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Crystal growth of PbFCl by modified Bridgman method

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Abstract

Lead fluoride chloride (PbFCl) crystal was grown by modified Bridgman method. The result of X-ray powder diffraction pattern (XRD) was well accordant with the data of JCPDS card. The transmittance spectrum was first reported without absorption band from 270 to 800 nm. Three emission bands were first observed at room temperature when excited by ultraviolet light.

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1. Introduction

It has been about one century since people synthesized PbFCl. Some concerns were given to its ionic conductivity properties [1–3], optical [4–7], photoconductivity [8], and theoretical [9] study. But little practical application was found for PbFCl because it is difficult to grow large crystal. PbFCl (Fig. 1) has a tetragonal layered structure (space group P4/nmm, D_{4h}^{7}) [10], which consists of two adjacent planes of chloride ions perpendicular to the *C*-axis. So it will cleave easily along (0 0 1) plane that makes it difficult to grow large ingot. Crystals grown from solution [11] and zone refining method were reported [1,12]. For PbFCl which belongs to halide crystals, even traces of oxygen contamination in the lattice of PbFCl will affect its properties. Precipitation of PbFCl from solution was abandoned because of inevitability of incorporation OH^- ions. Zone refining technique is a kind of traditional method in PbFCl growth that was initiated in 1973 [1] and has been used till today. The growth was carried in the pure nitrogen atmosphere. After 5–8 times of zone refining, small pieces of PbFCl crystal with an area of 1.5 cm^2 and 0.2 cm thick were obtained, however, they were slightly colored by impurities [12].

The process of zone refining in PbFCl growth is a little complex and the condition of growth is difficult to be controlled. In this paper we reported a simple and effective methods for growing PbFCl crystal. The transmittance and photoluminescence

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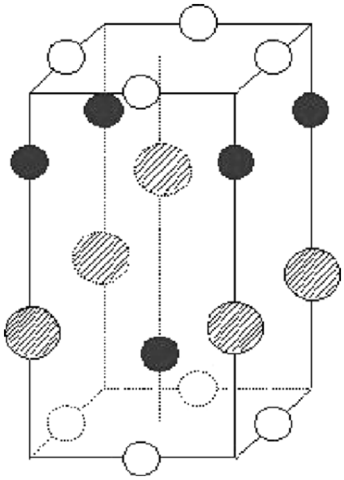

Fig. 1. Crystal structure of PbFCl: open circles F, black circles Pb, dash line circles Cl.

spectra of PbFCl crystal made at room temperature were also reported.

2. Crystal growth

PbF_2 (99.999%) and $PbCl_2$ (99.5%) powders were used as starting materials. They were bought from market and not purified before the experiment. PbF_2 and $PbCl_2$ were weighted according to the 1:1 molar ratio. The starting materials were thoroughly mixed and put into the capillary platinum crucible. PbFCl crystals were grown by unique modified Bridgman method developed in Shanghai Institute of Ceramics, Chinese Academy of Sciences (SICCAS). In order to eliminate the oxygen contamination brought by the air, the powder of raw materials was compressed as dense as possible and the crucible was sealed directly in the dry air. Then the crucible was placed into a typical Bridgman furnace. The furnace was heated at a certain rate. The temperature was regulated with a proportional integral differential (PID) controller. After the charge was completely molten, the crucible was lowered down through the temperature gradient zone at a rate of 1 mm/h. After all the melt passed the growth face, the furnace was cooled at a rate of 20°C/h. The growth speed of different planes exhibits great anisotropy. (1 0 0) Plane grows much faster than (0 0 1) plane, so PbFCl will cleave easily along the (0 0 1) plane. Fig. 2 shows the picture of large PbFCl plate grown in SICCAS. The crystal size is the largest in all reported ones according to Refs. [1,12].

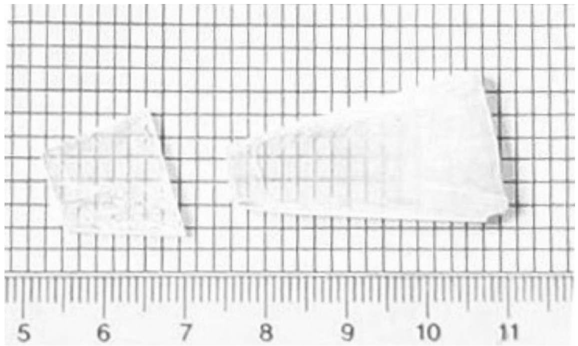

Fig. 2. PbFCl crystals grown by modified Bridgman method.

3. Experimental results and discussion

3.1. X-ray diffraction pattern

X-ray powder diffraction analysis was used to determine the phases existed in the ingot. The sample was collected from the middle part of the ingot and was ground into a fine powder. The result was shown in Fig. 3. Only PbFCl phase was found in the sample. The unit cell parameters were calculated according to the diffraction data by using a powder diffraction index program PTRUM. The unit cell parameters of PbFCl in the experiment are $a = b = 0.4111$ nm, $c = 0.7226$ nm, $V = 0.1221$ nm^3. The result was well accordant with the data of JCPDS card (No. 26-311).

