Improving radiation stability of yttrium ions doped PbWO$_4$ crystals by stoichiometric tuning

Xin Zhang a,∗, Jingying Liao b, Zhiwen Yin b, Xiaojing Wu a

a Department of Material Sciences, National Micro-analysis Centre for Microelectronic Materials, Fudan University, 220 Handan Road, Shanghai 200433, China
b Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

Received 10 October 2003; in final form 7 November 2003

Abstract

Light yield of some yttrium-doped PbWO$_4$ crystals increased after low dose irradiation, and the radiation hardness was sensitive to annealing temperature. The radiation instability was attributed to interstitial oxygen ions. In this study, the effect of melt stoichiometry on radiation instability was investigated. The results show that an excessive WO$_3$ in the starting materials can significantly improve the radiation stability of PWO:Y$^{3+}$. But an excessive PbO in the melt deteriorated the radiation stability. The extra amount of lead vacancies prevented the defect (Y$^{3+}$Pb) from forming [2(Y$^{3+}$Pb)$^–$O$^0$] cluster, thus improving the radiation stability of PWO:Y$^{3+}$.

© 2003 Elsevier B.V. All rights reserved.

1. Introduction

Because of its high density, fast decay time, short radiation length and low production cost, PbWO$_4$ crystals (PWO) have been paid more attention as a promising scintillator applied in high energy physics [1–3]. Due to the severe application environment with unprecedented levels of radiation [4], the ways to improve radiation resistance have also been carried out by means of raw material purifying, stoichiometrical tuning, high temperature annealing and heterovalent ions doping. Doping with trivalent and pentavalent ions such as Y$^{3+}$, La$^{3+}$, Lu$^{3+}$ and Nb$^{5+}$ could significantly improve the scintillation properties and radiation hardness of PWO [5–7].

Y$^{3+}$ doping and Y$^{3+}$/Nb$^{5+}$ co-doping were widely applied in large-scale PWO production. But some Y$^{3+}$ doping PWO crystals grown by Bridgman method in an air atmosphere showed exceptional irradiation behavior, namely, light yield increase after low dose rate irradiation. This phenomenon was accompanied with optical transmission change in the wavelengths from 380 to about 500 nm simultaneously [8]. In addition, radiation hardness was sensitive to annealing temperature. To suppress radiation instability in PWO:Y$^{3+}$, we investigated the relationship between radiation instability and stoichiometry of the starting materials of crystal growth. The experimental results show that an excessive WO$_3$ in the starting materials can significantly suppress the radiation instability in PWO:Y$^{3+}$, and transmission near the cut-off edge also improved. The mechanisms of an excessive WO$_3$ are also discussed.

2. Samples and experimental methods

The PWO crystals were grown by modified Bridgman method in an air atmosphere, and the purity of raw materials (PbO and WO$_3$ powders) was 99.999%. The crystallization orientation was [0 0 1], and the concentration of Y$^{3+}$ ion was 150 at. ppm (in the melt) in all samples. Since the radiation instability was more significant in the top of ingot than in the bottom,
the samples in this study were cut off from the top of each ingot. The details of the samples are listed in Table 1.

The recipe of annealing and irradiation for samples was as follows: annealing → $^{60}$Co irradiation at 0.35 Gy/h for 46 h → $^{60}$Co irradiation at 35 Gy/h for 46 h. The annealing procedures were carried out sequentially at 50, 100, 150, 200 and 250 °C in air. The soaking time is 24 h for annealing at 50 °C and 10 h for other annealing temperatures. Optical transmission and light yield measurements were followed right after each annealing and 5 h after each irradiation step.

The optical transmission was recorded along the longitudinal direction of each sample by a SHIMAZU-2501 spectrophotometer with an accuracy of ±0.002 Absorbency. Light yield at room temperature (20 °C) was measured by using a collimated $^{137}$Cs γ-ray source and Philip 2262 PMT on QVT Multichannel Analyzer test bench. The QVT is set in the internal gate trigger under $Q$ mode with a gate of 100 ns.

