Effects of Y concentration on luminescence properties of PbWO₄ single crystals

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Abstract

The effects of Y³⁺ doping at different concentration on the luminescence properties of PbWO₄ 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 PbWO₄:Y crystal samples were grown by modified Bridgman method and the concentration of Y³⁺ 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 PbWO₄ 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 Y³⁺. 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 Y³⁺ 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 Y³⁺ doping concentration influence on luminescence was also discussed in this paper.

Keywords: Y³⁺ doping, Bridgman technique; PbWO₄ single crystal; luminescence

1. Introduction

Lead tungstate PbWO₄ (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 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, Y³⁺, Gd³⁺, La³⁺, Lu³⁺ and Nb⁵⁺ 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 Y³⁺ and La³⁺, are believed to substitute for Pb²⁺ and induce an excess positive charge in the PbWO₄ host [9,10], which is compensated by lead vacancies (V_p) through the formation of defect complexes [2Re_p–V_p] [11]. Investigations of PWO crystals annealed in air have elucidated that interstitial oxygen (Oi) could also contribute to the defect structures under suitable conditions [10,12,13]. However, the behaviour and correlation of defect structures, including V_p, oxygen vacancies (V_O), Oi and Re_p, 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 Y³⁺-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 Y³⁺ at different doping level are discussed, especially heavy doping ones. Fourier transform infrared (FT-IR) spectra were employed to
Table 1
The lattice parameters of pure PWO and PWO:Y crystals in Fig. 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>(a= b=(\text{Å}))</th>
<th>(c= (\text{Å}))</th>
<th>Cell volume (Å(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PWO</td>
<td>5.462</td>
<td>12.043</td>
<td>359.266</td>
</tr>
<tr>
<td>PWO:Y ((x= 50 \text{ ppm}))</td>
<td>5.463</td>
<td>12.052</td>
<td>359.696</td>
</tr>
<tr>
<td>PWO:Y ((x= 10,000 \text{ ppm}))</td>
<td>5.464</td>
<td>12.051</td>
<td>359.714</td>
</tr>
</tbody>
</table>

elucidate this doping mechanism and information on the defects transformation at different Y\(^{3+}\) doping levels.

2. Experiment methods

Pure PWO and a set of Y\(^{3+}\)-doped PWO single crystals were grown by the modified Bridgman method from 5N PbO and WO\(_3\) powders in stoichiometric ratio. The PWO crystals grown were transparent, colorless and crack-free. The concentration of Y\(^{3+}\) was 50, 100, 500, 1000, 5000 ppm and 1.0 mol\% for PWO:Y crystals, respectively. All samples in dimension of 10 mm \(\times\) 10 mm \(\times\) 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 \(^{\circ}\)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 \(^{\circ}\)C was measured by using a \(^{137}\)Cs \(\gamma\)-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 diffracteur, Cu K\(\alpha\)). 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 Y\(^{3+}\) 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.

