A study of luminescence properties of (Gd^{3+}, Dy^{3+}, Nb^{5+})-doped lead tungstate single crystals

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Abstract

PbWO$_4$ single crystals doped with Gd^{3+}, Dy^{3+}, Nb^{5+} ions were grown using the modified Bridgeman method. Optical transmission, X-ray excited luminescence spectra, excitation and emission spectra have been investigated. All the doped PbWO$_4$ crystals exhibit improved transmittance in the short wavelength region, while Nb^{5+} doping makes the short wavelength cutoff sharper. Dy^{3+} and Nb^{5+} doping depresses the luminescence of PbWO$_4$ and the latter enhances the proportion of green component in spectra. In Dy:PbWO$_4$, the WO$_4^{2-}$ group could absorbs excitation energy, and transfers part of the energy to the Dy^{3+} ions, followed by the strong luminescence of Dy^{3+}. Gd:PbWO$_4$ is an exception because Gd^{3+} may be involved in the process of energy absorption and transfer the energy to the host. The luminescence of Gd:PbWO$_4$ has a similar intensity to that of pure PbWO$_4$ in the blue region, but the green component is decreased to some extent.
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1. Introduction

In the past decade, PbWO$_4$ crystals (or PWO) have been intensively investigated because they were chosen as scintillating crystals for the detectors of the Large Hadron Collider (LHC) at CERN [1,2]. With regard to the performance parameters of PWO, the luminescence spectrum, which consists of at least two main components a blue luminescence peak at 420 nm and green at 480–520 nm, are especially important to its employment as a scintillator and in the other high-energy physical region [3,4].

It has been established that the fast components in PWO scintillators mainly originate from the blue luminescence. Generally, photoluminescence measurements are applied to detect the luminescence of PWO, in which a xenon lamp is used in the excitation. This method cannot effectively be used to detect the luminescence for the scintillation crystal because it can only detect the slow component, but not for the fast one which is more important for excellent performance. X-ray excited luminescence (short for XEL) measurements,

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where X-rays are applied as the excitation lamp-house, can detect not only the slow luminescence but also the fast one. Of course, the host lattice involved plays a vitally important role. Many different ions have been doped into the PWO matrix to modify its luminescence and scintillation characteristics. PWO doping with trivalent ions at the level of several tens of ppm can give considerable improvement in the transmittance in the short wavelength region (350–500 nm) [5] and high radiation hardness [6].

It is the aim of this work to report on Gd^{3+}, Dy^{3+}, Nb^{5+} doping and the related changes of PWO luminescence characteristics detected by UV light and X-ray. Moreover, the transmittance features of doped PWO are reported.

2. Experiments

The PWO crystals investigated were grown from an initial mixture of stoichiometric PbO and WO_3 powders (>99.999%) under equivalent conditions using a modified Bridgeman method in the Shanghai Institute of Ceramics (SIC). The samples consist of pure PWO crystal, 200 at.ppm Gd:PWO, 0.5 mol% Dy:PWO and 1000 at.ppm Nb:PWO. They were cut into cubes of $15 \times 15 \times 20$ mm^3 in dimension with all facets polished and their opposing large faces perpendicular to *c*-axis.

First, optical transmission spectra were recorded using a Shimadzu UVPC spectrophotometer. Subsequently, the excitation and emission spectra were taken with a a Perkin Elmer LS-55 fluorescence spectrophotometer. Finally, XEL measurements are taken on a homemade setup FluorMain consisting of a X-ray excited luminescence spectrometer, where F-30 movable X-ray tube (W anode target) was used as the X-ray source. Luminescence spectra were obtained with a 44 W plate grating monochromator and a Hamamatsu R928-28 photomutiplier, with a computer acquired the data automatically. In the XEL experiments, a layer of Tyvek paper wrapped PWO crystals with only a single exposed facet was coupled to the grating of monochromator. The measurement were made with the same conditions (80 kV, 4 mA) at room temperature of 20 °C.

