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La^{3+} Distribution and Annealing Effects in La : $PbWO_4$ Crystal

NING LEI, BAOGUO HAN, XIQI FENG[1]), GUANQIN HU, YANXING ZHANG,
and ZHIWEN YIN

Laboratory of Functional Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, People's Republic of China

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The optical transmission spectra and irradiation induced absorption spectra were measured transversely point by point from the top to the bottom of La : $PbWO_4$ crystal. From the experimental results, it can be clearly seen that La^{3+} ions distribute inhomogeneously in the crystal, and have pronounced effect on suppressing its intrinsic absorption band at 350 nm. Therefore, the correlation between the transmission at 350 nm and the La^{3+} distribution concentration was reasonably discussed. Furthermore, high temperature annealing of the crystal in air can also influence its transmission spectra, and how this affects the formation of induced color centers being studied. The annealing temperatures taken are 600, 780, and 960 °C, respectively, and when annealed at 960 °C, La^{3+} diffusion in the crystal may occur, and thus induced color centers may decrease. Finally, it can be concluded that suitable La doping and annealing at appropriate temperatures can improve the radiation hardness of PWO crystal significantly.

1. Introduction

Optical properties of $PbWO_4$ (PWO) single crystals have been intensively investigated in recent years after recognizing its potential for application as a scintillator in high energy physics experiments [1 to 7]. Radiation hardness is the most important scintillation parameter because high energy physics applications create a rather severe environment with high dose radiation. Many research works have been done to improve the radiation hardness of PWO. One of the efficient methods is to dope trivalent or pentavalent ions. Recently, the improvements in the transmission in the wavelength range from 330 to 450 nm, in the radiation hardness as well as scintillation speed and also the disappearance of TSL peak above RT in La^{3+} doped PWO were separately reported [8, 9].

In addition, annealing at high temperatures can influence the defect absorption bands, and also has a great effect on the formation of color centers, thus, it is one of the important post-treatment methods to improve light yield, transmission, radiation hardness etc. of the crystal.

The aim of this paper is to report systematic studies of the effects of La^{3+} distribution concentrations in PWO crystal and the heat treatment of such crystal on its color centers and radiation hardness. It is the first time for us to report the correlation between La^{3+} distribution concentrations and defect absorption bands for different positions of the crystal.

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[1]) Correspondence author; e-mail: xqfeng@summ.shcnc.ac.cn

2. Experiments

The PWO crystal grown by modified Bridgeman method, has a La doping concentration in melt of about 50 at.ppm. The dimension of the sample used for transmission measurements and X-ray excited emission spectra is about 24 × 24 × 60 mm^3, and for TSL measurements polished plates were used with thickness of about 1 mm cut from the parent bulk sample at top and bottom. Transmission measurements were performed by Shimadzu UVPC2501 spectrophotometer, X-ray excited emission spectra were measured by our-made spectrophotometer (W target, 82 kV, 4 mA), TSL glow curve measurements were made at RT by FJ-427A thermoluminescence spectrometer. According to Baccaro [10] the same color centers can be observed after γ-ray (Co^{60}) and UV irradiation on PWO crystals. We used a 1000 W high voltage mercury lamp as irradiation source, and the time of irradiation was 25 min. Annealing treatments were taken at about 600, 780, and 960 °C in air for 24 h, respectively.

3. Results and Discussion

3.1 Before annealing

Because of the crystal growth method we used, the distribution of La^{3+} in PWO is very inhomogeneous. We measured the optical absorption transversely from the top to the bottom of sample point by point, and all position points are shown in Fig. 1. The transmission spectra of the sample are given in Fig. 2; from a to c, there are no obvious absorption bands, but the 350 nm intrinsic absorption band increased obviously from d to f, while La^{3+} concentration increases from f to a.

