous and switchable polarization.

A classic example of proper ferroelectric, BaTiO$_3$ has Ti$^{4+}$ ions in
the B site with no electrons in the 3d shell and they tend to form
strong covalent bonds with neighbouring O$^{2-}$ ions. The ferroelectricity
results by cooperative shifting of the Ti$^{4+}$ cation along the (111)
direction; this off-centering is stabilized by covalent bonding between
the oxygen 2$p$ orbitals and the empty $d$-shell of Ti$^{4+}$ [36, 63].

In BiFeO$_3$ and BiMnO$_3$, Bi$^{3+}$ plays the major role in the origin of
ferroelectricity [64]. In Bi$^{3+}$ ions, there are two outer 6$s$ electrons that
do not participate in chemical bonds. They are called lone pairs or
sometimes dangling bonds. They have a high polarizability—the
condition required for ferroelectricity in the classical description.
More microscopically, one can explain the origin of ferroelectricity in
these compounds by ordering of these lone pairs (with certain
admixture of $p$ orbitals) in one direction. Apparently this is what
happens in many Bi-containing ferroelectrics and multiferroics, such
as BiFeO$_3$. 
1.3.2 Improper ferroelectrics

In an improper ferroelectric, polarization is a secondary effect. Ferroelectricity is driven by an electronic degree of freedom, such as spin, charge or orbital ordering producing polarization as a by-product. Magnetoelectric multiferroics are examples of improper ferroelectrics, when a polarization is induced by an internal magnetic field [31, 58]. The known improper ferroelectrics can be sorted into three categories: geometric ferroelectrics, electronic ferroelectrics and magnetic ferroelectrics.

1.3.2.1 Geometric ferroelectrics

In improper geometric ferroelectrics, a structural phase transition at high temperatures causes the appearance of ferroelectricity. A prototypical compound is the family of hexagonal rare earth manganites (h-RMnO$_3$ with R = Ho-Lu, Y) [65]. The ferroelectricity in this class of compounds originates from the buckling of the MnO$_5$ polyhedra, combined with the displacements of R-ions and the layered MnO$_5$ network below the ferroelectric transition temperature of ~ 800 K. The Mn$^{3+}$ moments order in the temperature range of 80-120 K and the rare-earths moments order at temperatures below the magnetic ordering of Mn$^{3+}$.

1.3.2.2 Electronic ferroelectrics

Another group of improper ferroelectrics are charge-ordered insulators. Such an order can occur in a compound containing ions of mixed valence and with geometrical or magnetic frustration. LuFe$_2$O$_4$ is a well-known example of a charge ordered multiferroic compound, which shows improper ferroelectricity below 350 K [56]. Ferroelectricity in this material occurs due to a specific charge order in the triangular lattice. At temperatures above 350 K, an equal
number of Fe$^{2+}$ and Fe$^{3+}$ ions coexist randomly at the same site in the triangular lattice and thus, iron has an average valence of +2.5. However, at temperatures below 350 K, a charge redistribution takes place between the layers so that upper layer has a 2:1 ratio between Fe$^{2+}$ and Fe$^{3+}$ and the lower layer has the opposite, 1:2 ratio. In this manner, frustration in the triangular lattice can be broken and a charge ordered state emerges. Due to this specific charge ordered state, each plane in the bilayer structure acquires a net charge. Ferrimagnetic behaviour occurs below 240 K.

1.3.2.3 Magnetic ferroelectrics

In magnetic ferroelectrics, the polarization is induced by magnetic long-range order and so, this type of multiferroic shows unprecedented control of polarization under magnetic field. In the well-known example of TbMnO$_3$, the manganese moments order antiferromagnetically at $T_N = 41$ K and at 25 K, it undergoes another magnetic transition below which a cycloidal spin structure breaks the inversion symmetry and thus, induces ferroelectricity [66, 67]. In TbMnO$_3$ the polarization rotates (or “flops”) by 90 degrees when a critical magnetic field is applied along a certain direction [60]. In the case of HoMnO$_3$ [68], a collinear magnetic ordering with E-type magnetic structure gives rise to ferroelectricity. Since, the polarization and dielectric constants of a material are intimately linked; this kind of multiferroic shows a giant magneto-capacitance effect [68]. However, cross coupling between ferroelectricity and magnetism is only observed at low temperatures and high magnetic fields, since magnetism appears at low temperatures.
1.4 Symmetry

As the crystal symmetry plays a key role in ferroelectric properties, it is well clear that multiferroic property is closely linked to symmetry. The primary ferroic properties (Table 1.2) can be characterized by their behaviour under space and time inversion. Space inversion, for example, will reverse the direction of polarization (P), while leaving the magnetization (M) invariant. Time reversal, in turn, will change the sign of M, while the sign of P remains invariant. Magnetoelectric multiferroics require simultaneous violation of space and time inversion symmetry.

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<tr>
<th>Symmetry</th>
<th>Space Invariant</th>
<th>Space Variant</th>
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<tr>
<td>Time Invariant</td>
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1.5 Nanostructures

Most of the known single-phase bulk ME materials do not exhibit strong ME coupling, have Néel or Curie temperatures far below room temperature. But in the past few years, large ME effects in composites, laminates and more recently in nanostructured materials have been discovered [69]. The potential of ME nanostructures and their devices is almost limitless. But ME nanostructures are just in infant stage. Many open questions regarding the ME coupling in nanostructures remain: [7] how does the behaviour depend on the chemistry of the nanostructures? Is there a critical dimension below which the coupling will disappear or change in nature? Furthermore, the issue of the size and its correlation with the stabilization of the multiferroic behaviour is still a matter of much controversy [70].

Several phenomena occur at the point where the particle or crystallite size reaches a critical value. Since magnetism and
ferroelectricity are both cooperative phenomena, they display intrinsic size effect [71-74]. It is then interesting to explore whether the unique properties of intrinsic multiferroics are retained in their nanoparticles form with possible modifications/enhancements, so that multiferroics themselves can be integrated into nanoengineered configurations with potential beneficial effects [75, 76].

Size effects in ferroelectric materials have been investigated theoretically and experimentally for a long time [77]. Multiple reports on different compositions have addressed a finite crystallite size, in which the ferroelectric state becomes unstable [78, 79]. In BaTiO$_3$ nanocrystals, as the crystallite size decreases, the axial ratio c/a of tetragonality and the ferroelectricity decreases and the ferroelectric phase vanishes at a critical size of 48 nm [80]. At sizes below 100 nm, the tetragonality of PbTiO$_3$ shows a strong dependence on the crystallite size, transforming into a paraelectric cubic phase (c/a = 1) at a critical size of 7 nm. Selbach et al. [76] observed a similar dependence for BiFeO$_3$ nanoparticles, prepared by modified Pechini method.

In addition, several authors have reported change in the ferroic ordering due to size effects in different structures, observed through measurement of both Néel temperature as well as the Curie temperature at reduced dimensions [76-78]. Sun et al. [81] studied the behaviour of nickel nanowires and observed a reduction in the Curie temperature of the wire from 360 °C to 310 °C with a diameter reduction from bulk to 30 nm. Tanakaab et al. [78] observed a change in the Curie temperature of barium titanate particles from 400 K to ~190 K, as the particles were reduced from bulk values to 22 nm. They also noted that this was at the critical size for the structure, as they observed an orthorhombic-cubic transition occurring at smaller sizes. Zheng et al. [82] studied the finite size effect on Néel temperature in
antiferromagnetic nanoparticles and found the phase transition of
ball-milled CuO crystals to be reduced from 229 K to ~30 K, when
reducing the size to ~5 nm. This was lowered further to ~13 K as they
observed this transition in nanorods of 2-3 nm in diameter. Doing
measurements on $T_N$ as a function of crystallite size, Selbach et al. [76]
observed the antiferromagnetic to paramagnetic transition of the
BiFeO$_3$ nanocrystallites at sizes below ~50 nm.

1.6 Optical properties of multiferroics
Multiferroic materials also exhibit remarkable optical properties [83].
Several of the novel optical properties observed and predicted in
multiferroic materials depend on the inhomogeneous polarization
and magnetization across a multiferroic domain boundary. It is
known that these domains can be controlled using external magnetic
and/or electric fields, and it is this controllable response that makes
multiferroics attractive for tunable optical devices. However, exploiting
these properties for device applications will require the
ability to control the domain wall structure at small length scales.
Moreover, nanostructured single phase multiferroics may exhibit very
different optical properties than bulk or thin film samples, precisely
because of the absence of domain walls. In order to incorporate
multiferroics into optical applications, it will be necessary to address
at least three fundamental materials questions: precisely how do the
ferroelectric and magnetic domain walls respond to external magnetic
and electric fields? Can this behaviour be modulated by patterning on
the nanoscale? How does the optical response of multiferroic
nanomaterials differ from bulk samples?

Magnetoelectric multiferroics exhibit many optical properties
arising from the coexistence of ferroelectrically and magnetically
ordered phases. These properties suggest that multiferroic materials
could be useful in new types of optical devices. The optical-frequency dielectric response in these systems can be varied by 15% in a magnetic field, which could be useful for producing highly tunable optical filters [83]. One particularly novel aspect of multiferroics is that the ordered state breaks both spatial inversion symmetry and time-reversal symmetry. This results in striking effects in the nonlinear optical response, including shifts in the second harmonic generation intensity and the possibility of non-reciprocal refraction through a domain wall.

The rich palette of materials properties and specifically, the optical properties exhibited by multiferroics ensure that these systems will remain an active topic of research for years to come.

