

## The PbWO<sub>4</sub>:Nb single crystal growth and its optical properties

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### PbWO<sub>4</sub>:Nb 단결정의 성장과 그 광학적 특성

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**Abstract** High quality pure and Nb-doped PbWO<sub>4</sub> Single Crystal were grown from a 50%~50% mixture of Lead oxide (PbO) and Tungsten oxide (WO<sub>3</sub>) by Czochralski method in Iridium crucible. The stoichiometric deviation correspond to the selective loss of the crystal constituents is found to be responsible for the yellowish coloration of PbWO<sub>4</sub>. Through the X-ray powder diffraction experiment, we have investigated the lattice constant variations of each PbWO<sub>4</sub> crystals. We also present information on their photoluminescence (PL), optical absorption properties and Raman spectra. The temperature dependence of PL intensity and FWHM (Full Width Half Maximum) were measured in the temperature range 10 K~300 K. One observes a slight temperature dependence in the low temperature region and PL intensity decreases over 200 K by thermal quenching. The activation energy, Huang-Rhys coupling constant and inhomogeneous broadening acquired from their temperature dependence

**요약** Ir 도가니에서 PbO와 WO<sub>3</sub>를 50%~50% 혼합한 시료로부터 초코랄스키 성장방법에 의해 고품질의 순수한 PbWO<sub>4</sub>와 Nb 도핑한 PbWO<sub>4</sub>를 성장 시켰다. 결정을 성분의 선택적 결손에 부합하는 화학양론적 변화는 PbWO<sub>4</sub>의 노란색 형성에 원인이 되었다. X선 회절 실험을 통해서 각 PbWO<sub>4</sub> 결정의 격자상수 변화를 조사하였으며 광발광, 광흡수 및 라만 스펙트럼에 대한 특성들에 대해 조사를 하였다. 광발광은 10 K~300 K 온도 영역에서 측정 되었으며 낮은 온도 영역에서는 미흡한 온도의존성을 보였으며 200 K 온도 이상에서는 열적소광에 의한 광발광 강도의 감소를 보였다. PL 강도와 반치폭의 온도 의존성으로부터 각 PWO 시료에 대한 활성화 에너지, Huang-Rhys 결합상수, 비균질선폭계수를 구하였다.

### 1. Introduction

Although the PbWO<sub>4</sub>(PWO), also called Lead Tungstate compound have been researched since 1940's [1]. It was unnoticed by detector groups because of its relatively low light yield. Due to a strong thermal quenching at room temperature, the PWO compounds proved to have a very fast but relatively low light yield scintillation. But the PWO

single crystals have attracted interesting scintillator because of high density, short radiation length, short decay time, strong radiation hardness and cost. The optical and many other properties of PWO are affected by the presence of impurities like a foreign ions, the selective compound loss and defects found in the grown crystals during crystal growth and powder processing. This gives rise to the stoichiometric deviation that is the main

affection for the yellow coloration and other properties of PWO. In our experiment, Pb deficiency through the evaporation in the melting process was detected through the X-ray fluorescence (XRF) measurement. It is possibly related to yellowish PWO. Annealing over 15 hours at 850°C before growing and the very slow Temperature increasing process (40°C/h) improved transparency of PWO as restraining Pb evaporation. The nature of the color center in PWO is still unrevealed, but it is very sensitive to the growing condition such as gas atmosphere, the pressure, the kinds of crucible, and raw powder condition, etc. [2] From the optical absorption and transmittance measurement, we observed a significant absorption around 430 nm (2.88 eV) which in cases generates yellow coloration. The photoluminescence (PL) spectrum is peaked about 510 nm with a range from about 370 nm to 570 nm with the superposition of the two broad band at 450 nm and 510 nm respectively. PWO samples have similar PL spectrum. PL spectra of PWO reported the superposition of at least two components [3, 4].

The PL spectra was measured as function of temperature in the range 10 K~300 K. The activation energy acquired from the thermal quenching.