The irradiation induced absorption coefficient μ is defined as

$$\mu = 1/d \log [T_0/T_1], \tag{1}$$

where d is the thickness of the sample in cm and T_0 and T_1 are the initial transmission and that after an irradiation procedure, respectively. In Fig. 3, induced absorption spectra are given for all points, from a to f; the induced 420 nm color center absorption band increased gradually.

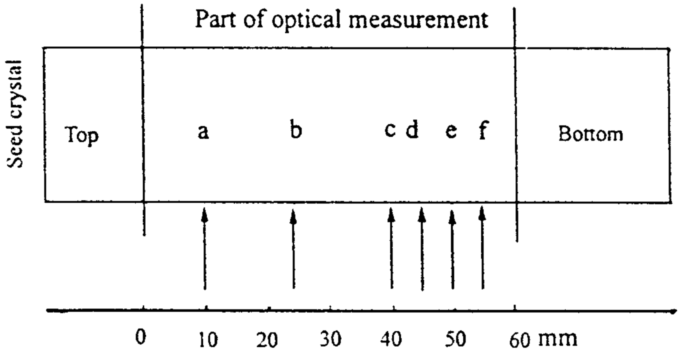

Fig. 1. Measuring positions of La : PWO sample, the top and the bottom are cut from the crystal for TSL measurement

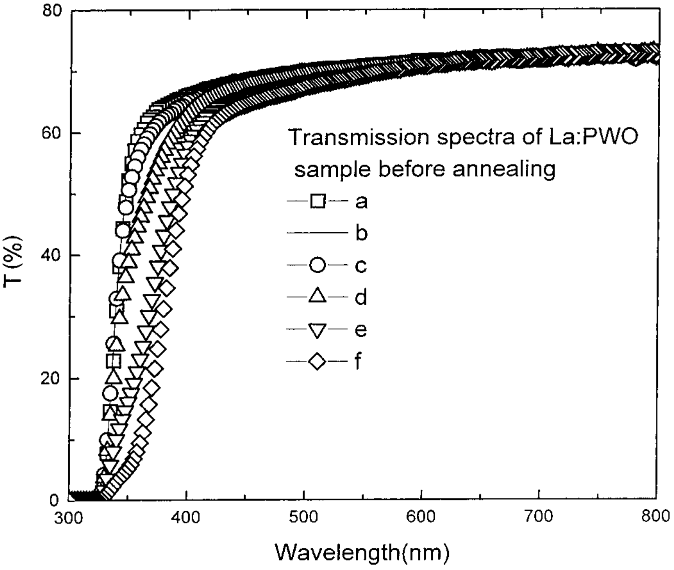

Fig. 2. Transmission spectra of La : PWO sample before annealing

Because the growth rate of PWO crystals is very slow, it belongs approximately to the steady-state growth, the distribution of La^{3+} in the sample can be expressed as follows [11]:

$$C_s = kC_0(1 - g)^{k-1}, \tag{2}$$

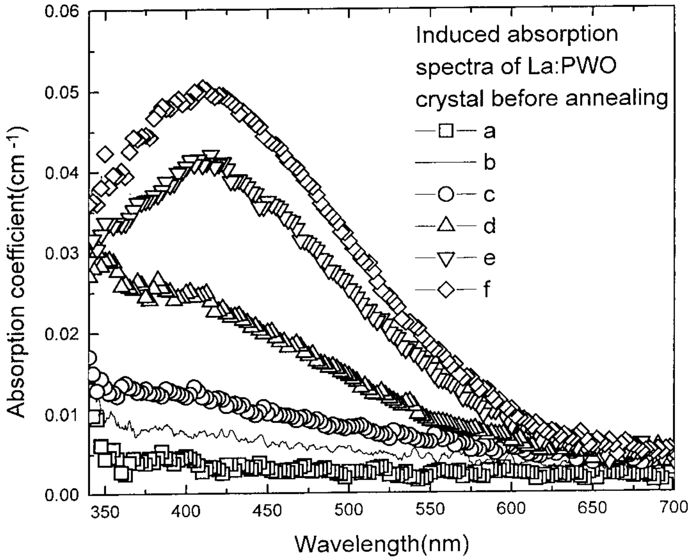

Fig. 3. Induced absorption spectra of La : PWO sample before annealing

Table 1
The solidification coefficient and La^{3+} average distribution concentration of measuring positions a to f