3. Results

Gd^{3+}, Dy^{3+} and Nb^{5+} doping can significantly improve the transmittance in short wavelength region (330–450 nm); and Nb^{5+} doping makes the short wavelength cutoff sharper (Fig. 1). This significant improvement was also reported in the previous researches [5]. The XEL spectrum of pure PWO can be defined as a superposition of at least three Gaussian components (Fig. 2a, the inset) with approximate peak wavelengths of: $I_1 \approx$ 430 nm, $I_2 \approx 520$ nm, and $I_3 \approx 620$ nm, which are distributed to self-trapped excited blue, green and red luminescence, respectively. The intensity of the luminescence of pure PWO in the blue range is higher than that of green component. Dy^{3+} and Nb^{5+} doping supress the luminescence of PWO (Fig. 2c and d). The luminescence of Dy:PWO is dominated by the blue luminescence component and the red component disappeases. The luminescence spectrum of Nb:PWO has a green luminescence componemt that is comparable to the blue one. Dy:PWO shows a sharp by distinct luminescence lines at 480 nm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) and at 572 nm ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) that coexist with the wide luminescence band from the PWO crystal host. By amplifying the spectra, a weak emission band of the Dy^{3+} 640 nm characteristic line ($^4F_{9/2} \rightarrow {}^6H_{11/2}$) can be also detected. The Gd^{3+} doped
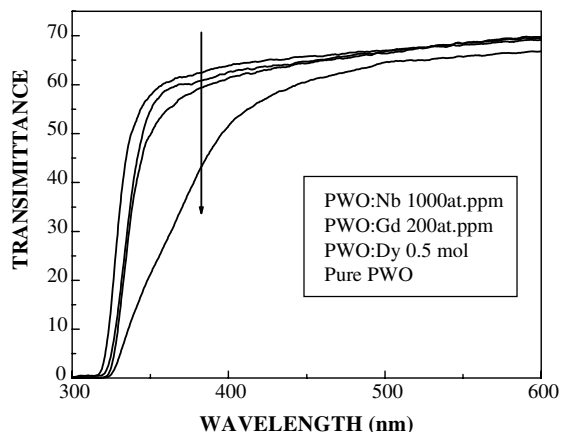

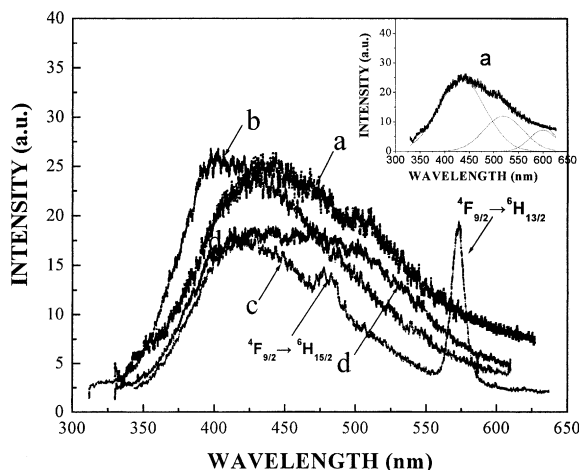Fig. 1. Comparison of the optical transmission spectra of the samples studied in this work.

Fig. 2. X-ray excited luminescence spectra of pure PWO crystal (a), 200 at.ppm Gd:PWO (b), 0.5 mol% Dy:PWO (c) and 1000 at.ppm Nb:PWO (d). Three Gaussian components of pure PWO is shown in the inset.

Fig. 4. Excitation and emission spectra of PWO doped Dy^{3+} 0.5 mol%. Emission spectra (a) $\lambda_{ex} = 310$ nm; (b) $\lambda_{ex} = 333$ nm; (c) $\lambda_{ex} = 352$ nm; (d) $\lambda_{ex} = 388$ nm; (e) $\lambda_{ex} = 453$ nm.

PWO has a similar luminescence intensity to that of the pure PWO crystal (Fig. 2b), but its ratio of green component to blue one is greatly decreased.