1.7 Rare earth chromites

Recently, Rao et al. reported that heavy rare earth chromites of the formula RCrO$_3$ with R = Ho, Er, Yb, Lu and Y belong to a new family of multiferroics, exhibiting canted antiferromagnetism at low temperatures ($T_N = 113–140$ K) and a ferroelectric transition ($T_{CE}$) in the 472–516 K range [84, 85]. Néel magnetic transition temperature ($T_N$) was found to decrease with the decrease in the radius of the rare-earth ion, while $T_{CE}$ increases slightly with decrease in size (Figure 1.3) [85]. Rare earth chromites possess a centrosymmetric orthorhombic structure with space group $Pnma$ (frequently given in its nonstandard setting $Pbnm$) and thus, non-compatible with ferroelectricity. However, the occurrence of the ferroelectricity has been attributed to chromium off-centering with a local character and a small value of displacement, leading to weak polarization [37, 86].

The dielectric constants of the rare earth chromites show a large dispersion below $T_{CE}$, but are frequency independent above $T_{CE}$, behaviour commonly observed in relaxor ferroelectrics [87]. Detailed
magnetic measurements have shown the weak ferromagnetic moment of the Cr\(^{3+}\) spins to be due to Dzyaloshinsky–Moriya (D–M) interaction in the chromites [88, 89]. Rare earth orthochromites show interesting magnetic properties, like temperature dependent spin re-orientation [90-96].

Rare earth chromites are p-type semiconductors with conductivities larger than the parent rare earth oxide, but comparable to that of the corresponding transition metal oxide [97]. The electrical transport properties of these solids can be explained in terms of the localized behaviour of the \(d\)-electrons; in all the systems investigated, there is an evidence for small polarons. Among the three series of rare earth compounds, namely chromites, manganites and ferrites, chromites exhibit the highest conductivity, lowest activation energy (\(E_a\)) and largest drift mobility. The conductivity of the chromites depends markedly on the R-ion [97]. In the high temperature region, activation energy (\(E_a\)) for conduction in the chromites is \(\sim 0.23\) eV. \(E_a\) values of chromites in the low temperature region show an increasing trend from Dy to Lu. The electrical conductivity at a given temperature decreases in the rare earth series from LaCrO\(_3\) to YbCrO\(_3\) [97]. The optical spectra of the RCrO\(_3\) compounds show that the R-O covalency increases, while the Cr-O covalency decreases down the rare earth series [98]. The decrease in the magnitude of conductivity of RCrO\(_3\) down the rare earth series may possibly be related to the decrease in the overlap of the cationic orbitals associated with the decrease in the Cr-O covalency and increased covalency of the R-O bond. A decrease in the probability of hopping of the charge carriers would be expected to accompany these changes in the bonding [97].

Rare earth chromites have been reported to show electronic sensitivity toward humidity [99, 100], methanol [101], ethanol [102, 103] and several gases [104], a property that is useful for potential
sensor applications. Furthermore, LaCrO$_3$ and its doped variants exhibited favourable sintering properties, high electrical conductivity and stability in reducing atmosphere, which make them promising candidates for application as interconnect materials in solid oxide fuel cells [105, 106] and as catalysts for hydrocarbon oxidation [107].

![Figure 1.3](image)

**Figure 1.3** Variation of the ferroelectric transition temperature, $T_{CE}$ and magnetic transition temperature, $T_N$ in the heavy rare-earth chromites [85]. CAFM, PM, FE and PE stand for the canted antiferromagnetic, paramagnetic, ferroelectric and paraelectric regimes, respectively.

### 1.8 Yttrium chromite

Among RCrO$_3$ compounds, yttrium chromite (YCrO$_3$) is important as a fundamental material, because it includes only spins of transition metals, so its magnetic structure is relatively simple compared to other crystals in this family [90, 108, 109]. Therefore, it is possible to study the effects originating from the electronic and magnetic structure of chromium ions directly, due to the lack of spin interactions between rare-earth and transition metal ions and optical absorption from rare-earth ions, which would be helpful to
understand the physical mechanism and possible application for
YCrO$_3$.

YCrO$_3$ was first reported by Looby and Katz in the year 1954 [110]. They indexed their powder pattern on a monoclinic cell with $a = c = 7.61$ Å, $b = 7.54$ Å and $\beta = 92^\circ 56'$. Later, Geller and Wood showed that YCrO$_3$ is iso-structural with orthorhombic GdFeO$_3$, which belong to space group $D_{2h}^{16}$ – $Pbnm$ with four distorted perovskite (ABO$_3$) units in the true crystallographic cell with lattice constants, $a = 5.247$ Å, $b = 5.518$ Å and $c = 7.54$ Å [111].

Pure YCrO$_3$ exists in two polymorphic modifications: orthorhombic (low-temperature form) and rhombohedral (high-temperature form) [112]. Reversible transformation occurs between them at ~930 °C [112]. The high-pressure evolution of the YCrO$_3$ perovskite structure has been investigated using synchrotron powder diffraction up to 60 GPa [113]. YCrO$_3$ perovskite did not change from its perovskite $Pbnm$ structure when compressed to 60 GPa at room temperature. However, YCrO$_3$ becomes more distorted with increasing pressure.

Crystals of YCrO$_3$ are canted antiferromagnets (weak ferromagnets) below the ordering temperature $T_N$ (140 K), in which a ferromagnetic component occurs in the crystallographic ‘c’ direction, due to canting of the two antiferromagnetic sublattices, which otherwise align along the easy direction parallel to the ‘a’ axis [108, 114, 115]. Weak ferromagnets are materials with basically antiferromagnetic ordering, in which a small ferromagnetic component is also present in the direction perpendicular to the axis of antiferromagnetism [116]. Magnetic measurements have shown the weak ferromagnetic moment of the Cr$^{3+}$ spins to be due to Dzyaloshinsky–Moriya interaction in the chromites [89, 116, 117].
Neutron diffraction data revealed a canted G-type antiferromagnetic structure for YCrO$_3$ [117].

In the YCrO$_3$ system, Cr$^{3+}$ ions with 3d$^3$ electronic configuration, sit in the octahedral geometry CrO$_6$, surrounded by six O$^{2-}$ ions that lead to the splitting of 3d$^3$ orbital into $t_{2g}$ and $e_g$ [118]. The $t_{2g}$ orbital is half filled and the $e_g$ ones is completely empty. The unfilled $e_g$ orbital hybridizes with the 2p orbital of O$^{2-}$, where two Cr$^{3+}$ ions interact via O$^{2-}$ ion in 180° position. Due to the Dzyaloshinsky–Moriya type antisymmetric exchange interaction [88, 89] of Cr$^{3+}$–Cr$^{3+}$ ions, which plays a very important role here, the Cr–O–Cr bond angle slightly deviates from 180°, resulting in residual electronic spin originating of the only $\Gamma_4$ ($G_x$, $A_y$, $F_z$, $F_2^g$) configuration [119, 120] from imperfect superexchange interaction and thus, the sample YCrO$_3$ is a canted antiferromagnet (CAFM) below $T_N = 140$ K with a weak ferromagnetic component.

A critical divergence in the magnetic susceptibility $\chi_{\perp}$, measured perpendicular to the antiferromagnetic ‘a’ axis, is expected to appear at $T_N$ in weak ferromagnets according to Borovik-Romanov’s theory [121]. The sharp peak in perpendicular susceptibility was experimentally observed by Morishita and Tsushima [113]. They observed that as a function of a magnetic field $H$, the value of the susceptibility at the peak varies with a $H^{-2/3}$ power law. Antiferromagnetic resonance in YCrO$_3$ single crystals was studied in pulse magnetic fields in 1-6 mm wave-length range [122]. For the magnetic field, $H_0$ directed along the a-axis, the spin-flop takes place at $H_0 = 33$ kOe. Domain structure in YCrO$_3$ single crystals was investigated over the temperature range 9-141 K by means of the Faraday effect [123]. The domain wall mobility in YCrO$_3$ was reported to be $\mu = 200$ cm/s Oe at 77 K.
The onset of the antiferro–paramagnetic transition has also been determined using electron paramagnetic resonance (EPR) and low-field microwave absorption (LFMA) techniques [124]. Below 140 K, a weak ferromagnetism is observed and it is attributed to canting of Cr$^{3+}$ ion sublattices in the antiferromagnetic matrix. LFMA technique also gives evidence of the magnetic order, suggesting a weak ferromagnetism at low temperature, with a very high detection sensibility.

Cr$^{53}$ nuclear magnetic resonance (NMR) has been observed in the rare earth orthochromites, YCrO$_3$, LuCrO$_3$, and EuCrO$_3$ [125]. In each compound, two quadrapolar split resonances are observed and tentatively identified as arising from spins in the wall and domain. The major contributor to the electric field gradient is lattice and this contribution is correlated with the anisotropic part of the hyperfine field. NMR studies on YCrO$_3$ shows a fast relaxation mechanism in the wall center. Comparison of the results of NMR with the data on wall mobility indicates that orthochromites are highly damped materials [126].