3.2. Transmittance

A piece of PbFCl crystal with the size of 15 mm × 10 mm × 3 mm was polished to 1 mm thick. Transmittance was performed by a Shimadu UV-2501 spectrophotometer. The result is shown in Fig. 4. Before our experiment no spectra of absorption and transmittance of PbFCl were obtained directly from sample because it is very difficult to grow large and transparent PbFCl crystal. The best way was to measure powder

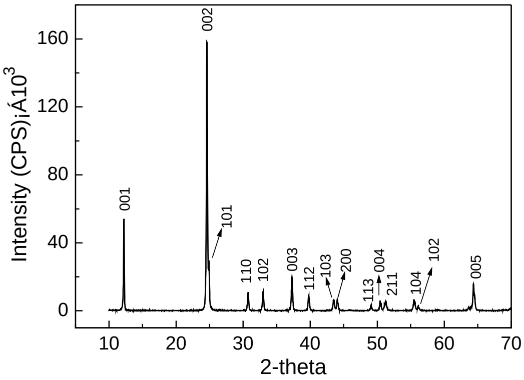

Fig. 3. X-ray powder diffraction patterns of PbFCl.

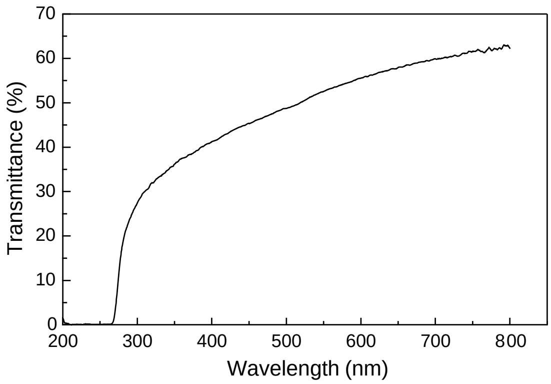

Fig. 4. Transmittance of PbFCl crystal in 1 mm thickness.

reflection spectra and to translate them into absorption spectra. Dependence of the absorption coefficient for PbFCl was derived by Kramers–Kroning analysis from the reflectance spectra at 84 K [5]. The absorption near 381 nm was found and was attributed to either oxide impurity or nonequimolar composition regarding F^- and Cl^- [4]. Good PbFCl plate was grown successfully by modified Bridgman method developed in SICCAS, and it is possible for us to obtain transmittance spectra of PbFCl directly from the crystal. No obvious absorption band is found from 270 to 800 nm. The result denotes that oxygen contamination was very slight in the process of crystal growth.

3.3. Photoluminescence

The photoluminescence of PbFCl was measured by a fluorescence spectrophotometer (Perkin-Elmer, LS55B) at room temperature. The slit width of 10 nm was selected in the measurement of excitation and emission spectra. The results were shown in Fig. 5. When PbFCl was excited by 258 nm ultraviolet light, a violet emission, a blue emission and a weak red emission were observed, with the peaks near 391, 421 and 760 nm, respectively. The photoluminescence of PbFCl at low temperature was studies in detail in 1970s [6,7]. A blue and a red emission were found when PbFCl was excited at 4.2 and 80 K. The temperature dependence of the intensities of the emissions of PbFCl indicates that both emissions were quenched above 175 K.

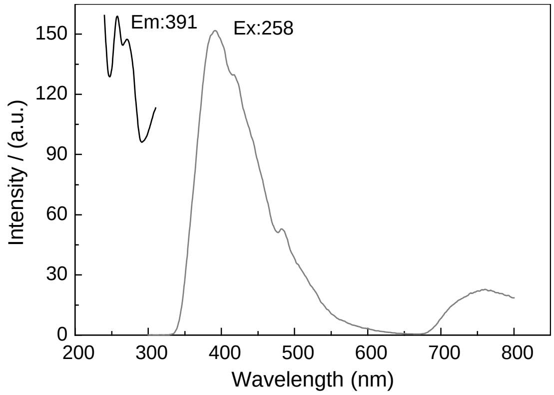

Fig. 5. The excitation and emission spectra of PbFCl at room temperature.

Two factors lead to the quenching of the photoluminescence of PbFCl. One is temperature, which is mainly dependent on the nature of the materials and hard to be improved. The other is the impurity that can be eliminated at a certain degree by purifying the raw materials and avoiding contamination during the process of crystal growth. Oxygen is considered to be a kind of primary luminescence quencher in halide crystals (CsI, NaI, BaF_2 and CeF_3). It can destroy the properties of halide crystals even if only trace of oxygen is remained in the materials. Our experiments indicate that if oxygen can be effectively excluded from the crystal, PbFCl appears as a strong violet emission at room temperature.

4. Conclusions

Large PbFCl crystal grown by Bridgman method was reported. The contamination of oxygen was effectively eliminated in the process of crystal growth. The XRD pattern proved that only PbFCl, instead of PbF_2 or $PbCl_2$ was only phase in the middle part of the ingot. The unit cell parameters of PbFCl in the experiment were $a = b = 0.4111\,nm$, $c = 0.7226\,nm$, $V = 0.1221\,nm^3$. The transmittance of PbFCl was first recorded directly without absorption band from 270 to 800 nm. PbFCl crystal could give off violet, blue and a weak red emission at room temperature when it was excited by ultraviolet light.

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