

Effects of Y concentration on luminescence properties of PbWO_4 single crystals

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Abstract

The effects of Y^{3+} doping at different concentration on the luminescence properties of PbWO_4 crystals have been investigated by means of Fourier transform infrared (FT-IR) spectrum, optical transmission, thermoluminescence (TL), X-ray excited luminescence (XEL), photoluminescence (PL) under excitation of UV light and light yield measurements. The series $\text{PbWO}_4:\text{Y}$ crystal samples were grown by modified Bridgman method and the concentration of Y^{3+} in the melt was in the range of 0–1.0 mol%. The slight blue-shift and evident red-shift of the absorption edge in PbWO_4 crystal were observed at low and heavy doping concentration, respectively. TL peaks in the range of from room temperature to 250 °C disappeared after the doping with Y^{3+} . With the increase of doping concentration, the luminescence intensity in the XEL and PL spectra was found to decrease accordingly, especially in the case of heavy doping. The measuring results demonstrate that Y^{3+} doping concentration below 100 ppm in the crystal seems to be the best for optimizing the optical and scintillation properties of the material. The mechanism of Y^{3+} doping concentration influence on luminescence was also discussed in this paper.

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1. Introduction

Lead tungstate PbWO_4 (PWO) crystals have drawn wide attention as a promising scintillator for radiation detection in high energy physics and nuclear physics due to its high density, short radiation length, small Moliere radius, fast decay time, non-hygroscopicity and low production cost [1–3]. To meet with the requirement of severe application environment with unprecedented levels of radiation in the experiments for example, CMS experiment in CERN [4], various ways to improve optical properties and radiation hardness of PWO crystals have been employed such as raw material purifying, heterovalent ions doping and high temperature annealing. Doping with trivalent and pentavalent ions, Y^{3+} , Gd^{3+} , La^{3+} , Lu^{3+} and Nb^{5+} et al., could significantly improve the optical properties and radiation hardness of PWO [5–8]. Considering the radius and

electronegativity, trivalent positive rare earth ions, such as Y^{3+} and La^{3+} , are believed to substitute for Pb^{2+} and induce an excess positive charge in the PWO host [9,10], which is compensated by lead vacancies (V_{Pb}) through the formation of defect complexes [$2\text{Re}_{\text{Pb}}-V_{\text{Pb}}$] [11]. Investigations of PWO crystals annealed in air have elucidated that interstitial oxygen (O_i) could also contribute to the defect structures under suitable conditions [10,12,13]. However, the behaviour and correlation of defect structures, including V_{Pb} , oxygen vacancies (V_{O}), O_i and Re_{Pb} , are still an open question despite many efforts having been made.

The aim of this paper is to present the optical and scintillation properties of a set of Y^{3+} -doped PWO single crystals grown by modified Bridgman method, such as optical transmission, thermoluminescence (TL), X-ray excited luminescence (XEL), photoluminescence (PL) and light yield. Based on the above measuring results and microstructure of PWO, different coordinate environment and doping mechanism of Y^{3+} at different doping level are discussed, especially heavy doping ones. Fourier transform infrared (FT-IR) spectra were employed to

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Table 1
The lattice parameters of pure PWO and PWO:Y crystals in Fig. 1

Samples	$a=b$ (Å)	c (Å)	Cell volume (Å ³)
Pure PWO	5.462	12.043	359.266
PWO: x Y ($x=50$ ppm)	5.463	12.052	359.696
PWO: x Y ($x=10,000$ ppm)	5.464	12.051	359.716

elucidate this doping mechanism and information on the defects transformation at different Y³⁺ doping levels.

2. Experiment methods

Pure PWO and a set of Y³⁺-doped PWO single crystals were grown by the modified Bridgman method from 5N PbO and WO₃ powders in stoichiometric ratio. The PWO crystals grown were transparent, colorless and crack-free. The concentration of Y³⁺ was 50, 100, 500, 1000, 5000 ppm and 1.0 mol% for PWO:Y crystals, respectively. All samples in dimension of 10 mm × 10 mm × 1 mm were cut from grown crystals and their orientations were confirmed by X-ray analysis, i.e. their two large polished faces are perpendicular to the c -axis.

