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Sb-doped lead tungstate (PWO) crystals were grown and investigated. The measurements of Sb content in crystals indicated that the segregation coefficient of Sb in PWO is about 0.63. Even with a little Sb^{3+} introduced into PWO crystal, the transmission, especially the light yield was enhanced significantly. Furthermore, after the Sb-doped PWO crystals were annealed, not only the fast component still remained a high percentage but also the radiation hardness was improved evidently. The main reason may be that Sb-doping can compensate the composition deficiency and then reduce the density of hole centers such as Pb^{3+} and O^-.

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Lead tungstate, $PbWO_4$ (PWO), is the first choice for detector material of electromagnetic calorimeter in the large hadron collider (LHC) at CERN due to its high density, short radiation length and fast decay time.[1] In recent years, many investigations have been devoted to the study of PWO and great progress has been made. Although full-size crystals can be grown successfully, most of them cannot satisfy the quality requirements for LHC. PWO crystal is grown from the melt of mixture of PbO and WO_3. Due to the high volatility of PbO, PWO crystal tends to be lead deficient,[2] resulting in hole centers in the crystal such as Pb^{3+} and O^- which are related to 350 and 420 nm absorption bands, respectively.[3] The existence of these hole centers will result in the degradation of optical transmission, light yield and radiation hardness of PWO crystal. In order to improve the properties of PWO crystal, some ions are usually introduced to compensate its composition deficiency and so reduce the density of defects.[4] For example, La^{3+} doping can improve the transmission and radiation hardness of PWO crystal. But in the meantime it seems to be harmful to the light yield.[5,6] In this work, we tried to introduce another kind of trivalent ion, Sb^{3+}, into PWO crystal. It was found that, in addition to improvement of transmission and radiation hardness, the luminescence intensity and light yield of Sb-doped PWO crystal were also enhanced.

The PWO crystals used in the experiments were grown by modified Bridgman method. The raw material of PbO and WO_3 were at least 99.99% pure. The samples were cut from two Sb-doped PWO crystals (Sb-doped 1 and 2) and an undoped one (undoped 3). For Sb-doped crystals, Sb was introduced into raw material in the form of Sb_2O_3. The initial concentration of Sb for Sb-doped 1 and Sb-doped 2 were 900 and 300 ppm, respectively. Information about the samples named as Sb900, Sb300 and undoped is listed in Table 1.

In order to determine the distribution of Sb in PWO crystal, atomic absorption spectrometry (AAS) analyses were performed on two Sb-doped crystals. The transmission spectra of samples were measured by a UV-256 spectrophotometer. The fluorescent spectra were recorded by a Perkin Elmer LS-50B spectrophotometer with a slit width of 15 nm. The x-ray stimulated luminescence (XSL) spectra of the samples were measured before and after annealing in oxygen-rich atmosphere at 960°C for 24 h. The light yield of sample Sb900 before and after irradiation under a radioisotope Co^{60} γ-ray source with a dose rate of 35 rad/h for 24 h were measured at the gate 100 ns.

For crystal Sb-doped 1, the concentration of Sb at two sides were measured, the results of AAS analyses showed that the concentration of Sb at the seed side is 30.7 ppm and that at the opposite side is 48.6 ppm. For crystal Sb-doped 2, only the concentration of Sb at the opposite side was measured, the results showed it was 10.8 ppm. These data indicate that the segregation coefficient k of Sb in PWO is less than 1. Accurate calculation shows that k is about 0.63. Another obvious conclusion is that the concentration of Sb in sample Sb900 is between 30.7 and 48.6 ppm while that in sample Sb300 is less than 10.8 ppm.

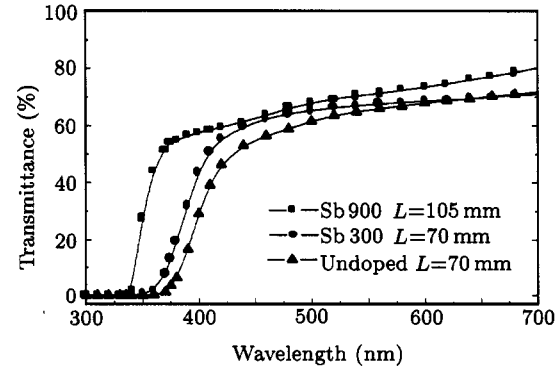

Fig. 1. Longitudinal transmission curves of Sb900, Sb300, and undoped.

