# Low dose rate irradiation behaviors of $Y^{3+}$-doped $PbWO_4$ crystals

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## Abstract

Light yield of some $Y^{3+}$: PWO crystals increases after irradiation, and is accompanied with transmission change in the wavelengths from 380 to 500 nm. The pre-existing 430 nm color centers or annealing induced ones are unstable during irradiation. These results interpret the temperature sensitivity of light yield and radiation hardness. A proper annealing temperature and the way to eliminate the instability are found out. © 2002 Elsevier Science B.V. All rights reserved.

*PACS:* 29.40.−n; 29.40.Mc

*Keywords:* $Y^{3+}$ doping; Bridgman technique; Lead tungstate; Scintillator

## 1. Introduction

Due to its high density, fast decay time, strong radiation resistance and low cost, $PbWO_4$ crystals have been paid more attention as a promising scintillator applied in high-energy physics. The scintillation properties and radiation hardness of PWO are crucial because of the severe application environment. The photoluminescence spectra of PWO are composed of two components with (i) the blue one peaking at 420 nm and (ii) the green one peaking at 480–520 nm. These spectra are ascribed either to regular $WO_4$ group, and defects associated with $WO_3$ [1] or "$WO_4 + O_i$" centers [2,3]. High-energy radiation does not influence the scintillation mechanisms of PWO, the light output degradation is caused by the creation of color centers originating with the absorption bands in the UV and the blue spectral regions [4].

Similar to the radiation-induced absorption bands (see Refs. [4,5]), the pre-existing 430 nm absorption band is also harmful in scintillation properties. Compared with radiation-induced color centers which can be effectively annihilated by annealing at 200°C, the as-grown 430 nm color centers are hard to eliminate even at a high temperature. Some as-grown PWO:$Y^{3+}$ crystals showed distinct 430 nm absorption band, and their light yield was sensitive to annealing temperature. In this work, the relationship among optical transmission, light yield and radiation hardness of PWO:$Y^{3+}$ crystals are investigated.

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## 2. Samples and experimental methods

The PWO samples (whose list is in Table 1) were grown by modified Bridgman method. The crystallization orientation was [0 0 1], and the concentration of $Y^{3+}$ ion is 150 at. ppm in all the samples. The ratio of PbO and $WO_3$ was selected as 1 according to the phase diagram of PbO–$WO_3$ system, which shows a congruent melt.

The recipe of experimental procedure for samples 509-1 and 509-2 was as follows: annealing $\rightarrow$ $^{60}$Co irradiation at 35 rad/h for 70 h $\rightarrow$ measurement $\rightarrow$ $^{60}$Co irradiation at 3500 rad/h for 70 h $\rightarrow$ measurement. The annealing procedures were carried out sequentially at $300°C(10 h)$ and $50°C(24 h)$. Optical transmission and light yield measurements were followed after each annealing and irradiation step. For samples 448-2 and 448-6, the annealing procedures were carried out sequentially at $50°C$, $100°C$, $150°C$, $200°C$, $250°C$ and $300°C$. The soaking time is 24 h for annealing at $50°C$ and 10 h for other annealing temperatures. A powerful 1000 W high-voltage mercury lamp performed the irradiation tests for 6 min. Optical absorption spectra were recorded after each annealing and UV irradiation step.

The optical absorption spectra were recorded by a Shimazu-2501 spectrophotometer. The light yield was measured by using a collimated $^{137}$Cs $\gamma$-ray source and Phillips 2262 PMT on QVT Multichannel Analyzer test bench. X-ray-stimulated emission spectra were measured on a home-made equipment using steady-state X-ray excitation (tube with Fe anticathode, 80 kV, 4 mA). The concentration of impurities was measured by ICP-AAS method ( see Table 2).

Table 1
Details of the sample segments

| Crystal ID | Dimension (mm³) | Remark |
|---|---|---|
| 448-2 | $26 \times 25 \times 80$ | Top |
| 448-6 | $24 \times 22 \times 80$ | Bottom |
| 509-1 | $21 \times 21 \times 115$ | Top |
| 509-2 | $21 \times 21 \times 115$ | Bottom |

Table 2
Concentration of dopant and impurities in samples 448-2 and 448-6 (unit: at. ppm)

| Dopant and impurities | Top part | Middle part |
|---|---|---|
| $Y^{3+}$ | 93 | 93 |
| $K^+$ | 15 | 7 |
| $Ca^{2+}$ | 32 | 41 |