The linear optical properties of YCrO$_3$ have been studied extensively [94, 127-130]. Absorption studies in YCrO$_3$ show several bands and sharp lines in the visible part of the spectrum, which is assigned to the optical crystal-field transitions in Cr$^{3+}$-ions [127, 129, 130]. Aoyagi et al. have reported the direct observation of Davydov splittings of zero magnon absorption lines in the transitions corresponding to the R-exciton (t$_{2g}^3$ 4A$_2$ → t$_{2g}^3$ 2E) lines in magnetically ordered states and the effects on the spectrum of an externally applied magnetic field [127, 131]. Davydov splittings of spin-forbidden exciton lines were due to spin-forbidden resonance energy transfers between the inequivalent magnetic ions and was found to be ~2 cm$^{-1}$ [131]. Allen [132] has reinterpreted the experimental results of
Aoyagi et al., a Cr$^{3+}$ spin reorientation induced by the field. Holmes et al. [133] have actually observed a spin reorientation by means of magnetization and magnetic susceptibility measurements, confirming this interpretation. They found that at 22 K the reorientation is complete at 11 kG. Meltzer et al. have investigated the R-line optical absorption spectra of Cr$^{3+}$ as a function of an applied magnetic field and concluded that the R-line spectrum of Cr$^{3+}$ can be understood by treating the excitations as Frenkel excitons [134]. The zero-magnon lines accompany very strong sidebands of electric dipole origin on the high energy side [128]. The temperature dependence of these sidebands suggests that the sidebands are mainly due to a combined exciton-magnon excitation [135].

Sugano et al. studied the exciton lines arising from the Cr$^{3+}$ R-line of YCrO$_3$ in magnetic fields ($H_0$) up to 50 kOe parallel to the $a$ axis [136]. The polarization of the high field spectrum is consistent with the selection rule for the $G_x$-type antiferromagnet, indicating a field-induced spin reorientation from $G_x$ to $G_z$ with the increase of a magnetic field parallel to the $a$-axis. The field-induced spin reorientation is further observed by Jacobs, Burne and Levinson in their magnetic measurements [137]. Application of a sufficiently strong magnetic field, $H_z$ along the antiferromagnetic easy axis ($x$) of YCrO$_3$ results in the smooth rotation of the antiferromagnetic vector in the $x$-$z$ plane, reaching the $z$ axis at the critical fields, $H_c = 40\pm1$ kOe at 4.2 K. A direct correspondence between Faraday rotation and magnetic circular dichroism structure and the absorption spectrum was observed in YCrO$_3$ in the vicinity of the $^4A_2$ - $^2E$ transition and attributed to magnon and phonon-assisted exciton transitions [138].

Measurements have been made of the fluorescence spectrum of Cr$^{3+}$ in YCrO$_3$ [139, 140]. Several very sharp emission lines, found at energies about 100 cm$^{-1}$ lower than the intrinsic $^4A_2$ to $^2E$ absorption,
were attributed to impurity-perturbed Cr\textsuperscript{3+} ions. Magnon sideband fluorescence is found at lower energy and results in the simultaneous optical de-excitation of a perturbed Cr\textsuperscript{3+} ion and the creation of a magnon on a neighbouring lattice site. The sideband is spin allowed, if the photon and magnon are created on the same sublattice and has electric dipole polarization.

Moreover, second harmonic generation (SHG) in YCrO\textsubscript{3} crystals has been reported [141, 142]. The origin of the SHG was assigned to magnetic-dipole transition from its spectral and polarization characteristics. The intensity of SHG shows a drastic change at the Néel temperature under magnetic field, which suggests the effects from magnetic ordering.

Raman spectra of YCrO\textsubscript{3} crystals were first reported by Udagawa et al. in 1975 [143]. \(A_{1g}\) and \(B_{2g}\) phonon frequencies near 560 cm\textsuperscript{-1} showed large blue shift from a little above \(T_N\) to lower temperatures. Such temperature dependence is understood by the magnetic ordering of Cr\textsuperscript{3+} ions, because these phonon modes are related only to the motion of Cr\textsuperscript{3+} and O\textsuperscript{2-} ions. Compared to the results presented in Ref. [143], two new lines, \(B_{1g}\) and \(B_{2g}\) at 556 and 611 cm\textsuperscript{-1} were registered by Todorov et al. in 2011 [144]. Based on performed lattice dynamical calculations, the observed lines were assigned to definite atomic vibrations. A systematic Raman scattering investigation of a series of nine \(RCrO_3\) (\(R = Y,\ La,\ Pr,\ Sm,\ Gd,\ Dy,\ Ho,\ Yb\ and\ Lu\)) powder samples were reported by Weber et al. in 2012 [145]. They have shown that the frequency of the \(A_{5}\) (5) correlates in a soft mode fashion with the magnitude of the octahedral rotation in \(RCrO_3\) and can thus be used to follow the distortion of the structure. Bhadram et al. have investigated the \(A\)-cation dependent spin-phonon coupling in rare-earth orthochromites, \(RCrO_3\) (\(R=\ Y,\ Lu,\ Gd,\ Eu\ and\ Sm\)) via Raman scattering through the magnetic phase transition [146]. All the
samples show phonon anomalies at $T_N$, but this is relatively weak in compounds with non-magnetic R-ion (Y, Lu and Eu). An anomalous hardening of the $A_g(1)$ mode is observed in all the samples, except in SmCrO$_3$, wherein a softening is observed. The observed hardening of $A_g(1)$ mode is consistent with the earlier observation, where a reduction in the unit cell volume is reported for YCrO$_3$ and is attributed to magnetostriction arising from Cr-ordering [143]. They concluded that spin-phonon coupling is present only in RCrO$_3$ with magnetic R$^{3+}$ ions.

In a comparative study on structural, optical and magnetic properties of orthorhombic perovskite-like isostructural compounds HoCrO$_3$ and YCrO$_3$, where in Ho$^{3+}$ is a magnetic ion and Y$^{3+}$ is non-magnetic, found almost identical structural parameters for both compounds, however a significant difference was observed in low wave number Raman active phonon modes [147]. Magnetization measurements reveal that Cr$^{3+}$ magnetic ordering temperature is insensitive to local fields (due to Ho$^{3+}$) and very sensitive to thermal cycling in the presence of an external applied magnetic field. This behaviour is related to magnetic disorder near the phase transition due to weak ferromagnetism and/or structural distortions, which is observed as thermal hysteresis.

Rao et al. reported breaks in the conductivity ($\log \sigma - 1/T$) plot for YCrO$_3$, DyCrO$_3$, HoCrO$_3$, YbCrO$_3$ and LuCrO$_3$ at 475, 510, 425, 490 and 485 °C respectively [96, 148]. Since no magnetic transitions were found in these compounds at these high temperatures [149], it was suspected that these breaks may correspond to ferroelectric-paraelectric transitions. This led to investigations of the dielectric properties of the heavy rare earth chromites. Recently, YCrO$_3$ has been reported to be a biferroic material, which shows weak ferromagnetism below 140 K ($T_N$) and a ferroelectric transition at 473
K \left(T_c\right), accompanied by a hysteresis loop \[83\]. The biferroic properties of YCrO$_3$ were confirmed in both bulk and thin film samples. The dielectric constant shows a large dispersion below $T_c$, but is frequency independent above $T_c$, a behaviour commonly observed in relaxor ferroelectrics \[86\]. The ferroelectric behaviour of the YCrO$_3$ pellets and films was also confirmed by their room temperature capacitance voltage (C-V) characteristics. The maximum polarization observed is $2 \mu\text{C/cm}^2$ at 300 K in the case of the pellet and $3 \mu\text{C/cm}^2$ at 178 K in the case of the thin film.

Unlike conventional ferroelectric systems, YCrO$_3$ is reported to possess a centrosymmetric (orthorhombic with $Pnma$ space group) crystal structure \[150-152\] and thus, non-compatible with ferroelectricity. The question therefore raised as to how to reconcile the existence of ferroelectricity in this material, since the presence of ferroelectricity requires the displacement of the B cation relative to the oxygen cage to create an electric dipole moment. First-principles density functional calculations have shown that the polarization found in YCrO$_3$ arising from the weak ferromagnetic instability is small and cannot explain the ferroelectric behaviour and therefore a new concept of “local noncentrosymmetry” has been suggested as the origin of the ferroelectricity in YCrO$_3$ \[83\]. Later, using neutron pair distribution function analysis, Ramesha et al. found that although the average crystal structure is centrosymmetric in the low-temperature ferroelectric state, YCrO$_3$ is locally noncentrosymmetric, characterized with a Cr off-centering displacement of the order of 0.01 Å along the z-direction, which seems to be temperature independent \[85\]. However, it is not yet clear the origin of the off-centering displacement of the Cr atom in YCrO$_3$. Ray et al. have determined structural instabilities of LaCrO$_3$, LuCrO$_3$, YCrO$_3$ and BiCrO$_3$ in their cubic perovskite structures with different magnetic orderings. They
proposed that the origin of small polarization and/or local noncentrosymmetry is probably from the relatively weak ferroelectric instabilities and their competition with various structural magnetic instabilities [118].

The onset of the ferro-paraelectric transition ($T_E = 430$ K) of YCrO$_3$, prepared by solid state reaction method has been determined using electron paramagnetic resonance and low-field microwave absorption techniques [153]. This transition that is associated with a local non-centrosymmetry promotes a spin redistribution of Cr$^{3+}$ ions, which creates changes in dynamics of microwave absorption in YCrO$_3$.

The biferroic properties of YCrO$_3$ were later confirmed in bulk, nanoparticles and thin film samples. Kim et al. reported the observation of both ferroelectricity and weak ferromagnetism in YCrO$_3$ crystals grown by the flux melting method [154]. Cheng et al. reported the observation of both ferroelectricity (at room temperature) and weak ferromagnetism in GdCrO$_3$ (170 K) and YCrO$_3$ (151 K) polycrystalline bulks and thin films, fabricated using conventional solid state reaction and PLD, respectively [155]. Duran et al. have investigated the electrical properties in YCrO$_3$ powder samples prepared by hydroxide precursor (nanoparticles), combustion and solid state reaction method [156-158]. All the samples showed a diffuse phase transition at about 450 K, typical of a relaxor ferroelectric. They found that the dielectric properties and conduction mechanism are greatly influenced by the synthesis route and the thermal history of the material. Seo et al. have investigated the multiferroic properties of YCrO$_3$ thin films grown by pulsed laser deposition on single crystal (001) Rh substrates [159]. The YCrO$_3$ thin films exhibited room temperature ferroelectricity with a remanent
polarization of about 9 μC/cm² as well as weak ferromagnetism below 150 K.