The optical transmittance of the samples before and after irradiation was recorded with unpolarized light using a Shimadzu UV-2501 spectrophotometer, the accuracy of which achieved ±0.002 abs. TL glow curves measurement after UV light irradiation were made at room temperature by FJ-427A thermoluminescence spectrometer at a heating rate of 2 °C/s. A 1 kW high voltage mercury lamp was used as UV light irradiation source to irradiate the samples for 20 min. The XEL spectra were measured on an X-ray excited spectrometer, FluorMain, where a F-30 movable clinical X-ray tube (W anticathode target) was used as the X-ray source, and operated under the conditions 80 kV, 4 mA at room temperature. PL spectra were taken with a fluorescence spectrometer, Perkin-Elmer LS-55, which has a Xe lamp as an excitation source. Light yield at 20 °C was measured by using a ¹³⁷Cs γ -ray source and Philip XP2262B PMT on QVT Multichannel Analyzer test bench with a gate width of 100 ns.

The crystal structure was confirmed by X-ray diffraction (XRD) method (Rigaku D/max 2550 V diffract, Cu K α). Samples for FT-IR measurement were also made from PWO:Y single crystals by grinding them into fine powders, and pressing with KBr into plates. FT-IR spectra of the samples were all collected on a Digilab-FTS-80 spectrophotometer.

3. Results and discussion

Since the heavy doping Y³⁺ concentration is up to 1.0 mol%, it is necessary to first confirm the structure of as-grown crystals. The phase analysis and lattice parameters measurement of pure PWO and PWO:Y crystals were performed by X-ray diffraction, and Si was used as a standard sample. The XRD profiles and lattice parameters are shown in Fig. 1 and Table 1. According to JCPDS 080476 cards all crystals are in perfect scheelite-type structure that means doping of Y at the designed concentrations does not change the crystal structure or induce a new phase.

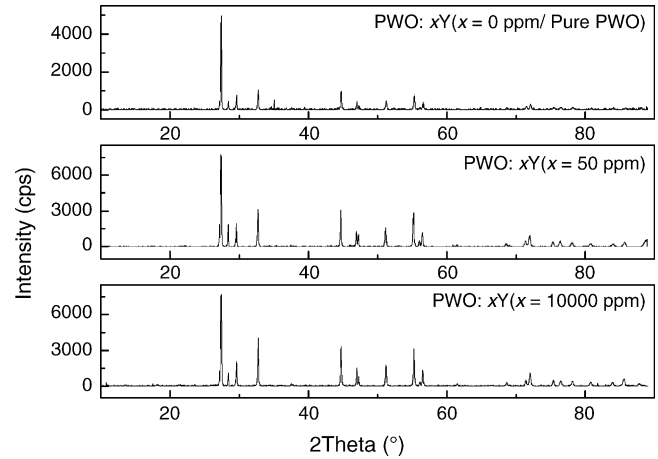


Fig. 1. X-ray powder diffraction (XRD) pattern of pure PWO and PWO:Y crystals grown by modified Bridgman method.

The FT-IR data (Fig. 2) help to further clarify the fact. The characteristic infrared absorption corresponding to W–O vibration appears in 1000–400 cm⁻¹; in particular the O–W–O stretches (ν_3 Au + ν_3 Au) occur in 900–750 cm⁻¹ [14]. Fig. 2 illustrates that a peak at $\rho_n = 780$ cm⁻¹ exists in these samples and the spectrum of PWO: 1.0 mol% Y crystal also shows great similarities to that of the pure PWO.

The optical transmission spectra of pure PWO and all Y³⁺-doped PWO crystal samples are showed in Fig. 3. Compared to that of pure PWO, optical transmission in the present PWO:Y³⁺ single crystals at low doping level (<100 ppm) has been improved evidently in short wavelength 330–420 nm region and its optical absorption edge is sharper than that of pure PWO with slight blue-shift. At higher doping level (>1000 ppm), however, an evident red-shift of the absorption edge for these samples is found compared to that of pure PWO.