measuring position	a	b	c	d	e	f
relative solidification coefficient g	0.25	0.40	0.55	0.60	0.65	0.70
La^{3+} distribution concentration (ppm)	79	59	42	36	30	25

where k is the segregation coefficient, C_0 is the La^{3+} doping concentration in the melt, g is the relative solidification coefficient (the ratio of the solidification part of the crystal to the whole length of crystal).

The size of light spot in the measurement is 6 mm, so it is appropriate to consider the average La^{3+} distribution concentration over 6 mm length, the expression is

$$\overline{C}_s = 1/\Delta g \int_{g-\Delta g/2}^{g+\Delta g/2} kC_0(1-g)^{k-1}\,dg = C_0/\Delta g[(1-g+\Delta g/2)^k - (1-g-\Delta g/2)^k], \tag{3}$$

where C_0 = 50 ppm, g is the relative solidification coefficient (the whole length of the crystal is 100 mm), Δg = 6/100 = 0.06, the segregation coefficient of La^{3+} in PWO crystal k = 2.25. The La^{3+} average distribution concentrations in the crystal are shown in Table 1.

From the above data we can know the correlation between the transmission at 350 nm and La^{3+} distribution concentration (Fig. 4), and the transmission of the crystal at 350 nm can improve greatly with increasing La^{3+} distribution concentration, but

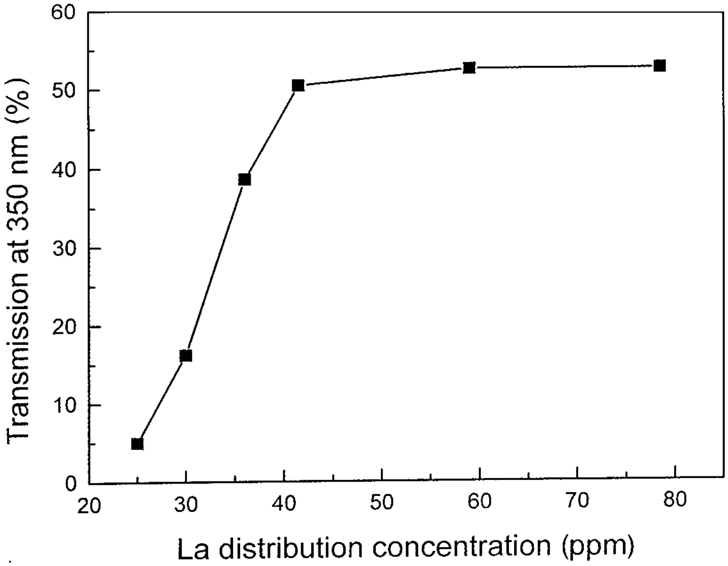

Fig. 4. Correlation between transmission at 350 nm and La distribution concentration in La : PWO sample

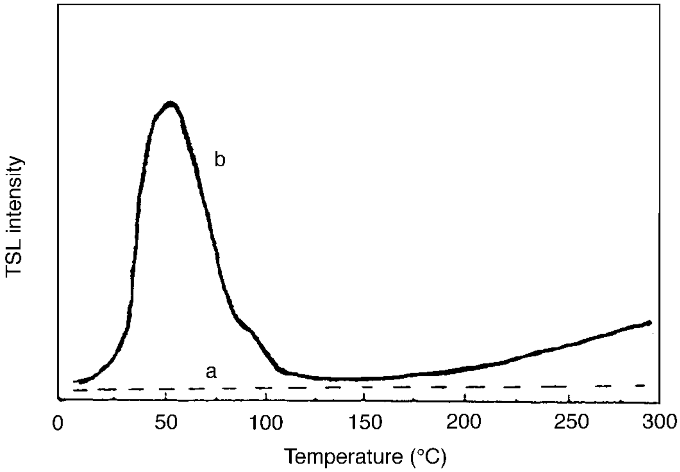

Fig. 5. TSL glow curve of La : PWO sample. (a) The top of sample, (b) the bottom of sample

