CHAPTER 5

BASIC CHARACTERISATION AND LUMINESCENCE STUDIES ON LEAD TUNGSTATE SINGLE CRYSTALS

5.1 INTRODUCTION

Crystals are grown for two main reasons: to understand how they grow and to use them for scientific and technological applications. Either to understand how growth processes influence perfection or to produce crystals of the perfection required for the end use, one must characterise the grown crystals by various techniques. It is the crystal grower's responsibility to relate the results of such studies to growth mechanisms - to the growth process - in a way enabling him to alter and control the process so as to control the characteristics - the perfection - of the grown crystal in desired ways (Laudise 1975). Consequently it is the purpose of this chapter to briefly outline some of the basic as well as applied characterisation methods and to elucidate these methods with a few results drawn from studies of lead tungstate single crystals grown by the author.

5.2 OPTICAL TRANSMISSION AND RADIATION DAMAGE

Generally lead tungstate single crystals are pale yellow in colour, i.e., they absorb light at around 430 nm and this absorption intensity is decreased by purification of raw materials, additional recrystallisation or vacuum annealing. This band, overlapping the luminescence spectrum, has a typical absorption coefficient at
the maximum of about $k=0.05 \text{ cm}^{-1}$ and leads to a relative light yield reduction by a factor of two for scintillation elements with a length of 200 mm or more (Annenkov et al 1996). The absorption intensity is increased when subjected to irradiation studies. In the present investigation, the crystals were subjected to optical transmission/absorption studies before and after $\gamma$-ray irradiation in order to estimate the radiation damage.

Attempts were made to study the colouration of the grown lead tungstate crystals by means of optical transmission in the UV-visible region. Since these crystals are finding applications in the field of radiation detection, any damage caused by radiation may in turn affect the optical transparency in the wavelength region of interest. Moreover, the grown crystals should have high degree of transparency in the emission wavelength region in order to get high luminescence output. Poor optical transmission of the crystals will limit the effective light yield detectable with photomultiplier tubes mounted at the end of long crystals (Kobayashi et al 1997).

5.2.1 Optical transmission studies on as grown crystals

The grown crystals were cut perpendicular to the growth direction into several wafers and were mechanically polished using diamond paste (particle size: 0.25$\mu$) to mirror finish. Some of the polished elements of lead tungstate crystals are shown in Figure 5.1. Transmission spectra of the polished samples obtained from top, middle and bottom portions of the crystal were recorded on a Hitachi 330 spectrophotometer and are given in Figure 5.2. As it can be seen from the spectra, there is no sign of absorption around 430 nm (corresponding to yellow colouration) for the samples cut from top and middle portions of the crystal whereas the bottom part showed slight yellow colouration as evidenced by an absorption dip in the transmission spectrum. When the crystal growth is carried out using pre-pulled
Figure 5.1 Some of the cut and polished PbWO$_4$ crystals
Figure 5.2 Optical transmission spectra of PbWO₄ samples obtained from (a) top, (b) middle and (c) bottom portions.
crystals as charge, i.e., under repeated crystallization, this absorption intensity is reduced and the whole length of the crystal showed almost uniform transmittance. Figure 5.3 shows the transmittance of PbWO$_4$ crystals grown using fresh charge and by repeated crystallisation at 430 nm with respect to boule length.

5.2.2 Optical absorption studies on γ-ray irradiated crystals

The radiation detectors such as lead tungstate crystals are sometimes used in strong radiation fields. The radiation sources may be various: protons, neutrons, electrons, γ-rays and other particles from particle accelerators, nuclear reactors, cosmic rays etc. Since the radiation detectors consisting of single crystals usually owe the good performance to optical transparency and luminescence of the crystals, any damaging effect on these two properties should be avoided. The primary effect of radiation damage is degradation in transparency rather than that in luminescence (Ishii and Kobayashi 1991). Decrease in optical transmission is especially dangerous in the γ-ray detectors for high energy applications.

Hence in order to study the effect of irradiation by γ-rays on the optical properties, measurements were made on the optical absorption. Samples from different portions of the crystal were cut and polished and were then subjected for this test. These samples were marked as A, B, C and D and are obtained from the bulk as represented in Figure 5.4.