The excitation and emission spectra of all the samples investigated are shown in Figs. 3–5. One can see that the shapes and intensities of the luminescence spectra obtained under X-ray and UV light excitation are slightly different. Note that, under X-ray, the whole crystal volume is excited,
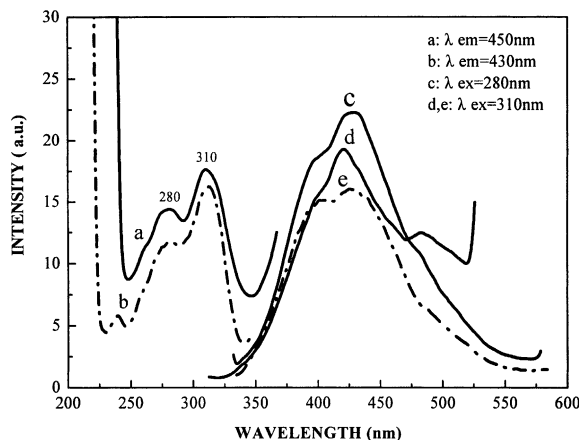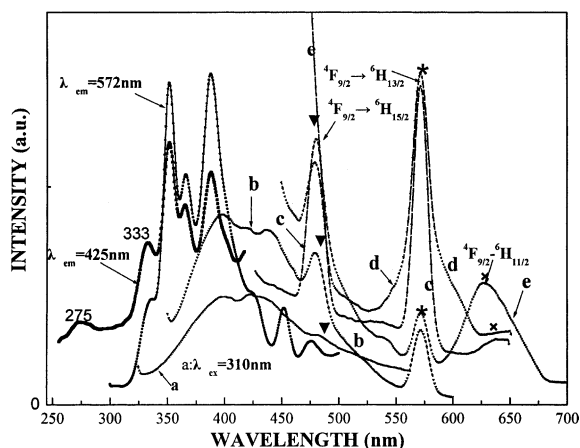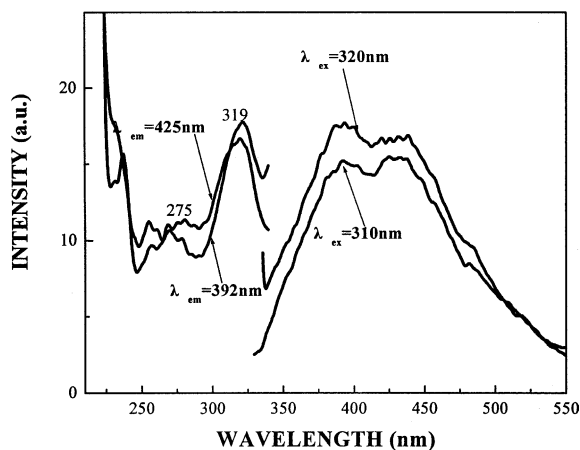

Fig. 5. Excitation and emission spectra of PWO doped with Nb^{5+} 1000 at.ppm.

Fig. 3. Excitation and emission spectra of pure PWO (solid line) and 200 at.ppm Gd:PWO (dash dot line).

so that a part of the luminescence can be reabsorbed, whereas UV light leads only to excitation within a thin surface; i.e. UV excitation only excites the surface luminescence, which is not that of the bulk luminescence of PWO crystals so that the effect of reabsorption will be small. For this reason the difference can be caused by different energy absorption taking into account that the PWO crystal has absorption in visible region (Fig. 1).

4. Discussions

In the case of pure PWO, the excitation spectrum for 450 nm emission has a wide broad band peaking at 310 nm, and a weaker band at 275 nm. The emission spectra for 310 nm excitation show a broad emission from 350 to 550 nm and that for 275 nm excitation presents a narrower emission land from 350 to 500 nm (Fig. 3). Gd:PWO has exactly the same excitation spectrum when excited by 280 nm (Fig. 3b and e) as that of pure PWO. It is very coincidental that the 274 nm excitation ($^8S_{7/2} \rightarrow {}^6I_{7/2}$) and the 311 nm emission ($^6P_{7/2} \rightarrow {}^8S_{7/2}$) of Gd^{3+} are located at exactly the same position in the excitation spectra of the pure PWO crystal. The 311 nm emission of Gd^{3+} ions can be absorbed by the PWO host and the energy transferred during the luminescence progress. So the luminescence of Gd^{3+} in PWO is quenched. Both the excited states $^6I_{7/2}$ and $^6P_{7/2}$ of Gd^{3+} ions are located in the conduction band of PWO. The luminescence from the 4f–4f transition of Gd^{3+} is slow; its quenching should not increase the slow components of luminescence in PWO. So the luminescence of Gd^{3+} doped PWO is dominated by fast components, and the intensity of blue luminescence is enhanced compared to pure PWO.