### 3. Experimental results

Fig. 1a and b present the transmission spectrums of the samples after being annealed at 50 and 250 °C. Comparing with the samples 12-1 and 16-1, the crystals with an excessive WO$_3$ in the melt (22-1 and 25-1) have better transmission from cut-off edge to about 500 nm. Moreover, the transmission curves are improved as increasing the amount of WO$_3$ in the starting materials. On the contrary, an excessive PbO in the melt leads to the appearance of 430 nm absorption band, especially in sample 16-1. The more PbO contains in the melt, the more distinct 430 nm absorption band the crystals have. According to our previous studies (see 8–10), the as

### Table 1

The details of the sample segments

<table>
<thead>
<tr>
<th>Crystal ID</th>
<th>Dopant/amount (at. ppm)</th>
<th>Stoichiometric ratio (PbO/WO$_3$) in the melt ($W_2 &gt; W_1$)</th>
<th>Dimension (mm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-1</td>
<td>Y$^{3+}$/150</td>
<td>PbO excess 1 + W$_1$</td>
<td>25 × 25 × 80</td>
</tr>
<tr>
<td>16-1</td>
<td></td>
<td>PbO excess 1 + W$_2$</td>
<td></td>
</tr>
<tr>
<td>22-1</td>
<td></td>
<td>WO$_3$ excess 1 – W$_1$</td>
<td></td>
</tr>
<tr>
<td>25-1</td>
<td></td>
<td>WO$_3$ excess 1 – W$_2$</td>
<td></td>
</tr>
</tbody>
</table>
grown or annealing induced 430 nm absorption band in Y$^{3+}$ doping PWO crystals grown by modified Bridgeman method are unstable under low dose rate irradiation.

Fig. 1c shows the induced absorption coefficient spectrum after 250 °C annealing treatment. The concentration of color centers created by different procedures can be estimated from optical transmission measurement since it is proportional to the induced absorption coefficient defined as:

$$\mu_{\text{treat}} = \ln(T_{\text{initial}}/T_{\text{treatment}})/d,$$

where \(d\) stands for the thickness of the sample. \(T_{\text{initial}}\) and \(T_{\text{treatment}}\) are the transmission before and after treatment, respectively. Since the transmission of as-grown samples is unreliable due to its sensitivity to annealing temperature, high temperature environment during the cooling down process in crystal growth may affect the transmission curve of as-grown crystals. We, therefore, regard the transmission after annealing at 50 °C as \(T_{\text{initial}}\) in Eq. (1), and the transmission after 250 °C annealing as \(T_{\text{treatment}}\). The annealing induced absorption coefficient \(\mu\) is positive from about 360–500 nm, so the optical transmission around 430 nm is deteriorated after annealing at higher temperature. Noticeably, the samples with an excessive WO$_3$ in the melt (22-1 and 25-1) also have better transmission stability to annealing temperature than those samples with a PbO compensation in the melt. Furthermore, the transmission stability is deteriorated as the amount of compensated PbO goes up.

Table 2 shows the results of light yield measurements at 20 °C with a gate width 100 ns. Positive light yield change means it increases after irradiation. Although large dose rate irradiation (35 Gy/h for 46 h) behaviors of the samples are almost the same (light yield decrease), changes of light yield are different during low dose rate irradiation. In the annealing temperature range from 50 to 250 °C, light yield of the samples with a PbO compensation in the melt (12-1 and 16-1) increase after $^{60}$Co 0.35 Gy/h irradiation, giving a positive light yield change. In addition, light yield changes of those samples increase as the annealing temperatures raise. So higher temperature annealing can significantly deteriorate the radiation stability of the PbO compensated samples. On the contrary, light yield changes of samples 22-1 and 25-1 (with an excessive WO$_3$ in the melt) are all negative in the temperature range from 50 to 200 °C, and slightly increase after irradiation while annealing at 250 °C. Thus, the samples with a WO$_3$ compensation in the starting materials have a better radiation stability than those samples with a PbO compensation.

Fig. 2 exhibits the radiation (dose rate 0.35 Gy/h for 46 h) induced absorption spectra of the samples annealed at different temperatures. In samples 22-1 and 25-1, the radiation induced absorption coefficients around 430 nm are positive in the temperature range from 50 to 200 °C. But being annealing at 250 °C, radiation induced absorption coefficients are negative around 430 nm after low dose rate irradiation, accompanied by light yield slight increase (see Table 2). On the contrary, samples 12-1 and 16-1 show positive light output changes after 0.35 Gy/h irradiation in the entire annealing temperature range, and the radiation induced absorption coefficients are also negative around 430 nm.