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 \((\nu_3Au + \nu_3Aa)\) occur in 900–750 cm\(^{-1}\) [14]. Fig. 2 illustrates that a peak at \(\nu_3= 780 \text{ cm}^{-1}\) 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 Y\(^{3+}\), doped PWO crystal samples are showed in Fig. 3. Compared to that of pure PWO, optical transmission in the present PWO:Y\(^{3+}\) 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 Y\(^{3+}\), 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 \(^{\circ}\)C, while the TL glow curve of PWO:Y shows a strongly
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, 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
two emission bands became the dominated component on the emission spectra of PWO:Y3+. However, with the increase of Y3+-doped concentration from 500 ppm to 1.0 mol%, the luminescence of PWO:Y3+ crystals became weaker and weaker. So we could imagine that in heavily Y3+-doped PWO, there might be some changes to regular tungsten groups [WO6]6−, which are assumed to be the blue luminescence centers in tungsten scheelite [18]. On excitation spectra of monitoring 430 nm emission, the peak at 315 nm shifts to short wavelength, becomes weaker and weaker and almost disappears when PWO doped with Y3+ concentration higher than 500 ppm. This indicates that heavy Y3+ doping annihilates intrinsic lattice defects and intensively suppresses exciton luminescence efficiency. The excitation mechanism might be influenced in the heavy-doped PWO:Y3+ 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 WO3 have different volatility due to their different vapor pressures. The PbO volatilizes more easily than the WO3 [19], consequently it can be assumed that oxygen vacancies cannot accommodate that much Pb2+ sites by means of the relaxation of scheelite-type PWO crystal lattice. At low Y3+-doping concentration (<1000 ppm) compared to pure PWO (Fig. 3). This may be assigned to the effect of localized defects [2(Re3+−O2−)−]. It has been reported that PWO can keep the scheelite structure well, even after heavily doping with La3+ up to 15 mol% [21], but it cannot accommodate that much Pb2+ in such a crystal [22]. The existence of O2− which has a similar influence on the absorption edge of PWO crystals as that of V0 in the lattice is supposed to be in the form of [2(Re3+−O2−)] to maintain the charge balance competed with V0 and support the scheelite structure in heavily La3+-doped PWO crystals [23]. Therefore, in this presented paper, with the increase of Y3+-doping concentration, the concentration of O2− probably becomes higher and higher, which may cause the red-shift of absorption edge of PWO:Y3+ (Fig. 3).

It also can be seen that, with the increase of Y3+-doping concentration, the luminescence of PWO:Y3+ crystals became weaker and weaker (Figs. 5–7). The light yield of heavily Y3+-doped PWO also decreases gradually (Table 2). These may be correlated to the aggregation of plenty of Y3+ 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 ion pairs or clusters might act as “killing sites” where effective nonradiative recombination of free electrons and holes occurs, hence intensively suppress the luminescence of PWO crystal.

![Fig. 7. The excitation spectra (monitoring 430 nm emission) of pure PWO crystal and Y3+-doped samples at RT.](image-url)

### Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>LY100ns (P.e./MeV)</th>
<th>Y dopant (ppm)</th>
<th>Size (mm3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PWO</td>
<td>17</td>
<td>0</td>
<td>10 x 10 x 20</td>
</tr>
<tr>
<td>PWO:Y</td>
<td>20</td>
<td>50</td>
<td>10 x 10 x 20</td>
</tr>
<tr>
<td>PWO:Y</td>
<td>23</td>
<td>100</td>
<td>10 x 10 x 20</td>
</tr>
<tr>
<td>PWO:Y</td>
<td>15</td>
<td>500</td>
<td>10 x 10 x 20</td>
</tr>
<tr>
<td>PWO:Y</td>
<td>14</td>
<td>1000</td>
<td>10 x 10 x 15</td>
</tr>
<tr>
<td>PWO:Y</td>
<td>9</td>
<td>5000</td>
<td>10 x 10 x 20</td>
</tr>
<tr>
<td>PWO:Y</td>
<td>5</td>
<td>10000</td>
<td>10 x 10 x 17</td>
</tr>
</tbody>
</table>

At 20°C, pedestal 66 channels, single photoelectron peak (SPP) 88 channels. LY100ns = N(SPP)/Pedestal/(SPP−Pedestal)×0.662 MeV.
based on $\text{WO}_4^{2-}$ groups. With increasing $\text{Y}^{3+}$ 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 $\text{Y}^{3+}$ 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 $\text{Y}^{3+}$-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. $\text{Y}^{3+}$ ion are tentatively considered to occupy mostly the Pb$^{2+}$-site and form a stable $[2(\text{YPb})–\text{V}_{\text{Pb}}^\prime\prime]$ dipole complex. In heavily $\text{Y}^{3+}$-doped PWO (>500 ppm), the existence of $\text{O}^{2-}$ in the lattice is supposed in the form of $[2(\text{YPb})–\text{O}_{2}^{-}]$ to maintain the charge balance competed with $\text{V}_{\text{Pb}}$ and support the scheelite structure of PWO crystals. At the same time, the formation of $\text{Y}–\text{Y}$ ion pairs or extended “$\text{Y}$-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 $\text{Y}^{3+}$ 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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References