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Annealing effects and radiation damage mechanisms of $PbWO_4$ single crystals

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The annealing treatments of a $PbWO_4$ crystal sample have been sequentially carried out in air from 640 to 1040 °C. After annealing at each temperature, the optical absorption spectra of the crystal have been recorded pre and post UV irradiation exposure. The experimental results show that annealing $PbWO_4$ crystals at a temperature above 740 °C in air can effectively wash out the intrinsic color centers causing a 350 nm optical absorption band and improve the radiation hardness of $PbWO_4$ crystals. In addition, during the radiation procedure, the conversions of the 350 nm intrinsic color centers to the 410 nm temporary color centers are evidenced in the experiments. Based on the earlier results, the annealing effects and the radiation damage mechanisms of $PbWO_4$ crystals are discussed. © *1999 American Institute of Physics.* [S0021-8979(99)00719-7]

INTRODUCTION

In recent years, $PbWO_4$ crystals (PWO) have attracted special interests because of plans to use them as a scintillator in detectors at the large hadron collider in CERN.[1–3] The luminescence properties of PWO have been intensively investigated during the past century, its excited luminescence spectrum exhibits the blue ($\lambda_{peak}=420\,nm$) and the green ($\lambda_{peak}=480–510\,nm$) emission components ascribed to regular lattice $(WO_4)^2$ and defect associated WO_3 centers, respectively.[5,6] The radiation hardness is particularly important in the case of PWO because high energy physics applications in the future create a rather severe environment with unprecedented levels of radiation.[4] The radiation experiments have shown that high energy radiation does not affect the scintillating mechanisms of PWO and the main effect of the irradiation on PWO is the creation of the color centers originating with the optical absorption bands in the UV and the blue spectral region.[3,7] Among the radiation induced absorption bands in PWO, the 410 nm absorption band is rather harmful to the scintillating properties of PWO, because it overlaps with the prime fast luminescence component—blue band ($\lambda_{peak}=420\,nm$), which leads to the degradation of light output of PWO.[1] Detailed works have been carried out to understand the origin of the absorption bands in PWO.[8,9,11] The absorption bands induced by irradiation are efficiently bleached by the treatment at 200 °C. On the contrary, the absorption bands induced during crystal growth or annealing at a high temperature are rather stable. We labeled these two kinds of color centers as temporary color centers and intrinsic color centers, respectively. Although this points to different mechanisms of stabilization for these two kinds of color centers, the centers themselves might be quite similar since just localized electrons and holes are responsible for the induced absorption bands.[10] Optical absorption bands of 350, 410, and above 500 nm exist in PWO, which have been considered to have originated from Pb^{3+} hole centers, O^- hole centers, and F kinds of color centers, respectively.[11] Now, the research work on PWO is in a crucial stage as the scheduled production date is coming near, but the radiation hardness of PWO still cannot meet the critical requirements of the applications in the future. The investigation of the radiation damage mechanisms has been still phenomenological up to now.[12–15]

In the present article, the sequentially annealing treatments of PWO from 640 to 1040 °C are reported. Experimental results show that annealing at a high temperature above 740 °C in air can effectively annihilate the 350 nm intrinsic optical absorption band and improve the radiation hardness of PWO. The experiments also provide more evidence for a deeper understanding of the microscopic radiation damage process of PWO.

EXPERIMENT

The PWO samples grown from 5 N raw material powders by the improved Bridgman method whose dimensions were about 15 mm×15 mm×3 mm, with the 15 mm×15 mm polished face perpendicular to the *c* axis of the crystal, were studied. The annealing treatments of the sample were sequentially performed from 640 to 1040 °C in air, and the detailed procedure was: 640 °C (6 h)→RT (room temperature for optical measurement)→740 °C (6 h)→RT→840 °C (6 h)→RT→920 °C (6 h)→RT→980 °C (6 h)→RT →1040 °C (6 h)→RT. The annealing process was controlled automatically by a computer system. After annealing at each temperature, the optical absorption spectra were measured pre and post UV radiation exposure with a SHIMAZU-2501 spectrophotometer whose accuracy achieved ±0.002 abs. A 1000 W high voltage mercury lamp was used to irradiate the samples and the radiation time was 10 min. As indicated by Dafinnei, the color centers induced by UV radiation are similar to that caused by γ-ray irradiation for $PbWO_4$ crystals.[15]

