Active Loss of Light Yield of $PbWO_4$:Y Scintillation Crystals After Irradiation

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PWO crystals doped with yttrium were grown with the Bridgman method in platinum crucible and by using an indigenously developed resistive heating furnace. After an exposure of γ-ray from a ^{60}Co source, with the dose rate of 15 rad/h for 20 h, the light output increases for about 15%, accompanied with vanishing of an optical absorption band at 420 nm. The excitation and emission spectra of PWO crystals were measured before and after irradiation with different dose rates. The optical absorption band at 420 nm was also found in the PWO sample annealed in oxygen-rich atmosphere. It is suggested that the absorption band at 420 nm is related to Pb^{3+} point defects existing in the PWO crystal. The unusual change of light output after irradiation probably results from the transformation of lead ions from Pb^{3+} to Pb^{2+}.

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Lead tungstate ($PbWO_4$) crystals are promising materials for electromagnetic calorimeters in high-energy physical experiments. The compact Muon solenoid (CMS) at CERN Large Hadron Collider has selected PWO crystals for its electromagnetic calorimeter. Such a calorimeter must withstand a hostile radiation environment with radiation levels as high as 0.3 Gy/h at its barrel part and up to 15 Gy/h in the end caps at the highest design luminosity.[1] As a scintillation crystal working in such high radiation environment, the deterioration of material performance under irradiation is an important factor to predict its lifetime and stability of parameters, especially the light output.

Usually, electromagnetic radiation reduces the crystal transmission through the formation of induced colour centres and some fraction of the scintillation light will be re-absorbed before it can reach the detector. The degradation of light output resulted from irradiation is called the passive loss.[2] However, an unusual change in transmission and light output was observed in some lead tungstate crystals grown in our laboratory: that is, their transmission and light output increase, rather than decrease, after irradiation.[3] This phenomenon is called the active loss. In this Letter, we present its optical transmission, excitation and emission characteristics and their relation to the point defects in PWO crystals.

Lead tungstate crystals were grown by a modified vertical Bridgman method. The charge was composed of PbO and WO_3 powders with purity of 99.99% and 99.999%, respectively. They were weighted in precise stoichiometric proportion of $PbWO_4$ and mixed in agate mortar fully. Sb_2O_3 was once used as dopant to decrease the defect density related to the vaporization of PbO, but its segregation coefficient in PWO is much less than 1.[4] In this experiment, Y_2O_3 was selected as a dopant because the radius of Y ions is closer to Pb ions than that of Sb. The doping amount was 200 ppm, which was based on our experimental experience. All starting materials were sintered in a platinum crucible to form polycrystalline grogs for the crystal growth. The orientation of the seed crystal was [001] in all our growth runs. Both the seed and the grog were put into platinum crucible and then heated to the melting point temperature of PWO. The crucible was kept at high temperature until all of the charge melted and then lowered at the rate of 1 mm/h. During the whole growth process, the temperature gradient at the interface between solid and melt was kept in the range of 25–30°C/cm.

The dimensions of the crystal bouls grown were $30 \times 30 \times 280$ mm. The samples used for test were cut in the shape of truncated pyramids with the bottom and top cross-sections of 26×26 mm and 22×22 mm, respectively, and a length of 230 mm. All the surfaces of the crystals were polished.

Both the photo-luminescence and photoelectron numbers of $PbWO_4$ crystals were measured at the California Institute of Technology. The absolute light output was tested by using a Hamamatsu R2059 PMT with a small ^{137}Cs source placed at the side of the crystal. The crystals were irradiated with a ^{60}Co source. An Hitachi F-4500 fluorescence spectrometer was used to record the excitation and emission spectra. The optical transmission of the crystals was measured with a Shimadzu UV-2501PC spectrophotometer equipped with a large sample compartment.

As shown in Fig. 1, the initial light output of the PWO:Y crystal, S111, with size of $22 \times 26 \times 230$ mm is 5.8 p.e./MeV within the time gate of 200 ns at 20°C. Then it was exposed to a ^{60}Co source with dose rate of 15 rad/h for twenty hours; the light output becomes 6.3 p.e./MeV, an increase of about 15%. This phenomenon is the so-called active loss. However, when the dose rate arises to 500 rad/h, the light output decreases to 5.3 p.e./MeV, which is less than the initial value. The light output increases and then decreases

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with the increase of the dose. The active loss of light output mostly appears in the PWO crystals prepared directly from the PbO and WO_3 powders. Even in the same ingot, this phenomenon is more significant at the top than that at the bottom of an ingot.

