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Nuclear Instruments and Methods in Physics Research A 489 (2002) 271–281

**NUCLEAR
INSTRUMENTS
& METHODS
IN PHYSICS
RESEARCH**
Section A

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The influences of monovalent ions on the stability of scintillation properties and radiation hardness of $\text{PbWO}_4:\text{Y}^{3+}$ crystals \star

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Received 24 January 2002; received in revised form 18 March 2002; accepted 22 March 2002

Abstract

Some Y^{3+} -doped PbWO_4 crystals grown by modified Bridgmann method showed exceptional behaviors, namely, light yield increased after low dose rate irradiation, and the radiation-induced absorption coefficient was negative around 430 nm. In this paper, the influences of monovalent ion impurities (Na^+ and K^+) on the stability of scintillation properties and radiation hardness were studied. The experimental results show that Na^+ ion enhances the absorption band at cut-off edge and at 430 nm, while K^+ ion only makes optical transmission unstable around 430 nm when the crystals were annealed at high temperatures. The contamination by Na^+ and K^+ ions makes scintillation properties and radiation hardness more unstable in the temperature range from 50°C to 350°C. The radiation-induced absorption coefficient is also negative around 430 nm. The charge compensation mode of K^+ ion along the crystal does not change, but those of Na^+ ion are different along the crystal. The concentrated Na^+ , K^+ and Y^{3+} ions, which occupied Pb sublattice, lead to the shortage of Pb vacancies (V_{Pb}''). Thus instead of the formation of $[2(\text{Y}_{\text{Pb}}^{3+})^{\bullet} - V_{\text{Pb}}'']$ ($(\text{Y}_{\text{Pb}}^{3+})^{\bullet}$ stands for the Y^{3+} ion occupying the Pb sublattice), Na^+ and K^+ ions compel the defect $(\text{Y}_{\text{Pb}}^{3+})^{\bullet}$ to form cluster $[2(\text{Y}_{\text{Pb}}^{3+})^{\bullet} - \text{O}_i'']$ or $[(\text{Y}_{\text{Pb}}^{3+})^{\bullet} - \text{O}_i'' + \text{hole}]$ in which the interstitial oxygen (O_i'') was considered to be the origin of light yield increase after low dose rate irradiation. © 2002 Elsevier Science B.V. All rights reserved.

PACS: 29.40.-n

Keywords: A1. Doping; A2. Bridgmann technique; B1. Lead tungstate; B2. Scintillator

1. Introduction

The single crystals of lead tungstate (PWO), have drawn wide attention as a promising scintillator for radiation detection in high-energy physics because of its high density, fast decay time, strong radiation resistance and low production cost [1–4]. It was established that the PWO emission spectrum consists of at least two emission components,

\star This work was supported by The National Nature Science Foundation of China (No. 59932002).

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the blue one peaking at 420 nm ascribed to the regular lattice of which the emitting level is also consisting of both lead and tungstate contributions [5], and the green one peaking at 480–520 nm [6] ascribed to some oxygen-related defect centers, WO_3 or $\text{WO}_4 + \text{O}_i$ centers [7]. It was also known that the scintillation mechanism of PWO was not damaged by high-energy irradiation and the light yield decrease was caused by the creation of color centers generating the absorption bands in UV and blue spectral regions [8]. The origin of these absorption bands between 380 and 500 nm was suggested to four kinds of color centers, such as two hole centers (Pb^{3+} and O^- , i.e. a hole is trapped by Pb^{2+} and O^{2-} ions, respectively) and electron centers (F^- and F , i.e. one and two electrons are trapped by oxygen vacancy, respectively) [9–11]. The comparatively detrimental one among these absorption bands peaks at about 420 nm, which overlaps with the prime fast luminescence ingredient, blue band.

Due to severe application environment with unprecedented high level of radiation [12], the ways to improve PWO radiation hardness have also been investigated by means of purifying raw materials, stoichiometrical tuning, high-temperature annealing and doping with heterovalent ions. Among these methods, 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, especially suppress the comparatively slow component, green and F center associated red components and the 350 nm intrinsic absorption band. Although the radiation-induced color centers in undoped PWO had been intensively studied [13,14], the pre-existing 430 nm color centers in as-grown $\text{PbWO}_4:\text{Y}^{3+}$ crystals which were introduced by impurities and the oxygen-rich growth atmosphere or improper high-temperature annealing were paid little attention on.

Compared with radiation-induced color centers which can be effectively annihilated by annealing at 200°C, the pre-existing 430 nm color centers are rather stable even at high temperature. Some Y^{3+} -doped PWO crystals behave exceptionally, namely, light yield and optical transmission increase in the wavelengths from 380 to about

500 nm simultaneously after low dose rate irradiation. In the near room temperature range from 50°C to 350°C, higher temperature annealing can enhance the absorption band around 430 nm. The pre-existing 430 nm color centers or annealing induced ones are unstable and can be “bleached” by low dose rate irradiation. The enhancement of green luminescence component was also observed [15]. A previous study [16] concluded that this phenomenon resulted from the enrichment of impurities, such as Na^+ , K^+ and Si^{4+} in the top part of crystals. Although concentrated Na^+ and K^+ ions could lead to distinct 430 nm absorption band in undoped PWO, their influence on the stability of scintillation properties, optical transmission and radiation hardness of $\text{PbWO}_4:\text{Y}^{3+}$ were not studied yet.