Fig. 4 presents the TL glow curves of pure PWO and Y³⁺-doped PWO crystal samples above RT after an exposure to an UV source for 20 min. It is observed that the TL glow curve of pure PWO is mainly composed of two bands peaked at around 85 and 160 °C, while the TL glow curve of PWO:Y shows a strongly

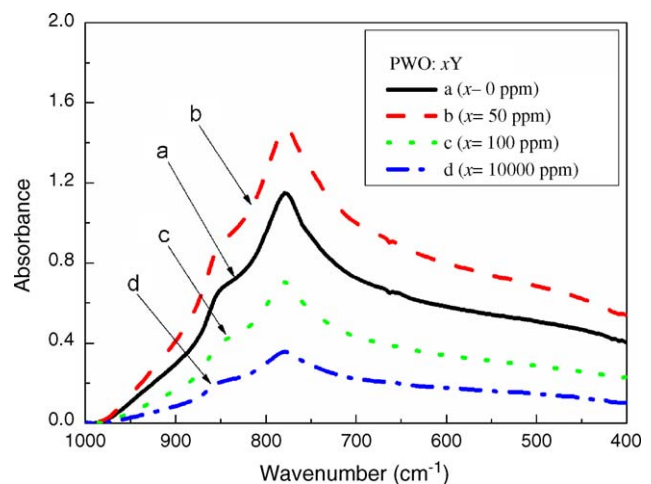


Fig. 2. Infrared spectra of PWO: x Y ($x=0, 50, 1000$ ppm and 1.0 mol%) crystals.

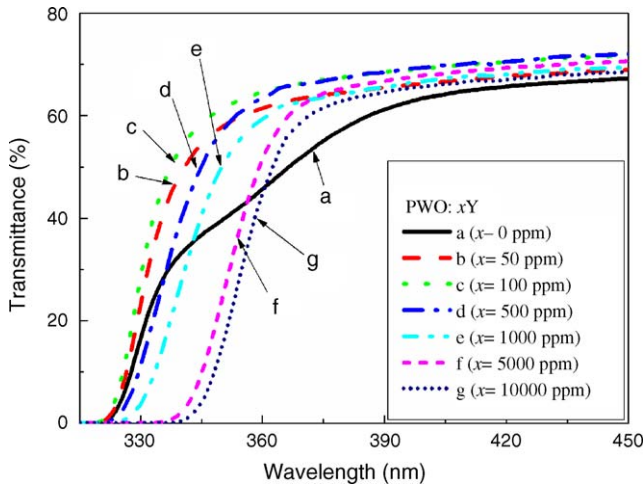


Fig. 3. Optical transmission spectra of pure PWO and PWO:Y crystals.

suppress in all peaks whose intensity is decreased almost by one order of magnitude, which is a significant lowering sign of intrinsic lattice defects in these doped PWO crystals. The suppression of these peaks indicates the disappearance of color centers with a result of inhibiting the absorption bands and improvement of the optical, e.g. optical transmittance and scintillation properties. The similar phenomena also occurs in doping of Gd^{3+} [15] and La^{3+} [16,17]. Because the electrons captured in traps above RT can be released from the traps and participate the process of luminescence and result in the fluctuation of light yield. Moreover, the temperature of application environment in high energy physics is RT. The suppression of TL above RT can improve the stability of light yield in a long term thus has great significance in radiation detection in high energy physics. As application concern, the doping Y^{3+} is a good way to improve the stability of light yield and other optical and scintillation properties of PWO crystals.

XEL spectrum of pure PWO (inset in Fig. 5) can be defined as a superposition of three Gaussian components with approximate peaked wavelengths: $I_1 = 400$ nm, $I_2 = 430$ nm and $I_3 = 480$ nm,

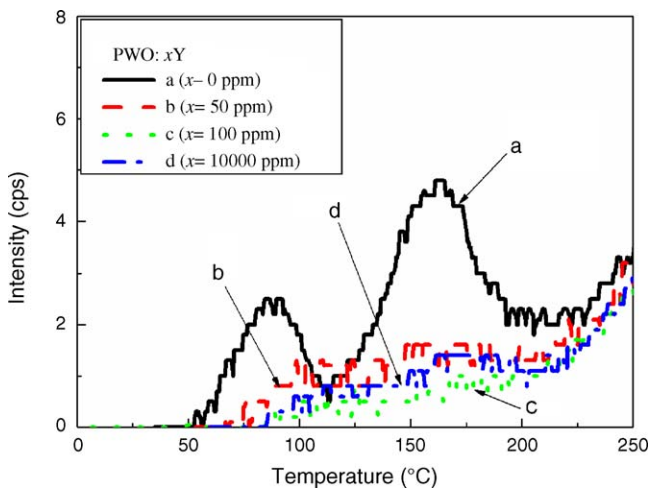


Fig. 4. Thermoluminescence glow curves of pure PWO and PWO: xY ($x=0, 100, 1000$ ppm and 1.0 mol%) single crystals between RT and 250 °C after UV irradiation for 20 min.