We observed 10 raman active mode and confirmed that there are two distinct W-O bond lengths in the PWO crystals through the Raman spectra measurement.

## 2. Experimental procedure

PWO single crystals were grown using radio frequency heating Czochralski crystal growing system with the 20 KW RF generator (CRYSTALOX(u.k.), MCG3, KBSI TAEGU BRANCH). Figure 1 is a schematic diagram of Czochralski crystal growing system. They were pulled from melt that was consisted of 50%~50% mixture of lead oxide (PbO) and Tungsten oxide (WO<sub>3</sub>) in the Ir crucible of 50 mm diameter in argon atmosphere. It was reported that the Pt crucible caused PWO to yellow coloration. Growing in O<sub>2</sub> atmosphere has same results. The PWO growing in a 50 mm diameter Ir crucible in Ar atmosphere is informed as best match for colorless PWO single crystals [5]. The pulling rate was 3 mm/h, the rotation rate 18 rpm. The melt temperature was controlled within an accuracy of

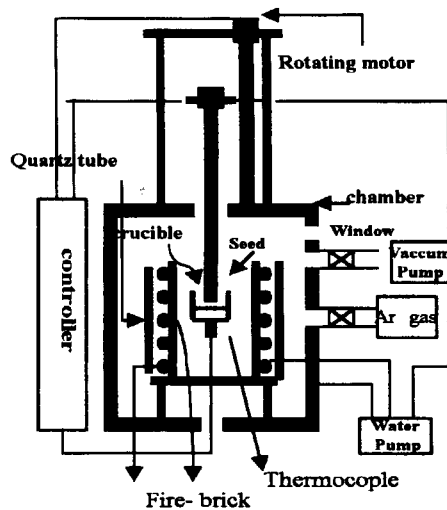


Fig. 1. Schematic arrangement of czochralski growing system.

0.1°C. The melting point of material was said to be 1123°C. The melting point of the material was found to get shifted towards higher temperature side after its first growing. Figure 2 is the experimental procedure.

For comparison, two other PWO samples (which is called PWO 4, PWO 5 by us) were doped with about 0.5 wt%, 4 wt% of Nb<sup>5+</sup> respectively. Samples were cut from the tail of the crystals. In case of the Nb-doped PWO single crystals, there have been found core that is generally formed along the growth direction in the center of crystal rotation. While PWO 4 with the size of about 15 mm in

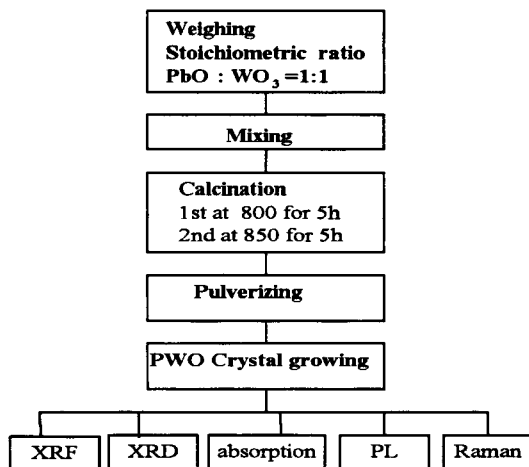


Fig. 2. Schematic diagram of the experimental procedure.

Table 1  
Tristimulus values of PWO(CIE)

	X	Y	Z
Colorless PWO	68.7161	70.3185	79.4071
Dark yellow	59.4477	64.3952	47.2857
Light yellow	64.7007	66.5599	71.7480
Nb doped	58.6897	60.0476	66.6310

diameter and 30 mm in length had core-defect size below 1 mm PWO 5 has shown an incomplete crystallization. The highly doped crystals like PWO 5 need a more careful treatment (pulling rate, rotation rate, etc.) during growing. For the most part, the formation of core originates from gases contained in the materials and impurities gathering caused by components deviation and the dislocation density also increase with growth rate. This can possibly be avoided if the temperature gradient in the melt can be greater than the equilibrium liquid temperature gradient at the interface. The starting materials need a sophisticated handling as well.