## 3. Results and discussion

Fig. 1 and Table 3 show the experimental results of samples 509-1, 2. They have been annealed at $300°C$ for 10 h, and all the segments exhibit 430 nm absorption band. The absorption intensity on top of the crystal is stronger. While exposed to $^{60}$Co irradiation at the dose rate of 35 rad/h, this absorption band vanishes, accompanied with an increase in the light yield and transmission change around 430 nm. But when exposed to high dose rate irradiation (3500 rad/h), wide absorption band from 350 nm to about 650 nm appeared, thus resulting in the degradation of light yield. The samples were then annealed at $50°C$, and this resulted in the disappearance of 430 nm absorption band which was eminent after $300°C$ annealing, light yield decreases after irradiation, irrespective of the dose rate being 35 or 3500 rad/h.

Fig. 2 exhibits the absorption spectra of the samples 448-2, 6 after annealing procedure. The absorption coefficient around 430 nm increases as the annealing temperature increases, and a saturation state (illustrated in Fig 2(a) and (b) as the saturation curve) occurs without reference to annealing temperature. The concentration of color centers created by irradiation can be estimated from the induced absorption coefficient defined as

$$\mu_{\text{treat}} = 1/d \ln(T_{\text{initial}}/T_{\text{treatment}})$$

where $T_{\text{initial}}$ and $T_{\text{treatment}}$ are the transmission before and after the treatment, and $d$ stands for the sample width. As illustrated in Fig. 2(c), the radiation-induced absorption coefficient $\mu$ is negative around 430 nm, and is positive at 350 and 500 nm. It is an interesting phenomenon that the annealing-induced unstable color-centers are
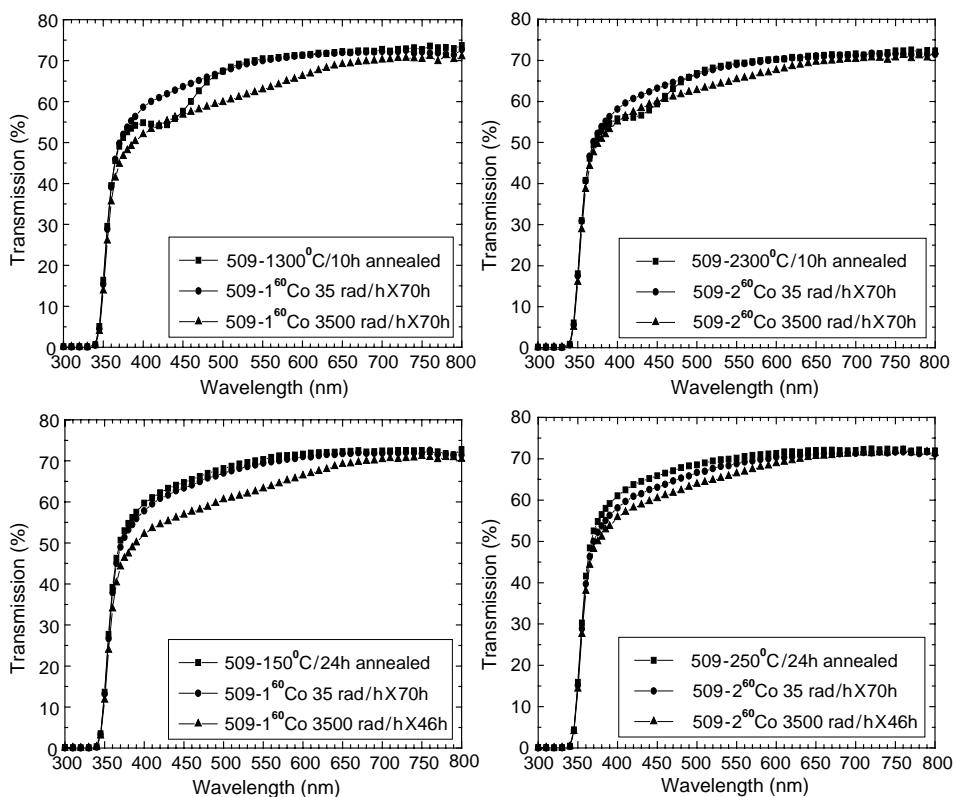
Fig. 1. Transmission spectra of samples 509-1 and 509-2 after annealing at 300°C, 50°C and irradiation.