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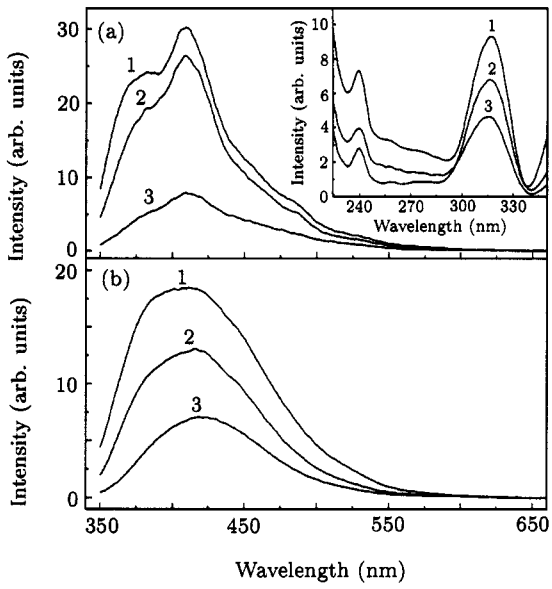

Fig. 2. Excitation and emission spectra of: 1, Sb900; 2, Sb300; and 3, undoped at $T = 300$ K. Insert: excitation for $\lambda_{em} = 420$ nm, (a) emission for $\lambda_{exc} = 240$ nm, (b) emission for $\lambda_{exc} = 317$ nm.

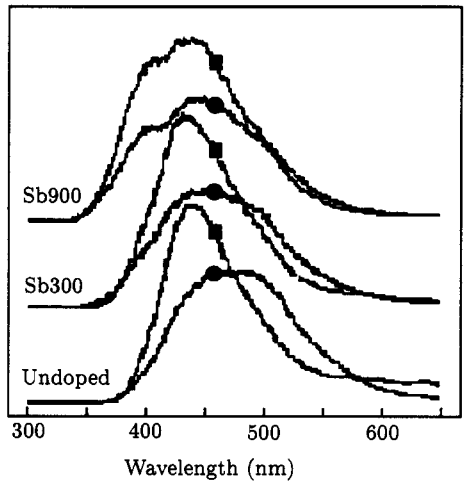

Fig. 3. XSL spectra of samples Sb900, Sb300, and undoped before (■) and after (●) annealing in oxygen-rich atmosphere at 960°C for 24 h.

Table 1. Dimensions and Sb concentration of samples.

Sample	Cut from	Dimension (mm)	C_{Sb} (ppm)
Sb900	Sb-doped 1	25×25×105	30.7–48.6
Sb300	Sb-doped 2	25×25×70	<10.8
Undoped	undoped 3	25×25×70	0

From transmission spectra of samples Sb900, Sb300 and undoped shown in Fig. 1, it can be seen that the undoped crystal has strong absorption in the near UV-blue region, while Sb-doping alleviates this absorption greatly and results in the blue shift of the cutoff wavelength. The emission and excitation spectra of samples Sb900, Sb300 and undoped shown in Fig. 2 indicate that three crystals have the same excitation peaks at 240 and 317 nm under the maximum emission $\lambda = 420$ nm. However, under some other maximum emissions, no new excitation peaks are detected. Excited by $\lambda = 240$ and 317 nm, their emission spectra also have similar shape with peak in the blue region. In addition, Sb-doping increases luminescence intensity with increasing Sb concentration.

The XSL spectra of samples Sb900, Sb300 and undoped are illustrated in Fig. 3. It can be found that before the crystals are annealed in oxygen-rich atmosphere the prevailing emission is located in blue region. After annealing, both Sb-doped and undoped crystals have the same trend of increase in green emission and decrease in blue emission, but Sb-doping seems to refrain this trend, the higher the Sb content in crystal, the less this trend. The luminescence of PWO crystal behaves very complex, either blue emission or green emission has both fast component with short decay time and slow component with long decay time. Detailed investigation obtained by time-resolved techniques indicated that blue emission is the main contribution to the fast component whereas the green emission to the slow component.[7] Therefore, the oxygen annealed Sb-doped crystal can maintain a high percentage of fast component.