PWO samples [colorless;PWO 1, dark yellow; PWO 2, light yellow;PWO 3, Nb doped (0.5 wt%): PWO 4] classified according to their color and doping amount and were cut and polished in the form of a plate 9×9×1 mm for the absorption, PL, Raman spectrum measurement. The Pb deficiencies were found as 0.35 %, 0.2 % and 0.07 % for PWO 1, PWO 2, PWO 3 through the XRF measurement. Table 1 indicate Tristimulus values of each sample in the CIE (commission Internationale de l'Eclairage). As the PWO is very brittle, it is cut by self-made cutter. The examples of PWO crystals grown by the Czochralski method are shown in Fig. 3.

### 3. Result

#### 3.1. The Structure of PWO

PWO is a tetragonal, scheelite-type crystal belong

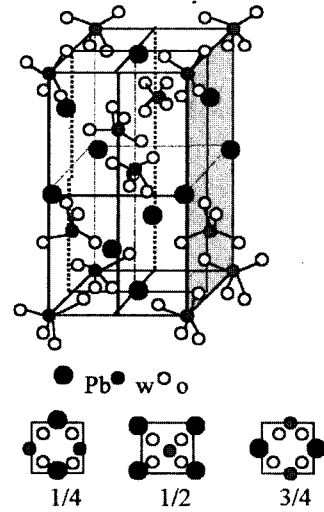


Fig. 4. The structure of PWO.

to the space group  $C_{4h}^6$  ( $I4_1/a$ ) and the point group  $C_{4h}$  ( $4/m$ ) [6]. The site symmetry at Pb and W positions is  $S_4$ . Ions are located in two types of oxygen tetrahedrons which are slightly rotated with each other. Each W ion is covalently bonded to the four nearest oxygen ions. The W-O bond lengths are 1.762 Å, 1.849 Å, and 1.859 Å estimated from Raman spectrum. Each Pb ion is surrounded by 8 oxygen atoms which belong to  $WO_4$  tetrahedrons. The bonding between Pb and oxygen ions is primarily ionic in character.

Lattice constants are  $a = b = 5.446$  Å,  $c = 12.082$  Å for colorless PWO from XRD measurement.

#### 3.2. X-ray Diffraction

The X-ray powder diffraction patterns for each sample were essentially the same and measured in the  $2\theta$  angle range from  $10^\circ$  to  $80^\circ$ . The powder X-ray diffraction patterns obtained are shown in Fig. 5. The lattice constants and unit-cell dimensions acquired from XRD are shown in Table 2.

#### 3.3. Absorption and transmission spectrum

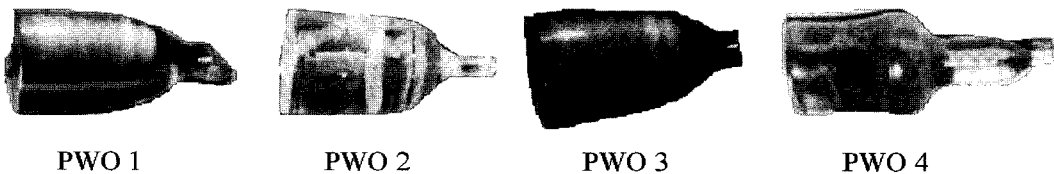


Fig. 3. PWO single crystals.