Prado-Gonjal et al. have performed a detailed investigation of the magnetic and dielectric properties of RCrO₃, synthesized by microwave-assisted technique and their correlations with particular focus on possible magnetoelectric or multiferroic behaviour [160]. No indications for a noncentrosymmetric space group and associated ferroelectricity were detected from XRD pattern, Raman spectroscopy and temperature-dependent dielectric permittivity data. No clear correlations of the magnetic and dielectric properties were found and major magnetoelectric coupling effects could not be detected. Thus, they concluded that microwave-synthesized RCrO₃ may not be classified as magnetoelectric or multiferroic materials.

Recently, Rajeswaran et al. have reported field-induced polar order below the Neel temperature of chromium in RCrO₃ containing magnetic R ions such as Sm, Gd, Tb, Tm and Er and no polar order, when the R ion is nonmagnetic (Lu and Y), indicating the absence of magnetoelectric coupling in YCrO₃ [161]. It is suggested that the polar order occurs in RCrO₃, due to the combined effect of the poling field that breaks the symmetry and the exchange field on the R ion from the Cr sublattice that stabilizes the polar state.

The effect of Mn substitution on the multiferroic properties of YCrO₃ and LuCrO₃ has been investigated [162]. Solid solutions of YCr₁₋ₓMnₓO₃ and LuCr₁₋ₓMnₓO₃ (x = 0.0–0.3) possess orthorhombic structures with Pnma and Pbmn space groups, respectively. Both the series of materials show canted antiferromagnetic behaviour with Tₙ decreasing with increasing x. They also exhibit ferroelectricity with the transition temperature decreasing with increase in x. The x = 0.3 compositions show improved magnetic properties with a ferroelectric transition in the 418–425 K range.
Amorphous YCrO$_3$ (a-YCrO$_3$) has been synthesized by Kim et al. in 2003 [163]. In 2012, a theoretical prediction of the structure of amorphous YCrO$_3$ was done by performing first principles calculations by means of two different methods, namely, molecular dynamics (MD) and the stochastic quenching (SQ) [164]. The structures obtained by the two methods are equivalent. In both amorphous structures, Cr atoms situated in oxygen octahedra resemble the local Cr environment in the orthorhombic perovskite structure. It was found that Cr$^{3+}$ atoms situated in slightly distorted oxygen octahedra throughout the amorphous structures and that the distribution of these octahedra is disordered. Cr$^{3+}$ local environment of the crystal that give rise to ferroelectricity in the orthorhombic perovskite structure is only slightly modified in the amorphous phase, which strongly suggests that the amorphous phase of YCrO$_3$ may also exhibit ferroelectric properties. The Cr-O-Cr angle, which is important due to its role in the stabilization of an antiferromagnetic state in YCrO$_3$ through super-exchange interaction is not preserved in the amorphous structures, indicate that the antiferromagnetic state may be difficult to realize in the amorphous phase [118].

Sandeep et al. have fabricated thin films of YCrO$_3$ by pulsed laser deposition [165]. The resulting films were amorphous and ferromagnetic beyond room temperature. Extensive studies on the films showed that these materials are not ferroelectric. Moreover, advanced spectroscopic techniques revealed that the amorphized state is metallic with Cr in a mixed valence state. The ferromagnetism is explained by evoking a number of coexisting effects, namely disordering of Cr-O-Cr bond angles, metallization, which introduces free carriers and the presence of mixed valence states (Cr$^{3+}$ in the bulk and Cr$^{4+}$ on the surface).
Bahadur et al. reported small-angle neutron scattering (SANS) investigation on pore characteristics and the effect of pore structure on the low and intermediate frequency (0.02–1000 kHz) dielectric response of YCrO$_3$ nanoceramic at different sintering temperatures [166, 167]. It has been observed that overall polydispersity of pore-size distribution decreases and loss peak of the ac dielectric response gets pronounced with a slight peak shift towards higher frequency with increasing sintering temperature. A transition from non-Debye response to near-Debye response was observed as the sintering temperature is increased beyond 1400 °C, which is attributed to the combined effect of pore–matrix interface smoothening, reduction of polydispersity of the pore-size distribution and breaking of the connectivity of the pores with increasing sintering temperature. Nyquist plot of YCrO$_3$ prepared by solution combustion method revealed non-Debye behaviour with two relaxation processes; grain and grain boundary contribution process [168].

The heat capacity of YCrO$_3$ below room temperature was reported by Stoppe et al. [169, 170] with a vacuum adiabatic calorimeter from 5-300 K. The heat contents of RCrO$_3$ (R = Dy, Ho, Yb and Y) were reported by Dzhaoshvili et al. [171] with a mixing method, that is to say a drop method, from 400 to 1500 K. Chen et al. [172], Dzhaoshvili et al. [173, 174], Kitayama and Iida [175] and Kawamura et al. [176] reported the Gibbs free energy of formation of RCrO$_3$ (R = La, Dy, Ho and Y) at high temperature by an e.m.f. method. The heat capacities of RCrO$_3$ (R = La, Pr, Nd, Sm, Gd, Dy, Ho, Er and Y) were measured by differential scanning calorimetry (DSC) from 150 to 450 K and also alternating current calorimetry (ACC) from 77 to 280 K [177]. Thermal anomalies due to magnetic transition were observed in all of the heat capacities of RCrO$_3$ and the transition
temperatures were in good agreement with the references by magnetic measurements.

Kim et al. reported the specific heat measurement on YCrO$_3$ single crystal in the temperature range 30-360 K using high sensitive microcalorimeter ($\sim 1 \, \mu$J/K) [154]. The sample showed a sharp ($\lambda$-shaped) peak in the specific heat at $T_N \approx 140$ K due to a canted antiferromagnetic ordering of Cr$^{3+}$ spins. The analysis of magnetic and phononic entropy of YCrO$_3$ suggest that there exist additional phonon modes beyond those of LaGaO$_3$, related to a broken inversion symmetry below $T_C = 500$ K. These results seem to be closely related to a comparative thermal conductivity study of YCrO$_3$ and LaGaO$_3$ by Zhou and Goodenough [178]. The phonon thermal conductivity of YCrO$_3$ is significantly suppressed below and above $T_N$ as compared with that of LaGaO$_3$. Without information of the occurrence of ferroelectricity in YCrO$_3$ [83], Zhou and Goodenough [178] have attributed their results to the bond-length fluctuation of YCrO$_3$ coupled to the magnetic fluctuation above $T_N$ that might come from an exchange striction driven by a strong spin–phonon coupling. Because the measured thermal conductivity is found to be much more suppressed even below $T_N$ as well as above, the inhomogeneous bond-length fluctuation driven by magnetic fluctuation alone might not be enough to account for the experimental observation. If inversion symmetry-breaking phonon modes related to short ranged or long ranged ferroelectric dipoles exist below $T_C$ and it gives the additional scattering of phonon thermal conductivity through the inhomogeneous bond-length fluctuation, one can expect both large excess entropy from the additional symmetry broken phonon modes and suppression of the phonon thermal conductivity over all temperatures.
In 2010, Duran et al. reported a spin reorientation transition at about 60 K, in addition to \( \lambda \)-type anomaly at \( T_N = 140 \) K [156]. It is possible that around 60 K, the antiferromagnetic easy x-axis results in a smooth rotation of the AFM-vector in the x–z plane as it was observed by Jacobs et al. [137].

\( \text{YCrO}_3 \) is a p-type semiconductor [179]. It has high thermal, [180] electrical, chemical, and structural stability [181] because of its high melting temperature (2290 ± 30 °C) [182]. Furthermore, \( \text{YCrO}_3 \) exhibit favourable sintering properties and high electrical conductivity [183]. These properties make \( \text{YCrO}_3 \) a promising candidate for many technologically demanding and challenging applications, such as interconnect materials in solid oxide fuel cells (SOFC), humidity sensor, oxidation catalysts and thermistor, in addition to the potential magnetoelectric application [163, 99, 184-187]. Alkaline earth metals were usually doped into A-site in \( \text{YCrO}_3 \) to enhance their utility by improving or changing physical and chemical properties [145, 188, 189]. In addition of working as interconnect, \( \text{YCrO}_3 \) based materials have been evaluated as potential anode for solid oxide fuel cell after multiple doping at A and B sites [190-193].

One aspect of fundamental interest to the study of multiferroics is the production of high quality samples of such materials for detailed study. Several synthesis techniques have been used to prepare \( \text{YCrO}_3 \), including solid state reaction method [194], liquid mix process [195], molten salt technique [109], citrate gel process [196], self-propagating high temperature synthesis method [197], sol-gel technique [183], solution combustion technique [198] and hydrothermal method [90].