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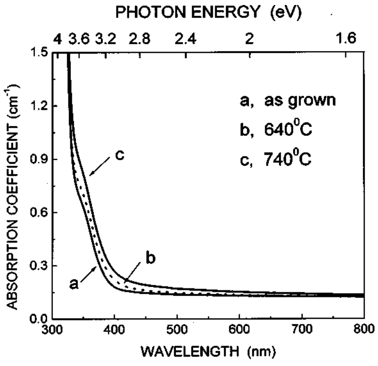

FIG. 1. The optical absorption spectra of the as-grown $PbWO_4$ sample and the samples as received after annealing at 640 and 740 °C.

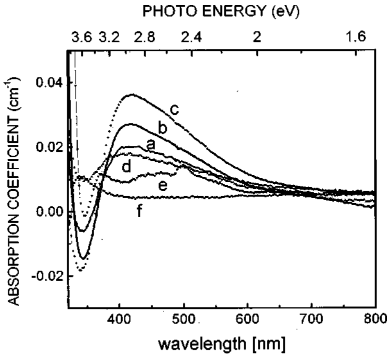

FIG. 3. The UV radiation induced absorption spectra of the $PbWO_4$, crystal samples as received after annealing at each temperature. (a) As-grown, (b) 640, (c) 740, (d) 920, (e) 980, and (f) 1040 °C.

The ORIGIN 4.0 software package was used to fit the measured spectra by the sum of gaussians in selected cases.

EXPERIMENTAL RESULTS

The optical absorption spectra taken after the PWO sample is annealed at temperatures from 640 to 1040 °C are given in Figs. 1 and 2. The optical absorption of the as-grown sample is shown by trace (a) in Fig. 1. There is significant absorption just beside the absorption edge. This absorption band is labeled as a 350 nm intrinsic absorption band. After the sample is heated to 640 °C in air for 6 h, the optical absorption around 350 nm increases and the subsequent annealing treatment at 740 °C further enhances this absorption band, as shown by trace (b) and trace (c) in Fig. 1, respectively. The change occurs after the PWO sample is annealed at 840 °C, as shown by trace (b) in Fig. 2. The optical absorption around 350 nm stops increasing but instead decreases. With the same treatments being repeated at 920 and 980 °C, the 350 nm band decreases rapidly, as illustrated by trace (c) and trace (d) in Fig. 2. After the final annealing treatment at 1040 °C, the 350 nm intrinsic optical absorption band initially existing in the as-grown PWO sample disappears, as evidenced by trace (e) in Fig. 2.

The annealing effects on the radiation hardness of the PWO sample are investigated in the following manner. As indicated in the prior section, high energy radiation does not affect the scintillating mechanisms of PWO and the main effect of the radiation on PWO is the degradation of the light output due to the 410 nm radiation induced absorption band which overlaps with the fast emission component—420 nm blue band.[3,5,6] Commonly, in the field of PWO, the intensity of the radiation induced 410 nm optical absorption band is used to evaluate the radiation hardness of PWO. The radiation induced absorption coefficient μ is defined as

$$\mu=\frac{1}{d}\log(T_0/T_1),$$

where d stands for the thickness of the sample in centimeters and T_0 and T_1 are the initial transmission and the transmission after an irradiation procedure, respectively.

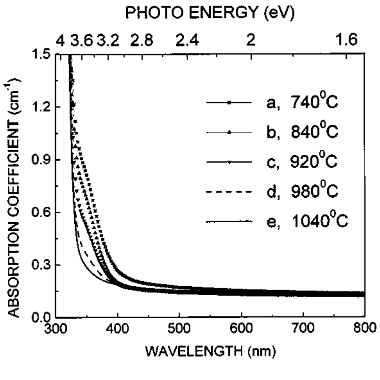

FIG. 2. The optical absorption spectra of the $PbWO_4$ samples as received after annealing at temperatures above 740 °C.