The optical absorption spectra of all the four samples are shown in Figure 5.5. It can be seen from the spectra that the samples A and B (obtained from top portion of the crystal) did not show any change in absorption spectra even after irradiation by γ-ray to 10$^5$ rad, i.e., the radiation damage is negligible for these two samples. However, samples C and D showed appreciable amount of absorption even before irradiation and the subsequent radiation damage upon γ-ray irradiation is
Figure 5.3 Optical transmission at 430 nm for crystals grown using (a) pre-pulled crystals and (b) synthesised charge.
Figure 5.4 Schematic representation of sampling positions
Figure 5.5 Optical absorption of PbWO$_4$ before (-----) and after (-------) gamma ray irradiation
more for these samples. Hence it may be concluded that the crystals for end use should be completely colourless to be highly resistant for high energy doses.

In addition to the change in the optical absorption, there was also a change in the UV cut-off wavelength. For samples A and B, the cut-off wavelength did not shift significantly whereas samples C and D showed a shift of about 20 nm towards higher wavelength side. This shift is attributed to the slight deviation from stoichiometry as the sample D is cut from the bottommost part which has been grown after considerable time gap leading to the evaporation of PbO or WO₃ (Korzhik et al 1996). This observation is further evidenced by TL study which is discussed below. It is also observed that the cut-off wavelength always shifted to higher wavelength side by a few nm upon irradiation.

5.3 LUMINESCENCE STUDIES

Luminescence is most conveniently defined as the radiation emitted by a molecule, or an atom, after it has absorbed energy to go to an excited state. It consists of fluorescence and phosphorescence (Hercules 1966). According to the original definition, fluorescence is a light emission which does not continue a measurable time after the end of the excitation process. Phosphorescence persists when the excitation is discontinued (Pringshein and Vogel 1943).

5.3.1 Mechanism of luminescence

Phosphor converts excitation energy into light, resulting in luminescence. The luminescence caused by radiation is called scintillation. The luminescence process in intrinsic inorganic scintillators is through electronic transition between various kinds of excited states and the lower states (Figure 5.6).
Figure 5.6 Scintillation processes in intrinsic inorganic crystals in terms of the radial dependence of the band structure.

Figure 5.7 Scintillation processes in intrinsic inorganic crystals in terms of band structure.
ionizes constituent atoms or excites valence band electrons. Ionization liberates electrons from their ionic bonds and raises them to the conduction band. Excitation forms a weakly coupled electron-hole pair, that is, an excitation whose energy state is just below the conduction band. The electrons drift about in the crystal and are easily captured by positive ions. A photon is emitted in this electron-hole recombination process in which the electron drops down to the valence band (Figure 5.7).

Although intrinsic crystals such as NaI and CsI belong to the oldest scintillation crystals studied, the doped scintillators of NaI:Tl or CsI:Tl became more popular than them, since NaI or CsI requires low temperature and/or UV light detection in order to get large light output. However, many intrinsic scintillation crystals have been developed since then and have become practical.

Extrinsic crystals are obtained by doping a pure host crystal with a small amount of metallic impurities such as Tl, Eu and Ce. These impurities are called as activators. The luminescence in these type of materials are mainly due to the presence of activators. The excitation energy is directly absorbed by the activator or indirectly transferred to the host lattice or other foreign ions which absorb the excitation energy (Ishii and Kobayashi 1991).

There are different types of luminescence depending upon the nature of excitation. It is called photoluminescence when excited with light (photons), cathodoluminescence when excited with electrons, radioluminescence when excited with radiation sources like gamma and X-rays and so on. The photoluminescence and thermoluminescence studies made on lead tungstate crystals are elaborately discussed in the following sections.
5.3.2 Photoluminescence studies on PbWO$_4$ crystals

Photoluminescence (PL) is the emission of electromagnetic radiation with the excitation of optical photons. The fluorescence emission band is always at the longer wavelength side of the excitation band. The shift of the emission band maximum with respect to the excitation band maximum is referred as Stoke's shift.