**1.9 \( \text{YFe}_{0.5}\text{Cr}_{0.5}\text{O}_3 \)**

In the perovskite materials, the magnetic properties are generally determined by the B-site cations and thus, alloying different magnetic
transition elements in this site may induce a variety of interesting phenomena, as has been observed by many authors [199-201]. Wold and Croft [202] have observed solid solubility between YFeO\(_3\) and YCrO\(_3\) in the YFe\(_{1-x}\)Cr\(_x\)O\(_3\) (0 ≤ x ≤ 1) system. YFe\(_{1-x}\)Cr\(_x\)O\(_3\) compounds revealed interesting magnetic properties [202, 203]. A systematic investigation of the magnetic properties of the series YFe\(_{1-x}\)Cr\(_x\)O\(_3\) has been performed by Kadomtseva et al. [205]. The compounds behave like weak ferrimagnets in the entire interval of concentration. The authors reported that the substitution of Cr\(^{3+}\) ions for Fe\(^{3+}\) ones induce anomalies in the temperature and concentration dependence of the magnetic moment. The results are explained by qualitatively assuming the presence of two uncompensated weak ferromagnets. The authors asserted that the most complicated region for the analysis of the magnetic behaviour is concentration near x = 0.5, where the used impurity-matrix model is completely failed.

Dahmani et al. [206, 207] discarded the spin glass model for describing these anomalies by supposing magnetic frustration interactions. Neutron diffraction measurements at room temperature have confirmed that the samples with high concentration of Fe are showing G-type antiferromagnetic ordering of the B-site ions magnetic moments. In the case of the non-substituted sample YCrO\(_3\), field-cooled magnetization (M\(_{FC}\)) that is proportional to the magnetic moment, follows a Brillouin function, but for the mixed compounds, the substitution shifts the magnetization away from the above simple behaviour. This effect is more pronounced in the case of YFe\(_{0.5}\)Cr\(_{0.5}\)O\(_3\), as this compound is known to exhibit the more anomalous properties. The results are explained by considering that the transition metal ions Fe\(^{3+}\) and Cr\(^{3+}\), having different electronic configuration, are randomly distributed in the octahedral site. This leads to a distribution of the weak ferromagnetic components inside the material. Weak
ferromagnetism observed in these compounds is considered to originate from small canting between the sublattices.

Early studies have established that the basic compounds, YFeO₃ and YCrO₃ are orthorhombically (Pnma) distorted perovskites [110]. Below their Néel temperatures of 648 and 140 K, respectively, the compounds order antiferromagnetically with G-type structure and their arrangement can be described by two cubic interpenetrating sublattices [208, 83]. Each ion has six antiparallel nearest neighbours. In the mother compounds YFeO₃ and YCrO₃, the small canting between the sublattices is responsible for the weak ferromagnetism that is induced by the Dzyaloshinsky–Moriya antisymmetric exchange and according to Moriya; the canting angle in this case is constant with temperature [116, 88]. In the mixed compounds, the hypothesis of a simple weak ferromagnetism with a constant canting angle although can explain the occurrence of hysteresis, but it cannot justify the non-Brillouin-like temperature dependence of the saturation magnetization. According to the empirical rules of Goodenough [209], it is expected that the superexchange coupling between two cations d³–d⁵ can be ferromagnetic, if the superexchange pathway is linear. However, Moskovin et al. [210] have reported that the superexchange angle is 146° and that this interaction is antiferromagnetic in the case of YFe₁₋ₓCrₓO₃ and cannot induce hysteresis behaviour. This fact is supported by the negative value of the paramagnetic Curie temperature.

Kovachev et al. have investigated the structural and magnetic properties of YFe₁₋ₓCrₓO₃ system, synthesized by self-propagation combustion techniques using neutron, X-ray diffraction and magnetic measurements [211]. The structural results for YFe₁₋ₓCrₓO₃ and the specific thermomagnetic behaviour of the system give a strong indication that replacement of Cr with Fe entails a substantially
modified antisymmetric exchange and frustrated magnetic interactions.

Yin et al. have investigated the structural, magnetic, electrical and dielectric properties of YFe$_{0.5}$Cr$_{0.5}$O$_3$, synthesized through a conventional solid-state reaction [212]. Powder X-ray diffraction showed that this compound possesses an orthorhombic structure with \textit{Pnma} space group. It exhibited a high magnetic transition temperature at around 250 K with weak ferromagnetic behaviour below this temperature. A rapid rise in the dielectric constant was observed above $T_N$, accompanied with a dielectric relaxation obeying the Arrhenius law, which is attributed to the hopping conduction of the localized charge carriers.

In YFe$_{1-x}$Cr$_x$O$_3$, it was predicted theoretically that a ferrimagnetic ground state results from antiferromagnetic coupling of weak ferromagnetic moments of Fe–O–Fe and Cr–O–Cr with that of Fe–O–Cr and hence, the magnetization reversal occurs in this system [205]. Very recently, temperature and magnetic field induced magnetization reversal with high compensation temperature ($T_{\text{comp}}$, the characteristic temperature where the material exhibits a net zero magnetization) of 248 K was observed in YFe$_{0.5}$Cr$_{0.5}$O$_3$, synthesized by the standard solid-state reaction [213]. Below $T_{\text{comp}}$, a tunable bipolar switching of magnetization is demonstrated by changing the magnitude of the field, while keeping it in the same direction, in contrast to ferro/ferrimagnets, where the switching between the two polar states is achieved by changing the polarity of the magnetic field. The observation of magnetization reversal in this system was ascribed to the competition between the single ion magnetic anisotropy (SIMA) and the antisymmetric Dzyaloshinsky–Moriya interaction. Further, an extraordinary coexistence of normal and inverse magnetocaloric effects (MCE) has been realized in YFe$_{0.5}$Cr$_{0.5}$O$_3$ above and below 260
K, respectively. YFe$_{0.5}$Cr$_{0.5}$O$_3$ exhibits the onset of AFM ordering at 274 K, which locates between the two Néel temperatures for YFeO$_3$ and YCrO$_3$, respectively.

Later, Mao et al. have reported the coexistence of sign reversal of both magnetization and exchange bias (EB) field in YFe$_{0.5}$Cr$_{0.5}$O$_3$ [214]. Above $T_{\text{comp}}$, only negative EB field appears, whereas the sign of the EB field below $T_{\text{comp}}$ can be reversed from positive to negative by applying a large cooling field. The competition between the DM interaction and the single ion magnetocrystalline anisotropy explained not only the magnetization reversal, but also the sign reversal of EB field.

Dasari et al. reported systematic and combined, experimental and theoretical studies on the magnetic properties of YFe$_{1-x}$Cr$_x$O$_3$ system [215]. They found that all the compositions exhibit weak ferromagnetism below the Neel temperature that decreases nonlinearly with increasing $x$, while certain intermediate compositions ($x = 0.4, 0.5$) show a compensation point and magnetization reversal. This unusual behaviour is explained based on a simple model comprising the isotropic superexchange and the antisymmetric Dzyaloshinsky-Moriya interactions. This model explained the magnetization behaviour in the entire range of doping and temperature, including the magnetization reversal, which results from an interplay of various DM interactions such as, Fe-O-Fe, Cr-O-Cr and Fe-O-Cr.

Recently, Rajeswaran et al. have reported the observation of ferroelectricity and magnetoelectric effect at $T_N = 260$ K in YFe$_{0.5}$Cr$_{0.5}$O$_3$ [200]. The origin of ferroelectricity is attributed to disordered cations of nonequivalent spins at the B-site of weakly ferromagnetic perovskites.
Later, Nair et al. have reported a relaxor-like ferroelectric transition (peak at ~507 K for 10 kHz) in the dielectric measurement for YFe$_{0.5}$Cr$_{0.5}$O$_3$, which can be attributed to the random distribution of Fe$^{3+}$ and Cr$^{3+}$ ions at the B-site [216]. Further, an anomaly is observed in the magnetization curve corresponding to this dielectric transition temperature (~507 K), which indicates the possibility of magnetodielectric effect in YFe$_{0.5}$Cr$_{0.5}$O$_3$. Neel temperature for YFe$_{0.5}$Cr$_{0.5}$O$_3$ is found to be ~275 K using temperature dependence of magnetization and neutron diffraction studies. Rietveld refinement of the neutron diffraction data divulges a canted G-type antiferromagnetic structure for YFe$_{0.5}$Cr$_{0.5}$O$_3$.

1.10 Motivation of the present investigation

A detailed review of the existing literature in YCrO$_3$ indicates the significance of synthesis at the nano-scale, where the materials display an enhanced properties or a completely new set of properties, which is usually absent in their classical dimensions. The physical properties of YCrO$_3$ ceramics were reported mostly in the bulk phases, such as single crystals and polycrystalline form. Although, there were few reports on the biferroic properties of YCrO$_3$ nanoparticles, yet the level of understanding with regard to the size effect on the ferroic properties is far from being satisfactory. Furthermore, the issue of the size and its correlation with the stabilization of the multiferroic behaviour is still a matter of much controversy. Recently, there were reports that microwave-synthesized YCrO$_3$ samples are not showing the biferroic behaviour. To date, there exist no systematic studies on the effects of particle size on multiferroic properties, as the synthesis of this complex oxide with a control over particle size and morphology is nontrivial. In this context, the synthesis and characteristic analysis of YCrO$_3$
nanoparticles with well-controlled size, shape and chemical homogeneity is interesting and essential to explore the possible size effect in this system.

