Chapter 3

CHARACTERIZATION TECHNIQUES

Abstract

The experimental techniques for the characterization of the grown crystals employed in the present work include X-ray analysis, Fourier Transform-Infrared spectroscopy, TG/DTA techniques, DSC, elemental analysis using (Inductively Coupled Plasma Atomic Emission Spectrometer (ICP – AES), and EDAX), electric conductivity using Impedance Analyzer Hewlett Packard (Japan) HP 4192A, Field dependence of dark and photo currents, microhardness measurements using Vickers microhardness tester and the dielectric properties of the crystals at microwave frequency by the cavity perturbation technique using a transmission type S-band rectangular wave-guide cavity resonator, HP 8510 C network analyzer and an interfacing computer. A brief description of the principles involved in these measurements is presented in this chapter.
3.1 INTRODUCTION

The growth kinetics of rare-earth mixed oxalate crystals is very important, in the contest of technological applications. These studies reveal the perfection of the crystals, influence of the methods on the growth of crystals and identification of the grown crystals. Study of the crystal habit forms an important part as it influences the physical properties.

Some of the experimental methods of characterization employed in the present work include X-ray analysis, Fourier Transform-InfraRed spectroscopy, TG/DTA techniques, DSC and elemental analysis using Inductively Coupled Plasma Atomic Emission Spectrometer (ICP –AES) and EDAX. The Impedance Analyzer Hewlett Packard (Japan) HP 4192A was used to study the electric property of the crystals. Microhardness of the crystals were tested using Vickers microhardness tester and the dielectric properties of the crystals at microwave frequency were studied by the cavity perturbation technique using a transmission type S- band rectangular wave-guide cavity resonator, HP 8510 C network analyzer and an interfacing computer. A brief description of the principles involved in these measurements is presented in this chapter.
3.2  X-RAY DIFFRACTOMETRY

The identity test of a crystal starts with the X-ray diffraction studies. X-ray diffraction provides an efficient and practical method for the structural characterization of crystals\textsuperscript{1,2}. It helps in determining the arrangement and the spacing of atoms in a crystalline material. The basic X-ray diffractometer consists of an X-ray tube generating the necessary radiation; a collimator to prevent the scattering of the beam; a sample holder in which the specimen is held or oriented; a goniometer on which a filter system and detector are mounted and rotated around the specimen and detector for measuring intensity of the diffracted X-rays. The relation between the wavelength ‘λ’ of the X-ray beam, the angle of diffraction ‘θ’ and the distance ‘d’ between the atomic planes of the crystal is given by the Bragg’s equation\textsuperscript{3}.

\[ 2d \sin \theta = n \lambda \]  \hspace{1cm} (3.1)

where ‘n’ represents the order of diffraction. In powdered diffraction method the crystal sample is in a finely powdered form, in which small crystals are oriented in every possible direction. When the X-ray penetrates through the material, a number of particles can be expected to be oriented in such a way as to fulfill the Bragg’s condition for reflection from every possible inter planar spacing.
In this work a fully computerized Bruker AXS D8 Advance X-ray diffractometer (Fig. 3.1) has been employed for the X-ray powder diffraction studies. This is a versatile, sensitive and high resolution X-ray diffractometer. It is equipped with a vertical theta-theta goniometer, variable width slits, a monochromator of the diffracted beam, 2.2 KW Cu- X-ray sources, a scintillator detector, and an automatic sample changer with nine slots. The collimated beam is directed on the sample.

**Fig 3.1:** Bruker AXS D8 Advance X-ray Diffractometer

The sample is held in the sample holder placed on a wide range goniometer. The goniometer rotates the sample to increase the randomness of the orientation of the crystals. The scanning speed of the specimen is fixed at 30°/s. The intensity of the diffracted beam against’
‘20’ values is recorded. The computer records the diffraction patterns obtained by automatic scanning. The lattice parameters of the crystals were determined by the analysis of this readings using software.

