Chapter 6
Conclusions and Future Prospects

The development of a multiferroic material, which has magnetoelectric properties i.e., ferroelectricity and ferromagnetism in the same phase at useful temperatures and a coupling between them, will be a milestone for the modern technology. Till date, there is only a few materials, which has magnetoelectric properties in the same phase at practically useful temperatures. Thus, the advances in applications and fabrication technologies in the recent years have not been impressive. The field of multiferroics can make significant strides towards room temperature functionality, if additional attention is given to utilizing the current materials and technologies widely used in the field today. In this thesis, the focus has been given to single-phase multiferroics, $\text{YCrO}_3$ and $\text{YCr}_{0.5}\text{Fe}_{0.5}\text{O}_3$. The present investigations brought out the potential of $\text{YCrO}_3$ and $\text{YCr}_{0.5}\text{Fe}_{0.5}\text{O}_3$ as multifunctional materials, with a variety of exciting functional properties.

One aspect of fundamental interest to the study of multiferroics is the production of high quality samples of such materials for detailed study. In the present work, the sol-gel method using PAA as the chelating agent is found to be an effective method for the synthesis of single-phase $\text{YCrO}_3$ nanoparticles, with an average particle size of about 15 nm at a temperature as low as 400°C. Compared with the previous works, this formation temperature is the lowest for
producing phase-pure YCrO$_3$. A remarkable control over the size, chemical homogeneity, agglomeration and stoichiometry of the nanoparticle is the most versatile advantage of this method. It is expected that this synthesis route may be extended to the synthesis of a variety of mixed oxide systems in nano regime.

YCrO$_3$ nanoparticles, with particle size in the range 15-38 nm as well as the bulk samples, exhibited a weak ferromagnetism below 140 K ($T_N$) and a ferroelectric transition at 471±1 K ($T_C$), thus confirming the multiferroic nature of the samples. From this, it is evident that the biferroic properties of YCrO$_3$ were retained in their nanoparticles form, within the range of our investigation. However, particle size is found to have a significant effect on dielectric constant, dielectric loss, conductivity and magnetization of the samples. No changes were observed in the transition temperatures, while the dielectric constant, dielectric loss, conductivity and magnetization of the samples were found to be enhanced with reduction in particle size. Microstructure is found to play a dominant role in determining the electrical properties of the samples.

A highlight of the present investigation is the presence of exchange bias effects in YCrO$_3$ samples, with average particle size of 15 and 22 nm, which is increasing with the decrease in particle size due to the increase in anisotropy. Exchange bias effect is technologically important for actual applications in magnetic recordable media, nonvolatile magnetic random access memories and other spintronic devices.

Another important finding of the present work is the discovery of a novel functionality for the ferroelectric-antiferromagnet YCrO$_3$ powder of optical limiting upon illumination by nanosecond (ns) laser pulses at 532 nm and femtosecond (fs) laser pulses at 800 nm. All the samples, with particle size in the range 15–200 nm, showed
strong optical limiting at both fs and ns timescales, so its action is truly broadband, useful for device applications. This opens up several new possibilities for device applications, exploiting the features of ferroelectricity, ferromagnetism and optical nonlinearity. The obtained nonlinearity fits to a three-photon like absorption process in the ns excitation domains and a two-photon like absorption process in the fs excitation domains. However, two-photon absorption followed by excited state absorption is found to be the major mechanism that contributes to the limiting in the ns timescales. Thus, a stronger limiting response is obtained with the longer ns pulses in comparison with the fs pulses. Particle size is found to have a crucial effect on the limiting performance of the samples and thus, providing a means to engineer its performance. The optical limiting response does not increase monotonously with size of particle. The optimal size of YCrO$_3$ for better limiting performance is found to be 64 nm in the present investigation.

