ELSEVIER

Journal of Crystal Growth 243 (2002) 539–545

JOURNAL OF CRYSTAL GROWTH

www.elsevier.com/locate/jcrysgro

Structural defects and characteristics of lead fluoride (PbF_2) crystals grown by non-vacuum Bridgman method ☆

Guohao Ren*, Dingzhong Shen, Shaohua Wang, Zhiwen Yin

Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Rd., 200050 Shanghai, People's Republic of China

Received 25 September 2000; accepted 20 June 2002
Communicated by G.B. Stringfellow

Abstract

A non-vacuum growth technique for pure cubic PbF_2 crystal was reported in this paper. It used a chemical as a scavenger to deprive the oxygen impurities in the raw materials and growth system and realized the growth of PbF_2 crystals under non-vacuum conditions. The needle-like defect existing in lead fluoride crystals was identified to be an orthorhombic phase of PbF_2 crystal. It can be eliminated effectively when annealed within a reduction atmosphere and at a temperature higher than 365°C. PbF_2 crystals grown with this method are characterized with a wide transparent region from 240 nm to 16.7 μm, a good energy resolution of $3.2\%/\sqrt{E}$, and a very high radiation hardness.

PACS: 61.72.Qq; 61.80.Ed; 81.10.Fq

Keywords: A1. Defects; A2. Bridgman technique

1. Introduction

During the search for new scintillation materials, a cubic form of lead fluoride crystal was found to be a promising Cherenkov radiator for electromagnetic calorimeters. The requirements for a Cherenkov radiator for total-absorption electromagnetic shower are as follows [1]: (1) short radiation length; (2) no fluorescence; (3) high refractive index; and (4) transparent, especially in UV region. To satisfy the above requirements, Williams [2] and Dalley [3] suggested that in the experiment to detect high-energy γ-rays, electrons, and positrons, the ideal material for such a detector would be a "transparent lead brick". A near approximation of this is cubic lead fluoride crystal. The most outstanding properties of PbF_2 are its high density (7.7 g/cm^3), short radiation length (0.93 cm), large average atomic number and good transmission extending to UV [4]. Its light output is sufficient to have a good electromagnetic energy resolution.

However, for a long time, the problems on crystal growing technique have not been resolved and the grown crystals cannot meet the needs for application in size or in properties. Since PbF_2

☆This work was supported by the National Natural Science Foundation of China (Project No. 59732040).

*Corresponding author. Tel.: +86-21-5992-6852; fax: +86-021-5992-7184.

E-mail address: rgh@mail.sic.ac.cn (G. Ren).

0022-0248/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S 0 0 2 2 - 0 2 4 8 (0 2) 0 1 5 7 9 - 8

crystals are easy to be contaminated by oxygen at high temperatures, they are usually grown with the vacuum method. However, the vacuum method costs are very high and cannot deoxidize effectively, so that there are always some needle-like defects and absorption of UV light in PbF_2 crystals. These defects greatly jeopardize the transmission and Cherenkov radiation intensity of the crystals. So, it is necessary to look for a new method for deoxidization in addition to purification of the raw materials.

Since the number of Cherenkov photons (dN) having a wavelength between λ and $d\lambda$ is given by [5]

$$dN \propto \lambda / d\lambda^2$$

higher transmittance in a short-wavelength region is an extremely important characteristic in order to collect more Cherenkov photons by photomultiplier. So, the transmission, especially at short wavelengths, is mainly used as a criteria to evaluate the crystal quality in this paper.

2. Experiment

The starting material used for growing cubic lead fluoride crystals was orthorhombic PbF_2 powder, which was synthesized by the following procedures: First, acetic lead with 4 N purity reacts with ammonium carbonate, resulting in lead carbonate

$$Pb(COOH)_2 + (NH_4)_2CO_3 = PbCO_3 + 2NH_4COOH.$$

Second, the solution containing NH_4COOH was filtered out of the system. Third, $PbCO_3$, the deposit from the solution, was fluorinated with HF at a high temperature

$$PbCO_3 + HF \rightarrow PbF_2 + CO_2 + H_2O.$$

The products were put in a vacuum oven and heated to about 120°C for a few hours. The components CO_2 and H_2O in the system were vaporized. According to X-ray diffraction (XRD) analysis, the produced white powder was orthorhombic lead fluoride (Fig. 1).