Advances in the development of new communication methods and new sources of radiation, particularly optical power sources, such as lasers had resulted in research oriented towards the protection from exposure to such sources. One major approach to laser protection is through the use of optical limiters. An ideal optical limiter should be transparent to low energy laser pulses and opaque at high energies, so that it can protect human eyes and optical sensors from intense laser radiation. Recently, nanomaterials have drawn significant attention as optical limiters. Further, control of the nonlinear optical properties by means of an external stimulus, such as magnetic and/or electric field presents remarkable applications. Optical limiting studies of YCrO$_3$ nanoparticles are attractive in this regard, as they possess a very high shelf life and remarkable thermal stability, which are important requirements for sustainable use with intense lasers. In fact, it is the physical and chemical stability of YCrO$_3$, which is an important attribute for an optical limiter, which prompted us to investigate their optical limiting properties. Optical limiting properties of YCrO$_3$ have not been investigated so far.

The ultimate goal for device functionality would be a single phase multiferroic with strong coupling between ferroelectric and ferromagnetic order parameters making for simple control over the magnetic nature of the material with an applied electric field at room temperature. There were reports that the magnetic transition temperature of YCrO$_3$ could be tailored close to room temperature by substitution of Fe$^{3+}$ ions for Cr$^{3+}$. Also there were reports of observation of ferroelectricity, temperature and magnetic field induced magnetization reversal, exchange bias effect and
magnetoelectric effect in YCr$_{0.5}$Fe$_{0.5}$O$_3$. Compared with other compounds exhibiting magnetization reversal, YCr$_{0.5}$Fe$_{0.5}$O$_3$ shows the higher $T_{\text{comp}}$. However, the effect of particle size on this unusual phenomenon of magnetization reversal, exchange bias effect, ferroelectricity and magnetoelectric effect of YCr$_{0.5}$Fe$_{0.5}$O$_3$ nanoparticles have not been studied so far.

By considering all the above mentioned issues, the present thesis aims:

- Synthesis of high quality samples of YCrO$_3$ with well-controlled size, shape and chemical homogeneity through a poly acrylic acid (PAA) assisted sol-gel route for detailed study and their structural characterization. This method has the advantage of simple, easily controllable and time and energy efficient preparation, which makes the process cost effective and gentle chemistry route, resulting in ultra fine and homogeneous powder.

- To explore the possible size effect on the magnetic and electrical properties of YCrO$_3$ nanoparticles and to compare the results with the corresponding bulk sample.

- To investigate the optical limiting properties of YCrO$_3$ nanoparticles using the open aperture Z-scan technique upon illumination by nanosecond (ns) laser pulses at 532 nm and femtosecond (fs) laser pulses at 800 nm.

- To explore the possible size effect on the optical limiting response of YCrO$_3$ nanoparticles, when compared with the bulk sample.

- Substitution of magnetic Fe$^{3+}$ for Cr$^{3+}$ and to investigate the structural, electrical, magnetic and magnetoelectric properties of YCr$_{0.5}$Fe$_{0.5}$O$_3$ nanoparticles. The results are to be compared with YCrO$_3$ nanoparticles.
1.11 Experimental details

This section deals with the details of the experimental techniques used and the basic operation principles of various structural and physical characterizations of the materials prepared.

1.11.1 Synthesis

1.11.1.1 Sol-gel method

The sol-gel process is a wet-chemical technique, widely used in the field of materials science and ceramic engineering. It has the advantage of good stoichiometric control and the production of ultrafine particles with a narrow size distribution in a relatively short processing time at lower temperatures [217]. This method is used primarily for the fabrication of typical metal oxide materials, starting from a chemical solution (sol), which acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers. Generally, the precursors will be metal alkoxides, metal nitrates or metal chlorides. The precursors undergo various forms of hydrolysis and polycondensation reactions. The formation of a metal oxide involves connecting the metal centres with oxo (M-O-M) or hydroxo (M-OH-M) bridges, thereby generating metal-oxo or metal-hydroxo polymers in solution. Thus, the sol evolves towards the formation of a gel-like diphasic system containing both a liquid phase and solid phase, whose morphologies range from discrete particles to continuous polymer networks [218].

We can chemically modify the precursors, which consist of a metal or metalloid element surrounded by various ligands, using certain chelating agents [219]. The nature of chelating agent greatly aids in the formation of a cross-linked gel, which may result in the control of properties of the nanostructured material formed in the
process. In a sol-gel process, where a chelating agent is used, the functional group of the chelating agent forms a chelate with cations, resulting in a sol. During the sol formation process, the chelating agent acts to distribute the cations atomistically throughout the polymeric structure and prevent cation segregation and thereby precipitation. Heating the sol to moderate temperature causes a condensation reaction via dehydration with the concurrent formation of water. As most of the excess water is removed, the sol turns into a gel and extremely high viscosity polymeric resins are formed. The gel can be either cross-linked or non-cross-linked, depending on the stoichiometry of the ratios of reactants. Calcination of the gel in air or other gases causes breakdown of the gel. While the chemical bonding of the cations to the polymeric chains is destroyed during pyrolysis, the high viscosity of the gel causes low cation mobility, which prevents the different mixed cations from segregation. Therefore, it is assumed during the calcination that there is little segregation of the various cations that remain trapped in the char. Subsequently, the cations are oxidized to form crystallites of mixed cation oxides.

1.11.1.2 Solid state reaction method

Ceramic or solid state reaction method is the most common and one of the simplest ways of preparing solids. It consists of heating together two or more non-volatile solids, which react to form the required product. The solid state reaction method can be used to prepare a whole range of materials, including mixed metal oxides, sulfides, nitrides, aluminosilicates, etc. This method is commonly used in both industries as well as in the laboratory and considered as a best way to synthesize oxide materials. The first high temperature superconductors were made by this method.
The simple procedure is to take stoichiometric amounts of oxides, grind them in a pestle and mortar to give a uniform small particle size and then heat in a furnace for several hours in a ceramic, alumina or platinum crucible, according to the required temperatures. Sufficient amount of some volatile organic liquid, preferably acetone or alcohol is added to the mixture to aid homogenization. This forms a paste, which is mixed thoroughly. During the process of grinding and mixing, the organic liquid gradually volatilizes and has usually evaporated completely after 10 to 15 minutes. For quantities much larger than ~20g, mechanical mixing is usually adopted using a ball mill and the process may take several hours. Pelleting of samples is preferred prior to heating, since it increases the area of contact between the grains. Although this method is being used widely, it has several disadvantages. Due to high temperature, a large amount of input energy is needed. This is because the coordination numbers in binary or ternary compounds are high and it takes a lot of energy to overcome the lattice energy, so that a cation can leave its position in the lattice and diffuse to different sites. Sometimes the phase or compounds may be unstable or decompose at such high temperatures [220].

1.11.2 X-ray diffraction

Phase formation of as-burnt and calcined chromite powder samples were studied by the powder X-ray diffraction (XRD) measurements performed on a PANanalytical X’pert Pro X-ray diffractometer (Cu Kα). In the powder, grains have random orientations. With random orientations, it is expected that most of the atomic planes lie parallel to the surface in some of the grains. Thus, scanning through different angles would be associated with different atomic spacing. A
powdered sample is packed on a sample stage, so that it can be irradiated by the X-ray.

To detect the diffracted X-rays, an electronic detector is placed on the other side of the sample from the X-ray tube and rotated the detector through different Bragg’s angles. The goniometer keeps track of the angle (θ) and the detector records the detected X-rays in units of counts/sec and sends this information to the computer. The operating parameters were; 40 kV and 35 mA with the Cu target, a step size of 0.02° and a count time of 4 s per step. After scan of the sample, the X-ray intensity (counts/s) was plotted against the angle, 2θ. The angle, 2θ for each diffraction peak was then converted to d-spacing, using the Bragg’s law;
\[ n\lambda = 2d \sin \theta \]  
(1.1)
where λ is the wavelength of X-ray and n is the order of diffraction.

The powder pattern is characterized by a set of line position, 2θ and a set of relative line intensities, I. But the angular positions of the lines depend on the wavelength used and a more fundamental quantity is the spacing, d of the lattice planes forming each line. Each pattern is described by listing the d and I values of its diffraction lines. Each substance is characterized by the d values of its 3 strongest lines. The d values together with the relative intensities are sufficient to characterize the pattern of an unknown crystal structure [220].

The crystalline phases were identified according to JCPDS (Joint Committee on Powder Diffraction Standards) data. The crystallite sizes of as-burnt and calcined powder samples were determined from X-ray line broadening, using the Scherrer’s equation [221] as follows:
\[ t = \frac{0.9\lambda}{B \cos \theta} \]  
(1.2)
where t is the crystallite size, λ is the wavelength of the radiation, θ is the Bragg’s angle and B is the full width at half maximum (FWHM).
Line broadening due to instrument was subtracted from the peak width before calculating the crystallite size using the following formula:

\[ B^2 = B_{\text{meas}}^2 - B_{\text{equip}}^2 \]  

(1.3)

where \( B_{\text{meas}} \) is the measured FWHM from peak, \( B_{\text{equip}} \) is the instrumental broadening [Standard Si sample was used, whose \( B \) value is 0.09821 at \( 2\theta = 29^\circ \), with \( (hkl) \) value (111)].

### 1.11.3 Transmission electron microscopy

Transmission electron microscopy (TEM) is a straightforward technique to determine the size and shape of nanostructured materials as well as to obtain structural information. In TEM, electrons are accelerated to 100 keV or higher, projected on to a thin specimen by means of a condenser lens system and penetrate into the sample [222]. TEM uses transmitted and diffracted electrons, which generate a two-dimensional projection of the sample. The principal contrast in this projection or image is provided by diffracted electrons. In bright field images, the transmitted electrons generate bright regions, while the diffracted electrons produce dark regions. In dark field image, the diffracted electrons preferentially form the image. In TEM, one can switch between imaging the sample and viewing its diffraction pattern by changing the strength of the intermediate lens. The greatest advantage that TEM offers are the high magnification, ranging from 50 to \( 10^6 \) and its ability to provide both image and diffraction information from a single sample.