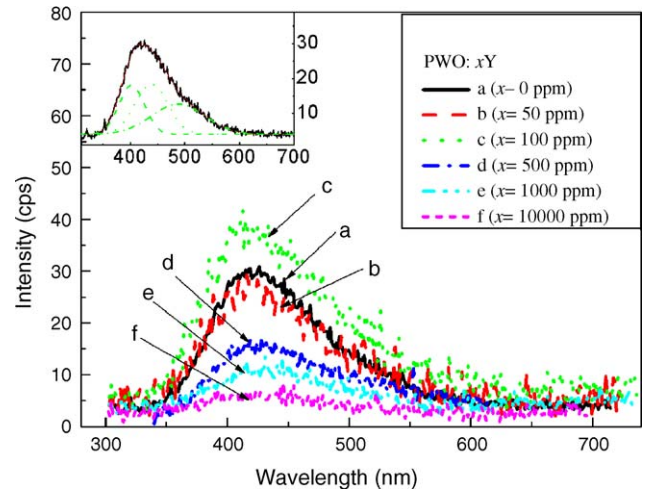


Fig. 5. XEL spectra of pure PWO crystal and PWO:Y crystal. In the inset, the XEL spectrum of pure PWO crystal is given approximated by three Gaussian fits with separate components given as peaking at about 400 nm (dash line), 430 nm (dot line) and 480 nm (dash dot line).

which are assigned to self-trapped excited blue and blue-green luminescence, respectively. In PWO:Y crystal, addition of Y ions at low concentration (Y/100 ppm) enhances the intensity of blue and green luminescence. However, with the increase of Y^{3+} -doped concentration from 500 ppm to 1.0 mol%, the luminescence of PWO:Y $^{3+}$ crystals became weaker and weaker (Fig. 5). The PWO: 1.0 mol% Y^{3+} decreased its luminescence intensity by a factor of about 6 compared to that of pure PWO. Luminescence of PWO: 1.0 mol% Y^{3+} presented nearly a straight line and was so weak that can hardly be detected under XEL measurement.

Emission spectra under 310 nm UV light and excitation spectra by monitoring 430 nm emission are shown in Figs. 6 and 7, which have a variety of results similar to that of XEL. The PL intensity of PWO:Y at low doping concentration (Y/100 ppm) (Fig. 6) was enhanced compared to pure PWO crystal. Two separate emission bands peaked at 400 and 430 nm were presented at high Y^{3+} doping concentration (>500 ppm). Moreover, these

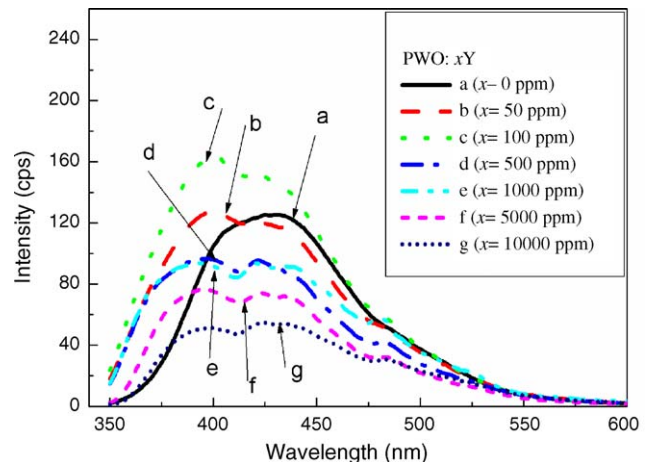


Fig. 6. The emission spectra (excited by UV light 310 nm) of pure PWO single crystal and Y^{3+} -doped PWO samples at RT.