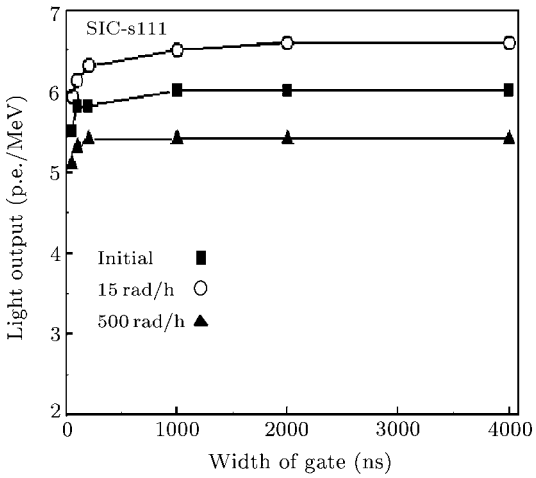

Fig. 1. Dependence of light yield of PWO crystal on the irradiation dose.

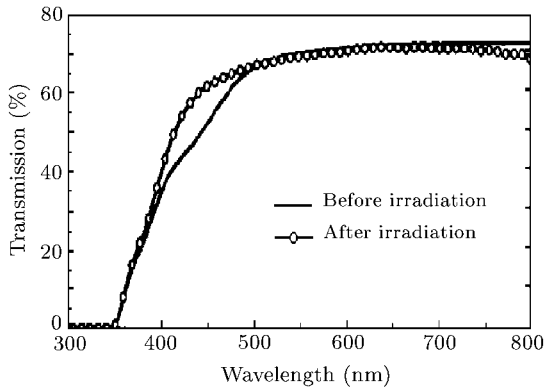

Fig. 2. Transmittance change of the PWO crystal before and after irradiation.

Accompanying the increase of light output, the transmission of the PWO crystal between 400 and 480 nm also increases after irradiation. The longitudinal transmittances before and after irradiation are shown in Fig. 2. It is clear that there is an absorption band between 400 and 480 nm in the crystal before irradiation. However, this absorption band vanishes after irradiation, and the transmission in this region rises higher than its initial value. Based on the shapes of transmission spectra, the PWO crystals can be classified into two types: one is characterized by the 430 nm absorption band at its initial transmission curve, the other has no such absorption band. It is very common that active loss of light output exists in the former case, and passive loss of light output exists in the latter case. This means that some kinds of defects, which are responsible for the 430 nm absorption in the active PWO crystals, are cured or bleached after irradiation with a low dose rate.

As shown in Fig. 3, the emission spectrum of the PWO:Y crystal can be fit into two peaks, 430 nm and 475 nm, which correspond to excitation peaks at 332 nm and 310 nm, respectively. The main excitation peak corresponding to 430 nm emission remains stable until 500 rad/h and then disappears. However, the second excitation peak corresponding to 475 nm emission decreases in intensity after irradiation with dose rate of 15 rad/h. It reappears until the dose rate reaches to 100 rad/h and then increases with the dose rate. The emission spectrum shows no obvious change when the irradiation dose rate increases from 100 to 500 rad/h except for the increase of luminescence intensity of the second component peaking at 475 nm.

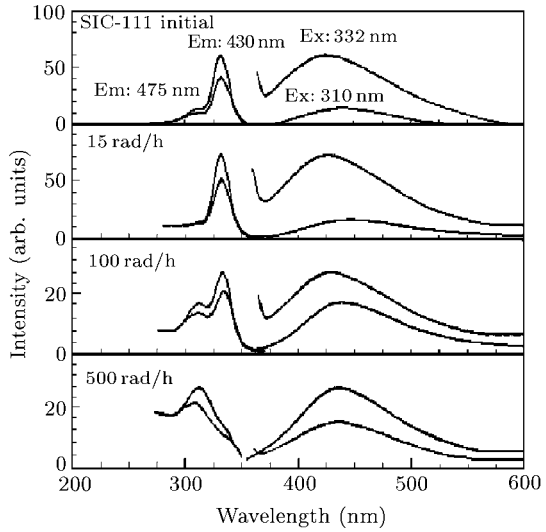

Fig. 3. Excitation/emission spectra of the PWO sample before and after irradiation with different doses.

Since the light output increases after irradiation of 15 rad/h accompanied with the disappearing of absorption band at 420 nm, it is reasonable to ascribe the active loss to the curing of colour centre related to the 420 nm absorption. However, there are many explanations for the origination of 420 nm absorption. For example, Nikl *et al.* proposed that the absorption band at 420 nm originated from an O^- hole centre in PWO crystals,[5] and in Han *et al.* once observed that UV irradiation caused an absorption band at 410 nm.[6] This process was explained to be O^{2-} transfer into O^- during irradiation and O^- to be responsible for the absorption at 410 nm. In this experiment, the absorption band at 420 nm was not enhanced, but reduced after irradiation with low dose rate. Therefore, it is unacceptable to ascribe the absorption at 420 nm to O^- defect centres. Based on the doping and annealing experiment, Annenkov *et al.* proposed that both trivalent lead and bismuth impurity ions provoked 420 nm absorption in PWO crystals.[7] Zhang *et al.* suggested that the increase of the light output after irradiation is originated from the interstitial oxygen ions (O_i) in PWO crystals, because the green scintillation components peaking at 460–500 nm were enhanced after

UV irradiation.[3] However, in the emission spectra of PWO after γ-ray irradiation with the dose rate of 15 rad/h (Fig. 3), the emission intensity in the green region was not enhanced; on the contrary, the excitation peaking at 310 nm, which corresponds to the green emission, was reduced greatly.