To know the emission characteristics, the sample is excited in the region where it has absorption and then the emission spectrum is recorded. The excitation spectrum can be recorded by fixing the emission where the emission is maximum (McKeever 1985).

a) Experiment 1

In one set of experiments, photoluminescence (excitation-emission spectrum) was measured using a fluorescence spectrophotometer (Hitachi F4500) in order to measure the luminescence from the surface of the well polished crystals. The dependence of the xenon light source intensity and the sensitivity of the photomultiplier tube on the wavelength were corrected. The slit width was 5 nm for both the excitation and emission.

The excitation-emission spectra for the top and bottom part of the crystals are given in Figure 5.8. The emission has a peak at 495 and 500 nm with the excitation full width at half maximum (FWHM) of 12 and 21 nm for top and bottom parts respectively. Though there is no much difference in emission peak wavelength the intensity has considerably reduced for the bottom part of the crystal. Correlating these results with the optical transmittance, one can come to a conclusion that the light output is largely dependent on the quality in transmittance in the range 350 - 500 nm (Senguttuvan et al 1997d).
Figure 5.8 Excitation-emission spectra of (1) top and (2) bottom part of PWO crystal; $\lambda_{ex}=308$ nm, $\lambda_{em}=495$ nm for (1) and $\lambda_{ex}=312$ nm, $\lambda_{em}=500$ nm for (2); Experiment-I.
**Experiment II**

In a separate set of measurements, the photoluminescence was measured for four samples obtained from different portions of the crystal using Shimadzu RF5000 fluorescence spectrophotometer having R-452-01 photomultipliers for photometry with a measuring wavelength range of 200-700 nm. The excitation source was a 150 W CW xenon lamp and the band width for the excitation and emission monochromators were set at 1.5 nm. In this case, the PL spectra were not corrected for the instrumental response. The excitation-emission spectra were measured for all the samples at identical conditions. Much care was taken to place the samples at similar positions during the measurement. Time duration of surface polishing was also kept uniform for all the samples. The resultant spectra are shown in Figure 5.9. On comparing the luminescence spectra with the optical absorption, it can be understood that the excitation-emission peak intensities are largely dependent on the optical quality of the samples. The samples which have better optical transmittance and hence lower absorption showed luminescence with higher intensity and narrow excitation peak with full width at half maximum (FWHM) as small as 15 nm (Senguttuvan et al 1997e). The emission curves are also narrow when compared to the results of previous experiment. The emission which peaked at 480 nm irrespective of the excitation wavelength differs from the previous experiment wherein the emission peaked at around 500 nm. Inaba et al (1995) have also reported the emission peaking at 480 nm.

From the above mentioned points it has further become evident that yellow colouration of the crystal is detrimental for getting intense luminescence. It is also clear from the two different experiments that the luminescence intensity gets reduced for the bottom part of the crystal. The values of peak excitation and emission wavelengths are given in Table 5.1.
Figure 5.9 Excitation-emission spectra for samples A, B, C and D; Experiment-II
Table 5.1

Excitation-emission wavelengths for PbWO₄ crystal in experiments I and II

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Sample</th>
<th>Excitation (nm)</th>
<th>Emission (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Top</td>
<td>308</td>
<td>495</td>
</tr>
<tr>
<td></td>
<td>Bottom</td>
<td>312</td>
<td>500</td>
</tr>
<tr>
<td>II</td>
<td>A*</td>
<td>308</td>
<td>480</td>
</tr>
<tr>
<td></td>
<td>B*</td>
<td>309</td>
<td>480</td>
</tr>
<tr>
<td></td>
<td>C*</td>
<td>311</td>
<td>480</td>
</tr>
<tr>
<td></td>
<td>D*</td>
<td>311</td>
<td>480</td>
</tr>
</tbody>
</table>

* Sample positions are shown in Figure 5.4

5.3.3 Thermoluminescence

Thermoluminescence (TL) or more precisely thermally stimulated luminescence is a type of luminescence which is emitted by giving a thermal stimulation to the sample. Any luminescence emission requires an excitation. In the case of TL, it is usually provided by irradiating the sample with X-rays or other ionizing radiations like α, β and γ-rays. Most of the ions produced recombine immediately. Some of the electrons produced during ionization, however, are captured in certain defect locations in the crystals which are deficient in negative charge. These electrons can stay in these locations for prolonged periods which depend on the stability of the configuration. The return of the electrons from the trapping sites and their recombination at an emitter site gives rise to the luminescent light called thermoluminescence. A specific property of TL is its emission in the form of glow peaks. The glow peaks appear when the sample temperature is raised.
after having been irradiated (excited). The rise in temperature of the sample reduces the life of the electrons in the trap, which leads to their ejection out of the traps at an exponentially increasing rate. This gives rise to a quick increase in the luminescent light emission. As the number of the trapped electrons starts getting exhausted, the light intensity decreases and finally falls to zero.