when the La^{3+} distribution concentration reaches 80 ppm, the 350 nm intrinsic absorption band disappears completely, and it cannot improve the transmission any more, even if the La^{3+} distribution concentration is larger than 80 ppm. So there is an optimism for La^{3+} doping concentration.

In fact, excess La^{3+} in crystals may create new killer sites at which effective nonradiative recombination of free electrons and holes occurs and leads to the strong lowering of light yield [2]. TSL peaks of the top and the bottom of crystal are shown in Fig. 5. The presence of 60 °C TSL peak which corresponds to the trap center in the bottom of the crystal was observed with respect to the top of crystal in untreated sample, which means La suppresses the formation of color centers [7].

There are two types of color center absorption bands which have the same wavelengths in PWO: 1. an intrinsic absorption band formed in the process of crystal growth; 2. an induced absorption band created by high energy particles or UV exposure. Possible differences exist in the color center stabilization, the former is stable, while the latter can be thermally bleached by heating for 2 h at 200 °C in air [1]. During the process of crystal growth, the evaporation of PbO may result in lead deficiency, the deficiency of Pb ions and resulting charge deficiency in the Pb sublattice can be most easily balanced by a simple increase of the concentration of temporary O^- and Pb^{3+}. In La : PWO, La^{3+} ions at Pb^{2+} sites introduce an excess charge into the Pb sublattice, which efficiently balances the charge deficiency for this sublattice and lowers the concentration of Pb^{3+} and O^- hole centers. Because radiation damage in the crystals appears to be due to the formation of color centers in crystals which may lead to the decrease of transmission, thus further decrease of light yield, so at the position points where La^{3+} concentration is higher, ist radiation hardness is also higher, and thus it is obvious that La doping can improve the radiation hardness.

The 350 nm intrinsic absorption band exists commonly in pure as-grown PWO crystals. Although its origin is still in debate, for example, Annenkev et al. [12] ascribed it to O^-, while Nikl et al. [1] to Pb^{3+}, there is good linear relation between the initial absorption of crystals at 350 nm and the absorption induced by irradiation in the greenred region [12, 13]. From transmission spectra, induced absorption spectra and TSL (Figs. 2, 3 and 4) we found the stronger the 350 nm intrinsic absorption band, the stronger is the 420 nm induced absorption band, maybe a transformation from 350 nm absorption band to 420 nm absorption band exists, while the emission spectra of PWO crystals lie in the blue-green region, which is in the same wavelength range as the induced absorption band, so the stronger the 350 nm absorption band in the crystal, the more emission light was absorbed by the crystal, and the lower is the light yield of crystal.

3.2 Annealing effects

After 600 °C annealing for 24 h, the 350 nm absorption bands of a and b show no essentially change, but from c to f, every absorption band is larger than that of the corresponding point in the untreated sample. Fig. 6 shows the absorption spectra, the 420 nm induced absorption bands of e and f increased greatly compared with the untreated sample.

After 780 °C annealing for 24 h, from d to f, each 350 nm absorption band is greater than that of the corresponding point in 600 °C annealing. The induced absorption spectra are given in Fig. 7, from d to f, the 420 nm induced absorption band increased further compared with 600 °C annealing. With 600 or 780 °C annealing, the part of crystal near the bottom becomes yellow under irradiation. After subsequent 960 °C annealing for 24 h, the 350 nm absorption band of c increased, but from d to f, the 350 nm absorption bands decreased compared with 780 °C annealing. The induced absorption spectrum is shown in Fig. 8, the 420 nm induced absorption band of c increased, but from d to f, every induced absorption band decreased greatly compared with 780 °C annealing, and the part of sample near the bottom becomes colorless. The real annealing curves reported in Fig. 9 show the relation between induced absorption at 420 nm and annealing temperatures.

