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Effect of Annealing on the Luminescene Property of $PbWO_4$ Crystals Grown by the Czochralski Method

PWO Crystals grown by the Czochralski method were annealed under different conditions. The transmittance of PWO crystal was decreased when it was annealed in an oxygen-rich environment; whereas it was increased when the crystal was annealed in vacuum. A mechanism on the transmittance change was proposed. The main peaks of X-ray exited emission spectra showed that both as-grown and vacuum-annealed crystals fit into blue light region with the latter one showing higher intensity. The oxygen-rich annealed crystal shifted to longer wavelength of green light region at lower intensity. The faster components in the light yield of crystals annealed in vacuum were higher correspondence to its higher intensity of the blue light.

Keywords: $PbWO_4$ crystals; annealing; transmittance; X-ray excited emission spectra; light field

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Introduction

Single crystals of $PbWO_4$ (PWO) became an interesting subject of optical study in the recent years due to its potential for future generation of fast, high density and radiation-hard scintillation detectors in high energy (KOBAYASHI et al., NEYRET et al., POLAK et al., ANNENKOV et al.). Although many theories have been raised on the luminescence properties and the mechanism of PWO crystal (EPELBAUM et al., ITOH et al. and HOFER et al.), there is a common view that the luminescence property is very sensitive to the growth condition, the dopants and the annealing process.

PWO crystals occur in nature as two polymorphs: (1) the tetragonal stolzite that crystallizes with a scheelite type structure (space group $I4_2/a$) and (2) monoclinic raspite (space group $P2_1/a$) (FUJITA et al.). The PWO crystals with the scheelite phase can be grown in laboratory, yet the crystals with the raspite phase can not be grown. The raspite phase transforms irreversibly into the stolzite form at 400 °C. PWO crystals can be grown by both Czochralski and Bridgman method (YAN, LECOQ). There are several advantages for the PWO crystals grown by the Czochralski method over those by the Bridgman method, for instance higher growth rate and lower inner stress that makes it easy to cut and polish. In the melt however, PbO and WO_3 vaporize differently which results in a stoichiometric deviation along the growth direction by an unsealed Czochralski method (PEIGNEUX). This causes the decrease on transmittance. In this paper we described the effect of annealing conditions on the luminescence property of PWO crystals by the Czochralski method.

Experiment

The crystals were grown by the Czochralski method. Pure starting materials of PbO and WO_3 (with purity of 99.995%) were used at molar ratio of 1:1. After being mixed for 20 h, the starting materials were loaded into a crucible and then placed into a heat resistant furnace. The temperature gradient was 30 °C/cm with the growth rate of 3 mm/h and the rotation rate of 25 rpm. The growth orientation was [001]. The size of this so-called "as-grown" crystal was about 25 x 25 x 100 mm (Fig. 1).