In the present paper, Na^+ and K^+ ion contained $\text{PbWO}_4:\text{Y}^{3+}$ crystals were studied, and the relationships between impurity contamination, optical transmission, light yield and the stability of radiation hardness were also investigated. The effect of doping and the origin of scintillation instability in $\text{PWO}:\text{Y}^{3+}$ are discussed.

2. Samples and experimental methods

The PWO crystals were grown from lead oxide (PbO) and tungsten oxide (WO_3) powders whose purity are 99.999% (5N) by modified Bridgmann method. The stoichiometric ratio between PbO and WO_3 was selected as 1 in preparation of raw materials for crystal growth. The crystallization orientation was [001]. Three samples were cut from the top, middle and bottom part of the ingot two-fold doped with Y^{3+} and Na^+ or K^+ , respectively, and two samples from the top and middle part of the Y^{3+} -doped ingot for comparison. The details of the samples are listed in Table 1. The same serial number before dash means the samples being cut from the identical ingot.

The recipe of annealing and irradiation for samples was in following sequence: annealing \rightarrow ^{60}Co irradiation at 0.35 Gy/h for 70 h \rightarrow ^{60}Co irradiation at 35 Gy/h for 70 h. The annealing procedures carried out sequentially at 50°C, 150°C

Table 1
The details of samples

Crystal ID	Dopant/dosage (ppm atom)	Location	Dimension (mm ³)
1-1	Y ³⁺ /150	Top	20 × 20 × 80
1-2		Middle part	
2-1	Y ³⁺ /150 Na ⁺ /100	Top	
2-2		Middle part	
2-3		Bottom	
3-1	Y ³⁺ /150 K ⁺ /100	Top	
3-2		Middle part	
3-3		Bottom	

and 350°C in air, and the soaking time is for 24 h at 50°C and for 10 h at 150°C and 350°C. Optical transmission and light yield measurements were followed after each annealing and irradiation step. Transmission and light yields remained constant after annealing, and were recorded 5 h after irradiation. X-ray excited emission spectra were measured before and after 0.35 Gy/h irradiation for the samples annealed at 350°C.

The optical absorption spectra were recorded along the longitudinal direction of each samples by a SHIMAZU-2501 spectrophotometer with an accuracy of ±0.002 Absorbency (Abs). The light yield was measured by using a collimated ¹³⁷Cs 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 X-ray stimulated luminescence spectra were measured under steady-state X-ray excitation on a homemade equipment (tube with Fe anticathode, 80 kV, 3 mA, emission wavelengths from 300 to 700 nm).

3. Experimental results

The transmission spectra of the samples annealed at 50°C for 24 h are shown in Fig. 1. Except for sample 2-1, in all samples 430 nm absorption band is not evident after annealing. For Y³⁺

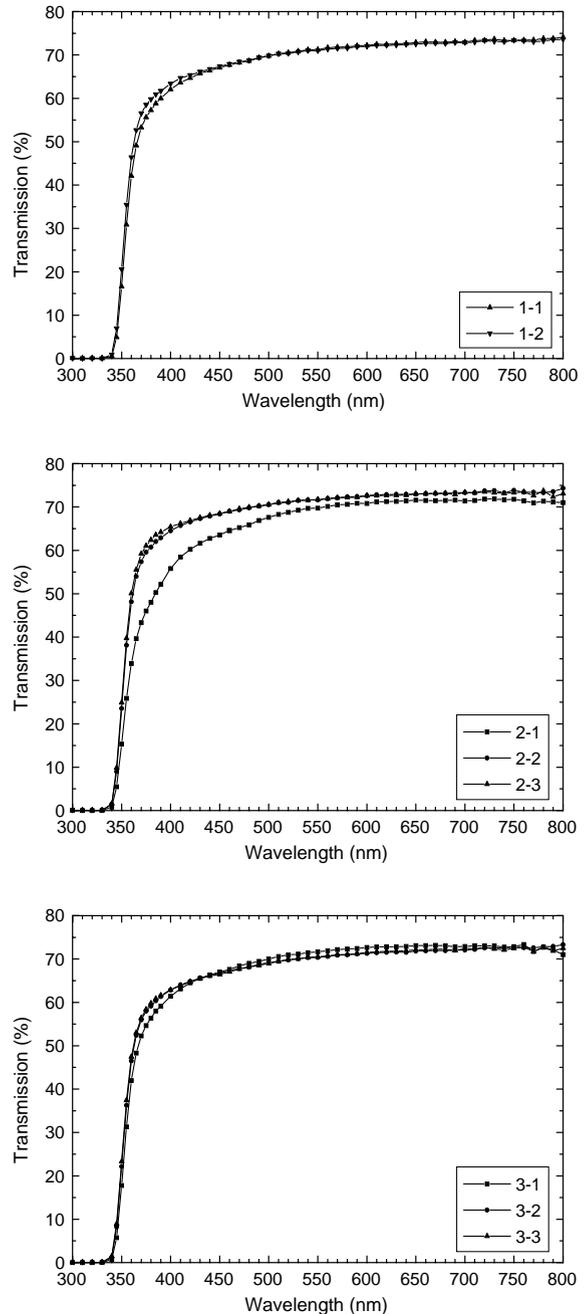


Fig. 1. Optical transmission spectra of the samples after annealing at 50°C for 24 h.