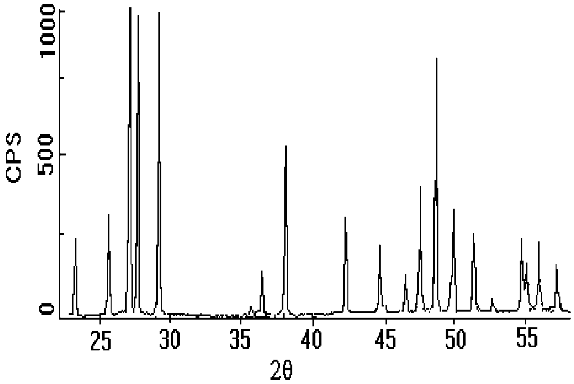

Fig. 1. XRD pattern of orthorhombic lead fluoride.

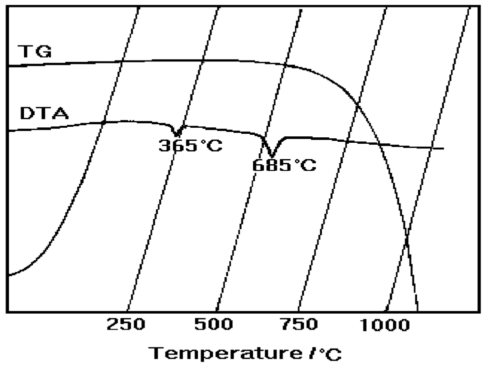

Fig. 2. DTA and TG curves of orthorhombic PbF_2.

Both DTA and TG curves of raw material were measured by NETSCH STA429 differential thermal analyzer. On the DTA curve (Fig. 2), there are two endothermal valleys: one is at 365°C, the other is at 685°C. The former corresponds to the phase transition of orthorhombic to cubic, and the latter corresponds to the melting of cubic PbF_2 crystal. However, this melting temperature is lower than that reported by Buchinskaya et al. [6], which may be caused by oxygen contamination during our measurement. So, in the crystal growth experiment, the temperature control was based on the data reported by Buchinskaya et al. [6] (that is 825°C).

The crystals were grown by a modified Bridgman method under non-vacuum conditions (Fig. 3). In this method, a chemical that can scavenge oxygen impurities, such as O^{2-} and

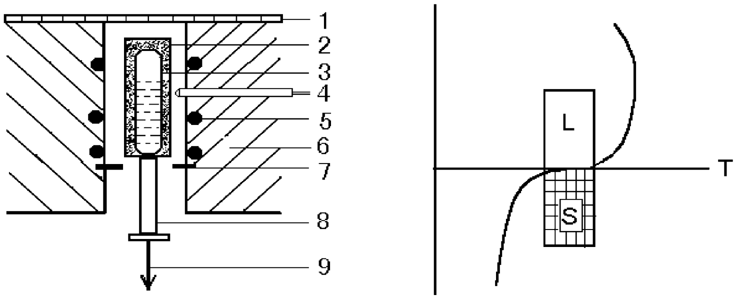

Fig. 3. Schematic diagram of furnace structure (a) and temperature curve (b). (1) furnace cover, (2) ceramic tube, (3) platinum crucible, (4) thermal couple, (5) heating elements, (6) refractory, (7) heat insulating plate, (8) pedistal, and (9) downward driving equipment.

OH^-, and does not cause any harmful effects on the crystal properties and growth equipment, was encapsulated in the crucible. Both PbF_2 powder and a little amount of scavenger were mixed thoroughly and then put into platinum crucible. The temperature of the furnace was controlled above the melting point of lead fluoride by a computer during the entire growing process. The temperature gradient near the solid and liquid interface was about 40°C/cm and the rate of crucible lowering was 1 cm/h.