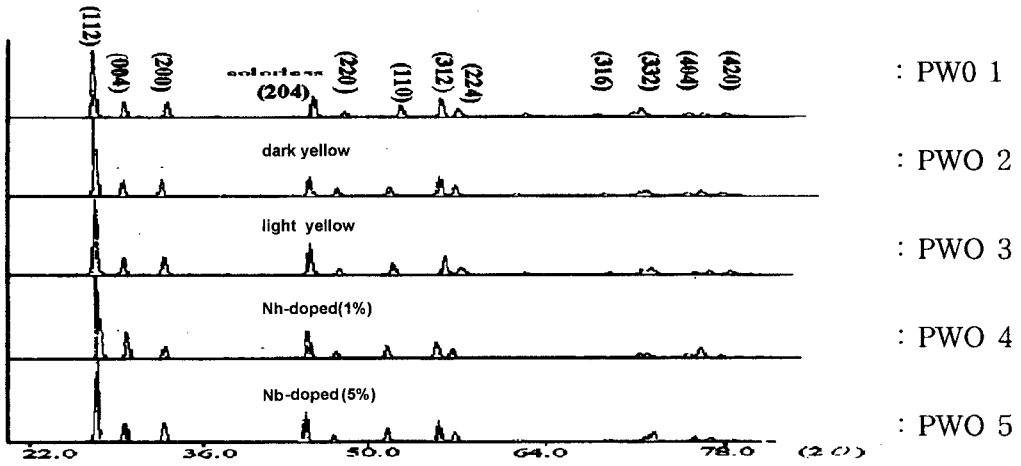


Fig. 5. The power X-ray diffraction patterns of PWO.

Table 2  
Unit cell dimensions of PWO

	a (Å)	c (Å)	V (Å <sup>3</sup> )	V/V <sub>0</sub>	c/a
PWO 1	5.446	12.082	358.3	1	2.213
PWO 2	5.460	12.021	358.4	1.0002	2.202
PWO 3	5.455	12.082	359.5	1.0033	2.215
PWO 4	5.455	12.039	358.2	0.9997	2.207
PWO 5	5.458	12.012	357.8	0.9986	2.2008

Transmission spectra, measured 1mm crystal thickness (PWO 1~4) from 250 nm to 900 nm with UV-VIS-NIR spectro photometer (Varian CARY 5G), are shown in Fig. 6. A significant absorption around 430 nm ( $\approx 2.88$  eV) was found for PWO 2, 3. It is believed to be due to the presence of holes

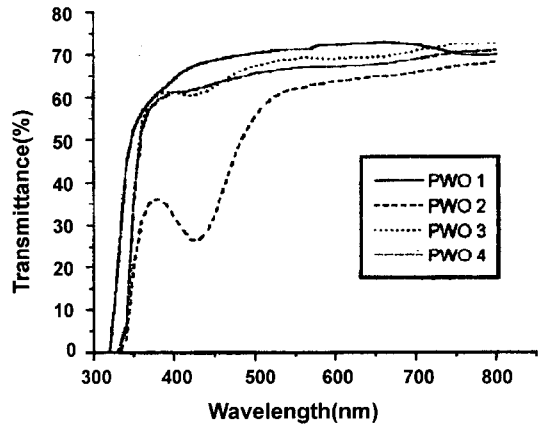


Fig. 6. Transmittance (%) of PWO.

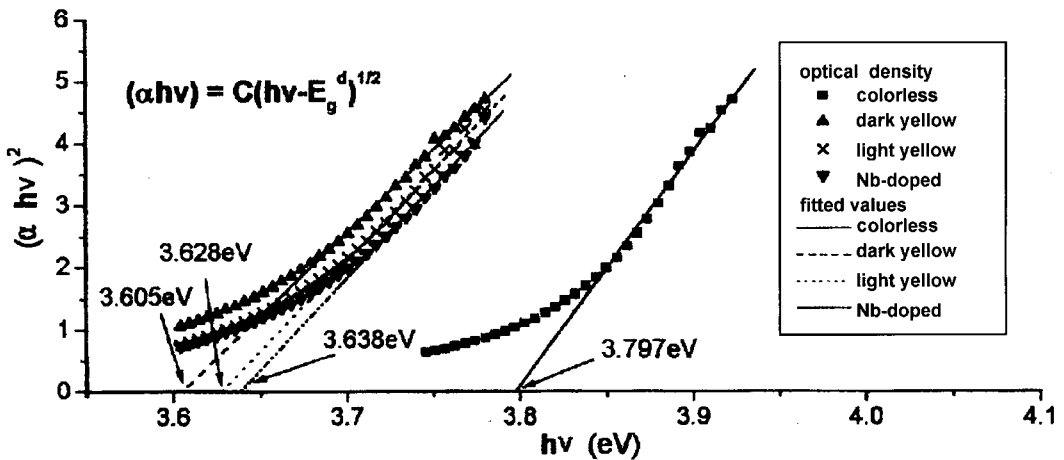


Fig. 7. The plots of  $(\alpha \cdot hv)^2$  vs. incident photon energy  $hv$  in PWO crystals at 300 K.

