ABSTRACT

The growth of large oxide crystals for use in the electronics industry has progressed significantly since the early 1960s. Today, parts fabricated from oxide single crystals are used as the active component in laser systems (Nd:YAG and ruby), substrates for silicon epitaxy (Al₂O₃), optical components (LiNbO₃ and PbMoO₄) and substrates for magnetic bubble devices (Gd₃Ga₅O₁₂). The dominant user of single crystals is of course the electronics industry and most of these crystals are grown from the melt by the Czochralski or crystal pulling technique.

In any melt growth process, the growth conditions change as the melt is consumed: for example temperature gradients change because of the steady lengthening of the crystal and the unequal thermal conductivities of crystal and melt; the melt volume decrease changes the convective flow, the solute concentration in the melt changes progressively. Moreover, the crystal-melt interface can become unstable which in turn will lead to so many complications.

The present study enumerates some fundamental aspects of the Czochralski growth of technologically important crystals of lead molybdate and lead tungstate. An introduction has been briefly outlined about the fundamental aspects of the melt growth process. The salient features of the crystal pulling technique along with the advantages and disadvantages are focussed. Specific mentioning has been made about the materials of interest to this thesis.
Crystal growth of lead molybdate was carried out using an indigenously developed resistive heating furnace. The description of the furnace construction along with experimental details are elaborately discussed. The problems associated with the growth are analysed one by one. The shape of the crystal-melt interface was studied for various other parameters. It was found that the shape of the interface was always convex and the reason for this nature is proposed. Crystals were grown under different conditions by changing crystal pulling rate, seed rotation rate and axial temperature gradient above the melt level. The incorporation of bubbles into the growing crystal was also analysed.

Various characterisation methods were adopted for analysing the quality of lead molybdate single crystals. Optical transmission which is an essential way of checking the quality of the crystals was employed for studying the optical properties. Etching is yet another method of understanding the defect nature present in the crystal. Lead molybdate crystals have been chemically etched with NaOH solution. The formation of film on the cut and polished surface upon etching was avoided and clear etch patterns were observed. Thermal etching was also adopted and several interesting features were found to appear on both (100) and (001) faces of the crystal. Different portions of the crystal revealed etch pits of different shapes. The Vickers microhardness and the work hardening coefficient were also determined. Atomic relocation was observed when micro-indented samples were subjected to thermal treatment. Possible reasons for the above said results are discussed.

Lead tungstate has also been successfully grown and the growth details are exclusively discussed. The problem of crystal cracking and yellow colouration has been avoided under optimised growth conditions. A separate furnace system has been designed and fabricated for use in the growth of lead tungstate single crystals. The low axial temperature gradient of the furnace helped avoid crystal cracking. The problem of increased crystal diameter in the initial
stage occurred very often and was overcome by careful adjustment of seed rotation rate. Crystal pulling rate was optimised and it was found that higher pulling rates (>3 mm h\(^{-1}\)) yielded crystals with poor optical quality, i.e., with voids/bubbles. Post-growth annealing was found to be very much important to get the crystal uncoloured and crack-free. The annealing duration was optimised and it was high enough to get the crystal crack-free and small enough to get it colourless.

Some basic characterisation studies like etching and microhardness were carried out and the results are discussed. Etching study consists of two parts namely chemical etching and thermal etching. Clear etch pits were observed by chemical etching and well shaped inclusion-like patterns were seen after thermal etching on both (100) and (001) faces. Optical transmission/absorption studies before and after gamma ray irradiation were carried out. It was found that the radiation damage was more for samples with yellow colouration than for colourless crystals. Excitation-emission spectra for different samples obtained from different portions of the crystals were analysed and it was found that the emission intensity varies with respect to the crystal quality. Most of the crystals emitted luminescence in the region 480 - 500 nm. Thermoluminescence measurements were also carried out after irradiating the samples with gamma ray to a dosage of 10\(^3\) rad. It was noticed that the TL glow curves were weak and different types of glow curves were obtained for different samples.