As grown ingots were cut, ground, and polished into samples with definite shape and size, the largest sample grown was $30 \times 30 \times 300\,mm^3$. The starting materials and samples after various treatments were examined by XRD. The impurities in raw materials were analyzed by atomic absorption spectrometry (AAS). The transmission of PbF_2 crystal was measured with Shimadzu UV-2501PC Spectrophotometer. The infra red absorption spectra were recorded with FTS-185 IR Spectrometer made by Bio-Rad company of USA.

3. Results and discussion

3.1. Structural defects

The most obvious structural defect existing in lead fluoride crystal is some needle-like defects, which are mainly located at the top end of the ingot. A thin section cut from this part of the crystal was observed with a polarizing microscope

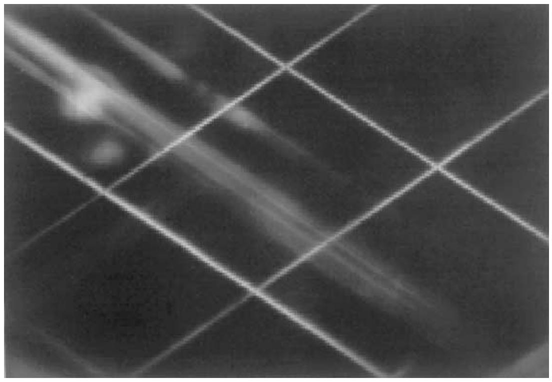

Fig. 4. Needle-like defects in cubic PbF_2 crystal (under cross-polarization light, 12.5×8).

and found that the needle-like structural defects have different interference color from the matrix; the former is white and the latter is always black or full extinction (Fig. 4). This showed that the needle-like defects are anisotropic crystallites and the matrix is an isotropic body. With an X-ray direction finder, the extending directions of the needle-like defects were confirmed to distribute along [1 1 1] and [1 1 0] directions of β-PbF_2 matrix. By means of electron microprobe analysis, no composition discrepancy was identified between the needle-like defects and the matrix. However, the X-ray powder diffraction pattern showed that there were two phases in the sample containing needle-like defects: one is cubic lead fluoride, the other is the orthorhombic phase of lead fluoride (Fig. 5).

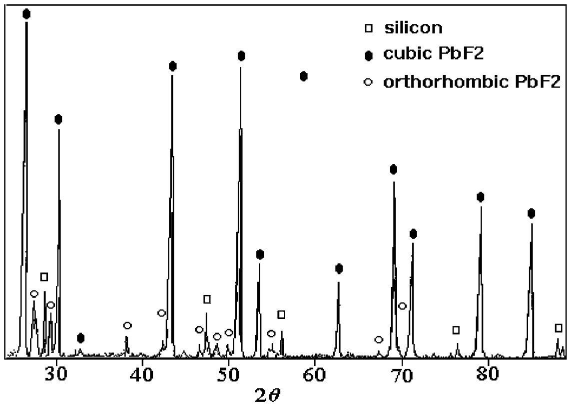

Fig. 5. XRD pattern of PbF_2 crystals containing needle-like defects.

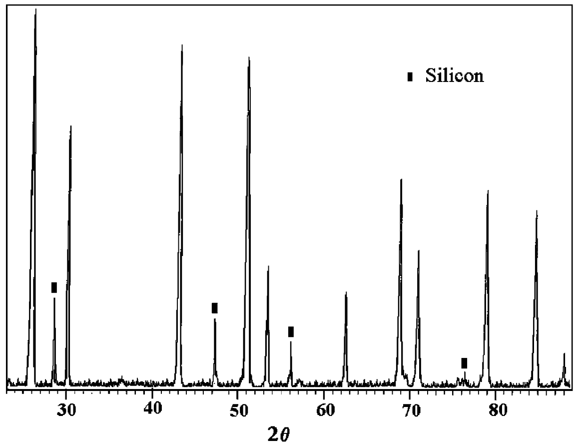

Fig. 6. XRD pattern of cubic PbF_2 crystals after annealing at 380°C for 4 h.

Since the orthorhombic phase can transform into the cubic phase at temperatures over 365°C (Fig. 2), a thin section sample ($10 \times 10 \times 3\,mm^3$) containing the defects was put into a platinum crucible and annealed in a reducing atmosphere at 380°C for about 4 h. The annealed sample did not show any cracking or decomposition. After being polished, it was observed again under cross-polarized light. The result demonstrated that there is no interference in the visual field. No matter how we rotate the stage from 0° to 360°, the needle-like defects can never be found. The XRD pattern showed that the orthorhombic phase of lead fluoride disappeared and that only the cubic phase in the sample remained (Fig. 6). From Fig. 7, it is clear that the transmittance of the sample is increased significantly after annealing.

Owing to the optical anisotropy inherent in orthorhombic lead fluoride (α-PbF_2), the white interference corresponding to the needle-like defects observed under polarized light is suggested to be α-PbF_2 phase. The annealing experiment further proved that α-PbF_2 can transform to β-PbF_2, resulting in the disappearance of the needle-like defects and increase of transmission.

In order to search the mechanism on the formation of needle-like defects, different amounts of scavenger were doped into the starting materials. Crystal growth experiments showed that the dosage of scavenger plays a key role to the quality

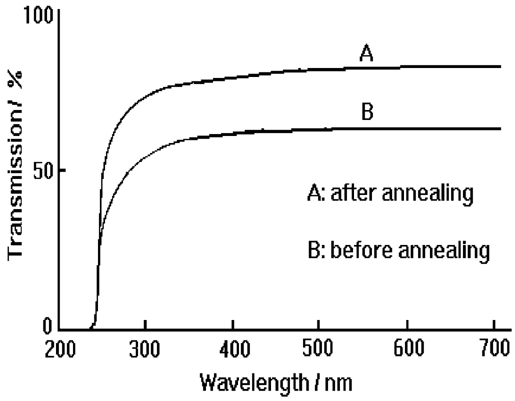

Fig. 7. Transmission curves of PbF_2 crystal containing needle-like defects before and after annealing.

of the lead fluoride crystals. As shown in Fig. 8, for both raw material No.1 and 2 when the doping amount goes up from 1 to 2 wt‰, the transmission of the crystals increases greatly. The cutoff edge of the crystal keeps constant for the same raw material whether transmission increases or decreases. When the doping amount is less than 1 wt‰, needle-like defects appear. If the doping amount is too low to deprive oxygen impurities from the raw materials, the grown crystal will become opaque. It was also analyzed by XRD and both cubic and orthorhombic phases were found in the XRD pattern. This implies that the formation of needle-like defects composed of

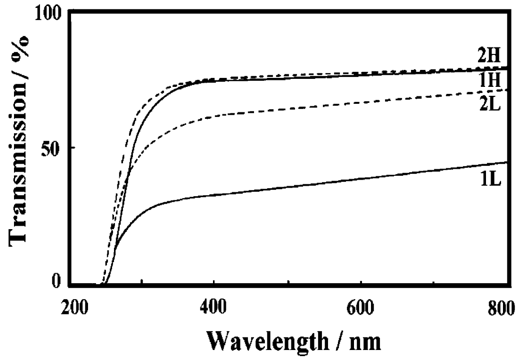

Fig. 8. Dependence of the transmission of PbF_2 crystals on the dosage of scavenger (1/2: batch number of the raw materials; H/L: dosage of scavenger is high or low).

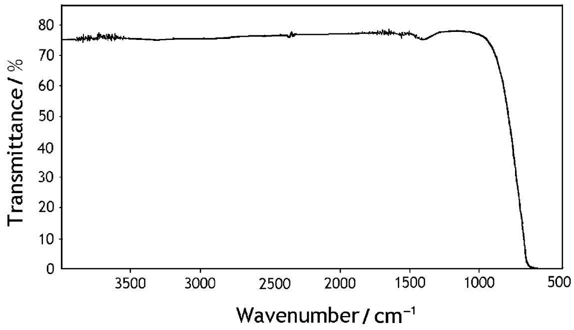

Fig. 9. The transmission of PbF_2 crystal versus wavenumber in infra-red region.

orthorhombic PbF_2 are related to the existence of oxygen impurities in the system. So, without scavenger, it is impossible to grow transparent lead fluoride crystals in ambient atmosphere. But if the doping amount of scavenger is too high, some of it will enter the crystals and cause the crystals to become fragile.

Therefore, the mechanism on the forming of these defects can be explained: β-PbF_2 transforms from cubic to orthorhombic phase under thermal strains. And the vanish of needle-like defects after annealing at temperatures higher than 365°C is ascribed to the release of thermal strain and phase transition from α-PbF_2 to β-PbF_2.

3.2. Transmission and absorption edge

The optical transmission versus wavelength for a crystal with thickness of 1 mm was measured with Shimadzu UV-2501PC Spectrophotometer. All curves are not corrected for absorption and reflection loss. As shown in Fig. 8, the intensity of the transmitted light at a wavelength longer than 250 nm is over 80%, then sharply decreases to zero at about 240 nm. The light with a wavelength shorter than 240 nm is absorbed completely, which means that the absorption edge of cubic lead fluoride crystal is 240 nm, that is 5.17 eV. Compared with other published results where the absorption edge was reported at 280 nm [7], the absorption edge of our PbF_2 crystals shifts about 40 nm toward the ultraviolet. Based on energy band theory, the energy gap of PbF_2 crystal is 5.84 eV [6] corresponding to 212 nm. The fact that the absorption edge of our PbF_2 crystal is closer to the theoretical one than that of other products, indicates that the non-vacuum method is superior to the vacuum method usually used for growing PbF_2 crystals.

The transmission of PbF_2 crystal versus wavenumber in the infrared region is shown in Fig. 9. It was measured with an FTS-185 IR spectrometer made by Bio-Rad company of USA. The thickness of the sample is 3 mm. The transmission at wavenumbers greater than 800 cm^{-1} is over 75% and then it decreases quickly to zero at wavenumbers from 800 to 600 cm^{-1}. The absorption edge of PbF_2 crystal in the infrared region is about 600 cm^{-1} or 16.7 μm. That means it is about 1.7 μm longer than that published earlier. Good transparency at wavelengths from 240 nm to 16.7 μm foresees that cubic lead fluoride can also be used as window materials.

3.3. Energy resolution

The energy resolution of 9 pieces of PbF_2 crystals ($30 \times 30 \times 166\,mm^3$) was tested in Mainz University of Germany. With direct electron beam on the crystals at a low rate, an energy resolution of 3.5% at 855 MeV was determined, and at 450 and 705 MeV the value is

$$\sigma/E = 3.2\%/\sqrt{E}.$$

With scattered particles from a liquid hydrogen target and for elastic electrons at 734 MeV, an energy resolution of 3.7% was obtained (Table 1). Woody et al. [8] have measured the energy resolution of PbF_2 crystals supplied by Optovac and have obtained a resolution of $\sigma/E = 5.95\%/\sqrt{E}$ for the 3×3 array and $\sigma/E = 5.70\%/\sqrt{E}$ for the 5×5 array at energies from 1 to 3 GeV. Compared with these test results, until now $3.2\%/\sqrt{E}$ represents the best energy resolution measured with PbF_2.

3.4. Radiation hardness

Radiation hardness is one of the key points in choosing materials for detectors in high-rate environments. To study the irradiation of PbF_2 crystals, a 166 mm long sample was irradiated by photons from a ^{60}Co source with a dose of 10 krad. Fig. 10 shows the transmission of the sample before and after irradiation (curves 1 and 2). All the curves in Fig. 10 were corrected for reflection loss and thickness. Curve 3 shows that there is a slight natural recovery from the radiation damage. When the irradiated crystal was bleached with 365 nm filtered light for a few minutes, the transmission could recover completely at longer wavelength, and only a little residual damage remained at very short wavelengths below 280 nm (curve 4), even though its radiation hardness is comparable with that grown by the vacuum method reported in Ref. [8].

Table 1
Energy resolution of lead fluoride crystals grown with non-vacuum method

Crystal size (mm)	Energy (MeV)	855	734	450–705
$30\times30\times166$	Resolution (%)	3.5	3.7	$3.2/\sqrt{E}$

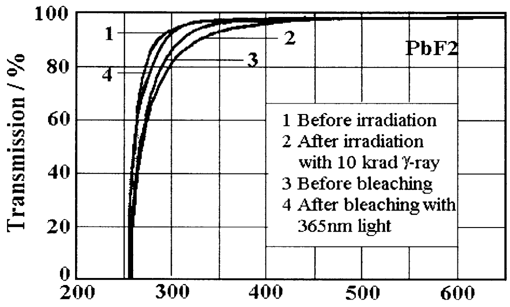

Fig. 10. Transmission of PbF_2 crystals before and after irradiation with 10 krad γ-rays as well as before and after annealing with 365 nm filtered light.

4. Summary

A new method for growing cubic PbF_2 crystal was presented. It uses a kind of scavenger to replace traditional vacuum equipment for scavenger oxygen impurities existing in the growing system and raw materials. The crystal quality is related to the content of the scavenger doped into the raw materials. If the content is too low, a kind of defect called needle-like defect will appear. It is confirmed that the defect is composed of orthorhombic PbF_2 crystalline, which are distributed along [1 1 1] and [1 1 0] directions of cubic PbF_2 matrix. Annealing at 380°C and under the condition of reduction atmosphere will eliminate these defects. It is suggested that these defects are caused partly by the transition of PbF_2 crystals from cubic phase to orthorhombic phase during the cooling process. Lead fluoride crystals grown with this method are characterized with a wide transparent region (240 nm to 16.7 μm), good energy resolution of $3.2\%/\sqrt{E}$, and very high radiation hardness.

Acknowledgements

The authors are grateful to Dr. Frank Maas of Mainz University for the provision of the test result of energy resolution and irradiation hardness of our lead fluoride crystals.

References

[1] Xu Zizong, et al., Techniques for Particle Detection, Shanghai Press for Sciences and Technology, Shanghai, 1981, pp. 159–166 (in Chinese).
[2] W.S.C. Williams, H.S. Caplan, Alead fluoride total-absorption spectrometer for high-energy electron and photons, Nature 17 (4571) (1957) 1185.

[3] E.B. Dally, R. Hofstadter, High energy γ-ray detector with good resolution, Rev Sci Instrum. 39 (1968) 658.
[4] R.D. Appuhm, et al., Electromagnetic calorimetry with lead fluoride crystals, Nucl. Instrum. Methods 350 (1994) 208.
[5] Yoshio Yoshimura, Akihiro Maki, New lead glasses for Cherenkov counters, Nucl. Instrum. Methods 126 (1975) 541.
[6] I.I. Buchinskaya, et al., PbF_2-based single crystals and phase diagrams of PbF_2–MF_2 systems (M = Mg, Ca, Sr, Ba, Cd), in: Jozef Zmija, et al. (Eds.), Solid State Crystals: Growth and Characterization, Proc. SPIE, Vol. 3178, Zakopane, Poland, 7–11 October 1996, pp. 59–63.
[7] D.F. Anderson, et al., Lead fluoride: an ultra-compact Cherenkov radiator for EM calorimetry, Nucl. Instrum. Methods 290 (1990) 385.
[8] C.L. Woody, et al., A study on the use of lead fluoride for electromagnetic calorimetry, IEEE Trans. Nucl. Sci. 40 (1993) 546.