trapped by lead ions, is found to be responsible for the yellowish coloration of PbWO<sub>4</sub> [7]. A hump in the transmission is observed over the range about 350 nm~430 nm. Figure 7 is the plots of  $(\alpha \cdot hv)^2$  vs. the incident photon energy  $hv$  in PWO crystals at 300 K. The optical band gap (E<sub>gd</sub>) was obtained from a direct transition formular (1)

$$\alpha \cdot hv = C(hv - E_g^d)^{1/2} \quad (1)$$

where C is constant. The optical band gap energy were 3.745, 3.587, 3.587, 3.588 eV for PWO 1~4 respectively.

### 3.4. Photoluminescence

The luminescence properties of PWO are due to not only to regular radiation center but also to centers related to point structure host defect. Several specialist investigate about its luminescence mechanism but many interpretations are not yet unified. The spectra of PWO samples photoluminescence at 300 K are shown on Fig. 8. PL spectrum is peaked about 510 nm with a range from about 370 nm to 570 nm with the superposition of the two broad band at 450 nm and 510 nm respectively. Excitation wavelength is used 325 nm He-Cd laser.

The blue luminescence reported that it is caused by 6p-6s<sup>2</sup> transition of Pb<sup>2+</sup> ions or due to a charge transfer transition between the tungsten group and Pb<sup>2+</sup> ions [8]. Van Loo concluded that green-yellow luminescence due to a charge transfer of an electron, which has been excited from the 6s<sup>2</sup> state of the Pb<sup>2+</sup> ions, occupying an empty d-state of the

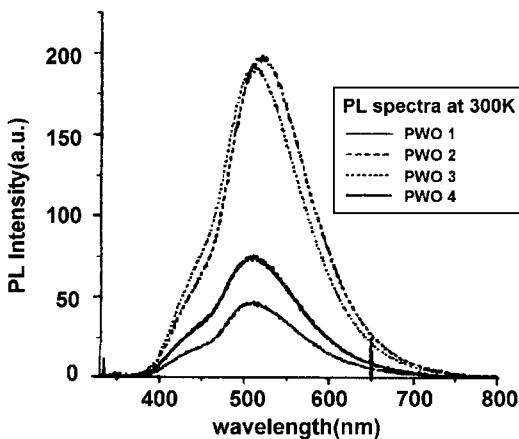


Fig. 8. The PL spectra of PWO at 300 K.

tungstate group to the 6s<sup>2</sup> state of the Pb<sup>2+</sup> ion [9]. Glasser has found several luminescence bands, a blue one, two green, one yellow and two red. The green luminescence has been explained as intrinsic luminescence of relaxed excitons of Pb-WO<sub>4</sub> type, yellow as WO<sub>3</sub> luminescence and red bands as F<sup>-</sup> center luminescence [10]. The PL spectra at different temperature in the range 10 K~300 K was shown Fig. 9(a) for PWO 1, Fig. 9(b) for PWO 4.

The temperature dependence of the intensity of the total PL of each PWO samples which were excited 325 nm ( $\approx 3.8$  eV) was presented in Fig. 10.