The effects of the incident ionizing radiations in insulating solids can be divided into two categories: (1) Atomic displacements by energetic heavy ions and by fast neutrons, (2) Ionization. The effects due to atomic or ionic displacements are called Frenkel or Schottky defects. The other category of radiation effects in insulating solids involves the electronic displacements. In this case the electrons and the holes liberated during the incidence of ionizing radiations are trapped at defect sites in the lattice. The trapping of an electron at a negative ion vacancy produces the well-known F centre. Similarly a hole can be trapped in the form of V\(_k\) centre. These defect centres involving the trapping of electrons or holes are called colour centres, since these absorb visible light of particular colours.

The trapped electrons and holes can return to their normal position if the irradiated sample is heated gently. The heat provides the activation energy to release the trapped charge from its potential well. The detrapped charge while returning to its normal position emits energy in the form of light called thermoluminescence (Sunta 1992).

**5.3.3.1 Thermoluminescence studies on PbWO\(_4\)**

The thermoluminescence glow curves over the temperature range 30-400°C were recorded after irradiating the samples with γ-ray to a dosage of 10\(^3\) rad. For this the samples were loaded in a \(\alpha\)Co γ-chamber. The dose rate was 26.4 Gymin\(^{-1}\) and the heating rate was 2°Cs\(^{-1}\).
Thermoluminescence measurements were made on two samples: A (completely colourless) and D (yellow coloured). Both the samples were irradiated with γ-ray simultaneously. The resulting curves (Figure 5.10) show that sample A has a stronger TL response than sample D, implying higher concentration of charge traps and luminescence centres in sample A (Woody et al 1996). However, the TL glow curves are rather weak. Sample A has only one peak at 210°C whereas sample D has two peaks one at 100 °C and the other at 200°C (Senguttuvan et al 1997e). The extra lower temperature peak of sample D has its consequences with the yellow colouration and hence with the off-stoichiometry (Sabharwal et al 1996).

5.4 DIFFERENTIAL THERMAL ANALYSIS

A grown crystal piece was powdered and the differential thermal analysis (DTA) measurement was carried out on Perkin-Elmer DTA instrument in oxygen atmosphere with a gas flow rate of 50 cc min⁻¹ and heating rate of 10°Cmin⁻¹. Al₂O₃ was used as standard to measure the absolute value of temperature reading. Figure 5.11 shows the DTA curve of PbWO₄ which indicates only one sharp endothermic peak at 1123.1°C corresponding to the melting point of the material.

5.5 ETCHING STUDIES

As reports on etching studies of lead tungstate crystals are not found in the literature, the author has carried out some investigations on the etching behaviour of the grown crystals. Both chemical and thermal etching studies were carried out. The experimental procedures and the results are discussed in the following sections.
Figure 5.10 TL glow curves for samples A and D obtained from top and bottom part of PbWO₄.
Figure 5.11 DTA curve for a PbWO$_4$ crystal
5.5.1 Chemical etching

A number of chemical reagents were examined for possible use as an etchant for PbWO₄ such as HNO₃, NH₄Cl, KOH and NaOH. The etched samples were immediately washed with deionized water and then with acetone and examined under an optical microscope for their microstructural morphologies. Figures 5.12a and 5.12b show the etch pit pattern on (001) face of the crystal etched in 1N NaOH solution for 5 and 20 min respectively. The same kind of etch patterns were obtained on both (100) and (001) faces when etched with KOH solution. Subgrain boundaries as line of oriented pits were also seen on both the surfaces. Figure 5.13 shows a subgrain boundary which is branched into three lines. An attempt to develop chemical polishing was unsuccessful. Since, PbWO₄ has a very weak cleavage plane, it was not possible to study the etching behaviour on cleaved surface.