Annealing experiment on the PWO crystal in oxygen atmosphere at 900°C demonstrates that an absorption band at 420 nm will be induced in the transmission spectrum of the PWO crystal (Fig. 4). At the same time, the transmission around 350 nm will be enhanced. The phenomenon that absorption at 420 nm was enhanced in oxygen atmosphere and reduced in vacuum was also observed in Yang's annealing experiment.[8]

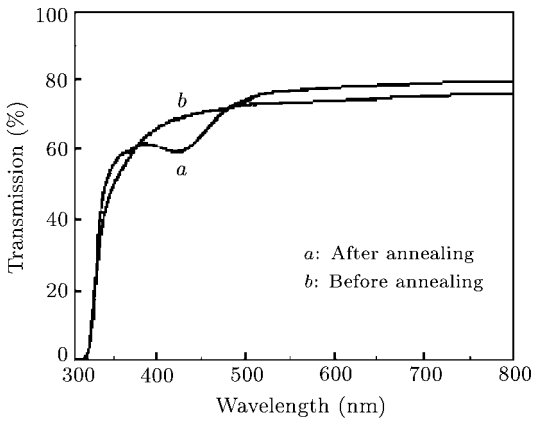

Fig. 4. Transmission of the PWO crystal before and after annealing at oxygen rich atmosphere.

As we know, PbO evaporation during growth of PWO crystals results in lead deficiency and oxygen deficiency. Therefore, lead vacancies V_{Pb}, which have two negative charges, and oxygen vacancies V_o, which have two positive charges, are predominant point defects in PWO crystals. Since the annealing in oxygen-rich atmosphere might induce the diffusion of oxygen into the PWO lattice, it may reduce the oxygen vacancy concentration. Such a process can be expressed by

$$1/2\,\mathrm{O_2} + [V_o]^{\bullet\bullet} \rightarrow \mathrm{O_O} + 2\mathrm{h}^{\bullet}. \qquad (1)$$

The produced holes in reaction (1) will be captured by lead ions, resulting in the transformation of lead ion form Pb^{2+} into Pb^{3+}, i.e.

$$\mathrm{Pb}^{2+} + \mathrm{h}^{\bullet} \rightarrow \mathrm{Pb}^{3+}. \qquad (2)$$

Pb^{3+} was suggested to be responsible for the optical absorption band at 420 nm.[7] Thus, annealing in oxygen-rich atmosphere will cause an absorption band at 420 nm. However, irradiation with γ-ray can promote reaction (2) from right to left,[6] thus reducing the concentration of Pb^{3+} and eliminating the absorption intensity at 420 nm. Since the emission peak of PWO crystals locates at 420 nm,[9] the elimination of absorption at 420 nm must result in the increase of light output of PWO crystals. Therefore, the active loss of PWO crystals after irradiation at low dose rate probably originates from the transformation of lead from Pb^{3+} to Pb^{2+}.

However, the active loss of light outputs were not found in the PWO crystals grown by Annenkov *et al.*, because they pulled the crystal within an isolated chamber filled with nitrogen.[7] Our PWO crystals are grown in air atmosphere, especially, the starting materials for the PWO growth are polycrystalline PWO synthesized from solid-state reaction in oxygen-rich atmosphere. Thus, it is inevitable for extra oxygen to enter the growth system. This process will induce the formation of trace Pb^{3+} ions. On the other hand, the growth direction of crystals in the Bridgman method is from bottom to top; this process can expel the extra Pb^{3+} to the top of the ingot, causing the concentration of Pb^{3+} at the top is higher than that at the bottom. This is why the active loss of the PWO crystal mostly appears at the top of the ingot. Therefore, the effective methods to overcome the active loss of light output in PWO should be avoiding oxygen contamination during the process of crystal synthesis.

In conclusion, in the PWO crystals grown with our modified Bridgman method, it was observed that the light output of the crystal increases for about 15% after irradiation with a low dose rate, accompanied by the vanishing of an optical absorption band at 420 nm. The active loss is suggested to originate from a point defect related with Pb^{3+} existing in PWO crystals. Pb^{3+} ions formed during the preparation of crystals are suggested to be responsible for the optical absorption at 420 nm. After irradiation with the low dose rate, Pb^{3+} ions can transfer into Pb^{2+} ions, thus eliminating the optical absorption at 420 nm and increasing the light output of PWO crystals. Therefore, irradiation at a low dose rate plays a role of bleaching on PWO crystals.

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