We have tuned the ferroic transition temperatures of YCrO$_3$ in the more accessible temperature range by making a solid solution of YCrO$_3$ and YFeO$_3$ and thereby, reducing the wide difference in transition temperatures (T$_C$/T$_N$). Sol-gel synthesized, single-phase YCr$_{0.5}$Fe$_{0.5}$O$_3$ nanoparticles, with an average particle size of about 20 nm exhibited a weak ferromagnetism below 280 K (T$_N$) and a ferroelectric transition at 346 K (T$_C$), confirming the multiferroic nature of the samples. The ferroelectric and magnetic transition temperature is found to be enhanced, when compared to YCrO$_3$ nanoparticles, prepared under identical conditions. Further, temperature induced magnetization reversal is observed. The sign reversal of magnetization can be applied for NMRAM and magnetic cooling/heating based constant temperature bath.
Another striking observation is the presence of exchange bias effects in YCr$_{0.5}$Fe$_{0.5}$O$_3$. Combining EB effect with magnetization reversal can exploit potential applications in spintronic devices with enhanced functionalities. Further, it displayed a strong magnetoelectric coupling effect at room temperature. Upon Fe substitution, we could thus reduce some inherent problems of YCrO$_3$, such as absence of magneto electric coupling, high dielectric loss and wide difference in transition temperatures.

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. The discovery of a new functionality of optical limiting and exchange bias effect in YCrO$_3$ shows that the potential of this material is nowhere near exhausted and leave a plenty of room for further discoveries. Thus, the present work is opening up a lot of new possibilities of technological applications.

Future scope of these investigations is related with the fabrication of these materials compatible for advanced applications. The discovery of a truly multiferroic single-phase material with room temperature functionality will be very useful towards a multiferroic device fabrication.

The optical limiting properties observed for YCrO$_3$ is ideal for the fabrication of efficient optical limiters in sensor protection applications. From a material point of view, it is advantageous to embed the samples in thin polymer films for optical and nonlinear applications. The polymer matrix serves not only as a medium to assemble the nanoparticles and stabilize them against aggregation, but also with its characteristic mechanical properties, is uniquely suited for device applications, as compared to samples dispersed in a solution. Highly transparent, monodispersed and freestanding films
of the composite could be obtained using spin coating technique and the fabrication of such films would be a significant development from the point of view of device applications.

Control of the optical nonlinear properties by means of an external stimulus, such as magnetic and/or electric field presents remarkable applications. The samples investigated in the present thesis are attractive in this regard. For instance, upon the application of the magnetic field, a drastic change in the SHG intensity has been observed in YCrO$_3$ crystals. Moreover, field induced spin reorientation have been observed in YCrO$_3$ by means of spectral changes of R-exciton lines corresponding to the $^4A_{2g} -^2E_g$ transition of Cr$^{3+}$. Thus, it will be interesting and essential to explore the optical limiting properties of the samples in the presence of an external field. In a typical device application, such control can turn out to be very useful.

The availability of high-quality thin-film multiferroics makes it easier to tailor their properties through epitaxial strain, atomic-level engineering of chemistry and interfacial coupling and is a prerequisite for their incorporation into practical devices. Thus, the fabrication of thin films of the present samples is imperative. Of the several growth techniques available, pulsed laser deposition stands far ahead than any other technique by virtue of its stoichiometry maintaining nature in the film as that of the target and non-equilibrium nature of its interaction with the target. The temperature dependence of the coercivity near the compensation point can be applied to writing and erasing in high-density magneto-optical recording media. By using films with compensation temperature, it is possible to attain a direct overwrite capability in magneto-optic thin films.
The multifunctional properties of the magnetoelectric materials (ferroelectric or ferromagnetic properties) are known to be tunable by introducing some defects. The swift heavy ion (SHI) irradiation is known to create the controlled defects in the materials, depending on the choice of ion and its energy. Moreover, SHI has been proved a good source to produce a wide variety of defects, which can create structural strain and disorder in oxide materials, responsible for modifying the physical properties of materials. Further, the interest in the swift heavy ion irradiation on oxides is, because of the effect of irradiation on the superexchange interactions, which are highly sensitive to any disorder in such materials. Thus, an analysis of the effect of SHI irradiation on the structural, electrical, magnetic and magnetoelectric properties is necessary for engineering multiferroic properties of materials.