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Influence of Y doping on the scintillation properties of $PbWO_4$ single crystals

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Abstract

Undoped and series of Y^{3+} doped $PbWO_4$ crystals were grown by the Czochralski method. The transmittance at 420 nm wavelength of $PbWO_4$ 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. Compared with undoped crystals, the transmittance and the ratio of the blue emission to green emission for $Y{:}PbWO_4$ were improved. It implied that Y doping prevented the creation of Pb^{3+} in the crystal. Correspondingly, the light yield of $PbWO_4$ by doping Y was increased. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: $Y{:}PbWO_4$ crystals; Czochralski method; Transmittance; Emission spectra; Light yield

1. Introduction

The $PbWO_4$ single crystals became a subject of increasing interest in the recent years due to their possible usage in the high energy physics field [1–3]. A dramatic increase of this research activity has been observed in connection with the planned construction of a $PbWO_4$ based electromagnetic calorimeter for the Large Hadron Collider (LHC) at CERN [4], but at least some problems have arisen which remained to be solved, for example: (1) an additional coloration of $PbWO_4$ crystals which exists mainly due to the presence of the absorption band around 420 nm and (2) the decreasing of light yield related to the defects of lead and oxygen vacancies (V_{Pb}, V_O) and induced color centers of Pb^{3+} [5] and O^- [6], etc. It was reported that doping, such as La^{3+} [7], Gd^{3+} [8], Nb^{5+} [9], could compensate the component deficiency, or eliminate the defects, improving the scintillation properties of $PbWO_4$. So Y^{3+} was doped into the crystals in this paper, and the $Y{:}PbWO_4$ crystals were grown by the Czochralski method.

$PbWO_4$ crystals occur in nature as two polymorphs: (1) the tetragonal stolzite that crystallizes

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with a scheelite type structure (space group $I4_2/a$) and (2) monoclinic raspite (space group $P2_1/a$) [10]. The $PbWO_4$ crystals with the scheelite phase can be grown in laboratory, yet the crystals with the raspite phase cannot be grown. The raspite phase transforms irreversibly into the stolzite form at 400 °C. $PbWO_4$ crystals can be grown by both Czochralski [11] and Bridgman methods [12]. There are several advantages for the $PbWO_4$ crystals grown by the Czochralski method over those by the Bridgman method, for instance, higher growth rate and lower inner stress that make it easy to cut and polish. However, PbO and WO_3 in the melt vaporizes differently which results in a stoichiometric deviation along the growth direction by an unsealed Czochralski method [13]. This might cause the decrease in transmittance.

2. Experimental procedure

Undoped and series of Y^{3+} doped $PbWO_4$ crystals were grown by the Czochralski method. The raw materials were PbO, WO_3 and Y_2O_3 with the purity of 99.99%. The atomic ratio of PbO to WO_3 was 1. The Y_2O_3 concentration was 30, 100 and 300 ppm for Y:$PbWO_4$, respectively. After being mixed for 20 h, the raw 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 $\varnothing$ 25 × 50 mm^2.

There existed the thermal stress inside the crystals because they were grown under a certain temperature gradient. Besides, chemical and structural stresses also co-existed in the crystals due to interaction of dopants and composition derivation, etc. However, the inner thermal stress could be partly eliminated by the 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 with the volume of 1 l at the rate of 400 ml/min when the oven temperature reached 460 °C. The crystal was annealed this way for 24 h. After being annealed, the crystals were cut from the top at the size of about 10 × 10 × 10 mm^3. Then the [001] faces were fully polished and the transmittance was measured on a SPEX1000M spectroscopy. The exposure time was 200 ms with a measuring pace of 5 nm. X-ray excited emission spectra were 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.

3. Results and discussion

Fig. 1 showed the effect of different annealing conditions on the transmittance of PWO crystals. The transmittance was increased when the crystal was vacuum annealed; in contrast, the transmittance, especially the transmittance at 420 nm wavelength, was decreased when the crystal was annealed under an oxygen-rich condition (in air); the crystal showed the color of yellow. There are two viewpoints on the absorption at 420 nm – the O^- absorption [6] and the Pb^{3+} absorption [5].

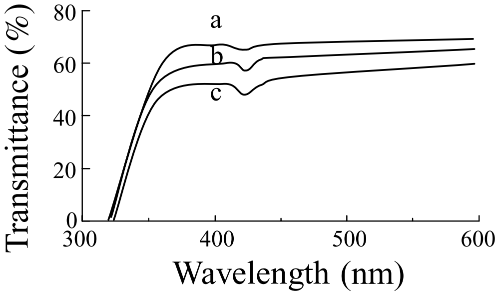

Fig. 1. The transmittance of $PbWO_4$ crystals under different annealing conditions: (a) crystal being vacuum annealed; (b) as-grown crystal; (c) crystal being oxygen-rich annealed.