When exposed to high dose rate irradiation (35 Gy/h), wide absorption bands from 350 to about 650 nm came into being in almost all samples which can be observed in normal PWO: Y$^{3+}$ crystals grown by Czochralski method, so they are not shown in Fig. 2.

Table 2
Light yield (100 ns, p.e./MeV) of the samples annealing at different temperatures and $^{60}$Co irradiation at the dose rate 0.35 and 35 Gy/h for 46 h

<table>
<thead>
<tr>
<th>Annealing treatment</th>
<th>Crystal ID</th>
<th>Light yield after annealing</th>
<th>Light yield after 0.35 Gy/h irradiation</th>
<th>Change (%)</th>
<th>Light yield after 35 Gy/h irradiation</th>
<th>Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 °C/24 h</td>
<td>12-1</td>
<td>12.1</td>
<td>12.0</td>
<td>-0.8</td>
<td>13.2</td>
<td>+9.1</td>
</tr>
<tr>
<td></td>
<td>16-1</td>
<td>10.2</td>
<td>11.1</td>
<td>+8.8</td>
<td>9.8</td>
<td>-3.9</td>
</tr>
<tr>
<td></td>
<td>22-1</td>
<td>14.7</td>
<td>14.0</td>
<td>-4.8</td>
<td>11.1</td>
<td>-24.5</td>
</tr>
<tr>
<td></td>
<td>25-1</td>
<td>15.1</td>
<td>13.6</td>
<td>-9.6</td>
<td>10.6</td>
<td>-29.8</td>
</tr>
<tr>
<td>100 °C/10 h</td>
<td>12-1</td>
<td>14.2</td>
<td>14.6</td>
<td>+2.8</td>
<td>12.6</td>
<td>-11.3</td>
</tr>
<tr>
<td></td>
<td>16-1</td>
<td>12.3</td>
<td>13.0</td>
<td>+5.7</td>
<td>10.5</td>
<td>-14.6</td>
</tr>
<tr>
<td></td>
<td>22-1</td>
<td>16.0</td>
<td>16.0</td>
<td>0.0</td>
<td>11.0</td>
<td>-31.3</td>
</tr>
<tr>
<td></td>
<td>25-1</td>
<td>17.0</td>
<td>15.7</td>
<td>-7.6</td>
<td>12.8</td>
<td>-24.7</td>
</tr>
<tr>
<td>200 °C/10 h</td>
<td>12-1</td>
<td>12.0</td>
<td>12.3</td>
<td>+2.5</td>
<td>9.4</td>
<td>-21.7</td>
</tr>
<tr>
<td></td>
<td>16-1</td>
<td>10.0</td>
<td>11.2</td>
<td>+12.0</td>
<td>9.1</td>
<td>-9.0</td>
</tr>
<tr>
<td></td>
<td>22-1</td>
<td>14.0</td>
<td>13.3</td>
<td>-5.0</td>
<td>9.8</td>
<td>-30.0</td>
</tr>
<tr>
<td></td>
<td>25-1</td>
<td>14.3</td>
<td>14.0</td>
<td>-2.1</td>
<td>10.2</td>
<td>-28.7</td>
</tr>
<tr>
<td>250 °C/10 h</td>
<td>12-1</td>
<td>11.8</td>
<td>12.9</td>
<td>+9.3</td>
<td>11.0</td>
<td>-6.8</td>
</tr>
<tr>
<td></td>
<td>16-1</td>
<td>9.2</td>
<td>11.5</td>
<td>+25.0</td>
<td>9.2</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>22-1</td>
<td>13.2</td>
<td>13.4</td>
<td>+1.5</td>
<td>10.6</td>
<td>-19.7</td>
</tr>
<tr>
<td></td>
<td>25-1</td>
<td>14.8</td>
<td>15.3</td>
<td>+3.3</td>
<td>12.0</td>
<td>-18.9</td>
</tr>
</tbody>
</table>
The same as our previous results [8–10], the transmission spectra after annealing at a given temperature are independent to annealing and irradiation history, and the transmission spectra after low dose rate irradiation are also independent to annealing temperatures. The formation of 430 nm absorption band by annealing and the disappearing of such band by low dose rate irradiation are reversible. So annealing induced absorption band peaking around 430 nm seems to be bleached under 0.35 Gy/h irradiation, and light yield increase relates to the bleaching some extent. There may be two steps taking place sequentially during irradiation: bleaching of 430 nm absorption band (accompanied with light yield increase) and the formation of wide absorption bands from 350 to about 650 nm (process of light yield degradation).

