Growth and characterization of scheelite crystals

A large number of tungstate (AWO₄) and molybdate (AMoO₄), where ‘A’ stands for large size divalent ions like Ca, Pb or Ba are naturally occurring crystals. Their scheelite structure is characterized by tetrahedrally coordinated (WO₄)²⁻/(MoO₄)²⁻ group positioned at four corners of a unit cell and the divalent A²⁻ located at bcc is octahedrally coordinated with oxygen ions [1]. The research interest in scheelite crystals dates back to early sixties, with investigation on CaWO₄ used as a laser host, where the laser action was achieved by doping the crystal with Nd³⁺ ions. Subsequently, the second harmonic generation in this crystal was also demonstrated [2]. Crystals of PbWO₄ (PWO) are extensively used as scintillation detectors. The scintillation emission in this case lies in blue region and it arises due to electronic transitions within the WO₄ groups. PbMoO₄ (PMO) crystals are used as acousto-optic modulator and this usefulness lies in independence of the deflection angle on polarization and also being a soft material. BaWO₄ (BWO) is the most promising universal Raman active crystal among all scheelite crystals [3]. Its important features are high gain in steady as well as in transient states and much lower decrease in Raman level even in pico-second pump laser pulses. Another iso-structural material viz. NaBi (WO₄)₂ (NBW), where mono and trivalent ions may occupy the same bcc position with equal probability, is reported as a promising Cherenkov detector for LHC experiments [4]. Rare-earth doped double tungstates [Re:NaT(WO₄)₂ with T being a Trivalent ion are also laser crystals having high conversion efficiency [5]. The applicability of nano-particles as photo-catalysts and ionic conductors of scheelites happens to be a subject of current interest.
Though scheelites have been investigated for over 50 years, issues related to their luminescent emission still remained unresolved. Some of them are listed as follows: (i) PMO crystal exhibits blue emission band only at low temperatures and no luminescence is observed at room temperature, (ii) the origin of UV emission band in BWO crystal still remains unresolved, (iii) PWO crystal shows good scintillation properties, but the analogous material BWO does not, (iv) resemblance in the optical properties of NBW, a double tungstate with mono tungstate PWO crystal. In this study, the above mentioned issues have been answered through a series of systematic experiments and theoretical calculations. The motivation behind selection of the thesis topic on “Growth and characterization of scheelite crystals” is essentially driven by the technological challenges involved in realizing these in the form of high quality single crystals and their characterization to address the unresolved issues mentioned above.

Scheelites in general are characterized by the presence of two emission bands in the blue and green regions, which arise due to electronic transitions within WO$_4$/MoO$_4$ groups [6]. The dependence of PMO luminescence on crystal stoichiometry with regard to both cationic and anionic sub-lattices is an important and novel outcome of this study. It may be mentioned that non-stoichiometry is inherent in multi-component systems and it has large influence on several of the material properties. Detailed investigations of this type have only been reported for couple of crystals viz. LiNbO$_3$ and GaAs. As the measurement of minute stoichiometric deviations is extremely difficult, crystals were grown from charges containing different amount of non-stoichiometry. But for the different compositions of the starting charges, all other conditions for crystal growth were maintained identical. The stoichiometric changes in anionic sub-lattice were affected by high temperature annealing treatment of the crystals under oxygen or vacuum. Optical absorption and photoluminescence measurements showed that the UV emission band is
the indeed a characteristic feature of BWO single crystal, which is quite distinct from other scheelites. The calculations of electronic and optical properties of BWO employing density functional theory (DFT) showed the absence of any contribution from cationic states to valence and conduction bands, indicating absence of excitonic emission, which makes BWO unsuitable for use as a scintillator. DFT calculations showed striking similarities in the band structure and optical properties of NBW and PWO crystals, in spite of having constituents of different valences.

The research work carried out and compiled here in the form of thesis has been published in of peer reviewed journals [Ref.7-17]. An overview of the thesis contents grouped under seven chapters is as follows.

**Chapter 1. Introduction**

The chapter begins with an introduction to scheelites crystals viz. PMO, BWO, NBW and the areas for further work are identified. The organization of the thesis is discussed and the important results obtained have been summarized.