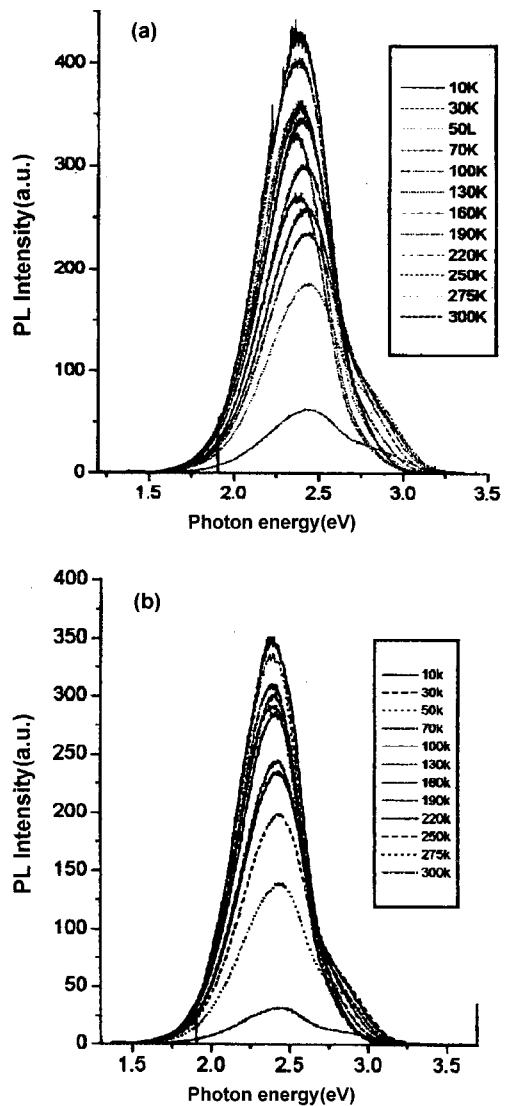


Fig. 9. TL PL spectra for PWO 1and PWO4 as function of Temp. (K).

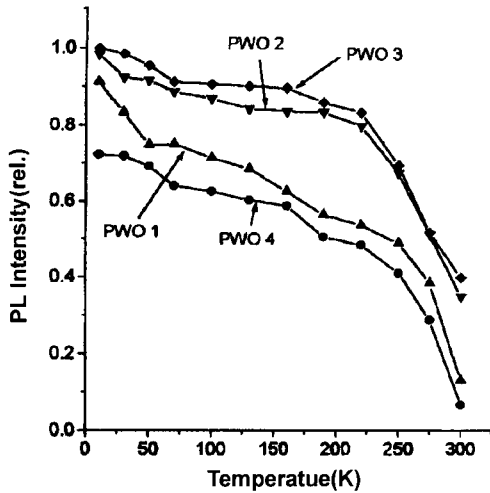


Fig. 10. The temperature dependence of the intensity of the total PL of PWO.

One observes a slight temperature dependence in the low temperature region and PL intensity decrease over 200 K by thermal quenching. It has been also found a strong thermal quenching close to room temperature and lead to a very fast decay but relatively low light yield compare with other tungstate crystals.

The thermal quenching can be represented as follow

$$I/I_0 = [1 + C \exp(-\Delta E/kT)]^{-1} \quad (2)$$

where  $\Delta E$  is the activation energy.

Figure 11 is the plots of  $\ln(I)$  vs. to the temperature (T).

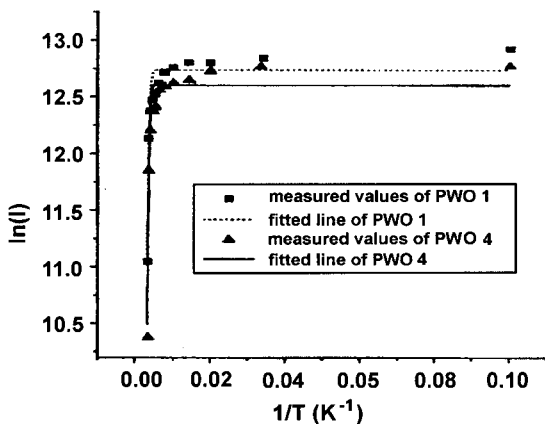


Fig. 11. The plots of  $\ln(I)$  vs. the temperature (T) about PL spectra.

