PREFACE

The modern technological developments mainly depend on the technologically important 'SMART' materials. In this regard the crystals having specific properties can be treated as the backbone of today's technological development. This led the investigators and scientists to concentrate on the developments of new variety of defect-free crystals of high degree of purity. Earlier crystal growth techniques were considered an art rather than science. Theories are now available on the growth of crystals so that crystal growth is no more an art. A variety of experimental techniques are developed and modified to such a level as to grow tailor made crystals for specific applications.

This thesis reports the studies on the growth of mixed rare earth hydrogen selenite crystals and a detailed study of its physical properties. The rare earth compounds have attracted considerable attention on account of their outstanding electric, magnetic and optical properties. Among the rare earth compounds hydrogen selenite crystals were selected because of their promising technical applications in optics and magnetism. Beside this the lack of work on the growth of these group of materials prompted the initiation of this work. This is the first time rare earth hydrogen selenite is grown by gel technique.

The thesis entitled 'Studies on the growth of mixed rare earth hydrogen selenite crystals and its properties' is a comprehensive account of investigations on the growth of praseodymium neodymium hydrogen selenite (PNHS), praseodymium samarium hydrogen selenite (PSHS), neodymium samarium hydrogen selenite (NSHS) in hydrosilica gel and their detailed characterisation, mechanical and magnetic property studies. Besides these this thesis discuss the result obtained on the growth of mono as well as mixed rare earth crystals. In the property studies a special emphasis is given on mechanical and magnetic properties.

The first chapter gives a general introduction to the theories and techniques of crystal growth methods for the growth of various types of crystals. The hydrosilica gel

method is a suitable technique for the growth of rare earth hydrogen selenite crystals due to their low aqueous solubility and increased thermal degradation behaviour.
The subject of gel growth is introduced in chapter 2. The advantageous of gel technique over the other conventional technique in growing certain types of materials especially hydrogen selenites are described. A survey of the literature concerning the subject and the various innovations of the growth methods are given.

The various experimental techniques employed for the present studies are discussed in chapter.3. These includes optical microscopy, X-ray diffractometry, FT-IR spectroscopy, UV-Visible absorption and emission spectroscopy, energy dispersive X-ray analysis (EDAX), thermogravimetric analysis (TGA), differential thermal analysis (DTA), microhardness measurements and magnetic susceptibility measurement (vibration sample magnetometer-VSM) etc.

Growth kinetics of the crystals at different conditions are elaborately discussed in chapter. 4. A detailed study of the growth of PNHS, PSHS and NSHS crystals have been described. The experimental setup, chemical reactions involved and effects of the change in different parameters on growth mode are also discussed. The effect of various growth parameters like the pH, density and age of the gel and concentration of the reactants are studied for each crystal. Appreciable changes in the habit of the crystals, nucleation density, the advancement of the crystallising region in the medium etc. are attributed to the changes of these parameters. It is observed that the low density and low pH of the gel favours the growth of good quality single crystals. Even though the quality of the crystals is high its dimensions are found to be small. As the pH and density of the gel increases, the nucleation density lowers which in turn enhances the size of the crystals but with diminished quality. These observations have been described with necessary explanations.

Characterisation of the material is quite tedious and painstaking and it needs a large variety of instruments. Faces of the crystal usually give a lot of information about the growth condition since it is the last stage of its growth. Metallurgical microscope has been employed to study surface features and quality of the crystals. The crystals are generally monoclinic with characteristic layer structures. Occasionally

rectangular crystals are also obtained. Etching can be utilised as a powerful tool to reveal the condition of the surface. Etching showed row of rectangular pits, which are assigned, to dislocations pile-ups.

Characterisation of the grown crystals has been done using different techniques. Powder diffraction data gave the unit cell parameters and crystal class to which it belongs. The absorption and emission spectroscopy gave evidence for the presence of different rare earth ions in the crystal.

The FT-IR spectroscopy and TG-DTA studies throw light to the functional group and molecular (chemical) formula of the crystals. The thermal analysis results obtained are discussed and it confirms the molecular formula. The percentage of incorporation of different rare earth ions were determined by energy dispersive X-ray analysis (EDAX). Detailed informations are given in chapter.5.

Chapter.6 reports the microhardnesss studies of grown crystal. The microhardness of mixed crystals of different stoichiometric combinations of rare earths are measured with the Vickers microhardness tester. The variation of the microhardness with load has been explained.

The importance of the magnetic properties of the rare earth elements and its compounds, lead to the study of magnetic moment and magnetic susceptibility of the grown crystals. Chapter.7 deals with the magnetic properties of the crystals. Detailed studies on all grown hydrogen selenite crystals and variations of magnetic moment with applied field and variation of Bohr magneton with stoichiometric combination are measured with a vibrating sample magnetometer (VSM). A detailed study has been presented in this part.

The concluding part, Chapter. 8 of the thesis give a summary of the work and a bird's eye view of the possible direction of future research.

A major part of the work is published in international journals and presented in various seminars. The list of publications is appended.

Research papers published/communicated for publication

1. Growth and characterisation of samarium hydrogen selenite single crystals, Indian journal of pure and Applied physics, Vol. 36, June 1998, pp. 319-321

2. Thermal decomposition studies of mixed rare earth hydrogen selenite crystal, Journal of thermal analysis. (accepted)

3. Magnetic moment and susceptibility measurement studies of double rare earth hydrogen selenite crystals, The journal of magnetism and magnetic materials (in press)

4. Vickers micro-indentation studies of some single rare earth hydrogen selenite single crystals(Crystal research technology- Communicated)

5. Growth characterisation and property studies of praseodymium samarium hydrogen selenite crystals(Indian journal of physics-Communicated)

6. Microhardness measurement studies of mixed rare earth hydrogen selenite crystals grown under ambient condition.(Journal of material sciences-Communicated)

Papers presented in Seminars and Conferences

1. Synthesis and characterisation of neodymium samarium selenite crystals in hydrosilica gel, proceedings of Seventh national seminar on crystal growth 6-8 Jan, 1997, Crystal research centre, Alagappa University, Karaikudy-630 003

2. Growth and fluorescence study of neodymium praseodymium selenite crystals, proceedings of National Laser Symposium 1997, 6-8 Feb 1997, CAT, Indore

3. Growth and characterisation of neodymium hydrogen selenite crystals, proceedings of XXVIII National seminar on crystallography September 24-26 1997, Mahatma Gandhi University, Kottaym.

4. Growth study of neodymium praseodymium hydrogen selenite crystals, proceedings of National conference on Advances in Condensed matter physics, Feb 26-28, 1998 Pondicherry University, Pondicherry.

5. Fluorescence study of praseodymium samarium selenite crystals grown under ambient conditions, proceedings of National laser symposium, December 14-16, 1998, IIT Kanpur.

6. Magnetic moment and susceptibility measurement studies of praseodymium neodymium hydrogen selenite crystals, proceedings of DAE- Solid state physics symposium-1998, Dec 27-31 1998, Kurukshetra University, Kurukshetra, Haryana.

7. Growth and magnetic property studies of praseodymium hydrogen selenite crystals VIIIth National seminar on crystal growth, 3-5, February 1999, Crystal growth centre, Anna University, Chennai 600 025.