5.5.2 Thermal etching

To get a more detailed understanding of the crystal inhomogeneity and inclusion - related imperfections, thermal etching was performed on cut and polished PbWO₄ crystals. Some of the polished samples were loaded in platinum boat and heated at 950°C for 15 h for thermal etching studies. The thermal etch pits normally result from the thermal motion of atoms when a defect-containing material is heat treated at a temperature close to the melting point and depend largely on the minimisation of surface free energy (Sangwal and Rodriguez-Clemente 1991). Upon heat treatment, there will be i) release of stress energy stored in a defect site and ii) movement of defect sites (Zeng 1996a). Figures 5.14a and 5.14b show some representative micrographs of thermal etch pits on (100) and (001) faces of the crystal, respectively, after heat treatment at 950°C for 15 h. In addition to the thermal etch pits, some inclusions were also observed which are often triangular/hexagonal shaped (Figure 5.15). It has not been possible to determine the
Figure 5.12 Etch pit pattern on (001) face when etched for (a) 5 min and (b) 20 min.

Figure 5.13 Subgrain boundaries revealed on (001) face of PbWO$_4$. 
Figure 5.14 Thermal etch pits observed on (a) (100) face and (b) (001) face of PbWO₄.

Figure 5.15 Triangular/hexagonal shaped inclusions observed on PbWO₄ crystal surface.
nature of this kind of inclusions. But the decomposition (surface reaction) of PbWO$_4$ into Pb$_2$WO$_4$ upon heat treatment at 950°C (which is close to the melting point of Pb$_2$WO$_4$) is a plausible cause. The other predicted reason is the presence of some specific impurities in the starting materials. The same kind of observations made on CaWO$_4$ (Nassau and Broyer 1962) and on some molybdates (Brixner 1973) showed that they were Pt inclusions. But in this study the possibility of Pt inclusion is ruled out as they (triangular/hexagonal patterns) formed only upon post-growth heat treatment.

5.6 MICROHARDNESS MEASUREMENTS

Vickers microhardness was measured on both (100) and (001) surfaces using diamond pyramid microindenter fitted with a metallurgical microscope. The indentation was carried out at room temperature for 10 s for all loads. The details of experimental arrangements are as described in Chapter 3.

The microhardness values were calculated using the equation (3.1). Figure 5.16 shows the variation of Vickers microhardness with applied load for (100) and (001) faces of PbWO$_4$ crystals. It is to be noted that the hardness values decrease initially with increase in load and remain constant thereafter. This is because the law of geometrical symmetry, which sates that for all pyramidal indenters the hardness of a given material should be independent of the normal load (Brookes 1983), holds for indentations made at normal loads above some particular value (say 100 gf in this study) But at loads below this level, there are many exceptions. The major part of the more reliable data shows that the hardness tends to increase with decreasing load as discussed for lead molybdate in Chapter 3.

Figure 5.17 shows log d vs log P plot and the values of work hardening coefficient, n, have been calculated by least square fit method. The fact that the
Figure 5.16 Variation of Vickers microhardness of PbWO$_4$ with applied load on (100) and (001) faces
Figure 5.17 Log d vs log P plot for PbWO$_4$ crystal on (100) and (001) faces
decrease in hardness with increase in load for n<2 has already been postulated by Onitsch (1950).

5.7 CONCLUSIONS

Optical transmission studies of the crystals showed gradual decrease in optical quality from the top part of the growing crystal and repeated crystallisation improved the transparency of the crystals in the lower wavelength region (340 - 500 nm). Radiation damage studies were carried out and it was found that the optical damage was more for the yellow coloured sample obtained from the bottom portion of the crystal than for the uncoloured sample obtained from the top portion of the crystal. The measured excitation-emission spectra are consistent with the literature and it is clear that the emission intensity has strong relation with the optical transmittance, i.e., the spectra evidenced decrease in emission intensity for the bottom part of the crystal due to poor optical quality. Chemical etching revealed etch pit formation and subgrain boundaries. Other studies such as thermal etching and differential thermal analysis have been proved to be convenient tools to measure the degree of perfection of the grown crystals.