Table 2 lists the light yield and light yield loss after irradiation of sample Sb900 before and after annealing. In agreement with the high luminescence intensity shown in Fig. 2, all the light yield of sample Sb900 are high. Moreover, the light yield loss decreases evidently after annealing, which means that the radiation hardness is improved greatly.

Table 2. Light yield (LY) and loss of Sb900 before and after irradiation under Co^{60} γ-ray source with a dose rate 35 rad/h for 24 h in units of photoelectron/MeV.

Before anneal	Before irradiation	18.0
	After irradiation	13.4
	LY loss	26%
After anneal	Before irradiation	15.8
	After irradiation	15
	LY loss	5%

Generally speaking, Sb^{3+} tends to occupy Pb^{2+} site because the radius and electron negativity of Sb^{3+} (0.93 Å and 1.8) are close to those of Pb^{2+} (1.20 Å and 1.6). Doping of Sb_2O_3 would result in an excessive charge in Pb^{2+} sublattice, thus decrease the density of Pb^{3+} and O^- related to the absorption bands at 350 and 420 nm. As a scintillation crystal, PWO crystal has the weak luminescence, the above results indicate that Sb-doping can improve it. The possible explanation for it may be that Sb^{3+} does not influence Pb^{2+} in the PWO crystal, while the blue emission of the crystal originates from the regular WO_4^{2-} activated by the sensitization of Pb^{2+} with an allowed transition $^1A_1 \rightarrow {}^3T_1$.[8] Although Sb^{3+} tends to occupy Pb^{2+} site, due to the fact that the radius of Sb^{3+} is some smaller than that of Pb^{2+}, it is difficult for Sb^{3+} to exclude Pb^{2+} then to occupy its site stably. Therefore, Sb^{3+} ions can only compensate the Pb^{2+}

deficiency by entering the vacancy rather than substitute for Pb^{2+}. With the growth of the crystal, PbO volatilizes further, more and more Sb^{3+} should enter the lattices. The above analyses can also explain the result that the segregation coefficient of Sb in PWO crystal is less than 1. At high temperature, both Pb^{2+} and O^{2-} in PWO crystal are supposed to be movable and annealing in oxygen-rich atmosphere should influence the defects related to V_{Pb} and V_O. On one hand, oxygen should move into the crystal by diffusion, thus decrease the density of V_O; On the other hand, Pb^{2+} should move out of the crystal and some additional Pb^{3+} and O^- hole centers may be induced. Because the diffusion of Pb^{2+} and oxygen depends on vacancy density, the little change of luminescence of Sb-doped crystals caused by annealing can be attributed to the low vacancy density in crystals. As already mentioned above, Sb-doping can compensate the lead deficiency of PWO crystal, it means that Sb-doped PWO crystals will have lower V_{Pb} density. Meanwhile, because V_O may exist in crystal as a kind of defect to balance the local charge deficiency at V_{Pb} site, Sb-doped PWO crystals will have lower V_O density, too. So due to the lower vacancy density, when Sb-doped crystals were annealed, the diffusion of Pb^{2+} and oxygen become weaker, i.e. oxygen annealing had less effect to their luminescence. Previous works on influence of annealing in different atmosphere (vacuum, inert gas, air and oxygen atmosphere) on the luminescence of PWO crystal indicated that the change of luminescence was strongly dependent on partial pressure of oxygen in annealing atmosphere.[9] It means that the diffusion of oxygen plays a more important role when PWO crystals are annealed. Therefore, although Sb-doped PWO crystals had lower vacancy density, due to the easier diffusion of oxygen, annealing in oxygen-rich atmosphere can still compensate O vacancies, then the radiation hardness should be improved.

In conclusion, Sb is an effective dopant to improve the scintillation properties of PWO crystals because not only Sb-doping can enhance the light yield and transmission, but also the annealing in oxygen-rich atmosphere has little effect to the luminescence of Sb-doped crystals. Moreover, considering the low light yield of PWO crystal at room temperature, the most outstanding advantage of Sb-doping is to enhance the light yield of PWO crystal.

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