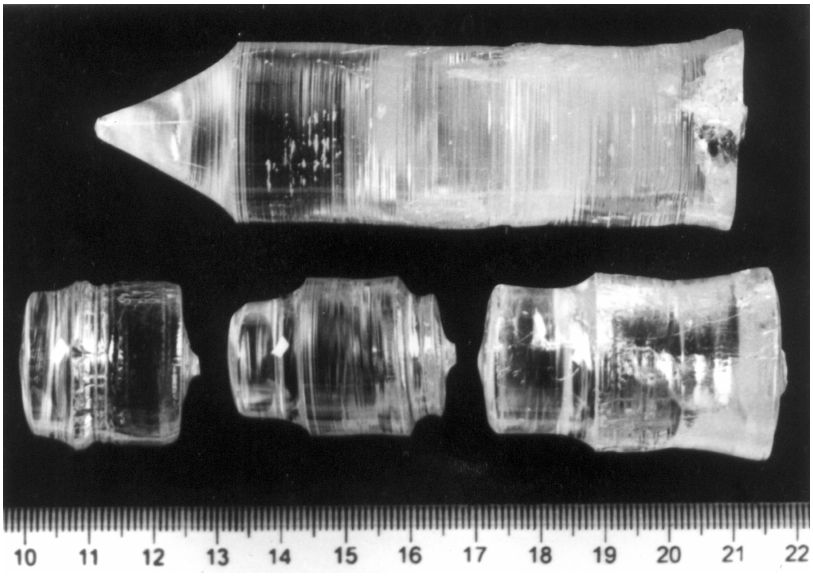

Fig. 1: Photo of as-grown crystals

There existed thermal stress inside the crystals because they were grown under certain temperature gradient. Besides, chemical and structural stress also co-existed in the crystals due to interaction of dopants and composition derivation, etc. However, all the inner stress could be eliminated by annealing process. The annealing conditions could affect the luminescence properties of crystals. One was the vacuum annealing. The crystal was heated at the rate of 50 °C/h until reaching 920 °C when it was placed into the tube furnace. The furnace was pumped under vacuum and the crystal was annealed at 920 °C for 24 h. Afterwards, the crystal was cooled at the rate of 50 °C/h. The vacuum pump was turned off at the room temperature. For the oxygen-rich annealing process, the crystal in a tube furnace was heated in the same way. Oxygen began to be blown into the furnace at the rate of 400 mL/min when the oven temperature reached 460 °C. The crystal was annealed this way for 24 h or 48 h. After being annealed, the crystals were cut from the top at the size of about 10 ×10 × 10 mm. Then the [001] faces were fully polished and the transmittance was measured on a SPEX1000M spectroscopy. The exposure time was 200 ms with measuring pace of 5 nm. X-ray excited emission spectra was measured at a voltage of 80 kv, with the target of W and the slit width of 5 nm. With ^{137}Cs being the radiation source, the light yield was collected by a XP2262 photomultiplier tube and integrated in a charge-sensitive ADC varying the gate width between 0.25 and 4 μs.

Results and Discussion

1. Transmittance spectra

Fig. 2 shows the effect of different annealing conditions on the transmittance of PWO crystals. The pale yellow as-grown crystals had main absorption peak of 420 nm. The transmittance at this wavelength was increased when the crystal was vacuum annealed; in contrast, it was decreased when the crystal was annealed under an oxygen-rich condition. When the crystal annealed under an oxygen-rich condition was re-annealed under vacuum, the yellow color vanished.

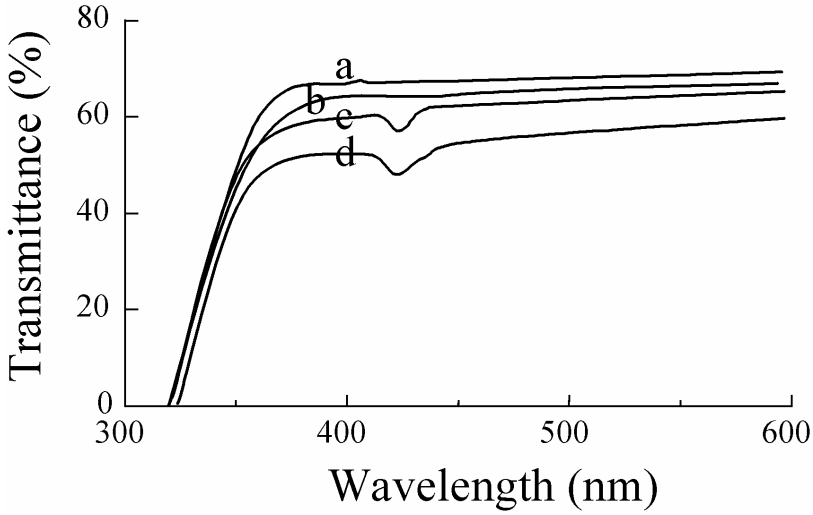

Fig. 2: The transmittance of PWO crystals under different annealing conditions: a: crystal being vacuum annealed; b: crystal being re-annealed under vacuum after being oxygen-rich annealed; c: as-grown crystal; d: crystal being oxygen-rich annealed.