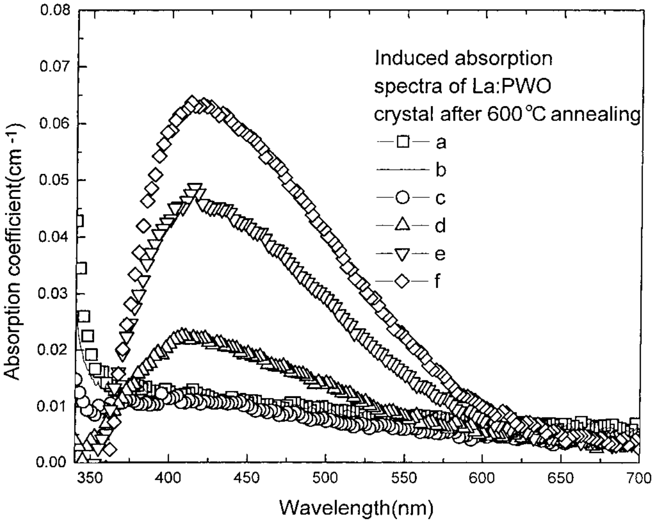

Fig. 6. Induced absorption spectra of La : PWO sample after 600 °C annealing

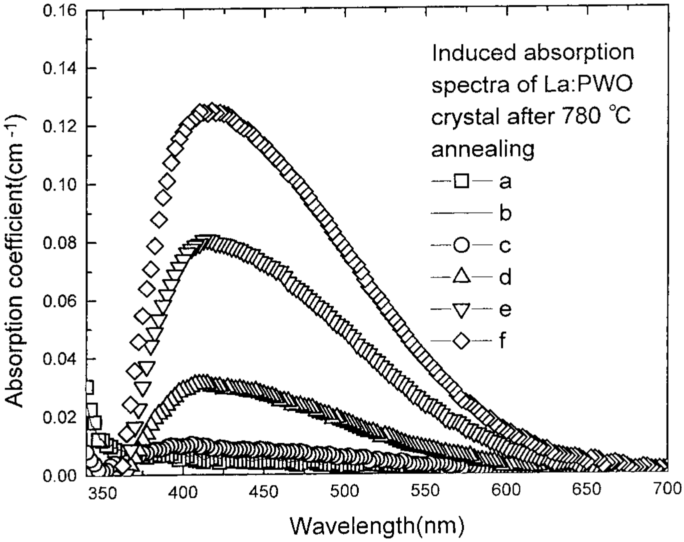

Fig. 7. Induced absorption spectra of La : PWO sample after 780 °C annealing

The emission peak wavelengths are 429, 431, 429 and 433 nm for untreated and 600, 780 and 960 °C annealed samples, respectively. The annealing does not change emission mechanism which is important to application.

The annealing at 600 or 780 °C in air induces the diffusion of oxygen ions into the PWO, the increase of both $Pb^{3+}$and O^{-} leads to a further increase of the 350 and 420 nm absorption bands, the part of sample near the top (rich-La) has essentially the same absorption band. After annealing at 960 °C, we observed different phenomena, the 350 and 420 nm absorption bands in the part of sample near the bottom (poor-La)