From the experimental results, an excessive WO₃ in the starting materials can significantly improve the transmission of PbWO₄ from the cut-off edge to about 500 nm, thus suppress radiation instability in PWO:Y³⁺ crystal.

4. Discussion

This exceptional phenomenon only existed in some Y³⁺- or Gd³⁺-doped PWO crystals [11], and was firstly attributed to the concentrated impurities, such as Na⁺, K⁺ and Si⁴⁺ whose segregation coefficient are smaller than 1 [12]. It was found out that Si⁴⁺ ion did not influence the radiation stability of PWO:Y³⁺ [13]. Although concentrated Na⁺ ions led to the appearance of distinct 430 nm absorption band, this absorption band was not ‘bleached’ under low dose rate irradiation. The contamination of K⁺ and Na⁺ ions strongly influenced the radiation stability only in the case of PWO with high concentration of Y³⁺ ion [9]. Furthermore, it was suggested that interstitial oxygen ions (Oᵢ₀₀) resulting from oxygen-rich atmosphere during crystal growth and annealing procedure was the origin of the exceptional irradiation behaviors [10,14].

In modified Bridgman method, the polycrystalline PWO prepared by solid phase reaction in air atmosphere was used as the starting materials, and the growth procedure was also carried out in an oxygen-rich environment. The platinum crucibles were designed with a vent hole (its diameter was about 0.5 mm) to avoid inflation of gas that contained in the starting materials. The slow lowering speed of the crucibles made the PWO ingots experienced a high temperature annealing in situ during cooling down procedure. So the formation of interstitial oxygen ions (Oᵢ₀₀) seems inevitable.
Due to PbO evaporation, a large amount of lead vacancies (VPb) existed in as-grown PWO, and led to the formation of 350 and 430 nm absorption band [15]. The 350 and 430 nm absorption bands were tentatively attributed to the formation of color centers (Pb3+ and O−) [16,17] or defect clusters ([O2−–VPb–O−–VPb–O32−] and [O2−–VPb–O2−]) [18]. The charge equilibrium modes of doped rare earth ions (Re3+) were proved by the observation of dielectric relaxation in PWO:La3+ crystal [19]. The observed polarization was attributed to the formation of 350 and 430 nm absorption bands [15]. The formation of Y3+ and OOi is in all probability if the concentration of VPb were not high enough in the top part.

The analysis mentioned above gave useful clues for eliminating the radiation instability in PWO:Y3+. Although PbO compensation in the starting materials was an effective way to eliminate VPb, proper amount VPb is needed for local charge compensation because of enrichment of Y3+ ions and oxygen-rich growth atmosphere. So on account of formation energy, the additional amount of VPb favors the extra Y3+ ions combine with VPb into defect cluster [2(YPb3+)+Vn/0Pb], and suppresses the formation of defect cluster [2(YPb3+)+O0i]. Moreover, it also can keep the crystal in a negative charge environment, prevents the OOi which is also negative charge centers from entering into crystal. Although increasing the amount of OWO3 in the melt can significantly suppress the radiation instability of PWO:Y3+, overabundant VPb is harmful to radiation hardness. Thus the stoichiometric ratio must be carefully controlled in the growth of PWO:Y3+.

5. Conclusion

An excessive of OWO3 in the starting materials can significantly suppress the radiation instability in PWO:Y3+, and improved the transmission of PbWO4 from the cut-off edge to about 500 nm. While the compensation of PbO in the melt deteriorated the radiation stability of PWO:Y3+ crystal. The extra amount of lead vacancies in the top part of the ingots prevented the defect (Y3+Pb)+ from forming defect cluster [2(Y3+Pb)+O0i], in which interstitial oxygen ion is caused by enrichment of Y3+ ion and O2-rich growth atmosphere. Thus suppress the exceptional irradiation behaviors.

Acknowledgements

The authors would like to acknowledge helpful assistance on light yield experiments by Dr. Jiangujun Xie and Dr. Hui Yuan.

References