PREFACE

Beauty has always been a source of joy to mankind. As man moved out of ignorance and darkness and stepped into the bright light of progress and civilization, his thirst for beauty led to many wonderful creations and discoveries that became important pillars supporting the edifice of civilization. Crystals also attracted men's eyes because of their beauty. In early times, men were fascinated by their varied shapes and hues. In recent times their importance has shifted mainly to their tremendous use in electronics and solid state devices.

The growth and characterization of single crystals have become an increasingly important and active branch of science in the modern world because of the growing demand for synthetic crystals. Today, crystal growth forms one of the main pillars of modern technology. Crystal growth as a science is mostly concerned with the chemistry and physics of heat and mass transfer in fluid-solid transitions and in a wide sense, with the technology of controlling phase transitions that lead to solids. Growing crystals in gels is probably the most versatile among the various techniques of crystal growth from solutions at ambient conditions.
The present thesis entitled "ON THE GROWTH OF RARE EARTH MIXED CRYSTALS OF BARIUM MOLYBDATES AND COPPER OXALATES" deals with an investigation on the growth of mixed crystals of samarium barium molybdate, neodymium barium molybdate, praseodymium barium molybdate, samarium copper oxalate, neodymium copper oxalate and praseodymium copper oxalate crystals in silica gel media and its physico-chemical characterization.

The thesis consists of mainly, three parts and an appendix. Part I comprises of the first three chapters. The first chapter deals with the introduction, existing information, structure and symmetry, properties and habits of rare earth mixed barium molybdates and copper oxalates. Chapter two gives a brief discussion on the different types of gel, their growth procedures and growth characteristics. Chapter three deals with the different experimental techniques used during studies like X-ray, IR, Raman, uv-visible, EDAX, thermal analyses (TGA, DSC/DTA) etc.

Part II comprises of 4 chapters. Chapters 4, 5, & 6 deal with the growth and characterization of samarium barium molybdate, neodymium barium molybdate and praseodymium barium molybdate respectively. In the seventh chapter detailed discussions are included on the main growth characteristics of these crystals.
The effect on the growth due to various parameters like concentration of outer electrolytes, inner electrolyte, pH of the gel, ageing etc. are discussed in each case and the optimum condition of growth is established. The depth of precipitation and partial dissolution were found to be directly proportional to the concentration of the outer electrolyte and inversely proportional to the inner electrolyte in this multicomponent system. Lower pH values were favourable for thicker precipitate and dissolution regions. It was found that in the case of molybdates precipitation cum dissolution process lead to crystallization of the crystals. Silica gel is a polymerised form of silicic acid and it is a fine-pored adsorbent. The outer electrolyte was adsorbed into the gel to form colloidal precipitate. The acidity present in the gel brought about the dissolution of the precipitate, thereby leading to crystallization. These crystals were identified and characterized by different methods like X-ray, IR, Raman, EDAX, XRF, thermal analyses. It was concluded that any rare earth from the lanthanide series can be substituted in the place of the rare earth to obtain this type of crystals, having a general formula, which are supposed to be important in ferroelastic, ferroelectric, laser and acousto-optic fields.
Part III consists of 4 chapters from 8-11. The first three chapters deal with the growth kinetics, identification and characterization of samarium copper oxalate, neodymium copper oxalate and praseodymium copper oxalate respectively. The eleventh chapter deals with a detailed discussion of the general procedure of growth, the effect of variation due to different parameters of these crystals etc. As the top nutrient diffused into the gel, it reacted with the inner electrolyte and produced a precipitate band. From this colloidal particles of the precipitate, nucleation started to form crystals. As the concentration of the outer electrolyte increased, the depth of precipitation and crystallization region increased as in the two component systems.

The morphology of the crystals and spherulites formed are also discussed in detail in this chapter. The crystallinity is proved by the X-ray analysis. IR and Raman analyses give the evidence of the presence of water of crystallization and oxalato complexes. EDAX, DSC and TGA give the percentage composition of each component and the different stages of mass variation with temperature. ICP and XRF data support the results of EDAX. The surfaces of these crystals are etched to obtain the surface details. From these studies it is found that the rare earth component can be substituted by other rare
earths, to grow the respective rare earth mixed crystals of copper oxalate having same general properties and formula.

The appendix is set apart for the Liesegang ring phenomenon in molybdates. The existing laws are just reviewed and the validity of the ring system under various internal growth parameters are investigated.

In preparing the literature concerning various aspects of the work presented in the thesis, over 400 references have been included.

A major part of the work included in this thesis has been published/presented in the following journals/conferences.


7. Studies on \( \text{La}_x \text{Cu}_{3-x} \text{C}_0 \cdot \text{nH}_0 \) crystals grown in \( 1-x \) hydrosilica gel. Crystal Research Technology 25(1990)7.


12. Growth and characterization of \( \text{Sm}_{2.67} \text{Cu}_{2.47} \cdot \text{C}_0 \cdot \text{135H}_0 \cdot \text{2} \cdot \text{2} \). Journal of Crystal Growth (communicated).


17. Thermal studies of mixed crystals of praseodymium copper oxalate. 5th session, Kerala Science Congress, Kottayam (accepted for presentation) (1993).

19. Rare earth barium molybdates - their growth, properties, characteristics - in general (communicated).

20. Rare earth (Sm, Pr & Nd) mixed copper oxalates - nature and formula. J. of Crystal growth (communicated).