doping and Y³⁺/K⁺ co-doped samples, the transmission curves of the top, middle and bottom part are not easily to be distinguished from each

other. In Na^+ ion concentrated part, sample 2-1, optical transmission is deteriorated in the wavelengths from 350 to 500 nm. Comparing with samples 1-1 and 3-1, two notable absorption bands can be differentiated in sample 2-1, one peaks at about 430 nm, another near the cut-off front about 380 nm. Compared with other parts of $\text{Y}^{3+}/\text{Na}^+$ co-doped crystals, the absorption band of the top part is more obvious than that of the bottom and middle part. So the monovalent ions, such as Na^+ and K^+ , have different influences on the properties of PWO crystals. This may originate from the discrepancy in charge compensation mode, which will be discussed in next section.

Fig. 2 presents the annealing induced absorption coefficient spectra of the samples after annealing at 150°C and 350°C for 10 h. 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

$$\mu_{\text{treat}} = 1/d \ln[T_{\text{initial}}/T_{\text{treatment}}]$$

where d stands for the thickness of the samples. T_{initial} and $T_{\text{treatment}}$ are the transmission before and after treatment, respectively. It must be pointed out here that it is difficult to obtain the transmission of as-grown samples due to its annealing temperature sensitivity, the high temperature during the cooling down process in crystal growth may affect the absorption curve of as-grown crystals. So we regard the transmission after annealing at 50°C as T_{initial} in the equation. As can be seen from Fig. 2, the annealing induced absorption coefficient μ is positive from about 350 to 500 nm and increases as the annealing temperature goes up. Therefore it can be easily deduced that the optical transmission around 430 nm is deteriorated after annealing at higher temperatures. In addition, the $\text{Y}^{3+}/\text{Na}^+$ and Y^{3+}/K^+ co-doping samples have higher induced absorption coefficient if they are compared with Y^{3+} doping samples at the same location of the ingot.

Fig. 3 exhibits the radiation-induced absorption coefficient spectra of the samples annealed at different temperatures and being irradiated at 0.35 and 35 Gy/h. The optical transmission spectra of samples 2-3 and 3-3 have the same shape as the

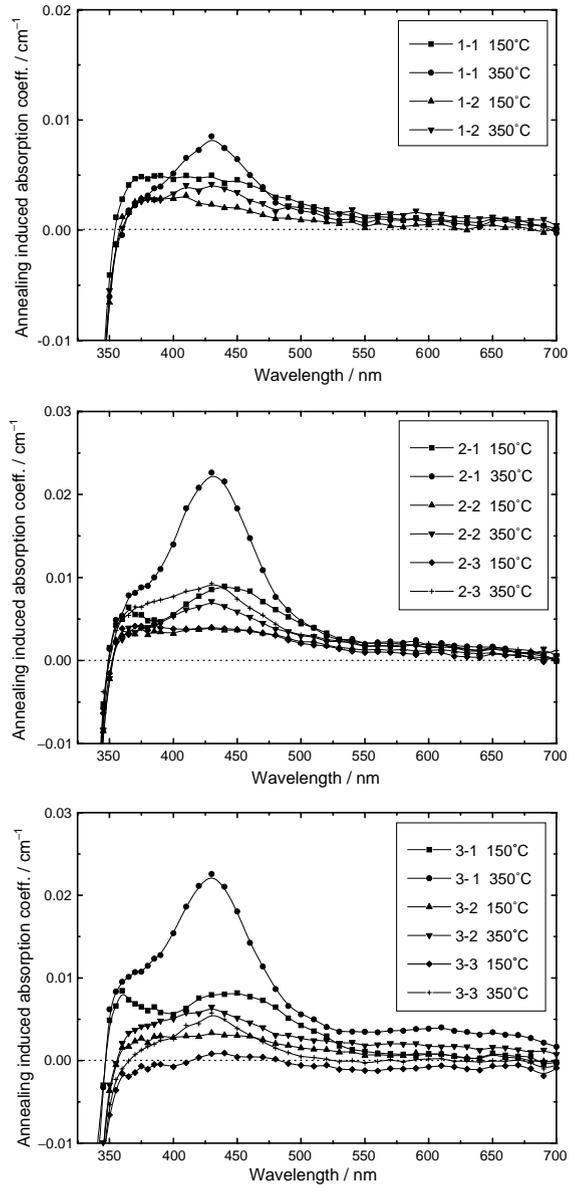


Fig. 2. Annealing induced absorption coefficient spectra of the samples.