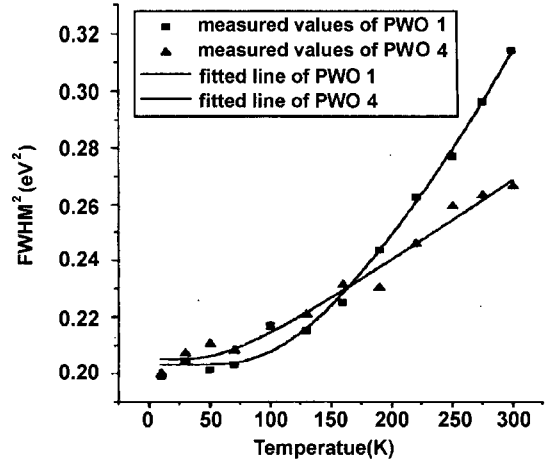


Fig. 12. Plots of  $(FWHM)^2$  vs. the temperature (T) about PL spectra.

$\Delta E$  is amount to 0.35, 0.20, 0.16 and 0.42 eV for PWO 1~4.  $H(0)$  is, FWHM at absolute temperature zero, given by

$$H(0) = 2\sqrt{2\ln 2S} \hbar \omega \quad (3)$$

where S is Huang-Rhys coupling constant.

The temperature dependence of FWHM of PL spectra described as follow

$$H(T)^2 = H(0)^2 \coth \frac{\hbar \omega}{2kT} + H_{inh}^2 \quad (4)$$

where  $H_{inh}$  is the inhomogenous brodenning. Figure 12 is the plots of  $(FWHM)^2$  vs. the temperature (T) for PWO 1, 4 and it used same plotting for PWO 2, 3 as well. S and  $H_{inh}$  are 41, 49, 47, 43; 52, 63, 59, 65 for PWO 1~4 respectively.

### 3.5. Raman spectra

Group-theoretical analysis of the scheelite structure  $C_{4h}^6$  space group gives the distribution of the vibrations into the irreducible representations as follows

$$\Gamma = 3A_g + 5B_g + 5E_g + 3A_u + 3B_u + 4E_u \quad (5)$$

$A_g$ ,  $B_g$ , and  $E_g$  are Raman active and  $A_u$ ,  $B_u$ ,  $E_u$  are infrared active. Figure 13(a) is PL spectrum of PWO 1 in the range of about 325~340 nm and was found several sharp peak. The first line in Fig. 13(a) represent as peak position (nm), the second line as the each peak frequencies and the third line as the shift values calculated from the excited laser

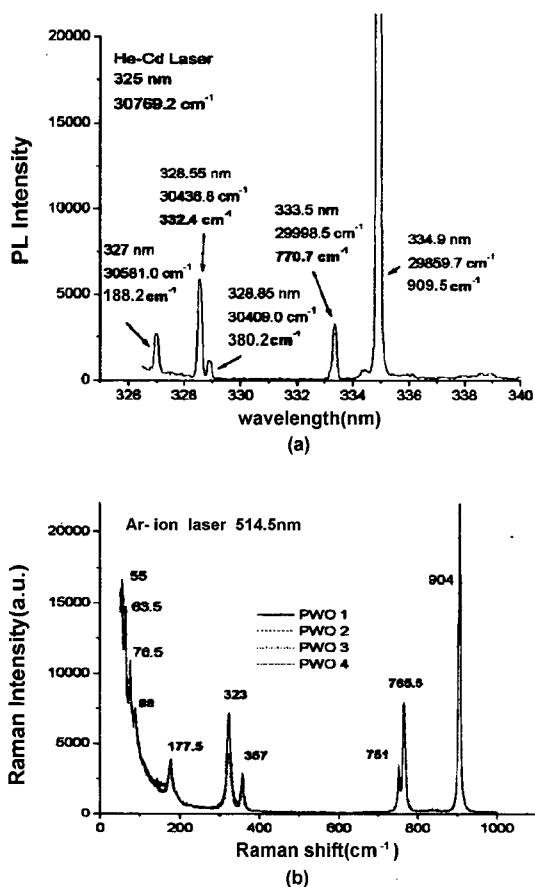


Fig. 13. (a) PL spectrum of PWO 1 in the range of about 325–340 nm (b) Raman spectrum of PWO.

frequency (325 nm : 30769.2 cm<sup>-1</sup>) This values were corresponded to Raman shift. Figure 13(b) is the Raman spectrum of PWO.