High resolution transmission electron microscope (HRTEM) [223] can generate lattice images of the crystalline material allowing the direct characterization of the sample’s atomic structure. The resolution of the HRTEM is 1 nm or smaller. However, the most difficult aspect of the TEM technique is the preparation of samples.
Selected area electron diffraction (SAED) offers a unique capability to determine the crystal structure of individual nano materials and the crystal structure of the different parts of a sample. A small area of the specimen can be selected from a high resolution transmission image and its electron diffraction pattern (rings or spots) can be produced on the screen of the microscope by making appropriate arrangement of the lenses of TEM. This is an optional arrangement in HRTEM. The SAED allows the researcher to determine lattice constant of the crystalline material, which can help in species identification. Basically diffraction patterns are distinguishable as spot patterns resulting from single crystal diffraction zones or ring patterns obtained from the randomly oriented crystal aggregates (polycrystallites). For nanocrystallites, the diffraction patterns will be diffused ring patterns [224, 225].

In the present investigation, the size and morphology of the samples were determined using JEOL JEM-2100 transmission electron microscope (200 kV).

1.11.4 Energy dispersive X-ray spectroscopy

Energy dispersive X-ray spectrometer (EDS) attached to the transmission electron microscope analyzes characteristic X-ray radiation emitted from the specimen, when the electron beam interacts with the specimen. The main use of EDS is to accurately determine the composition of the sample under investigation. Upon exposing the samples to high energy electron beams, the various atoms present in the sample emit characteristic X-rays, which can be observed as several distinct peaks on an energy scale. The intensities of the peaks can be compared with the peaks of a standard sample to obtain the relative amounts of each atomic species, whereby accurate composition of the sample can be determined. The use of EDS has
been demonstrated in oxide nanoparticle research in a number of reports [226, 227].

The elemental composition of the present samples was determined using EDS attached with SEM (Swift-ED Oxford Instruments) and TEM (Oxford INCA).

1.11.5 Scanning electron microscopy

Scanning electron microscopy (SEM) is one of the most widely used techniques for morphology studies and surface characterization. It provides images of the morphology and microstructures of the bulk and nanostructured materials and devices. The resolution of SEM approaches a few nanometers and the instrument operates in the range of 10-30,000 nm. SEM image is obtained by scanning an electron beam over the sample surface and detecting the yield of low energy electrons (secondary electrons) and high energy electrons (back scattered), according to the position of the primary beam. The secondary electrons, which are responsible for the topological contrast, provide mainly information about the surface morphology. The backscattered electrons, which are responsible for the atomic number contrast, carry information on the sample's composition [228].

In the present study, JEOL JSM-6390 scanning electron microscope was employed to analyze the morphology of the samples.

1.11.6 Fourier transform infrared spectroscopy

Vibrational motion of chemical bonds occurs in the infrared region of the energy beam. Fourier transform infrared (FTIR) spectroscopy exploits this phenomenon. When a sample is exposed to infrared energy, it couples with the energy of the sample, if the impinging IR energy is in resonance with the energy of the chemical bond in the
sample. The intensity of the beam is measured before and after it interacts with the sample. The incident radiation can be detected in transmission or reflection experiments. The intensity is then plotted as a function of the frequency in the IR spectrum [229]. Thus, infrared spectroscopy is a useful technique for characterizing materials and obtaining information on the molecular structure, dynamics and environment of a compound. In an infrared spectrum, the absorption or transmittance peaks correspond to the frequencies of vibrations between bonds of the atoms making up the material. From the characteristic peaks, different functional groups present in the compound can be identified. This aspect makes infrared spectroscopy quite useful in material characterization. FTIR spectra of the present samples were recorded using Shimadzu 8400S FTIR spectrophotometer.

1.11.7 Dielectric measurements

The dielectric constant of the samples can be calculated using the equation,

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A}$$  \hspace{1cm} (1.4)

where $C$ is the capacitance measured by LCR meter, $d$ is the thickness of the pellet, $A$ is the surface area of the pellet and $\varepsilon_0$ is the permittivity of free space.

The theory involved for the evaluation of ac conductivity from dielectric constant values may be briefed as follows. Any capacitor when charged under an ac voltage will have a loss current due to ohmic resistance or impedance by heat absorption. For a parallel plate capacitor of area of cross section, $A$ and separation, $d$ the ac conductivity is given by the relation,

$$\sigma_{ac} = \frac{J}{E}$$  \hspace{1cm} (1.5)
where $J$ is the current density and $E$ is the field density. But, we know that the electric field vector,

$$ E = \frac{D}{\varepsilon} $$

(1.6)

where $D$ is the displacement vector of the dipole charges and $\varepsilon$ is the complex permittivity of the material. Also, the electric field intensity ($E$) for a parallel plate capacitor is the ratio of potential difference between the plates of the capacitor and the inter-plate distance.

$$ E = \frac{V}{d} $$

(1.7)

where $V$ is the potential difference between the plates of the capacitor and $d$ is the inter-plate distance.

Since the current density, $J = dq/dt$ and $q$ is given by $\frac{Q}{A} = \frac{V \varepsilon}{d}$, where $Q$ is the charge in coulombs due to a potential difference of $V$ volts between two plates of the capacitor,

$$ J = \frac{\frac{dq}{dt}}{dt} = \frac{d}{dt} \left( \frac{V \varepsilon}{d} \right) $$

$$ J = \frac{\varepsilon}{d} \frac{dV}{dt} = \frac{\varepsilon}{d} Vj\omega $$

(1.8)

Substituting for $E$ and $J$ from equations (1.7) and (1.8) we get,

$$ \sigma_{ac} = \frac{J}{E} = \varepsilon j \omega $$

(1.9)

Considering, $\varepsilon$ as a complex entity of the form $\varepsilon^* = (\varepsilon' - j\varepsilon'')$ and neglecting the imaginary term in the conductivity, we can write

$$ \sigma_{ac} = \omega \varepsilon'' $$

(1.10)

But, the loss factor or dissipation factor in any dielectric is given by the relation,

$$ \tan \delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} $$

(1.11)

Hence, from the dielectric loss and dielectric constant, ac conductivity of the samples can be evaluated using the relation,

$$ \sigma_{ac} = 2\pi f \tan \delta \varepsilon_0 \varepsilon_r $$

(1.12)
where \( f \) is the frequency of the applied field and \( \tan \delta \) is the loss factor [230].

The samples for dielectric measurement were pressed by applying a uniaxial force of 5 tonnes for 3 min using a hydraulic press to get compact circular pellets with dimensions 10 mm in diameter and approximately 1.0 mm to 1.5 mm in thickness. LCR meter is compactable with such dimension of the pellets. Silver paint was used on both sides of the pellets as electrodes. The pellets were then placed in a tube furnace for taking measurements at various temperatures. The temperature control was performed with DPI-1100 dry temperature calibrator of the tube furnace. The capacitance and loss factor was measured using LCR HITester (HIOKI 3532-50) in the frequency range of 500 Hz–1 MHz and over a temperature range of 303-623 K. After obtaining capacitance and dielectric loss from the instrument, the dielectric constant and the ac conductivity of the powder samples were calculated using the relation (1.4) and (1.12).

### 1.11.8 Magnetic measurements

Various magnetometers have been devised to study magnetic materials. A vibrating sample magnetometer (VSM) is one among the instruments that is used relatively widespread for magnetic measurements. A vibrating sample magnetometer operates on Faraday's law of induction, which tells us that a changing magnetic field will produce an electric field. This electric field can be measured and provides us information about the changing magnetic field.

In a VSM, the sample to be studied is placed in a constant magnetic field. If the sample is magnetic, this constant magnetic field will magnetize the sample by aligning the magnetic domains or the individual magnetic spins, with the field. The stronger the constant field, the larger the magnetization. The magnetic dipole moment of
the sample will create a magnetic field around the sample, sometimes called the magnetic stray field. A transducer converts a sinusoidal ac drive signal provided by a circuit located in the console into a sinusoidal vertical vibration of the sample rod and the sample is thus made to undergo a sinusoidal motion in a uniform magnetic field. Coils mounted on the pole pieces of the magnet pick up the signal resulting from the sample motion. As the sample is moved up and down, the magnetic stray field change as a function of time and can be sensed by a set of pick up coils. The signal has the same frequency of vibration and its amplitude will be proportional to the magnetic moment, amplitude and relative position with respect to the pick-up coils system. The greater the magnetization, greater will be the induced current.

The induction current is amplified by a transimpedance amplifier and a lock-in amplifier. The various components are interfaced via a computer. Controlling and monitoring software, the system can tell us how much the sample is magnetized and how magnetization depends on the strength of the constant magnetic field. For particular field strength, the corresponding signal received from the probe is translated into a value of magnetic moment of the sample. When the constant field varies over a given range, a plot of magnetization versus magnetic field strength is generated. Using VSM, the hysteresis loop parameters namely, saturation magnetization (\( M_s \)), coercive field (\( H_c \)), remanence (\( M_r \)) and squareness ratio (\( M_r/M_s \)) can be derived. A cryogenic setup attached to the sample permits low temperature measurements.

