

PREFACE

The rapidly developing applications of natural and synthetic crystalline materials **in** industries impelled a new upsurge in solid state physics in general and materials science in particular. The need of better quality crystals in industries and technology has kept the human race developing their knowledge in the field of crystal growth. Today people try to synthesise the better quality crystals, which are rare in nature or not yet grown, adopting different techniques of crystal growth and study their physical and chemical properties in detail.

The alkaline earth metal molybdates and tungstates which are formed from the elements of group II and VI of the periodic table have got wide applications in various fields such as lasers, luminescence and many acousto-optical and opto-electronic devices.

Calcium molybdate, CaMoO_4 , belongs to isomorphic and isostructural series of Scheelite type divalent metal ion compounds having the general formula ABO_4 . It

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crystallizes in the bipyramidal form with space group C_{4h}^6 in the tetragonal system. Since this material has got a very high melting point (1450°C) and is insoluble in water, the main resource to get it has been its growth from melt. It was conjectured that CaMoO_4 can be grown in single crystalline form from flux. Many crystal growers have employed flux technique for the growth of CaMoO_4 crystals, but in most of these attempts both the crystal size and the quality were not worth appreciable^{time}. It was, therefore, decided to carry out a systematic study on the flux growth of single crystals of calcium molybdate and their important properties like dielectric, electrical, magnetic and mechanical. The results are presented in the form of a thesis.

The thesis has been divided into three parts. In the part I (Chapters 1 to 3) a succinct review of the existing information about CaMoO_4 has been given in chapter 1. The existing theories of crystal growth and dissolution are presented in chapter 2. The chapter 3 deals with some prominent experimental techniques employed during the present investigation.

The part II deals with studies carried out for the crystallization of calcium molybdate. The chapter 4

deals methodically with the flux growth of calcium molybdate single crystals. The search for the suitable flux was made out of a wide range of possibly useful compounds, namely, LiCl, KCl, Na₂MoO₄, Li₂MoO₄, etc. LiCl was found to be the best amongst them. The role of growth parameters, like composition of the starting materials, growth temperature, soak period, cooling rate, etc. on the morphology, size and perfection of crystals are also briefly explained in this chapter.

The characterization of the grown crystals is carried out using X-ray diffraction, EDAX, Magnetic effects, etc. The data collected by characterization work finds place in chapter 5.

The chapter 6 deals with the kinetics of calcium molybdate crystallization from the unstirred molten solutions of low-to-medium supersaturation of lithium chloride. The diffusion rate constants K_{D1} and K_{Dw} are determined at both the temperatures. The growth is found to be diffusion-controlled upto an extent of 63 %. The effect of variation of the crystallization temperature on the crystal size and their number is also quantitatively studied in this chapter.

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The part III concerns with the measurements and discussion of the useful, pertinent properties (mechanical and electrical) of the grown crystals. The chapter 7 deals with the micromechanical investigations carried out on the as-grown (011) and the cleaved (001) planes of crystals at room temperature. The anisotropy in hardness with quenching and annealing, in the temperature range 525-775°C, are also studied. The development of crack patterns around the indentation marks and their variation with loads is also studied and explained in this chapter.

In the chapter 8 are presented dielectric measurements carried out on the polycrystalline pellets and the platy single crystals. The variation of dielectric constant with applied frequency, pelletising pressure, temperature, etc. are investigated and explained in this chapter. The concept of polarization effect contributing to the dielectric constant is advocated in this chapter.

The chapter 9 comprises the effect of variation of temperature on the electrical conductivity studied on pelletised samples and single crystals in

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the temperature range 313 to 773 K. The electrical conductivity has been explained in (two different) lower and higher temperature regions and thus the energy of formation of Frenkel defects has been estimated.

Finally, the far-reaching conclusions of the thesis and the scope of the future work are precisely narrated in chapter 10.