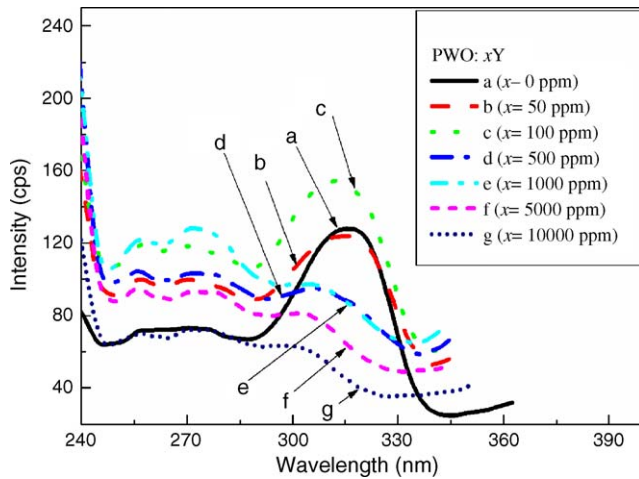


Fig. 7. The excitation spectra (monitoring 430 nm emission) of pure PWO crystal and Y^{3+} -doped samples at RT.

two emission bands became the dominated component on the emission spectra of $PWO:Y^{3+}$. However, with the increase of Y^{3+} -doped concentration from 500 ppm to 1.0 mol%, the luminescence of $PWO:Y^{3+}$ crystals became weaker and weaker. So we could imagine that in heavily Y^{3+} -doped PWO, there might be some changes to regular tungsten groups $[WO_4]^{2-}$, which are assumed to be the blue luminescence centers in tungsten scheelite [18]. On excitation spectra of monitoring 430 nm emission, excitation peak at 315 nm shifts to short wavelength, becomes weaker and weaker and almost disappears when PWO doped with Y^{3+} concentration higher than 500 ppm. This indicates that heavy Y^{3+} doping annihilates intrinsic lattice defects and intensively suppresses exciton luminescence efficiency. The excitation mechanism might be influenced in the heavy doped $PWO:Y^{3+}$ crystals due to probable new trap centers in the PWO lattice, which are involved in the energy transfer and storage processes in this crystal.

It is well known that during PWO crystal growth, the raw materials PbO and WO_3 have different volatility due to their different vapor pressures. The PbO volatilizes more easily than the WO_3 [19], consequently it can be assumed that oxygen vacancies and lead vacancies are dominant intrinsic defects in PWO crystals. The vacancies can destroy the local charge balance. The charge of V_{Pb} may be compensated by adjacent polarized mobile hole centers/color centers (Pb^{3+} or O^-) which are likely responsible for the absorption at 330–420 nm region in pure PWO crystals [10]. In Y^{3+} -doped PWO crystals, the ionic radius of Y^{3+} (1.02 Å) is close to that of Pb^{2+} (1.20 Å) and both ions incline to eight-fold coordination [29], so Y^{3+} ions may occupy the Pb^{2+} sites by means of the relaxation of scheelite-type PWO crystal lattice. At low Y^{3+} -doping concentration (<100 ppm), Y^{3+} ion is supposed to occupy the Pb^{2+} -site and formed stable $[2(Y_{Pb}^{3+}) \bullet - V_b^{''}]$ dipole complexes, in other words, low level doping of Y^{3+} ions in PWO can lessen the intrinsic V_{Pb} concentration and simultaneously restrict the production of V_O in the crystal. Consequently the concentration of Pb^{3+} and O^- can be decreased and the transmittance of PWO at 330–420 nm region is also improved evidently (Fig. 3). The absorption edge of PWO

Table 2

The light yield (LY) of pure PWO and Y^{3+} -doped PWO crystals at 100 ns gate width (P.e./MeV)

Samples	LY _{100ns} (P.e./MeV)	Y dopant (ppm)	Size (mm ³)
Pure PWO	17	0	10 × 10 × 20
PWO:Y	20	50	10 × 10 × 20
PWO:Y	23	100	10 × 10 × 20
PWO:Y	15	500	10 × 10 × 20
PWO:Y	14	1000	10 × 10 × 15
PWO:Y	9	5000	10 × 10 × 20
PWO:Y	5	10000	10 × 10 × 17

At 20 °C, pedestal: 66 channels; single photoelectron peak (SPP): 88 channels. $LY_{100ns} = (N_{Signal\ channels} - Pedestal) / (SPP - Pedestal) / 0.662\ MeV$.