samples in top and middle part of ingot, and vary little before and after irradiation. So they are omitted in Fig. 3. Tables 2–4 show the results of light yield measurements at 20°C and a gate width 100 ns. Positive light yield change means it increases after irradiation. The light yield of nearly

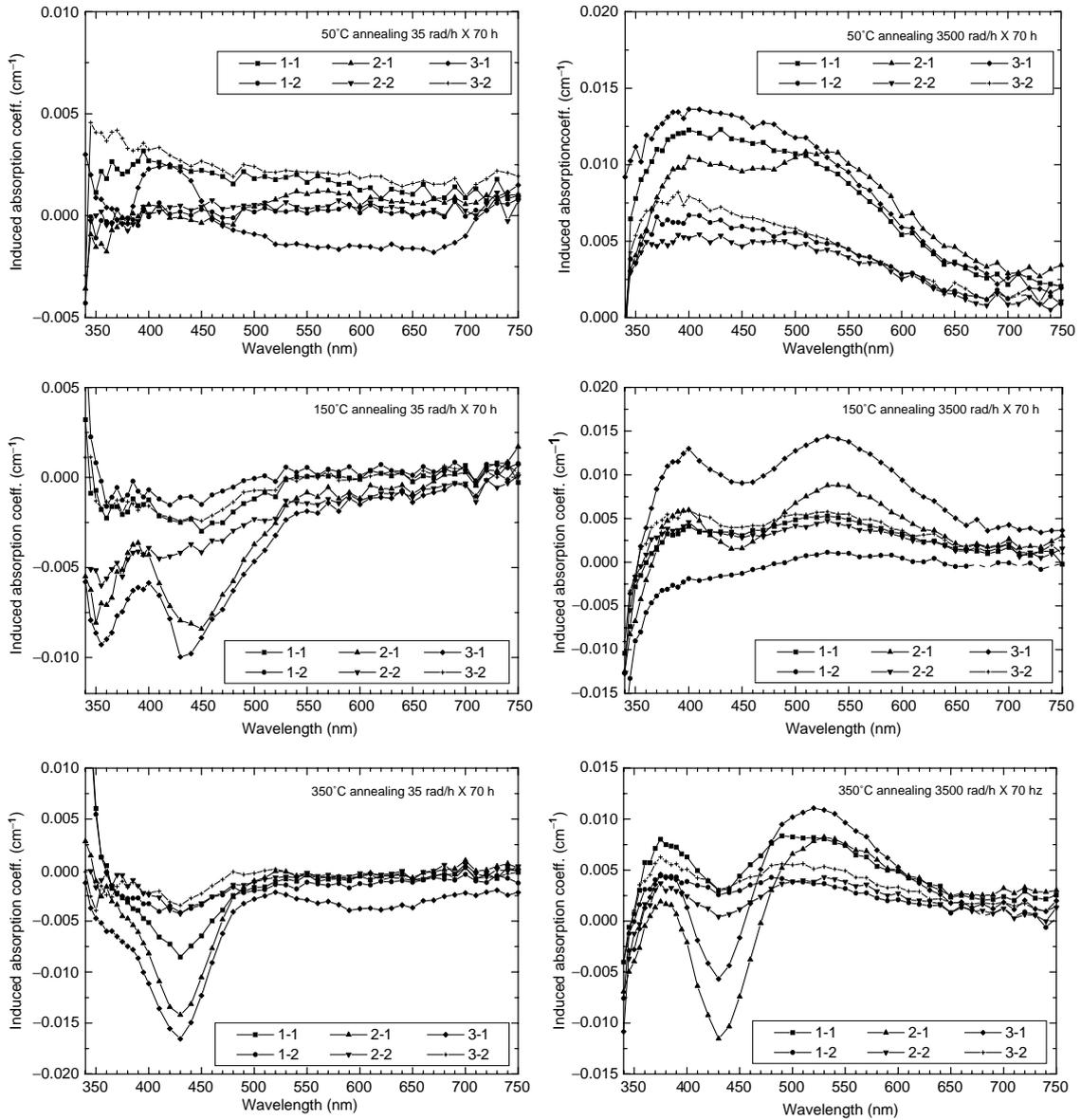


Fig. 3. Radiation-induced absorption coefficient spectra of the samples after being annealed at different temperatures.

all samples annealed at 50°C/24 h decrease after ⁶⁰Co irradiation no matter the dose rate is 0.35 or 35 Gy/h. Comparing with light yields after annealing at 50°C, higher temperatures (150°C and 350°C) annealing decrease light yields of all samples. Moreover, the radiation-induced absorption coefficients are negative around 430 nm after

low dose rate irradiation, accompanied by light yield increase simultaneously. Therefore the annealing induced absorption band peaking around 430 nm seems to be effectively “bleached” under 0.35 Gy/h irradiation, and light yield increase relates to the bleaching of 430 nm color centers to some extent. When exposed to high dose rate

Table 2

Light yield (unit: photon electron/ MeV, i.e., p.e./MeV) results of the samples annealed at 50°C for 24 h and ^{60}Co irradiation at dose rates 0.35 and 35 Gy/h for 70 h

