8.1 Introduction

The growth techniques, characterisation and the measurement of various properties of the mono and mixed rare earth hydrogen selenite crystals have been discussed in the preceding chapters. Even though some work has been reported in the past on the growth of hydrogen selenite crystals, there is no exhaustive information available on the growth and properties of the rare earth hydrogen selenite crystals. It seems appropriate here to include a summary of the actual observations and findings from the studies reported in the previous chapters. This chapter gives general conclusions extracted from the experimental observations and findings and their scope for future research.

8.2 Conclusions

Hydrosilica gel is observed as a good medium for growing good quality crystals of mono and mixed rare earth hydrogen selenite crystals. The ability of the controlled diffusion of ions through hydrosilica gel really enhances the quality of the grown
crystals. The optimum conditions for the growth of high quality single crystals were
determined by adjusting the various growth conditions and results are abbreviated
below.

**Optimum conditions for growing rare earth hydrogen selenite crystals**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel density</td>
<td>1.03 gm/cc</td>
</tr>
<tr>
<td>Gel age</td>
<td>22 hrs</td>
</tr>
<tr>
<td>PH of the gel</td>
<td>6.5</td>
</tr>
<tr>
<td>Conc. of inner reactant</td>
<td>0.5 M selenous acid</td>
</tr>
<tr>
<td>Conc. outer reactant</td>
<td>0.5 M rare earth nitrates</td>
</tr>
<tr>
<td>Growth period</td>
<td>6 weeks</td>
</tr>
</tbody>
</table>

The changes in the morphology of the crystals depend upon the growth conditions.
Concentration of the feed solution and pH of the medium are vital factors in
moulding the shape of the crystals. The variations of the nucleation density with the
varying parameters have been studied extensively. The morphology and growth
patterns of all the grown crystals are similar in many respects. The
microphotographs of the crystals have been presented to elucidate the various
morphologies.

The surface features of the grown crystals were apparently the same. All the grown
crystals were layered in nature. The etching studies show etch pits arranged in
parallel lines parallel to the longer edges of the crystals. The observed etch pits are
rectangular in shape, deep and with pointed bottom. These etch pits reveal the
defects segregated along the major axis of the crystal.

The X-ray powder diffraction analysis of all the grown crystals gives their lattice
parameters. It is observed that all the grown crystals are in the monoclinic system
with space group P2_1/c. The FT-IR studies show the presence of various functional
groups. The bands at 3500-3100 cm\(^{-1}\) is due to the vibration of the water molecule.
The SeO_3^{2-} vibrations lie between 840 cm\(^{-1}\) and 440 cm\(^{-1}\). A very significant band at
1227 cm$^{-1}$ is ascribed to hydrogen selenite (HSeO$_3$). The bands at 1640 cm$^{-1}$ and 2405 cm$^{-1}$ show the presence of OH molecules.

The UV-visible and emission spectra analysis of rare earth hydrogen selenite reveals the presence of rare earth ions present in the crystals. The EDAX studies were carried out to identify various rare earths present in the grown crystals qualitatively and quantitatively. The thermodynamic studies show the validity of the proposed chemical formula of the crystals. The various steps during the thermal decomposition of mixed rare earth hydrogen selenite crystal is depicted as

$$2[RR_1(HSeO_3)(SeO_3).2H_2O] - 1H_2O \rightarrow RR_1Se_4O_{11} .4H_2O - 4H_2O \rightarrow RR_1Se_4O_{11} - 1/2SeO \rightarrow \frac{1}{2}[4RR_1Se_7O_{20}] - \frac{1}{2}SeO_2 \rightarrow RR_1Se_3O_2 - 2SeO_2 \rightarrow RR_1SeO_3 - 1SeO_2 \rightarrow RR_1O_3$$

The differential thermal analysis shows five endothermic peaks in accordance with the mass loss as shown in TG curve except for the decomposition of RR$_1$Se$_4$O$_{11}$, that is an exothermic peak. This peak can be regarded as an elimination of SeO$_2$ and simultaneous crystallographic transformation.

The mechanical and magnetic properties of the crystals are studied in detail. The microhardness measurements reveal the mechanical strength of the crystals. All the grown crystals show poor mechanical resistance. For mixed crystals at constant load the hardness increases to a maximum value at equal percentage of the components and then decreases to a minimum level when the other rare earth component is predominant. The mono rare earth hydrogen selenite shows low hardness values. The hardness reaches the maximum value for the 50:50 composition. This may be explained as follows. When the components i.e. in a lower concentration the minority atoms might be going to the structure replacing other component as an interstitial. When the components are in equal proportions atom will get a chance to arrange in an orderly way since it will have minimum energy configuration.
The magnetic susceptibility and effective magnetic moment of the stoichiometrically different doubly mixed crystals were calculated by recording the variation of the magnetic moment with external field. Effective magnetic moments observed and theoretically calculated are in good agreement. This suggests that the rare earth ions are weakly perturbed by the crystalline lattice and the atomic properties of the rare earth ions are retained in the mixed states. The magnetic moment of the mono rare earth hydrogen selenite shows a linear change with varying external magnetic field.

8.3 Scope for future research

There is vast scope for continuing fruitful research in the rare earth hydrogen selenite crystals. The rare earth materials are highly attractive due to their outstanding physical properties. The hydrosilica gel medium can be utilised as a successful medium to grow different mono and mixed rare earth hydrogen selenite crystals. In this thesis, measurements on only a few of the physical properties of the crystals are reported and there is scope for more research on several other properties hitherto unexplored. Since these lanthanum based compounds are playing a dominant role in high $T_c$ superconductors$^{1,2,3}$ these mixed crystals may be good candidates for investigation in that field. Rare earth crystals show photoluminescence properties. By growing mixed crystals of different stoichiometry one can tailor the properties and photoluminescence studies in the case of hydrogen selenite crystals may offer exciting possibilities due to the presence of chalcogenide ions.

In short the mixed rare earth hydrogen selenite crystals have great potential in the technical field due to their varied physical properties. Their exciting magnetic and luminescent properties may lead them into fruitful technological applications.

References