The effects of the annealing treatments in air on the radiation hardness of PWO are noticed in Fig. 3. As given by trace (a), UV irradiation induces a structured 410 nm absorption band in the as-grown PWO sample, indicating that the initial radiation hardness of the PWO sample is weak. After the sample is heated to 640 °C in air for 6 h, UV radiation induced absorption spectra of the sample is recorded at room temperature, the 410 nm band grows evidently as shown by curve (b). After repeating the same treatment at 740 °C, the 410 nm band grows more, shown in curve (c), the radiation hardness of the sample is further annihilated. This trend reverses after annealing the sample at 920 °C [curve (d)], the 410 nm radiation induced band stops growing but decreases. With further increasing annealing temperature, the 410 nm band continues to decrease and the radiation hardness is improved continuously, shown in curves (d), (e), and (f). After the final treatment at 1040 °C, the radiation hardness of PWO becomes quite rigid and no structured 410 nm radiation induced absorption band is present through UV radiation, as shown by curve (f).

Additionally, the experimental results provide us with some significant information about the creation and the annihilation of the color centers during irradiation. In the as-grown sample and the samples as received after annealing at 640 and 740 °C, the radiation induced absorption spectra show an interesting behavior. In other words, the values of the radiation induced absorption coefficient μ are negative around 350 nm, just at the position of the 350 nm absorption band, which means the concentration of the color centers causing 350 nm absorption band decreases during irradiation procedure. The decrease of μ around 350 nm correlates with the increase of μ around 410 nm, showing there probably exist the conversions of the intrinsic color centers causing the 350 nm absorption band to the temporary color centers causing the 410 nm absorption band during irradiation.

DISCUSSION

PWO tend to be ''lead deficient'' because of the evaporation of PbO during crystal growth.[16] The resulting lead vacancies each have two effective negative charges relative to the lattice and are ordinarily balanced by oxygen vacancies, F^+ centers (one electron in oxygen vacancy) and hole centers.[11] Since there is only one prominent intrinsic optical absorption peak (at 350 nm) ascribed to Pb^{3+} hole centers observed in the as-grown PWO sample, it can be considered that lead vacancies in the PWO sample used for this study are mainly balanced by oxygen vacancies and Pb^{3+} hole centers together.

We offer the following explanation of the data presented in Figs. 1 and 2. Annealing the PWO sample in air (oxygen abundant atmosphere) is actually an oxidation process of the sample. Oxygen vacancies would be filled in, as a result of oxygen ion diffusion in the sample. To keep the charge conservation, more Pb^{3+} hole centers should be introduced. This is evidenced by the data presented in Fig. 1, which shows that after annealing at 640 and 740 °C the 350 nm intrinsic optical absorption band has increased. However, an immediate question from the data presented in Fig. 2 is why the 350 nm band stops increasing but instead decreases at higher annealing temperatures at which the oxygen ion diffusion in the sample might be more effective. We interpret it to mean that further oxidation of the Pb^{3+} ion to the Pb^{4+} ion happens at a temperature higher than 740 °C. The conversion of the Pb^{3+} ion to the Pb^{4+} ion could happen. First, Pb^{4+} is one of two stable valance states of the Pb ion. Second, taking into account the sheelite structure of PWO, the Pb^{4+} ion provides one more electron with the surrounding eight oxygen ions compared to the Pb^{3+} ion, thus loosening the distortion of the local space configuration. Then the stability of the Pb^{4+} ion is enhanced in this way. The Pb^{4+} ion is a close shell ion, whose related optical absorption bands are within the absorption edge of PWO. Therefore, with the conversion of Pb^{3+} hole centers to Pb^{4+} ions being induced during annealing at the temperatures above 740 °C, the 350 nm intrinsic optical absorption band caused by Pb^{3+} hole centers continues to decrease. Eventually, the annealing crystal at 1040 °C has washed out the color centers originating from the 350 nm band.