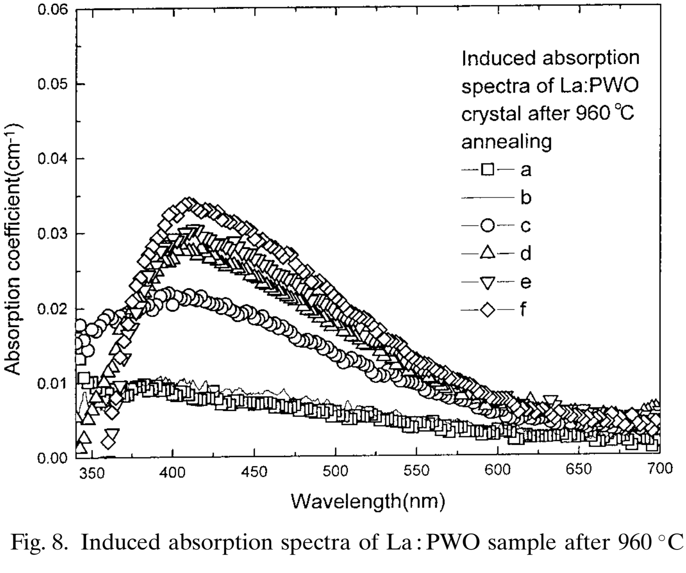

Fig. 8. Induced absorption spectra of La : PWO sample after 960 °C annealing

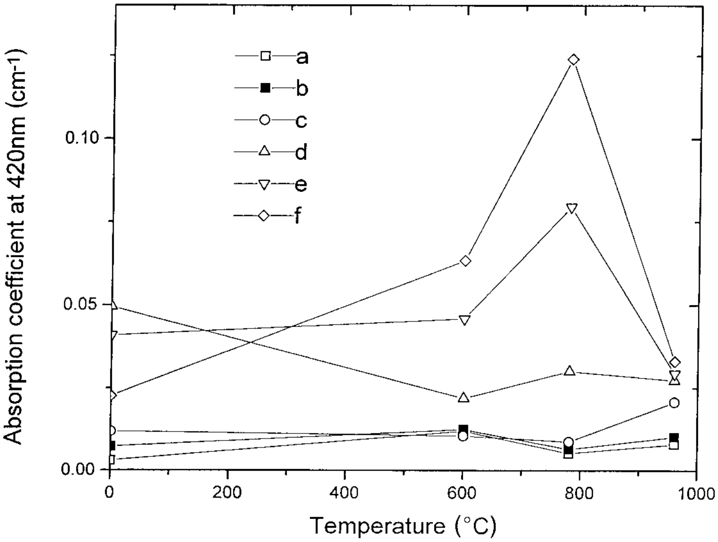

Fig. 9. Real annealing curves, showing the relation between induced absorption at 420 nm and annealing temperature

decreased greatly, while those in the part of sample near the top increased little, because there is a great La concentration gradient in the crystal, maybe there is La^{3+} diffusion from the top of sample to the bottom, the La concentration is redistributed in PWO (as can be seen from Figs. 8 and 9, point c induced absorption and intrinsic absorption band increased continuously at the three annealing temperatures, but those of points d, e and f decreased suddenly at 960 °C annealing). Another possible explanation is the thermal decomposition of color centers at high temperature. More detailed work is in progress. For pure PWO crystals annealing in air (24 h, 980 °C) lowers the transmission below 500 nm [5]. The sample was also irradiated at high dose with high dose rate (Co^{60}, 3 kGy/h, 8×10^4 Gy) after 960 °C annealing. The transmission spectra before and after irradiation show only little change, and the induced absorption coefficient at 420 nm of point f is smaller than 0.02 cm^{-1}, so we found such crystal has good radiation hardness.

4. Conclusion

The La^{3+} distribution in PWO crystal is very inhomogeneous, it suppresses the formation of color centers. There is a correlation between the transmission at 350 nm, induced absorption at 420 nm and La^{3+} distribution concentrations in the crystal. La^{3+} may diffuse in the crystal at high temperature, suitable La doping and annealing at appropriate temperature can actually improve the radiation hardness of PWO crystal.

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