The Dy:PWO crystal shows a complex structure of excitation and emission spectra (Fig. 4). The excitation spectra for 425 nm emission show a new peak at 333 nm, meanwhile the 310 nm peak that dominates the emission of pure PWO crystal disappears. Excitation spectra monitored for 572 nm emissions consist of several peaks at 353, 387, 454 and 480 nm, which are all located on the intrinsic emission band of pure PWO crystal; meanwhile the 480 nm is also a characteristic emission of Dy^{3+}. The emission spectra of Dy:PWO excited by 310 nm UV light (Fig. 4a) show an intrinsic luminescence band of PWO host (350–550 nm), on which only a very weak characteristic line 480 nm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) of Dy^{3+} can be seen. When excited by 333 nm, the 480 nm line becomes sharper and the 572 nm characteristic line ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) emerges (Fig. 4b). The intensity of green luminescence for 352 and 388 nm excitation (Fig. 4c and d) decreases, and the 572 nm characteristic line of Dy^{3+} presents a drastic intensity increase compared with that for 480 nm emission; meanwhile the 640 nm characteristic line ($^4F_{9/2} \rightarrow {}^6H_{11/2}$) appears. The emission spectrum for 453 nm excitation (Fig. 4e) has an intense 640 nm luminescence line of Dy^{3+} and a weak 572 nm line with the disappearance of 480 nm emission. It should be noted that the profiles of the excitation spectra from the 572 nm band is very similar to that of 425 nm band. All these indicate that the emission of the Dy^{3+} ions excited by the UV light might be produced through host-sensitization. It is its structure that provides the fundamental condition for energy transfer from the host to the Dy^{3+} ions in Dy:PWO. It is very reasonable that energy transfer takes place between the Dy^{3+} ions from shorter wavelength emission to long wavelength, that is to say, in Dy:PWO, the WO_4^{2-} group could absorb the excitation energy, and then transfers part of the energy to the rare-earth ions Dy^{3+}, followed by the strong luminescence of Dy^{3+}. The green luminescence of PWO might also contribute to the luminescence of Dy^{3+}, hence the intensity of green luminescence of PWO doped by Dy^{3+} decreases greatly. The excitation spectrum of Nb:PWO (Fig. 5) has a similar shape to that of pure PWO, but its emission for 275 and 310 nm excitation all show stronger green emission, which is consistent with the results of the XEL measurements.

In general, based on radius and electronegativity, trivalent ions are supposed to occupy the Pb^{2+} site and induce an excess positive charge into the crystal, which is compensated by V_{Pb} through the formation of a dipole complex $[2La_{pb}–V_{pb}]$ [7]. Many researches have confirmed that PWO doped with trivalent ions show the absence of the slower recombination decay components and dominated blue luminescence component in its whole luminescence [6]. As can be seen in the XEL spectrum of (Dy, Gd):PWO, Nb doping is different from trivalent ion doping. Recent research [8] confirmed that in Nb:PWO, where Nb^{5+} ions replace the W^{6+} sites the spectrum does not show dielectric relaxation prosess like that of trivalent ion doping. This result reveals that the charge compensation differs from that of trivalent ions. Its charge compensation in Nb:PWO mechanism might include the production of oxygen vacancies [9]. The oxygen

vacancies can suppress the difference of $([V_{Pb}] - [V_O])$, so that Nb:PWO shows a better transmission at short wavelength than that of trivalent ion doping. Here we suggest that the V_F^- center is the origin of 350 nm intrinsic color center, and the transmittance at short wavelengths is mainly influenced by $([V_{Pb}] - [V_O])$ [10]. Nb doping enhances green luminescence in the PWO crystal compared to that of trivalent ions doping, for example Gd^{3+} and Dy^{3+} in this work. Further research work should be carried out on this doping mechanism.

5. Conclusion

Gd^{3+}, Dy^{3+}, Nb^{5+} doping improves the transmittance of PWO crystals in the short wavelength region, while Nb^{5+} doping makes the short wavelength cutoff sharper. Dy^{3+} and Nb^{5+} doping depresses luminescence of PWO, while Nb:PWO shows a higher proportion of green component in whole spectrum. In Dy:PWO, the WO_4^{2-} group could absorb excitation energy, and then transfers part of that energy to the rare-earth Dy^{3+} ions, followed by the strong luminescence of Dy^{3+}. Such luminescence centers can effectively increase the light yield of PWO, if much longer integration time gates can be used. In contrast to Dy^{3+} doping in PWO, Gd:PWO is an exception because Gd^{3+} ions may be involved in the process of energy absorption and transfer of the energy to the host. The Gd^{3+} doped PWO has a similar luminescence intensity to that of the pure PWO crystal in the blue region, but the green component is decreased to some extent.

Acknowledgements

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