Crystal ID	Annealed (p.e./MeV)	^{60}Co 0.35 Gy/h for 70 h (p.e./MeV)	Light yield change (%)	^{60}Co 35 Gy/h for 70 h (p.e./MeV)	Light yield change (%)
1-1	13.3	11.4	−14.3	9.5	−28.6
1-2	15.2	14.4	−5.3	13.3	−12.5
2-1	9.7	9.0	−7.2	8.3	−14.4
2-2	17.4	15.3	−12.1	15.3	−12.1
2-3	14.7	13.7	−6.8	15.8	+7.5
3-1	10.2	9.5	−6.9	7.3	−28.4
3-2	15.7	15.0	−4.5	13.0	−17.2
3-3	14.4	14.7	+2.1	14.3	−0.7

Table 3

Light yield (unit: photon electron/ MeV, i.e., p.e./MeV) results of the samples annealed at 150°C for 10 h and ^{60}Co irradiation at dose rates 0.35 and 35 Gy/h for 70 h

Crystal ID	Annealed (p.e./MeV)	^{60}Co 0.35 Gy/h for 70 h (p.e./MeV)	Light yield change (%)	^{60}Co 35 Gy/h for 70 h (p.e./MeV)	Light yield change (%)
1-1	10.2	11.5	+12.7	8.4	−17.6
1-2	13.4	14.1	+5.2	11.4	−14.9
2-1	7.8	9.4	+20.5	6.2	−20.5
2-2	15.0	15.8	+5.3	12.9	−14.0
2-3	13.1	130.8	+5.3	12.0	−8.4
3-1	8.5	10.0	+17.6	5.3	−37.6
3-2	13.4	14.3	+6.7	11.2	−16.4
3-3	13.2	14.2	+7.6	12.2	−7.6

Table 4

Light yield (unit: photon electron/ MeV, i.e., p.e./MeV) results of the samples annealed at 350°C for 10 h and ^{60}Co irradiation at dose rates 0.35 and 35 Gy/h for 70 h

Crystal ID	Annealed (p.e./MeV)	^{60}Co 0.35 Gy/h for 70 h (p.e./MeV)	Light yield change (%)	^{60}Co 35 Gy/h for 70 h (p.e./MeV)	Light yield change (%)
1-1	10.6	12.6	+18.9	7.0	−34.0
1-2	13.6	14.2	+4.4	11.3	−16.9
2-1	6.9	8.5	+23.2	5.7	−17.4
2-2	15.0	15.4	+2.7	11.9	−20.7
2-3	12.5	13.9	+11.2	11.9	−4.8
3-1	7.2	7.7	+6.9	6.0	−16.7
3-2	13.4	14.1	+9.7	11.1	−17.2
3-3	12.7	13.5	+6.3	11.9	−6.3

irradiation (35 Gy/h), wide absorption bands from 350 to about 650 nm came into being which can be observed in PWO:Y^{3+} crystals grown by Czochralski method. Thus the formation of wide absorption bands which overlap with the blue and green luminescence components results in light yield decrease.

It can be concluded that there are two steps taking place sequentially during irradiation. The first one is the bleaching of the unstable 430 nm color centers, accompanying with light yield increase. The second one is the formation of wide absorption bands from 350 to about 700 nm, leading to the degradation of light yield. It must be mentioned here that the processes of annealing induced absorption and irradiation bleaching are

reversible. If the samples were annealed at 350°C again after irradiation, the absorption band peaking at 430 nm appears again.

X-ray excited emission spectra of samples 1-1, 2-1 and 3-1 annealed at 350°C for 10 h were measured before and after irradiation, and the results are presented in Fig. 4. The luminescence spectra of samples show that a new emission peak does not appear after ^{60}Co radiation, only the emission intensity enhances in the wavelengths from 350 to 550 nm. Previous studies [8] have showed that high-energy radiation does not influence the scintillation mechanisms of PWO, so the light yield increase merely relates to the optical transmission change at the wavelengths from about 350 to 500 nm.