Table 3  
Assignments of the fundamental vibrational modes of PWO

R. K. Khanna v (cm <sup>-1</sup> )	A. Jayar -aman v (cm <sup>-1</sup> )	Our measure-ment	
76		76.5	Pb <sup>2+</sup> -Pb <sup>2+</sup> St (B <sub>g</sub> )
61	67	63.5	Pb <sup>2+</sup> -Pb <sup>2+</sup> St (E <sub>g</sub> )
52	59	55	WO <sub>2</sub> <sup>2-</sup> -WO <sub>2</sub> <sup>2-</sup> St (B <sub>g</sub> )
86	80	88	WO <sub>4</sub> <sup>2-</sup> -WO <sub>4</sub> <sup>2-</sup> St (E <sub>g</sub> )
187	182		R <sub>x,y</sub> (E <sub>g</sub> )
178		177.5	R <sub>z</sub> (A <sub>g</sub> )
322	329	323	v <sub>2</sub> (A <sub>g</sub> WO <sub>4</sub> <sup>2+</sup> bend)
322		323	v <sub>2</sub> (B <sub>g</sub> )
348			v <sub>4</sub> (B <sub>g</sub> )
353	360	357	v <sub>4</sub> (E <sub>g</sub> WO <sub>4</sub> <sup>2-</sup> bend)
748	755	751	v <sub>3</sub> (E <sub>g</sub> W-O bend)
764	769	765.5	v <sub>3</sub> (B <sub>g</sub> W-O bend)
900	903	904	v <sub>1</sub> (A <sub>g</sub> W-O stretch)

The observed Raman frequencies for PWO are listed in Table 3 which was compared with an observed Raman modes by Jayaraman [11] and R.K. Khanna [12].

W-O bond lengths were acquired from the equation (4) which is plotted by F.D. hardcastle and I.E. Wachs and through correlating W-O Raman stretching mode wavenumber to their reported crystallographic bond lengths of Tungstates [13].

$$\nu = 25.823 \exp(-1.902 R) \quad (6)$$

Where R is the W-O bond length.

We estimated the W-O bond length for 751, 765.5, 904 cm<sup>-1</sup> raman stretching mode, it were 1.762 Å, 1.849 Å, 1.859 Å. There are two distinct W-O bond lengths in the PWO crystals.

A lower Raman stretching mode wavenumber indicates a more regular structure. PWO has the most regular tetrahedron compare with other tungstates.

#### 4. Conclusions

The pure and Nb-doped PWO, grown by the Czochralski method with Iridium crucible. The stoichiometry deviation is mainly responsible for PWO yellow coloration like Pb deficiency detected from XRF measurement. The lattice constants are a = b = 5.446 Å, c = 12.082 Å for PWO 1 and a = b = 5.455 Å, c = 12.039 Å. The lattice constant a is increased with yellow coloration. PWO 2 and 3 has shown A significant absorption around 430 nm (≈2.88 eV). The optical bandgap energy estimated as 3.745, 3.587 eV, 3.587, 3.588 eV for PWO 1–4 respectively from optical absorption measurement. PL spectrum is peaked about 510 nm with a range from about 370 nm to 570 nm with the superposition of the two broad band at 450 nm and 510 nm respectively.

One observes a slight temperature dependence in the low temperature region and PL Intensity decrease over 200 K by thermal quenching. The activation energy are amount to 0.35, 0.16, 0.20 and 0.42 eV for PWO 1 4 using thermal quenching. The sharp peaks of PL spectra correspond to the Raman spectra of PWO. The bond lengths for W-O stretching mode are 1.762 Å, 1.849 Å, 1.859 Å. There are two distinct W-O bond lengths in the PWO crystals.

### Acknowledgements

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