3.3 FOURIER TRANSFORM INFRA RED SPECTROSCOPY

This technique is one of the most important and widely used spectroscopic techniques of analyzing quantitatively the structural units of the unknown compounds. It helps to identify the functional units, internal structure of the molecules and nature of the chemical bonds of a compound. Absorption of infrared radiations is confined largely to molecular species for which small energy differences exist between various vibrational and rotational states. When the frequency of the incident radiation coincides with the vibrational frequency of the molecule, resonance occurs and absorption of energy takes place. When the molecules return from the excited state to the ground state the absorbed energy is released resulting in distinct peaks in the IR spectrum. Thus IR absorption bands reveal the state of the molecules present in the sample. IR spectroscopy is classified into three regions of the electromagnetic spectrum.

a) NIR (Near IR) (12000 -4000) cm$^{-1}$

b) MIR (Mid IR) (4000 -200) cm$^{-1}$

c) FIR (Far IR) (200 -10) cm$^{-1}$
The Mid IR ranges encompasses a vast amount of analytical applications. It provides a unique fingerprint of the molecules, which can be clearly distinguished from the absorption patterns of other vibrations. Conventionally there are two methods adopted for recording IR spectrum of the solid sample, one is the mull method and the other is KBr pellet method. The powdered sample is dispersed in the mulling agent made of ‘metal oil’ (nugol) and the slurry thus formed is placed in the spectrometer. The KBr pellet method is more popular and has several advantages over the mull method, such as low scattering loss, higher spectral resolution, the homogeneity of the sample etc. In this study the KBr pellet method was used to record the IR spectra of the oxalate crystals of Rare Earths. The weight of the sample required for the analysis is about 5 gm.

Thermo Nicolate Avator 370 spectrometer (Fig 3.2) was employed to obtain infrared absorption spectrum using KBr pellet method. It consists of a source of IR radiation and a sensitive transducer. All absorption bands in the range 400cm\(^{-1}\) to 4000cm\(^{-1}\) can be recorded in the instrument with high resolution.

In Fourier Transform IR spectroscopy, the infrared radiation is analyzed by means of a scanning interferometer instead of a monochromator. The IR wavelength is split into two beams. After
reflection the two beams recombine at the splitter and constructive and destructive interference takes place for any particular wavelength depending on the optical path. The resulting interferogram containing all the information is reconstructed into the spectrum with the help of the mathematical programming called Fourier Transformation.

![Fig. 3.2 Thermo Nicolate Avator 370 spectrometer](image)

3.4 THERMAL ANALYSIS – TG/DTA

Thermal methods are based upon the measurement of the dynamic relationship between temperature and some property of a system such as mass, heat of reaction or volume. Of the various thermal methods, thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) are most important.
In thermogravimetric analysis, the mass of the sample is recorded continuously as a function of temperature as it is heated or cooled at a controlled rate\textsuperscript{10, 11}. A plot of mass as a function of temperature (thermogram) provides both qualitative and quantitative information. The apparatus required for thermogravimetric analysis includes a sensitive recording analytical balance; a furnace; a furnace temperature controller, programmer and a recorder that provides a plot of sample mass as a function of temperature. Often an auxiliary equipment to provide an inert atmosphere for the sample is also needed. Change in the mass of the sample occur as a result of the rupture or formation of various physical and chemical bonds at elevated temperature that led to the evolution of volatile products or formation of reaction products. Thus the TGA curve gives information regarding the thermodynamics and kinetics of various chemical reactions, reaction mechanisms, intermediate and final products.

In differential thermal analysis (DTA) the heat absorbed or emitted by a chemical system is observed by measuring the temperature difference between the system and an inert reference compound- such as alumina, silicon carbide or glass beads. As the temperature of both are increased at a constant rate\textsuperscript{12}, the corresponding deviation of the sample temperature from that of the reference ($\Delta T$) versus the programmed temperature ($T$) is
recorded and it explains whether the transition is endothermic or exothermic. The DTA studies along with TGA provide detailed information regarding the dehydration, decomposition and the phase transitions of a material during heating.

The thermal characteristics of the grown crystals were studied using Perkin Elmer, Diamond TG/DTA (Fig. 3.3). The temperature range selected for the present study was from ambient temperature to 1200°C.

![Fig. 3.3 Perkin Elmer, Diamond TG/DTA](image)

### 3.5 THERMAL ANALYSIS – DSC

Differential Scanning Calorimetry (DSC) is a thermoanalytical technique in which the difference in the amount of heat required to increase
the temperature of a sample and reference are measured as a function of temperature. Both the sample and the reference are maintained at very nearly the same temperature throughout the experiment. Generally the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will need to flow to it than the reference to maintain both at the same temperature. Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic. As the sample undergoes exothermic process less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and the reference, Differential Scanning Calorimeters are able to measure the amount of energy absorbed or released during such transitions.