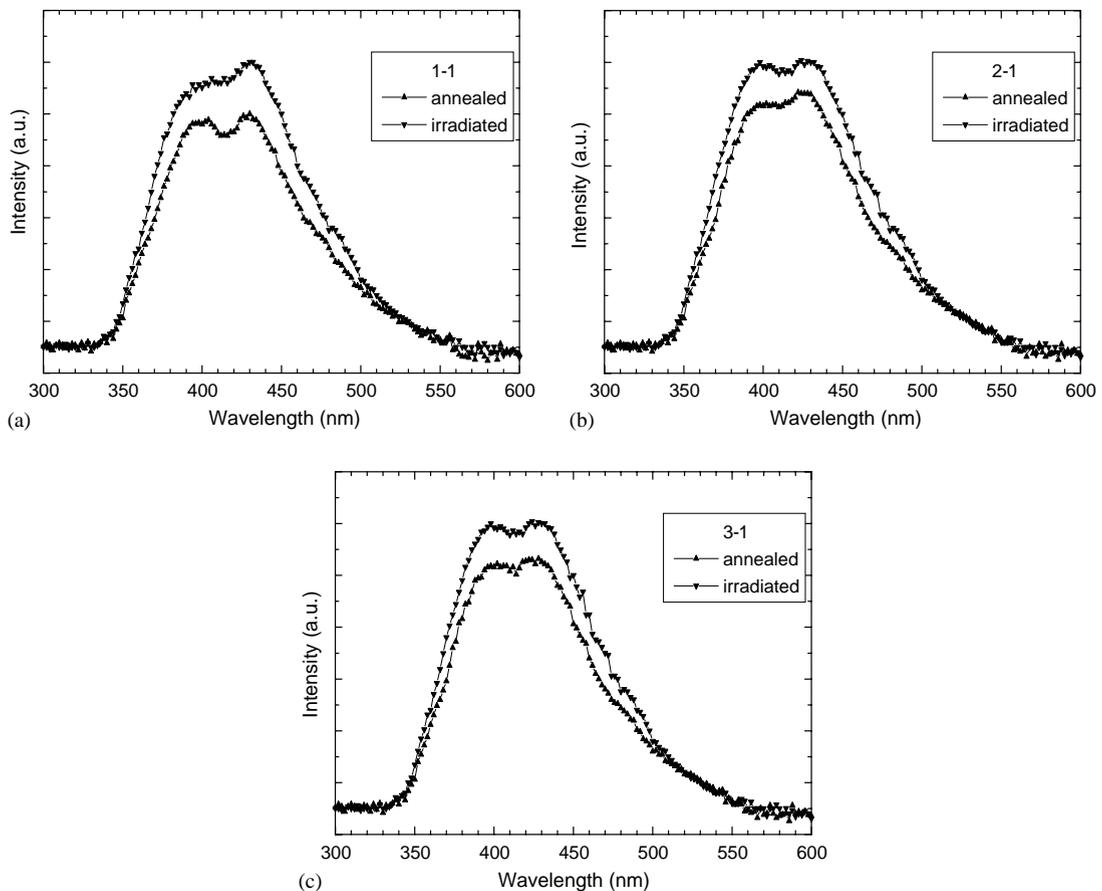


Fig. 4. X-ray excited emission spectra of samples.

The above-mentioned behaviors of Y^{3+} -doped crystals that show contrary results to the irradiation results of undoped crystals and the crystals doped with other ions concerning the induced, respectively, bleached absorption band were discovered firstly in Y^{3+}/Sb co-doped crystals [16]. According to large-scale experiments that are not discussed in the present paper, this phenomenon only exists in some Y^{3+} or Gd^{3+} [17] doped PWO crystals.

4. Discussion

PbO evaporation during growth procedure results in lead deficiency in PWO crystals [18], so V_{Pb} (stands for Pb vacancy) and V_O (stands for O vacancy) are predominant point defects in as-grown PWO. In undoped PWO crystals, besides the $V_{Pb}:V_O$ pairs charge equilibrium mechanism, the lead deficiency introduced additional V_{Pb} which have two effective negative charges relative to the lattice could be compensated by the defect clusters $[O_2^{3-}-V_{Pb}-V_O-V_{Pb}-O_2^{3-}]$, $[V_F^- - V_O - V_F^-]$ in short. The defect V_F^- in the form of $[V_F^- - V_O - V_F^-]$ and V_F^0 ($[O_2^{3-}-V_{Pb}-O_2^{3-}]$) were the origin of the 350 and 420 nm absorption bands, respectively [19].

Doping with trivalent ions [20–23], such as La^{3+} , Y^{3+} , Gd^{3+} and Lu^{3+} , can significantly improve the optical transmission and radiation hardness of PWO crystals, especially suppress the 350 nm intrinsic absorption band. From the observation of dielectric relaxation in PWO: La^{3+} crystal, the existence of V_{Pb} was confirmed [24], and the concentration of mobile defects was reduced while increasing the amount of La^{3+} ion. The observed polarization was tentatively attributed to the formation of $[2(La_{Pb}^{3+})^{\bullet}-V_{Pb}^{\prime\prime}]$ dipole complexes, in which $V_{Pb}^{\prime\prime}$ (as mobile defects in undoped PWO) was incorporated into immobile ones. Therefore, integrating V_{Pb} into dipole complexes prevents it from forming $[V_F^- - V_O - V_F^-]$ which correlates to the 350 nm absorption band, thus improving the optical transmission and radiation hardness of PWO scintillating crystals. The computer simulation results [25] of extrinsic defects in PWO proved that trivalent ion introduced positive charge defect $(M_{Pb}^{3+})^{\bullet}$ where M^{3+}

occupied the Pb^{2+} sublattice and was compensated by V_{Pb} in the form of $[2(M_{Pb}^{3+})^{\bullet}-V_{Pb}^{\prime\prime}]$ (M^{3+} stands for trivalent ion) for local charge equilibrium. With the mechanism mentioned above, Y^{3+} ion which in this respect is similar to the La^{3+} ion could form defect cluster $[2(Y_{Pb}^{3+})^{\bullet}-V_{Pb}^{\prime\prime}]$. Except for the top part of the ingot, the concentration of Y^{3+} ions is comparatively constant because the segregation coefficient of Y^{3+} is close to 1 (0.94 ± 0.04 [16]). The distribution characteristic of Y^{3+} ions is favorable to suppress the defect cluster $[V_F^- - V_O - V_F^-]$ along the length of crystal if we take into account the PbO evaporation during the growth procedure. Thus in accordance with a previous study [26] in which the crystals were grown by Czochralski method in Russia, Y^{3+} doping and Y^{3+}/Nb^{5+} co-doping were widely applied in large-scale PWO crystal production.