The experimental results presented in Figs. 3–5 provide more evidences for a deeper understanding of the microscopic radiation damage process of PWO. During UV irradiation, the creation of the color centers is essentially a three-step process consisting of: (i) creation of hot electrons and holes by UV radiation exposure; (ii) their separation during subsequent cooling down and diffusion processes; and (iii) free carriers are trapped in suitable lattice sites, thus creating the color centers. In the case of PWO, the creation of Pb^{3+}, O^-, F (two electrons in O vacancy), and F^+ (one electron in O vacancy) centers have been reported. As given by curve (c) in Fig. 3, the UV irradiation induced absorption spectra measured after the sample is annealed at 740 °C is most structured and gives a reasonable chance for unambiguous decomposition into gaussian curves. Coinciding with the results reported in Ref. 11, four gaussian curves are attempted to fit the spectra. We have gotten four independent radiation induced absorption bands peaking at 410, 495, 550, and 350 nm, which have been tentatively ascribed to O^-, F, F^+, and Pb^{3+} hole centers, respectively.[8,9,11] The 350 nm band shows negative μ values, which indicates that the concentration of the 350 nm intrinsic color centers decreases during irradiation. In the following section, we will pay more attention to the creation of 410 nm color centers because it is the root course of the radiation damage of PWO.

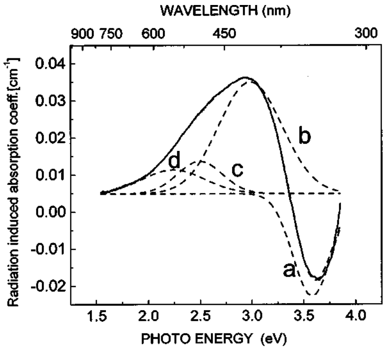

FIG. 4. The Gaussian curve fit result of the UV-radiation induced absorption spectra taken after the PWO sample is annealed at 740 °C.

A convenient treatment of color centers which is used to predict their concentrations is to consider them as chemical species. We thus try to write transitions of one type of color centers into another as chemical reactions and predict the final concentration from law of mass action. During irradiation, the creation and the annihilation of electron or hole centers happen at the same time. For example, during the irradiation procedure, free holes tend to be trapped at the oxygen ion, thus forming O^- hole centers. Meanwhile, the existed O^- hole centers also have a chance to trap a free electron, and convert back to O^{2-} ions. The competitive pro-

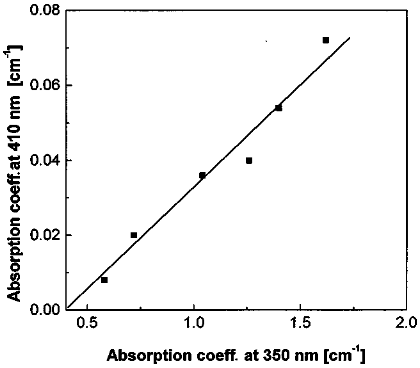

FIG. 5. A plot of the intrinsic absorption coefficient at 350 nm versus the UV-radiation induced absorption coefficient at 410 nm at each annealing temperature.

cesses for the creation of Pb^{3+}, O^-, and F centers are iterated by Eqs. (1)–(6), respectively. (Since the behavior of F^+ centers is similar to that of F centers in the experiments, we only consider F centers in this study in order to have a more concise discussion.)

$$\text{Pb}^{3+} \text{ hole centers:} \quad \text{Pb}^{2+}+h\rightarrow\text{Pb}^{3+}, \tag{1}$$

$$\text{Pb}^{3+}+e\rightarrow\text{Pb}^{2+}. \tag{2}$$

$$\text{O}^{-} \text{ hole centers:} \quad \text{O}^{2-}+h\rightarrow\text{O}^{-}, \tag{3}$$

$$\text{O}^{-}+e\rightarrow\text{O}^{2-}. \tag{4}$$

$$\text{F electron centers:} \quad V_\text{O}+2e\rightarrow\text{F}, \tag{5}$$

$$\text{F}+2h\rightarrow V_\text{O}. \tag{6}$$

Whether the creation of the color centers is through the annihilation can be determined by the change of their related optical absorption bands after UV irradiation exposure. As illustrated by Fig. 4, UV radiation has induced the 410 nm band related to O^- color centers and the earlier 500 nm band related to F kinds of color centers. On the contrary, it has annihilated the 350 nm band ascribed to Pb^{3+} hole centers. This indicates the processes described by Eqs. (2), (3), and (5) are the dominant reactions for the sample used in this study during UV radiation exposure. Transforming Eqs. (2), (3), and (5) like (2)+(3)→(7), (5)+2×(3)→(8), we obtain