DSC curves of the crystals under study were recorded by using Mettler Toledo DSC 822 e (Fig. 3.4). Its temperature range is from -150°C to maximum 700°C. The weight of the sample required for the analysis is about 10-50 mg.
ELEMENTAL ANALYSIS USING INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETER (ICP –AES)

The atomic spectrum emitted by a sample is used to determine its elemental composition in this instrument. The wavelength at which emission occurs identifies the element, while the intensity of the emitted radiation quantifies its concentration.
In the present study (Fig. 3.5) was used to identify the elements. It is a flexible axial and radial view instrument, with high concentration capabilities. Powerful TEVA Software, CID Detector, Microwave Digestor for sample digestion and 5 – 10 ml of aqueous solution of the samples are needed for the identification of the elements.

3.7 MICROHARDNESS MEASUREMENTS

To study the microhardness property of crystals the indentation technique has been employed. A Vickers micro hardness tester is employed for this purpose. The specimen (grown crystals) to be indented is mounted on a platform and a most planar region is selected by viewing through a microscope. The indenter button is pressed during which a red light glows till the end of indenting. The indenting time is 10 seconds. After the completion of indentation, a yellow lamp glows. The position of the indenter is observed through the microscope and the measurements are taken.

The diagonal length of such indentation marks are measured and the Vickers hardness numerical (VHN) is calculated using the formula

\[
VHN = \frac{2P \sin \frac{\theta}{2}}{d^2} \frac{\text{Kg}}{\text{mm}^2}
\]

\[\ldots\ldots\ldots(3.2)\]
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where \( P \) is the load applied in units of kilogram weight, \( \theta \) is the angle between the opposite faces of the indenter and \( d \) is the average diagonal length in mm.

For \( \theta = 136^\circ \) as in the case with Vickers Pyramidal indenter, the formula is

\[
VHN = \frac{1.854 \times P}{d^2} \text{ Kg mm}^2
\]

\[ \cdots \cdots (3.3) \]

3.8 ELECTRICAL CONDUCTIVITY MEASUREMENTS USING IMPEDANCE ANALYZER

Dielectric constants, dielectric loss and the electrical conductivity of the grown samples were determined by using HP 4192A Impedance Analyzer.

The HP 4192A Impedance Analyzer (Fig. 3.6) performs both network analysis and impedance analysis on devices such as telecommunications filters, audio/video electronic circuits, and basic electronic components. The HP 4192A can measure 11 impedance parameters (|\( Z \)|, |\( Y \)|, \( \theta \), \( R \), \( X \), \( G \), \( B \), \( L \), \( C \), \( D \), \( Q \)) over a wide range |\( Z \)|: .1 m\( \Omega \) to 1 m\( \Omega \); |\( Y \)|: 1 nS to 10 S

The built-in frequency synthesizer can be set from 5Hz to 13 MHz with a maximum resolution of 1 mHz. This feature allows accurate characterization of high Q devices such as crystals. Test signal level is
variable from 5 mV to 1.1V with 1 mV resolution. Also, an internal dc bias voltage source provides ± 35V at 10mV increments.

Fig. 3.6. HP4192A Impedance Analyzer

Measurements of dielectric constants and dielectric loss were done directly from the Analyzer itself. Electric conductivity of the pellet samples of the crystals were calculated using the formula

\[ \sigma = 2\pi f \varepsilon_0 \varepsilon_r \tan\delta \]  

where \( \sigma \) is the electrical conductivity, \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon_r \) is the dielectric constants of the samples and \( \tan\delta \) is the dielectric loss of the samples respectively.
3.9 PHOTOCONDUCTIVITY

Photoconductivity refers to the difference of electrical conductivity of a device with and without illumination. Measurement of photoconductivity consists of I-V measurements conducted under dark and illumination.