Monovalent ions in PWO, such as Na^+ and K^+ , may engender defect clusters in the form of $[2(A_{Pb}^+)'-(V_O)^{\bullet\bullet}]$ (A^+ stands for monovalent ions) [25]. But in this study, Na^+ and K^+ ions have different impacts on properties of PWO: Y^{3+} crystals. The concentration of Na^+ and K^+ ions are 100 ppm atom in the melt, but the typical values tested by Glow Discharge Mass Spectrometry Method in PWO grown from 5N raw materials are always below 15 ppm atom. So the concentration of Na^+ and K^+ ions in the samples is higher than those in the corresponding part in PWO: Y^{3+} samples. The contamination of Na^+ and K^+ does not result in the emergence of absorption band peaking at cut-off front and 430 nm in the bottom and middle part of the ingots. In the top part, Na^+ ion doping leads to the formation of absorption band peaking at 430 nm and cut-off edge while K^+ ion doping does not. It can be deduced that the charge compensation mode of K^+ ion along the length of crystal is the same, namely, in the form of $[2(K_{Pb}^+)'-(V_O)^{\bullet\bullet}]$ which does not lead to the appearance of two absorption bands mentioned above. Although the charge equilibrium modes of Na^+ in the bottom and middle part of crystals are the same as K^+ ion, the style is different at the top as can be seen from Fig. 1. The formation of two absorption bands could be originated from the two

following ways. Firstly, in Y^{3+} ion concentrated part, the defect $(Y_{Pb}^{3+})^{\bullet}$ is located near $(Na_{Pb}^+)'$, so instead of $[2(Y_{Pb}^{3+})^{\bullet} - V_{Pb}^{\prime\prime}]$, the formation of cluster $[(Na_{Pb}^+) - (Y_{Pb}^{3+})^{\bullet}]$ mitigates the effects of Y^{3+} ion on defect cluster $[V_F^- - V_O - V_F^-]$; secondly, the negative charge center $(Na_{Pb}^+)'$ is compensated by a hole nearby, or the defect $(Na_{Pb}^+)'$ in the form of $[2(Na_{Pb}^+) - (V_O)^{\bullet}]$ is near the $[V_F^- - V_O - V_F^-]$ and V_F^0 ($[O_2^{3-} - V_{Pb} - O_2^{3-}]$), thus stabilizes the hole trapped by oxygen ions.

After annealing at 50°C , sample 2-1 cut from top part of Na^+ ion contained ingot shows remarkable absorption band at 430 nm and near cut-off front. But light yield decreases after low dose rate irradiation, and the 430 nm absorption band is almost unchanged after irradiation. Therefore, it is not necessarily the case that light yield increase after irradiation accompanies the appearance of 430 nm absorption band before irradiation in PWO: Y^{3+} crystals. For annealing at higher temperatures, sample 2-1 exhibits higher induced absorption coefficient around 430 nm. After low dose rate irradiation, this annealing induced absorption band vanishes. The K^+ ion concentrated sample 3-1 is different, there is no appearance of absorption band after annealing at 50°C . Sample 3-1 shows stronger 430 nm absorption band than sample 1-1 when annealing at higher temperatures. The irradiation behaviors of sample 3-1 are the same as those of sample 2-1 after annealing at 150°C and 350°C . We can classify the 430 nm color centers into two types according to the stability under low dose rate irradiation, one is introduced directly by Na^+ ion contamination as in undoped PWO, this type of 430 nm color centers are hardly to be eliminated even at high temperatures and stable at room temperature and under 0.35 Gy/h irradiation as well. The other is introduced by annealing and can be bleached under irradiation. Therefore from comparison of Na^+ and K^+ ion doping experiments, it can be concluded that the instability of light yield and radiation hardness is because of the annealing induced unstable color centers. In addition, those exceptional irradiation behaviors are not the results of Na^+ and K^+ ion contamination, but correlate indirectly to the enrichment by the ions that occupy Pb sublattice.