The temperature dependent measurements can be done by two different means called zero-field-cooled (ZFC) and field-cooled (FC) magnetization techniques. Zero field cooled measurements provide a means of investigating various magnetic interactions. In ZFC mode, a
sample is cooled to liquid helium temperatures under zero applied magnetic fields. Then, small uniform external field is applied and the net magnetization is measured, while heating the sample at a constant rate. For small magnetic particles, this curve has a characteristics shape. As the particle cools in a zero applied magnetic field, they will tend to magnetize along the preferred crystal directions in the lattice, thus minimizing the magnetocrystalline energy. Since the orientation of each crystallite varies, the net moment of the system will be zero. Even when a small external field is applied, the moments will remain locked into the preferred crystal directions, as seen in the low temperature portion of the ZFC curve. As the temperature increases, more thermal energy is available to disturb the system. Therefore, more moments will align with the external field direction in order to minimize the Zeeman energy term. In other words, thermal vibration is providing the activation energy required for the Zeeman interaction. Eventually, the net moment of the system reaches a maximum, where the greatest population of moments has aligned with the external field. The peak temperature is called blocking temperature ($T_B$), which depends on particle volume. As temperature rises above $T_B$, thermal vibrations become strong enough to overcome the Zeeman interaction and thus randomize the moments [231].

Field cooled measurements proceed in a similar manner to ZFC, except that the constant external field is applied while cooling and heating. The net moment is usually measured while heating. However, the FC curve will diverge from the ZFC curve at a point near the blocking temperature. This divergence occurs because the spins from each particle will tend to align with the easy crystalline axis that is closest to the applied field direction and remain frozen in that direction at low temperature. Thermal remanent magnetization (TRM) curves are obtained by field cooling to the measurement start
temperature. The field is then removed and the magnetization is recorded as a function of temperature, while the sample is heated. It is important to note that ZFC, FC and TRM are nonequilibrium measurements [232].

The magnetic measurements of the present samples were carried out using Lakeshore vibrating sample magnetometer 7410 and Oxford Instruments model vibrating sample magnetometer. FC-ZFC modes of the VSM were employed for the measurements. In the ZFC mode, the sample was cooled in the absence of a field and the magnetization was measured during warming, by applying a nominal field of 200 Oe. In the FC mode, the sample was cooled in presence of a field and the magnetization was measured during warming, under the field of 200 Oe. Hysteresis loops were recorded at different temperatures.

1.11.9 Z-scan technique

Z-scan is a very commonly used experimental configuration to investigate the nonlinear optical properties of various materials. This is proposed as a technique with complete theory by Sheik Bahea et al. in 1990 [233, 234]. The technique is based on the principle of spatial beam distortion, but offers simplicity as well as high sensitivity comparable to interferometric methods. When a high irradiance laser beam propagates through any nonlinear material, photoinduced refractive index variations may lead to self-focusing of the beam. The propagation of laser beam inside such a material and the ensuing self-refraction can be studied using the Z-scan technique. It enables one to determine the nonlinear properties of solids, ordinary liquids and liquid crystals. The experimental set up for single beam Z-scan technique is given in Figure 1.4.
In the single beam configuration, the transmittance of the sample is measured as the sample is moved along the propagation direction of a focused Gaussian beam. A laser beam propagating through a nonlinear medium will experience both amplitude and phase variations. If transmitted light is measured through an aperture placed in the far field with respect to focal region, the technique is called closed aperture Z-scan [233, 234]. In this case, the transmitted light is sensitive to both nonlinear absorption and nonlinear refraction. In a closed aperture Z-scan experiment, phase distortion suffered by the beam while propagating through the nonlinear medium is converted into corresponding amplitude variations. On the other hand, if transmitted light is measured without an aperture, the mode of measurement is referred to as open aperture Z-scan [234]. In this case, the throughput is sensitive only to nonlinear absorption. Closed and open aperture Z-scan graphs are always normalized to linear transmittance i.e., transmittance at large values of $|Z|$. Closed and open aperture Z-scan methods yield the real and imaginary part of nonlinear susceptibility, respectively. Usually closed aperture Z-scan data is divided by open aperture data to cancel the effect of nonlinear absorption contained in the closed aperture measurements.
The new graph, called divided Z-scan contains information on nonlinear refraction alone.

In a Z-scan measurement, it is assumed that the sample thickness is much less than Rayleigh’s range $z_0$ (diffraction length of the beam), defined as $z_0 = k \omega_0^2 / 2$, where $k$ is the wave vector and $\omega_0$ is the beam waist radius given by, $\omega_0 = \frac{f \lambda}{D}$, where $f$ is the focal length of the lens used, $\lambda$ is the wavelength of the source and $D$ is the beam radius at the lens. Z-scan technique is highly sensitive to the profile of the beam and also to the thickness of the sample. Any deviation from Gaussian profile of the beam and also from thin sample approximation will give rise to erroneous results. For ensuring that the beam profile does not vary appreciably inside the sample, the sample thickness should always be kept less than the Rayleigh’s range.

Large nonlinearities in materials are commonly associated with a resonant transition that may be of single or multiphoton nature. The nonlinear absorption of such materials is manifested in the open aperture Z-scan measurements. For example, if nonlinear absorption like two photon absorption (TPA) is present, it is manifested in the measurements as a transmission minimum at the focal point [235]. On the other hand, if the sample is a saturable absorber, transmission increases with increase in incident intensity and results in a transmission maximum at the focal region [235]. The coefficients of nonlinear absorption can be easily calculated from such transmittance curves.

In the present investigation, open aperture Z-scan technique is employed to measure the nonlinear absorption in the sample. A more detailed description of the experimental set up is given in Chapter 4.
1.11.10 Magnetoelectric coupling

The magnetoelectric effect is usually described mathematically by the linear magnetoelectric coupling coefficient ($\alpha$), which is the dominant coupling term in a nonlinear coupling expression. There are basically three direct methods to measure ME effect, namely: static, quasi-static and dynamic method. In the static method, the ME signals is measured as a function of increasing magnetic field using a high input impedance electrometer. While poling and measuring, the space charges may built-up at electrodes, which could lead to erroneous results [236]. For the quasi-static case, the ME signals is measured as a function of time using a high input impedance electrometer, while the applied dc magnetic field is varied with time [237]. However, this quasi-static method cannot solve the problem of charge accumulation, especially for polycrystalline samples. Recently, a dynamic technique has been developed to study ME effect [238]. The dynamic method is similar to quasi-static method, but ac-magnetic field was superimposed over time varying dc-magnetic field. The bias of ac-magnetic field is employed for not to allow the charges to built up at the electrodes.

The philosophy of the dynamic technique is to measure the effective value of the small ac ME voltage ($V_{out}$) appeared across the sample when applying a small ac magnetic field instead of measuring the ME charge or voltage as in the static method. This method also allows one to measure the phase shift of the signal. However, this phase shift is approximately constant during varying the bias field measurements. By changing the dc magnetic bias field, one can explore the ME effect at different working points of the sample. By changing the frequency of the ac field, one can study the response of
the sample under different time scales. Since the ME signal in this method has a well-defined frequency (determined by the driving current) and is measured by a lock-in amplifier, the noise is dramatically reduced and the problem of charge accumulation is avoided. These are the advantages of this method. However, due to the assumption that the ac field is much smaller than the dc one, this method will give information about the ME effect at low-ac magnetic field, but at different working points of the magnetostrictive component. Since an ac magnetic field is employed, an induction voltage always exists, contributing as zero signals. To avoid it, the lock-in amplifier has to work in differential mode to subtract the common-mode induction contribution. Using this mode, not only the zero-signal problem is solved, but also the calibration is not needed, since with good cable (well shielded, low capacity) and good connection, the ME signal is zero without sample or with a non-ME samples.

In the present investigation, the dynamic lock-in technique is used to measure the room temperature magnetoelectric effect across the sample. Figure 1.5 shows the schematic diagram of the experimental set up used to measure the magnetoelectric effect using dynamic lock-in technique. The dc magnetic bias field up to 5 kOe is produced by an electromagnet (EM). The measurements were done with superimposed small amplitude of ac magnetic fields generated by Helmholtz coils (HC). The sine output of the internal function generator of a lock-in amplifier was given to a power amplifier (PA) and the amplified current fed the Helmholtz coils, which provides ac magnetic fields. The ac magnetic field at the center of the Helmholtz coils was monitored using Hall probe (HP) with Gauss meter (GM). In addition, the strength of the magnetic field was estimated by measuring the ac voltage developed across a standard resistor.
connected in series with the Helmholtz coils using a digital multimeter.

Figure 1.5 Schematic diagram of the experimental set up to measure the magnetoelectric coefficient using dynamic lock-in technique: where SMU - source measure unit, PA - power amplifier, HC - Helmholtz coil, EM - electromagnet, HP\textsubscript{ac} - HP\textsubscript{dc} and GM\textsubscript{ac} - GM\textsubscript{dc} are the Hall probes and Gauss meters for ac and dc magnetic fields, respectively [240].

The sample is placed in the magnetic field with its surface perpendicular or parallel to the field direction, according to the longitudinal and transverse measurement, respectively. Both ac and dc magnetic fields were kept parallel to the direction of polarization (longitudinal mode). The reorientation of the electrical dipoles in the sample by an ac magnetic field induces an ac voltage on the top and bottom surfaces of the sample through magnetoelectric coupling, which was measured using the lock-in amplifier in the differential mode to eliminate the errors due to Faraday induction. The ME coefficient, $\alpha_{ME}$ can be calculated using the relation, $\alpha_{ME} = \frac{dE}{dH} = \frac{1}{t} \frac{dV}{dH} = \frac{V_{out}}{H_{0} t}$, where $V_{out}$ is the ac magnetoelectric voltage appearing across the
sample surface (measured by the lock-in), $h_0$ is the amplitude of the ac magnetic field and $t$ is the thickness of the sample [239, 240].

References

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