Photoconductivity measurements were carried out on the pellet samples of the rare earth oxalate crystals by fixing it onto a microscope slide. The sample was connected in series with a DC power supply and KEITHLEY123 Pico ammeter. The sample was covered with a black cloth and the voltage applied was increased from 0 to 5 volts. The dark current is recorded. The sample was illuminated by the radiation from 100 mW halogen lamp containing iodine vapour and tungsten filament. The photocurrent was recorded for the same values of the applied voltage. Field dependence of dark and photocurrents were plotted.

3.10 MICROWAVE DIELECTRIC STUDIES

The dielectric properties of rare earth mixed oxalate crystals had been studied by the cavity perturbation technique at microwave frequency. Using such a technique, a rectangular wave-guide resonator in the S-band is used to measure the dielectric constant of solid-state materials.
The experimental set up consists of a transmission type S-band rectangular wave-guide cavity resonator, HP 8510C network analyzer and an interfacing computer. Cavity perturbation technique is employed for the study. Closed section of a wave-guide constitutes a cavity resonator. Electromagnetic energy is coupled to the cavity through coupling incises at the ends of the cavity. A non-radiating slot is provided at the broad wall of the cavity for the introduction of the sample. On exciting the cavity resonator in the TE$_{10p}$ mode, the cavity resonates at different frequencies depending on its dimensions. The basic principle involved in this technique is that the field within the cavity resonator is perturbed by the introduction of the dielectric sample. The resonant frequency and the quality factor of the cavity get shifted due to perturbation.

The complex frequency shift is related to the quality factor as

$$\frac{d\Omega}{\Omega} = \frac{d\omega}{\omega} + \frac{f}{2} \left( \frac{1}{Q_s} - \frac{1}{Q_0} \right)$$

…………(3.5)

where $Q_s$, $Q_0$ are the quality factors of cavity resonator with and without the sample.

Quality factor $Q$ is given by, $Q = \frac{f}{\Delta f}$
where ‘f’ is the resonant frequency and ‘Δf’ the corresponding 3dB bandwidth.

The real part $\varepsilon_r'$, of the complex permittivity is usually known as dielectric constant. The imaginary part $\varepsilon_r''$, of the complex permittivity is associated with dielectric loss of the material.

$$\varepsilon_r' = 1 + \frac{f_0 - f_s}{2f_s} \left( \frac{V_0}{V_s} \right)$$

$$\varepsilon_r'' = \frac{V_0}{4V_s} \left( \frac{Q_0 - Q_s}{Q_0 Q_s} \right)$$ ………..(3.6) ………..(3.7)

The effective conductivity $\sigma$ is given by

$$\sigma = \omega \varepsilon'' = 2\pi f_0 \varepsilon_r''$$

The dielectric loss of a material will be usually expressed by a term loss tangent or tan $\delta$.

$$\tan \delta = \frac{\varepsilon_r''}{\varepsilon_r'}$$ ………..(3.8)

Using the above relations, the real part $\varepsilon_r'$ of the complex permittivity, imaginary part $\varepsilon_r''$, of the complex permittivity, the effective conductivity $\sigma$ and loss tangent ‘tan $\delta$’ of the samples were calculated.
3.11 ENERGY DISPERSIVE ANALYSIS BY X-RAYS (EDAX)

Energy dispersive analysis by X-rays is an analytic technique used to determine the chemical composition of a material. When a beam of electrons strike a specimen, a fraction of the incident electrons excite the atoms of the specimen, which then emit X-rays when they return to their ground state. The energy of these X-rays is strictly related to the atomic number of the elements excited and therefore their detection forms the basis of elemental analysis in the electron microscope.

An energy dispersive spectrometer consists of a polychromatic source, a sample holder and a detector. The crystals were mounted on the holder, the surfaces of which are coated with a thin layer of gold to make them electrically conductive. The surfaces are examined in the EDAX analyzer. A lithium drifted silicon p-i-n diode held at liquid nitrogen temperature is used as the detector of the emitted X-rays. A beryllium window covers the cooled detector. The output pulses are stored in a multichannel analyzer. In the multichannel energy dispersive instrument, all of the emitted X-ray lines are measured simultaneously. This method is a non-destructive one and can detect all elements having atomic number greater than eleven\textsuperscript{14}. In the present study the EDAX analysis of the samples had been carried out using a link AM 10000 instruments.
3.12 REFERENCES