**Chapter 2. Experimental**

This chapter begins with an introduction to crystal growth techniques with particular emphasis on Czochralski technique. The crystal puller system used and the conditions determining the growth of PMO, BWO and NBW have been discussed. Various characterization techniques used in the present work and information sought from each of the measurements are described. The techniques mainly include X-ray diffraction, Differential thermal analysis, UV-VIS optical
absorption and reflectivity spectra, photoluminescence, thermo luminescence and X-ray fluorescence measurements.

**Chapter 3. Theoretical Calculation**

The density functional theory (DFT) for ‘First principles calculations’ using Linearized augmented plane wave (LAPW) method, as embodied in the Wien2k program has been applied [11]. Details of DFT along with approximations for charge density, potentials and basis sets used for solving the Kohn-Sham equation are given. The details of GSAS program based on Rietveld method of structural refinement are described in details. Determination of absorption coefficient, refractive index, electron energy loss spectrum and reflectivity from energy dependence of real and imaginary parts of dielectric constants as calculated from the electronic response using Kramers-Kroening relation have also been given.

**Chapter 4: Investigations on Lead Molybdate crystals**

The chapter highlights the need for studying this material, essentially to bring out some unresolved issues. PMO is considered as one of the best candidates for studying influence of non-stoichiometry on crystal properties. This is because melt grown PMO crystals are inherently deficient in MoO$_3$ due to much higher vapor pressure of one of the constituent oxide viz MoO$_3$ near growth temperatures. Investigations on PMO crystals for the first time have shown that optical absorption and luminescence properties are a sensitive function of its stoichiometric composition. Both green and blue emissions bands were observed at room temperature itself, in crystals possessing minor stoichiometric deviations [7-9]. Another set of studies showed that though the source of strong coloration in PMO is the presence of extrinsic impurities; non-
Stoichiometry in both cationic and anionic sublattices also plays a significant role in its coloration [10-11]. Excitonic transitions observed in PMO have been understood by invoking theoretical calculations of electronic band structure and optical properties [12].

**Chapter 5: Results on optical properties of Barium Tungstate**

The characteristics of BWO that are distinctly different from analogous materials are described. Optical absorption and photoluminescence studies carried out on single crystal samples annealed under different ambient showed that the absence of coloration and the presence of UV emission bands are both related to inherent oxygen deficiency [13]. DFT calculations showed BaWO$_4$ as a direct band gap crystal having less dispersive valence and conduction bands as compared to other scheelites and therefore exhibit narrow line width in the Raman active vibrational mode. The properties of BWO are found to be quite different from other scheelites like PWO, because of its very different electronic structure [14].

**Chapter 6: Investigations on optical properties of Sodium bismuth double tungstate**

NBW crystal exhibiting ultra high radiation hardness is considered as prospective substitute for PWO scintillator in the energy range of GeV – TeV. Though the applicability of this crystal as Cherenkov detector was demonstrated in Desy, HERMES [4], it has not been used in LHC due to difficulties in realizing large size single crystals of requisite quality. Conditions under which high optical 90 mm long crystals of 20 mm dia could be realized are described. The experimental results concerning optical absorption of differently treated NBW crystals and theoretical calculation of its crystalline & band structures and other optical properties are summarized. The band structure calculations showed that the energy levels of W and O are the prime contributors
in the formation of valance and conduction bands similar to those reported for PWO crystals [15]. Investigations on the origin of radiation induced coloration in this crystal are also dealt in the details. Single crystals grown from re-crystallized charges were found to discolor to a smaller extent on gamma-ray exposures exceeding $10^6$ Grey [16].

**Chapter 7: Conclusion**

Novel findings of the investigations carried out on these three crystals have been listed out in this chapter. The dependences of optical absorption, photoluminescence and radiation induced coloration on the stoichiometric composition for all the three crystals have been brought out. Though changes in optical absorption on high temperature annealing are well known but demonstrating an equal role of non-stoichiometry with regard to anionic and cationic sub-lattices on crystal luminescence is the novel contribution of this work. During initial investigations on luminescence from scheelites, the absence of room temperature PL was reported for PMO crystals [18]. We have however observed both blue and green emission bands from PMO crystals for a particular proportion of PbO and MoO$_3$. The underlying inference drawn from the study is that the characteristics of a material should come with a tag related to its preparatory conditions. Theoretical calculations are important not only in predicting applicability of a given crystal, but it also gives an idea about the limit to which crystal quality can at best be achieved. Information regarding special features that can be extracted from a given material can also be predicted from these calculations. The chapter concludes with some of the aspects that are yet to be answered/explored, setting the tune for the future work.
References:


