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Optical Absorption on Cubic β-PbF$_2$ Crystals *

REN Guo-Hao(任国浩), SHEN Ding-Zhong(沈定中), WANG Shao-Hua(王绍华), YIN Zhi-Wen(殷之文)

Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050

The transmission spectra of cubic β-PbF$_2$ crystals grown by the non-vacuum Bridgman method were measured with a spectrophotometer. It was found that there are several optical absorption bands peaking at 300 nm, $390-400$ nm, as well as at 460 nm. According to composition analysis, doping and annealing experiments, it is suggested that the absorption at 300 nm originates from the electron transition of Ce ions from $4f \rightarrow 5d$. The absorption at $390-400$ nm may result from the colour centres related to oxygen impurities. In addition, the sample recrystallized from the coloured β-PbF$_2$ crystal exhibits a new absorption band at 460 nm, which might be caused by trace lead vacancies.

For a long time, the cubic lead fluoride (β-PbF$_2$) crystal has been investigated as a Cherenkov radiator for electromagnetic calorimetry.[1] Its most outstanding properties are high density (7.77g/cm^3), short radiation length (0.93 cm), large average atomic number as well as a transmission extending to ultraviolet. The light output is sufficient to allow a good electromagnetic energy resolution.

Since the number of Cherenkov photons (dN) is given by[2]

$$\mathrm{d}N \propto \mathrm{d}\lambda/\lambda^2,$$

it is very important to raise the transmittance, especially in the short wavelength region, so that as many Cherenkov photons as possible could be collected for photomultipliers. Therefore, the transmission, particularly at the short wavelength, is an important standard for evaluating the crystal quality in applications.

For a long time, the problems of crystal growing techniques have not been resolved and the grown crystals cannot meet the needs for applications whether in size or in their properties. Various crystal defects have existed in the lattice, such as scattering particles and various colour centres resulting in optical absorption,[3] deteriorating the physical properties. In this letter, we will mainly discuss the optical absorption phenomena appearing in PbF$_2$ crystals.

The cubic PbF$_2$ crystals were grown from orthorhombic PbF$_2$ powder by the non-vacuum modified Bridgman method. In order to scavenge the oxygen impurities, such as O^{2-}, OH$^-$, in the system completely, a chemical that can scavenge oxygen impurities effectively and does not cause any harmful effects on the crystal properties and growth equipment was doped into the starting materials. The raw materials and the scavenger were mixed thoroughly and then put into a platinum crucible. The temperature of the furnace was controlled by a computer and kept above the melting point (822°C) of lead fluoride during whole growth process. The temperature gradient at the interface between the solid and liquid was about 40°C/cm and the lowering rate was 1cm/h.

The crystal ingots were cut, ground and polished into various samples with different sizes. The largest sample has the dimensions of $30\times30\times300$ mm.

The starting materials and sample obtained at various stages were examined by a RAX-10 x-ray diffractometer. The impurities in the raw materials were analysed by an atom absorption spectrometer (AAS). The transmission of the PbF$_2$ crystal was measured by a Shimadzu UV-2501PC spectrophotometer.

The transmission of six PbF$_2$ crystals as a function of wavelength is shown in Fig. 1(a). A visible absorption band, peaking at 300 nm, was found in the transmission spectra. It exhibits a weak absorption shoulder when measured along the longitudinal axis of the crystal, but it becomes very sharp when measured transverse to the longitudinal axis of the crystals (Fig. 1(b)). The absorption intensity decreases from the bottom to the top of the crystals. This means that the absorption intensity at the starting point is stronger than that at the finishing end.

The impurities in PbF$_2$ crystals with and without absorption have been analysed by AAS. Compared with the sample without 300 nm absorption, the sample with 300 nm absorption contains more Ca, Ba and Mg. Thus, these impurities were previously regarded as the cause of the 300 nm absorption.[4]

To judge if the above conjecture is true or not, trace amounts of CaF$_2$, BaF$_2$ and MgF$_2$ were doped into the PbF$_2$ starting material. The doping amount varied from 100 to 2000 ppm. The transmission of the doped PbF$_2$ crystals demonstrates that there is no obvious absorption effect in all these doped samples. Therefore, it is inconceivable to ascribe 300 nm absorption to these impurities.

It has been noted that the absorption phenomena peaking at 300 nm not only exists in the PbF$_2$ crystal, but also in other fluoride crystals, such as BaF$_2$, CaF$_2$ and Na$_{0.4}$Yb$_{0.6}$F$_{2.2}$. The absorption is proven to be related to cerium impurity in these crystals.[5$-$7]

Different amounts of cerium fluoride impurity were doped into PbF$_2$ raw materials to examine its influence on the absorption bands in PbF$_2$ crystals. The

grown crystals were measured with a spectrophotometer. As shown in Fig. 2, an obvious absorption band peaking at 300 nm appears in the transmission spectra. Its absorption intensity increases with the doping amount. When the content of the dopant reaches to 1 wt%, the absorption edge shifts from 250 to 300 nm. This demonstrates that cerium impurity is quite sensitive to 300 nm light. Even if there is even a small amount of cerium ions in PbF_2 crystal, a visible absorption at 300 nm will appear. The absorption intensity is proportional to the content of cerium ions. The absorption is also stronger at the seed end than that at the top end.
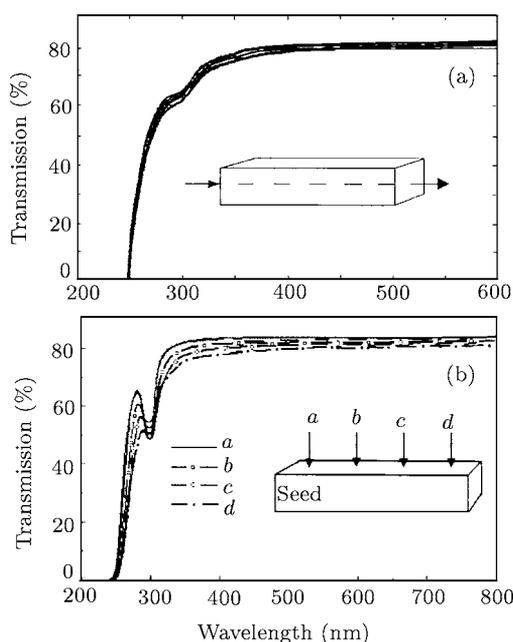
Fig. 1. Transmission spectra of PbF_2 crystals along (a) and transverse to (b) the growth direction.
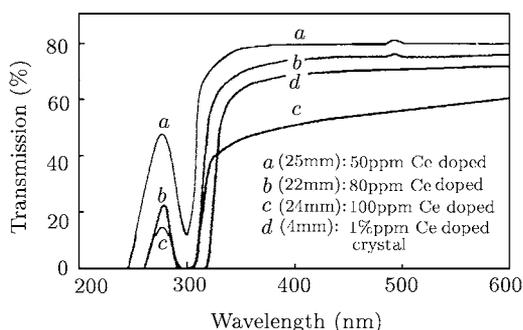
Fig. 2. Transmission spectra of PbF_2 crystals doped with different amounts of cerium ions.

The content of Ce in the PbF_2:Ce crystal was analysed with AAS. It was found that its concentration gradually decreases from the seed end to the finishing end. This variation corresponds to the dependence of absorption intensity at 300 nm on the position.

As we know, the electron configuration of Ce^{3+} is $4f^1$, its excited-state and ground-state configurations

are $5d^1$ and $4f^1$ respectively. In addition, $4f^1$ yields two levels: $^5F_{5/2}$ and $^2F_{7/2}$, separated by 2000 cm^{-1} due to spin-orbit coupling (Fig. 3). The transition from $^5F_{5/2}$ to $5d^1$ corresponds to a wavelength of 303 nm. Usually, the effect of crystal field on $4f^1$ is very weak. When the transition from $^5F_{5/2}$ to $5d^1$ takes place, an optical absorption band related to this transition will appear.
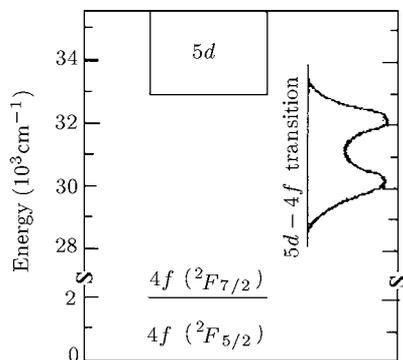
Fig. 3. Energy level of cerium ion (Ce^{3+}).
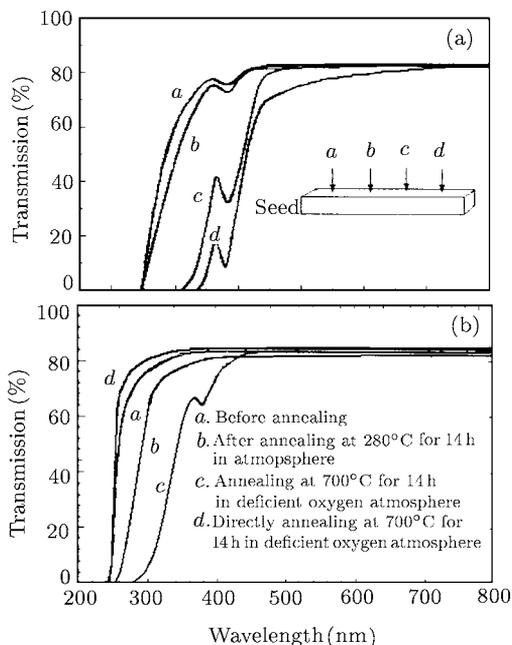
Fig. 4. Transmission spectra of yellowish PbF_2 crystals transverse to the growth direction (a) and those of colourless crystals annealed at different conditions (b).

In fact, cerium is a common impurity in fluoride crystals, because fluorides are usually synthesized by combining HF with other compounds, as shown in reaction (1). Generally, HF is produced by the following chemical reaction:

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4. \qquad (2)$$

Since the radius of Ce^{3+} ions (10.1 pm) is similar to that of Ca^{2+} ions (9.9 pm), it can substitute Ca^{2+} and becomes a very common impurity in natural fluoride

(CaF$_2$) minerals.[8] When CaF$_2$ is used as the raw material to produce HF, cerium ions were brought into fluoride products. Thus the effective way to overcome the 300 nm absorption band is to purify HF.

Besides the absorption band at 300 nm, there is another absorption band peaking at 390 nm, in some PbF$_2$ crystals (Fig. 4(a)). This absorption is responsible for the faint yellow coloration of the PbF$_2$ crystal. The intensity of coloration depends on both raw materials and the position of the crystals. This absorption band only exists in some crystals, not in all crystals. Even in the same crystal ingot, the absorption intensity decreases from the top to the bottom. If the absorption is strong enough, the crystal will exhibit a faint yellow colour. Usually, the top of the crystal is yellow, and the bottom of the crystal is colourless. The coloration varies with the absorption intensity at 390 nm.
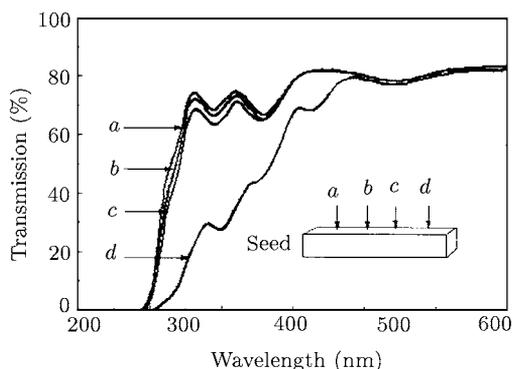
Fig. 5. Transmission spectra of PbF$_2$ recrystallized from the faint yellow crystal charge.

Comparing the chemical composition of the faint yellow samples with that of the colourless samples, no distinct difference can be found among their impurity elements. Therefore, it is difficult to identify which impurity is responsible for the 390 nm absorption.

Annealing experiments under different atmospheres show that a colourless crystal becomes faint yellow and exhibits an absorption valley at about 380 nm after annealing in an oxygen atmosphere (Fig. 4(c)). Conversely, the crystal annealed within a no-oxygen atmosphere has no absorption effect at any wavelength in its whole transmittance region (Fig. 4(b)). In the above two annealing experiments, the former contains oxygen, and the latter does not. Therefore, it is reasonable to ascribe the 390 nm absorption band appearing in the former annealing experiment to oxygen. Because the absorption wavelength induced in the annealing experiment under an oxygen atmosphere is very similar to that in the grown crystals, it is suggested that the 390 nm absorption in PbF$_2$ crystals originates from the colour centre related to oxygen impurity.

In fact, the point defects induced by the doping of oxygen have been reported in CaF$_2$ crystals.[9] After irradiation by x-ray at 80 K, the $F_H(O^{2-})$ and V_K centres appeared. Crystals containing the above defect exhibit an absorption band peaking at 3.35 eV,

corresponding to a wavelength 380 nm. Since it is rather similar to the absorption wavelength in PbF$_2$ crystals (390 nm) and both of these are caused by oxygen, we assume that there are also colour centres similar to F_{2H}^+ centres in PbF$_2$ crystals, which result in the absorption at 390 nm.

The third absorption appeared at 460 nm (Fig. 5), which exists in PbF$_2$ crystals recrystallized from the yellowish crystal charge. Based on x-ray fluorescence spectrum (Table 1), this kind of crystal contains less impurities than the colourless crystal, but is deficient in the lead element. Thus, the 460 nm absorption is recognized to be the role of the colour centre related to Pb deficiencies, rather than impurities.

Table 1. X-ray fluorescence intensity of yellowish and colourless PbF$_2$ crystals.

Seq.	Sample	Colour	Pb(kcps)	F(kcps)
1	169A	Faint yellow	627.890	5.178
2	169A	Faint yellow	629.885	5.169
3	169A	Faint yellow	627.293	5.211
4	169B	Faint yellow	628.846	5.155
5	169B	Faint yellow	627.565	5.174
6	169B	Faint yellow	629.522	5.155
Average from 1 to 6			628.500	5.178
7	S97A	Colourless	627.932	4.904
8	S97A	Colourless	629.272	4.932
9	S97A	Colourless	630.557	4.894
10	S97A	Colourless	629.594	4.921
11	S97B	Colourless	629.454	4.957
12	S97B	Colourless	628.455	4.976
13	S97B	Colourless	628.008	4.980
Average from 7 to 13			629.039	4.938

In conclusion, it is suggested that the 300 nm absorption band appearing in the PbF$_2$ crystal originates from the transition $4f \rightarrow 5d$ of Ce^{3+} impurity ions. Ce^{3+} impurities can be traced back to the mineral CaF$_2$, which is used to produce HF, one of the starting materials to synthesize PbF$_2$ crystals. By special purification of HF, the 300 nm absorption band disappears in the grown PbF$_2$ crystals. An annealing experiment under oxygen atmosphere proves that the optical absorption at 390 nm, which is responsible for the faint yellow coloration of the crystal, is related to oxygen impurity. The 460 nm absorption may result from the colour centre caused by lead deficiency.

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