PREFACE

Crystal growth is a vital and fundamental area of material science and engineering, since crystals of suitable size and perfection are required for fundamental data acquisition and for other millions of applications. These days, the synthetic growth of crystals is an important part of the modern world. The present boom in IT depends on semiconductor crystals. The list of the uses of crystals is endless.

Crystal growth occurs from the addition of new atoms, ions, or polymer strings into the characteristic arrangement, or lattice, of a crystal. This happens in two stages: nucleation and growth. In the first stage, a small nucleus containing the newly forming crystal is created. Nucleation occurs relatively slowly as the initial crystal components must "bump" into each other in the correct orientation and placement for them to adhere and form the crystal. After crystal nucleation, the second stage—growth rapidly proceeds. Crystal growth spreads outwards from the nucleating site. In this faster process, the elements which form the motif add to the growing crystal in a prearranged system, the crystal lattice, started in crystal nucleation.

This thesis entitled “Growth and characterization of certain pure and doped phosphate crystals” presents a detailed account of the growth of the pure crystals namely, calcium hydrogen phosphate, barium hydrogen phosphate and strontium hydrogen phosphate in hydro silica gel and doped with neodymium. The grown crystals were characterized by different techniques. The influence of various parameters like gel pH, gel density, gel aging, concentration of reactants etc. on growth and morphology of these crystals were also investigated.

The thesis is divided into seven chapters. Chapter 1 deals with theories of nucleation, kinetics of crystal growth and various growth methods. Chapter 2 is divided into two parts. The first part describes the art and
science of growing crystals in gel medium in detail. The advantages of
gel method over other growth methods are discussed. It introduces
phosphate crystals and the importance of neodymium doping. The
second part consists of the various techniques used for characterization
and are discussed in detail. The characterization techniques employed
are X-ray powder diffraction analysis, Fourier Transform Infra Red
Spectroscopy, Thermal analysis, Energy Dispersive Spectrum Analysis,
X-Ray Fluorescence Spectroscopy, Optical Microscopy, Scanning
Electron Microscopy, UV-Visible Spectroscopy and Microwave Dielectric
studies. Thermal analysis includes TGA, DTA, DTG and DSC.

Chapter 3 discuss the growth of pure and neodymium doped calcium
hydrogen phosphate single crystals. The characterization includes
XRD, FTIR, Thermal analysis, XRF and EDS The optimum conditions
for the growth of good quality single crystals were found out. The
nature of the crystals was found to vary from micro crystals to well
faceted platelet and acicular crystals of average dimension
20mmx7mmx1mm.

Chapter 4 gives the discussion of the growth of pure and neodymium
doped barium hydrogen phosphate single crystals. The characterization
includes XRD, FTIR, Thermal analysis and EDS. The optimum
conditions for the growth of good quality single crystals were found out.
The nature of the crystals was found to vary from micro crystals to well
faceted platelet crystals of average dimension 4mmx2mmx1mm.

Chapter 5 deals with the growth of pure and neodymium doped
strontium hydrogen phosphate single crystals. The characterization
includes XRD, FTIR, Thermal analysis and EDS. The optimum
conditions for the growth of good quality single crystals were found out.
The nature of the crystals was found to vary from micro crystals to well
sized spherulitic crystals of average dimension 3mm. Based on thermo
gravimetric analysis and differential thermal analysis, the different
stages of thermal decomposition of the crystals were evaluated.
Chapter 6 deals with the Micro topography, Optical and Dielectric studies of the grown crystals. Surface Morphology was studied in detail by Optical Microscopy. It was confirmed by the studies of Scanning Electron Microscopy. The morphologies are distinct in each case. Based on the surface studies growth mechanism has been explained. Etching method has been employed to study imperfections like dislocations. Triangular and rectangular etch patterns were obtained. Successive etching is carried out in order to establish the linearity of the dislocations. Optical studies were conducted by UV-Visible absorption spectral analysis. Energy-level assignments were made by comparison with crystal spectra. The UV-Visible absorption studies confirm the presence of Nd$^{3+}$ ions in each crystal from their characteristic absorption peaks. The absorption spectra of rare earths in the optical region arise from the transition within the 4f configuration. Due to the shielding habit of the 5s$^2$, 5p$^6$ shells perturbation by surrounding neighbours does not take place resulting sharp line spectra.

The dielectric properties of materials have been studied by the cavity perturbation technique at microwave frequency. The dielectric constant $\varepsilon'$, Imaginary part $\varepsilon''$, the effective conductivity $\sigma_e$, and loss tangent $\tan\delta$ are determined and represented graphically.

Chapter 7 deals with the study of the Liesegang patterns observed during the growth of calcium hydrogen phosphate and strontium hydrogen phosphate crystals in gel medium. The study of this beautiful phenomenon is highly useful to study the diffusion of different types of ions and the growth of crystals in general. The generic laws have been verified. The diffusion coefficients were estimated.

Most of the work presented in this thesis have either been presented in seminars or published in International journals or are in the process of publication. A list of such publications is appended below.