Table 3
Radiation hardness test results of samples 509-1 and 509-2 (gate: 100 ns, unit: photons/MeV)

| Crystal ID | 300°C/10 h annealing | 35 rad/h irradiation/ change (%) | 3500 rad/h irradiation/ change (%) | 50°C/24 h annealing | 35 rad/h × 70 h irradiation/ change (%) | 3500 rad/h irradiation/ change (%) |
|---|---|---|---|---|---|---|
| 509-1 | 11.5 | 14.4/+25.4 | 8.0/−30.3 | 12.2 | 11.9/−2.9 | 9.6/−21.9 |
| 509-2 | 13.2 | 14.9/+13.0 | 11.4/−13.7 | 14.2 | 13.6/−4.4 | 11.9/−16.5 |

around 430 nm, but it seems that they are "bleached" by irradiation.

As listed in Table 2, the distribution of $Y^{3+}$ ions in sample 448 is the same and the concentration of $K^+$ ion is a typical one in PWO crystals, irrespective of the increase or decrease in light yields after irradiation. The concentration of $Ca^{2+}$ ions must be high at the bottom part if we take into consideration that the segregation coefficient of $Ca^{2+}$ ion is larger than 1.

The X-ray-excited emission spectra of sample 448-2, 6 are presented in Fig. 3. They indicate that no new emission peaks appear after UV radiation, only the emission intensity is enhanced in the wavelengths from 350 to 550 nm. If we observe Fig. 2 (a) and (b), it can be easily deduced that the percentage of light yield change in the bottom part of 448-6 sample is larger than that of the top part of sample 448-2. As illustrated in Fig. 2(c), the optical transmission from 460 nm to about 550 nm
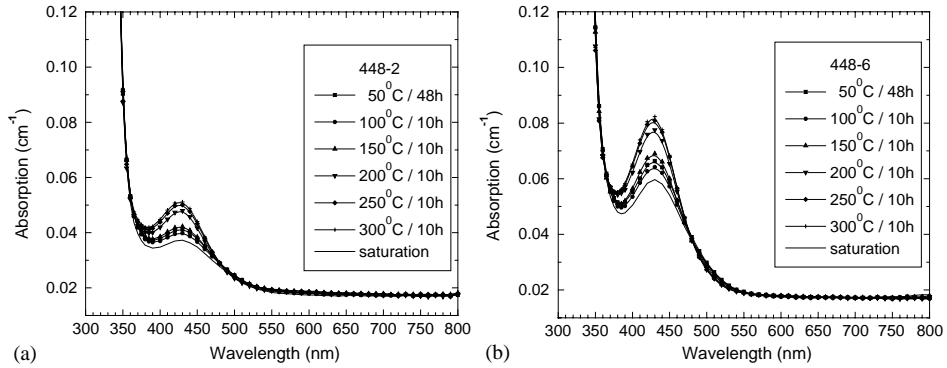
Fig. 2. Absorption and radiation-induced coefficient spectra of samples 448-2 and 448-6.
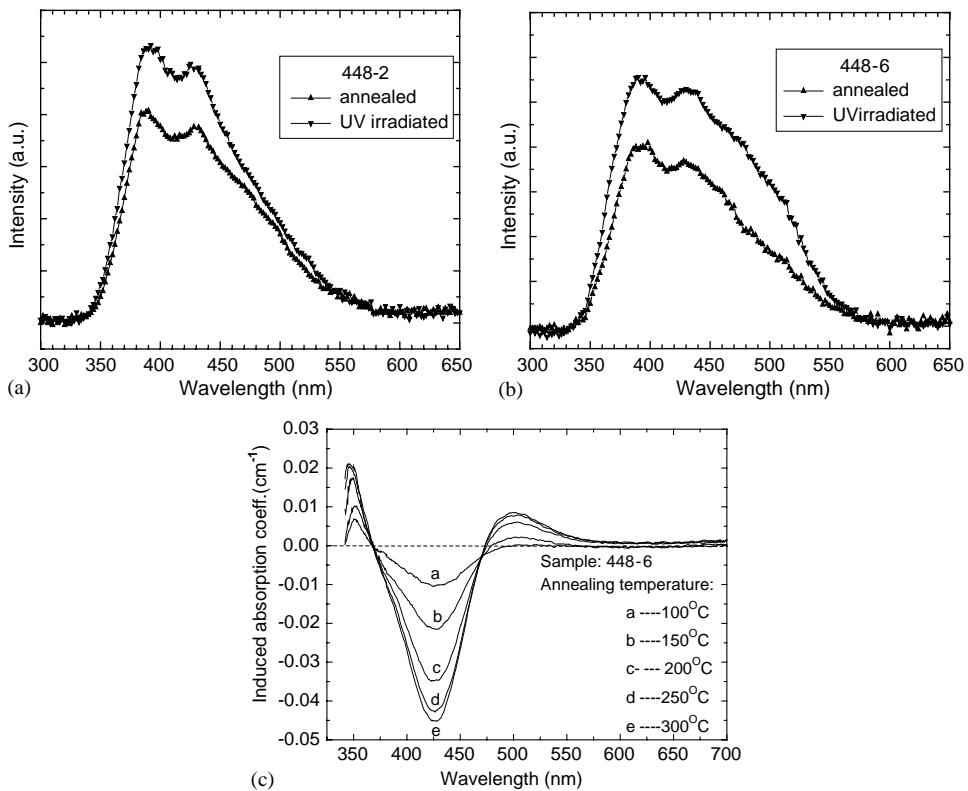