There are two viewpoints on the absorption at 420 nm--the O^- absorption and the Pb^{3+} absorption. It was reported that in a CaS crystal, the higher the temperature was, the higher the concentration of F (Vs + 2e) center over that of F^+ (Vs + e) center was (Rennie). There was equilibrium between the F center and the F^+ center. We assume that the same principle applies to the PWO crystals; otherwise, the annealing under oxygen-rich atmosphere could induce the diffusion of oxygen ion into PWO crystals thus lowering the oxygen vacancy concentration. The relative concentration of F (V_o + 2e) center to that of F^+ (V_o+ e) center was increased to achieve charge balance. The existing capacity of O^- is reduced in the same manner. Therefore the Pb^{3+} in the crystals resulted in the absorption at 420 nm. In fact, PbO could be oxidized into Pb_3O_4 or even PbO_2 in the air at the temperature of 390 °C or above. From analysis of the volatile composition, it was found that there were Pb^{3+} and Pb^{4+} containing compounds at higher concentration in the residue on the wall. It was known that Pb^{4+} could not induce absorption due to its electronic configuration of $4f^{14}5d^{10}$. Pb^{3+} could be transformed into Pb^{2+} under vacuum, therefore the absorption at 420 nm was weakened and furthermore the transmittance was enhanced.

2. X-ray excited emission spectra and light field

Fig. 3 shows X-ray excited emission spectra for crystals annealed in different atmosphere. It was observed that the as-grown crystals fit into the blue light region with main peak at 464 nm. The blue light intensity was improved for the crystal being annealed in vacuum. However, for the crystal being annealed under oxygen-rich environment, the emission was shifted to longer wavelength with main absorption peak at 516 nm in the green light region. Interestingly, when this crystal was annealed again in vacuum, the main emission peak was shifted back to the blue light region.

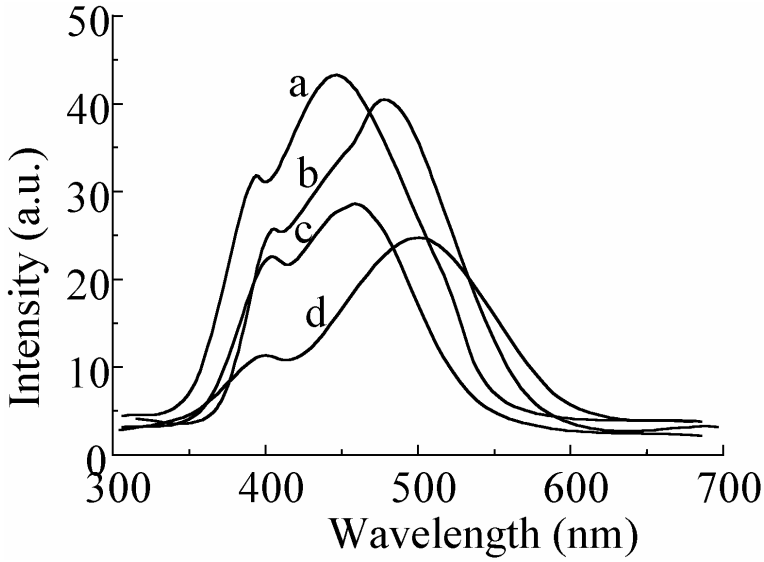

Fig. 3: X-ray excited emission spectra of PWO crystals being annealed under the following conditions: a: crystal being vacuum annealed; b: crystal being re-annealed in vacuum after being oxygen-rich annealed; c: as-grown crystal, d. crystal being oxygen-rich annealed.

Comparing Fig .3 with Fig.2, it was found that the absorption peak at 420 nm was related to the emission of green light. But their origination was different because no emission of blue light for PWO crystal exited by the light of 420nm was obtained. The shorter the response time to the radiation was, the higher the intensity ratio of blue light to green light was. Table 1 showed the light field of crystals under different annealing conditions. The faster componenents in the light yield of crystal annealed in vacuum was higher correspondence to its higher intensity of blue light.

Table 1: Light field of PWO crystals in different annealing conditions.

Crystal	LY measured within 100ns (p.e./MeV)	Fraction of the LY emitted within 30ns (%)	Maxium wavelength of radio luminescence (nm)
As-grown	12	70	464
Vacuum annealed	17	85	460
Vacuum annealed after oxygen-rich annealed	15	65	480
Oxygen-rich annealed	9	55	516

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