There existed V_{Pb} and V_O in the crystals because the vaporization rate of PbO was faster than that of WO_3 in the growth process. O^- and Pb^{3+} were formed in order to compensate the charge balance. The vacuum annealing might induce the diffusion of oxygen ions out of the $PbWO_4$ thus increasing the oxygen vacancy concentration. Pb^{3+} was reduced to Pb^{2+} and the O^- center concentration was increased to maintain the above-mentioned charge balance. The annealing in air was likely to induce the reverse process of oxygen diffusion into the crystal, namely the increase of Pb^{3+} and decrease of O^- center concentration. The transmittance at 420 nm was increased when the crystal was vacuum annealed, whereas it was decreased when the crystal was annealed in air. This might imply that the absorption had resulted from Pb^{3+}. 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. It was found that there were Pb^{3+} and Pb^{4+} containing compounds at higher concentration in the volatile 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.

Fig. 2 showed the transmittance of Y:$PbWO_4$. Compared with undoped $PbWO_4$, the transmittance at 420 nm was obviously improved by Y doping. And the transmittance was increased with the increasing of Y ions concentration. Y ion was in a trivalent state, which would predominantly replace the Pb vacancy, preventing the creation of the Pb^{3+}. So the transmittance at this wavelength was increased.

Fig. 3 showed X-ray excited emission spectra for undoped and Y doped $PbWO_4$ crystals vacuum annealed. It was observed that there existed blue and green emission in $PbWO_4$ crystals. The emission wavelength was shifted to the shorter one for the Y doping crystal, namely the blue light intensity was improved and the green light intensity was decreasing. The luminescence decay time was shorter if the blue emission components were higher [14]. So the blue emission was called as the fast component, whereas the green emission as the slow one. The blue emission was ascribed to the regular WO_4^{2-} group [15], while the green one was related to the defect WO_3 group [16], possibly with an F center nearby [17]. Y doping replaced the V_{Pb} and reduced the defects in the crystals, improving the blue light component. The blue light component became higher with the increasing of Y concentration. However, the growth of doped crystals with higher concentration was difficult because the polycrystals were easily formed in this case.

Comparing Fig. 3 with Fig. 2, it was found that the green emission components were higher if the absorption at 420 nm in $PbWO_4$ crystals was improved. There seemed to be a correction between the 420 nm absorption and the green emission. But their origin was different because no emission of green light for $PbWO_4$ crystal excited by the light of 420 nm was obtained. Table 1 showed the light

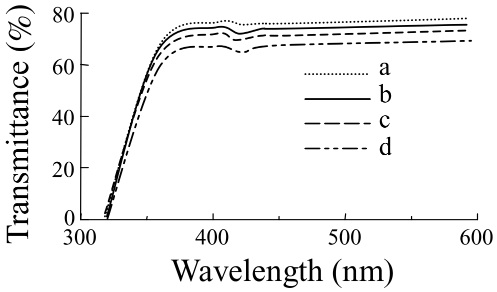

Fig. 2. The transmittance of $PbWO_4$ crystals: (a) Y doping with concentration of 300 ppm; (b) Y doping with concentration of 100 ppm; (c) Y doping with concentration of 30 ppm; (d) undoped.

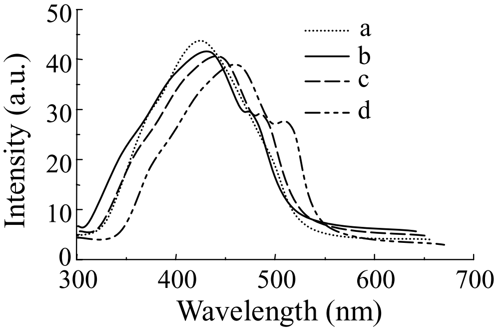

Fig. 3. X-ray excited emission spectra of $PbWO_4$ crystals being vacuum annealed: (a) Y doping with concentration of 300 ppm; (b) Y doping with concentration of 100 ppm; (c) Y doping with concentration of 30 ppm; (d) undoped.

Table 1
Light field of undoped and Y doping $PbWO_4$ crystals vacuum annealed

$PbWO_4$ crystal	LY measured within 100 ns (p.e./MeV)	Fraction of the LY emitted within 30 ns (%)
Undoped	17	80
Y (30 ppm) doping	27	90
Y (100 ppm) doping	29	92
Y (300 ppm) doping	33	95

field of crystals. The faster components in the light yield of crystal doped Y were of higher correspondence to its higher intensity of blue light.

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