In modified Bridgmann method, the polycrystalline PWO prepared by solid-phase reaction in air atmosphere was used as the starting materials for PWO growth. This leads to the inevitable oxygen contamination in the materials. Moreover, the crystal growth was carried out in almost sealed Pt crucibles that can avoid the PbO evaporation to a large extent. In addition, PWO grown by Bridgmann method contains more Y^{3+} ions than those grown by Czochralski method, especially in the final crystallization parts even if the concentrations of Y^{3+} ions in the melt are the same. The effective segregation coefficient of Na^+ , K^+ and Y^{3+} ions are smaller than 1, so the ions are concentrated in the top of ingot. Those ions occupy Pb sublattice, and may result in V_{Pb} shortage in which V_{Pb} is needed by defect $(Y_{Pb}^{3+})^{\bullet}$ for charge equilibrium. Local charge balance modes of Y^{3+} ions may be different along the length of ingot. In the bottom and the middle part, Y^{3+} ions integrate V_{Pb} into defect cluster $[2(Y_{Pb}^{3+})^{\bullet} - V_{Pb}^{\prime\prime}]$ due to low concentration. The concentrated Y^{3+} , together with the enrichment of Na^+ and K^+ ions that also reduce the concentration of V_{Pb} by means of occupying Pb sublattice, may lead to V_{Pb} shortage for charge equilibrium in the top part. So it is possible to form defect cluster $[2(Y_{Pb}^{3+})^{\bullet} - O_i^{\prime\prime}]$ or $[(Y_{Pb}^{3+})^{\bullet} - O_i^{\prime\prime} + \text{hole}]$ in which the interstitial O ion ($O_i^{\prime\prime}$) was considered to be the origin of the light yield increase after low dose rate irradiation [27]. In this study, we consider that the defect cluster $[(Y_{Pb}^{3+})^{\bullet} - O_i^{\prime\prime} + \text{hole}]$ is bleached under low dose rate irradiation, and also is the origin of enhancement of green component. The Na^+ and K^+ ion contamination is not only harmful to radiation resistance itself, but also to the stability of radiation hardness and scintillation properties of PWO by the way of occupying Pb sublattice and leading to consequent shortage of V_{Pb} .

Present results show that the green component originates from the " $WO_4 + O_i^{\prime\prime}$ " centers, and the enhancement of green component is also observed in our previous study [15]. The analysis mentioned above gave useful clues for eliminating the instability of radiation hardness and scintillation properties. It is most important to purify the raw materials, especially reduce the concentration of

Na^+ and K^+ ions and produce proper amount of V_{Pb} that is needed for local charge compensation because of enrichment of Y^{3+} ion and V_{Pb} shortage at the top part of the ingot. The existence of V_{Pb} in melt has two effects on PWO. Firstly, it prevents the formation of defect cluster $[2(\text{Y}_{\text{Pb}}^{3+})^{\bullet}-\text{O}_i^{\prime\prime}]$ and compels $(\text{Y}_{\text{Pb}}^{3+})^{\bullet}$ to integrate V_{Pb} into $[2(\text{Y}_{\text{Pb}}^{3+})^{\bullet}-V_{\text{Pb}}^{\prime\prime}]$. Secondly, it keeps the crystal in a negative charge environment, thus prevents the interstitial oxygen and monovalent ions which are also negative charge centers from entering into crystal.

Our experiments with V_{Pb} compensator and V_{Pb} creator dopants showed that an increase of V_{Pb} compensator leads to the emergence of the prominent 420 nm absorption band which is unstable under low dose rate irradiation and temperature fluctuation. On the contrary, V_{Pb} creator dopant produces proper amount of V_{Pb} needed by positive charge center $\text{Y}_{\text{Pb}}^{3+}$ where the Y^{3+} ions occupy the Pb sublattice at the top part, thus suppresses the exceptional irradiation behaviors in Y^{3+} -doped PWO crystals. The doping experimental results validate the conjecture that $\text{O}_i^{\prime\prime}$ is responsible for the exceptional irradiation behaviors of some Y^{3+} doping PWO crystals. Based on the studies, proper dopant that acts as V_{Pb} creator has been found out, and the unstable 430 nm color centers have been suppressed successfully.

5. Conclusion

The pre-existing or annealing induced 430 nm color centers in $\text{PWO}:\text{Y}^{3+}$ are unstable and can be “bleached” by irradiation. The unstable color centers correlate to the enrichment of Y^{3+} , Na^+ and K^+ ions in the top of crystals. The charge compensation mode of K^+ ion along the length of crystal is the same, namely, in the form of $[2(\text{K}_{\text{Pb}}^+)']-(V_{\text{O}})^{\bullet\bullet}]$. The charge equilibrium modes of Na^+ in the bottom and middle part are the same as K^+ ion, but the mode is different in the top of the crystals. The results of annealing and irradiation experiments of the samples reveal that $\text{O}_i^{\prime\prime}$ is responsible for light yield enhancement after low dose rate irradiation, and give useful clues to

suppress the instability of scintillation properties. Based on this study, experiments on new dopant acting as a V_{Pb} creator were carried out to completely eliminate $\text{O}_i^{\prime\prime}$ aiming at producing radiation hard crystals that meet the technical specification established by CERN for CMS experiment.

Acknowledgements

The authors would like to acknowledge helpful assistance on X-ray excited emission experiments by Professor Dingzhong Sheng and Doctor Bo Gong.

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