Fig. 3. X-ray-excited emission spectra of samples 448-2 and 448-6.

is deteriorated by radiation, but the emission intensity in these band increases. The green scintillation components peaking at 460–500 nm are enhanced after UV irradiation. There may be a sensitization that effectively transfers energy of UV irradiation to the green luminescence centers. The origin of blue scintillation components enhancement may relate to the annihilation of 430 nm color centers or the same sensitization and the green components. It was considered that

the enhancement of blue and green components had the same origin-interstitial oxygen ion [6].

The introduced $Y^{3+}$ ions can cause a positive charge defect $(Y_{Pb}^{3+})^{\bullet}$ which was compensated by $V_{Pb}$ (lead vacancy) in the form of $[2(Y_{Pb}^{3+})^{\bullet}\text{-}V''_{Pb}]$ [7]. Integrating the extra $V_{Pb}$ into defect cluster can avoid the formation of $[V_F^- \text{---} V_O \text{---} V_F^-]$ which was probably considered to be the origin of 350 nm intrinsic color centers [8]. The distribution characteristic of $Y^{3+}$ ions is beneficial in suppressing the defect cluster $[V_F^- \text{---} V_O \text{---} V_F^-]$ along the crystal if we take into account that the segregation coefficient is smaller than 1. On account of the technical differences, PWO crystals grown by Bridgman method contain more $Y^{3+}$ ions, especially, in their crystallization parts. In addition, the technique for preventing PbO evaporation that was applied in growth may lead to $V_{Pb}$ deficiency in $Y^{3+}$-ion concentrated part. Therefore, local charge equilibrium mode of $Y^{3+}$ ion changes: it is possible to form $[2(Y_{Pb}^{3+})^{\bullet}\text{---}O''_i]$ in which the interstitial oxygen ions ($O''_i$) were most probably considered as the origin of the light yield increase after irradiation [6]. Present results show that the green component originated from the "$WO_4 + O_i$" centers, and also the enhancement of green scintillation component is observed.

Contrary to the results obtained with samples 509-1, 2, the percentage of light yield increase in samples 448-2, 6 in the bottom is larger than that in the top. This outcome implies that the light yield increase may not relate to impurities in the crystals. In sample 448-2, 6, it was possible to have correlation with enrichment by $Ca^{2+}$ ions in the bottom. From the viewpoint of ion radiuses, $Ca^{2+}$ ions (0.112 nm) can occupy the $Pb^{2+}$ (0.129 nm) sub-lattice easier than $Y^{3+}$ ions (0.102 nm), and moreover, it does not need extra negative charge for equilibrium. The concentrated $Ca^{2+}$ ions in the bottom can occupy $V_{Pb}$ which are needed by $(Y_{Pb}^{3+})^{\bullet}$ for local charge compensation that compel $Y^{3+}$ to form $[2(Y_{Pb}^{3+})^{\bullet}\text{---}O_i^{\cdot}]$. $V_{Pb}$ is needed for local charge compensation due to enrichment by $Y^{3+}$ ions. With our experiments with $V_{Pb}$ compensator and $V_{Pb}$ creator dopants, an appropriate amount of $V_{Pb}$ creator suppresses the exceptional irradiation behaviors.

## 4. Conclusion

The pre-existing or annealing-induced 430 nm color centers in PWO:$Y^{3+}$ are unstable. Low dose rate irradiation enhances the green scintillation components peaking at 460–500 nm. The results of the paper and the experiments of $V_{Pb}$ creator dopant reveal that $O''_i$ is responsible for light yield enhancement. Based on these studies, experiments on new dopant (acts as $V_{Pb}$ creator) were carried out to eliminate $O''_i$ aiming at producing radiation-hard crystals that meet the technical specification established by the CMS experiment at CERN.

## Acknowledgements

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