crystals is caused by the transition from the O 2p ground state to the W 5d excited state [20]. The slight blue-shift of absorption edge in low Y^{3+} -doped PWO crystals maybe due to the fact that the polarizability of Y^{3+} is less than that of Pb^{2+} , the substitution of Y^{3+} into the Pb^{2+} site in the lattice will make the polarization of O^{2-} decrease and thereby it will enlarge the energy of an electron transition from O 2p ground state to W 5d excited state. However, it also can be seen that an evident red-shift of the absorption edge occurred in PWO crystals with heavy Y^{3+} doping (>1000 ppm) compared to pure PWO (Fig. 3). This may be assigned to the effect of localized defects $[2(Re_{Pb}^{3+}) \bullet - O_i^{''}]$. It has been reported that PWO can keep the scheelite structure well, even after heavily doping with La^{3+} up to 15 mol% [21], but it cannot accommodate that much V_{Pb} in such a crystal [22]. The existence of O_i^{2-} which has a similar influence on the absorption edge of PWO crystals as that of V_{Pb} in the lattice is supposed to be in the form of $[2(La_{Pb}^{3+}) \bullet - O_i^{2-}]$ to maintain the charge balance competed with V_{Pb} and support the scheelite structure in heavily La^{3+} -doped PWO crystals [23]. Therefore, in this presented paper, with the increase of Y^{3+} -doping concentration, the concentration of O_i^{2-} probably becomes higher and higher, which may cause the red-shift of absorption edge of $PWO:Y^{3+}$ (Fig. 3).

It also can be seen that, with the increase of Y^{3+} -doping concentration, the luminescence of $PWO:Y^{3+}$ crystals became weaker and weaker (Figs. 5–7). The light yield of heavily Y^{3+} -doped PWO also decreases gradually (Table 2). These may be correlated to the aggregation of plenty of Y^{3+} ions in PWO crystals. It is well known that when the rare earth ions are doped in crystals with a sufficient high concentration, it might lead to the creation of Re–Re self-compensation ion pairs by means of an electron exchange force and result in the formation of new nonradiative centers that influence luminescence and optical properties. This phenomenon occurs commonly in many kinds of rare earth ions doped laser crystals, silicate scintillating glasses [24,25] and scintillation crystals [26,27]. From these viewpoints, we would like to suggest that when the concentration of Y ions in the PWO crystals is high enough, it might substitute the Pb-sites first and further go into mostly the interstitial site to forming Y–Y ion pairs or extended “Y-rich” defect clusters by means of electron exchange force. The so-called self-compensation pairs or clusters might act as “killing sites” [28] where effective nonradiative recombination of free electrons and holes occurs, hence intensively suppress the luminescence of PWO crystal

based on $[\text{WO}_4]^{2-}$ groups. With increasing Y^{3+} dopant in PWO crystal, effective nonradiative recombination augments resulting in awfully feeble luminescence intensity, as was verified in the results of XEL and emission of UV excitation in Figs. 5–7. However, the luminescence and doping mechanism of series Y^{3+} doping in PWO crystal really need more experiments to further clarify. And the related works are in progress.

4. Conclusions

A series of PWO:Y crystals with different dopant concentration has been grown by modified Bridgman method. The XRD profile, parameters of lattice and FT-IR spectra show that the as-grown PWO:Y crystals even at heavily Y^{3+} -doped concentration still maintains perfect scheelite-type structure. At low doping level (<100 ppm), optical transmission of PWO:Y crystals has been significantly improved, and its absorption edge slightly move toward violet. The luminescence intensity and light yield are also enhanced. Y^{3+} ion are tentatively considered to occupy mostly the Pb^{2+} -site and form a stable $[2(\text{Y}_{\text{Pb}})-\text{V}_{\text{Pb}}]$ dipole complex. In heavily Y^{3+} -doped PWO (>500 ppm), the existence of O^{2-} in the lattice is supposed in the form of $[2(\text{Y}_{\text{Pb}})-\text{O}_1^{2-}]$ to maintain the charge balance competed with V_{Pb} and support the scheelite structure of PWO crystals. At the same time, the formation of Y–Y ion pairs or extended “Y-rich” defect clusters by means of electron exchange force intensively suppress the luminescence of PWO crystal based on $[\text{WO}_4]^{2-}$ groups. With increasing Y^{3+} dopant in PWO crystal, effective nonradiative recombination augments resulting in awfully feeble luminescence intensity. For making clearer the nature of the doping mechanism of series PWO:Y and the processes of energy transfer and storage in PWO structure, further work is needed.

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