$$\text{Pb}^{3+}+\text{O}^{2-}\rightarrow\text{Pb}^{2+}+\text{O}^{-}, \tag{7}$$

$$V_\text{O}+2\text{O}^{2-}\rightarrow 2\text{O}^{-}+\text{F}. \tag{8}$$

The reactions deduced earlier uncover that the creation of 410 nm color centers during radiation as the root course of PWO radiation damage is stimulated in two main aspects. One is from the conversion of 350 nm intrinsic color centers, the other is oxygen vacancies trapped the electrons during radiation, which stabilizes the existence of 410 nm color centers. From the law of mass action, while the reaction equilibrium is achieved, we have

$$\frac{[\text{Pb}^{2+}][\text{O}^{-}]}{[\text{Pb}^{3+}][\text{O}^{2-}]}=K. \tag{9}$$

$[Pb^{2+}]$ and $[O^{2-}]$ as lattice sites approximately equal constant 1 so the equation becomes

$$\frac{[\text{O}^{-}]}{[\text{Pb}^{3+}]}=K. \tag{10}$$

Since the variation of the 350 nm band after radiation exposure is less than 5% of the intensity of the 350 nm band pre UV radiation in the experiments, $[Pb^{3+}]$ can be regarded to approximately equal to the concentration of the intrinsic Pb^{3+} hole centers induced during crystal growth or annealing treatments. By now a law describing the radiation damage process of PWO has been figured out, i.e., the stronger the 350 nm intrinsic absorption band, the higher the concentration of the 410 nm radiation induced color centers, and the poorer the radiation hardness of PWO. The radiation hardness testing results reported by Auffary *et al.* that PWO possessing the 350 nm intrinsic absorption band have poor radiation hardness[7] can be well explained by the law obtained here now.

Since it is difficult to accurately decompose the absorption spectra, here we approximately represent $[Pb^{3+}]$ and $[O^-]$ using the absorption coefficient at 350 nm in Figs. 1 and 2 and that at 410 nm in Fig. 3, respectively, to validate Eq. (10). A plot of the intrinsic absorption coefficient at 350 nm versus the radiation induced absorption coefficient at 410 nm is presented in Fig. 5. The ratio of them is close to a constant, which is in good agreement with Eq. (10). This result has further confirmed the rule of the radiation damage of PWO that the stronger 350 nm intrinsic optical absorption band, the poorer the radiation hardness of PWO.

By means of annealing the PWO sample at high temperatures above 740 °C in air, the 350 nm intrinsic color centers have been effectively washed out as shown in Fig. 2. On the other hand, with the sufficient diffusion of oxygen ion in the crystal, the oxygen vacancies V_O have also been eliminated. As a result, the radiation hardness of the PWO crystal has been effectively improved. The microscopic radiation process revealed in the experiments can also give a satisfactory explanation of the improvement of the radiation hardness by La doping.[17,18] The key point is that La doping can restrain the creation of the 350 nm intrinsic color centers during crystal growth.

CONCLUSION

The sequential annealing experiments from 640 to 1040 °C in air have revealed the whole process of the increase of the 350 nm intrinsic color centers during annealing at temperatures below 740 °C and their annihilation with increasing annealing temperatures.

The radiation hardness of the $PbWO_4$ crystal has been effectively improved by means of annealing the crystal at a high temperature in air. The conversions of the 350 nm intrinsic color centers to the 410 nm temporary color centers during UV radiation exposure has been observed in the experiments. The experiments clearly show that the creation of the 410 nm radiation induced color centers as the main aspect of the radiation damage of $PbWO_4$ crystals is stimulated by two predominant factors. One is the conversion from the 350 nm intrinsic color centers, the other is oxygen vacancy as electron trap centers traps electrons to form F kinds of color centers during irradiation, which stabilizes the existence of O^- hole centers. When these two factors have been removed by means of annealing the crystal at a high temperature in air, the radiation hardness of the $PbWO_4$ crystal are improved effectively.

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