



Study of effects of F/Cl ratio on crystal growth and X-ray excited luminescence of PbFCl

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Abstract

Lead fluoride chloride (PbFCl) crystals with different F/Cl ratio were grown by modified Bridgman method. The excess of PbCl₂ is favorable to the crystallization of transparent ingot. X-ray powder diffraction analysis was used to identify the phases in PbFCl ingots. The transmittance spectra of the samples indicated that the presence of PbF₂ or PbCl₂ did not cause extra absorption bands in PbFCl crystals. F/Cl ratio strongly affected the number of emission bands and their peak positions in X-ray excited luminescence of PbFCl.

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1. Introduction

Lead fluoride chloride (PbFCl) is a dihalide system that belongs to the MFX (M = Ca, Sr, Ba, Pb; X = Cl, Br, I) family [1]. As an X-ray storage phosphor, most of these materials have been widely investigated and have found their applications in medical imaging in the last two decades [2–3]. It has been nearly a century since PbFCl crystal was first synthesized from the solution [4]. However, only few articles on its photoluminescence at low temperatures, reflectivity as well as ionic conductivity have been published [5–9]. It

was reported that the dissociation of PbFCl into PbF₂ and PbCl₂ amounts to 32% at its melting point [10]. Some of PbF₂ or PbCl₂ will remain in the PbFCl ingots. So it is necessary to investigate the effects of the crystal growth and properties brought by the deviation of PbF₂ or PbCl₂. PbFCl crystal in small size can be grown by zone refining method but the process is rather complex and the growth conditions are difficult to be controlled [11–12]. A convenient way to obtain good PbFCl crystals is to use modified Bridgman method [13]. In this paper, three PbFCl samples of different composition were grown by modified Bridgman method. The crystal growth, transmittance and X-ray excited luminescence (XEL) were first discussed.

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2. Melting point of PbFCl

The melting point of PbFCl was measured using a differential thermal analysis (DTA). PbFCl has high volatility and can be easily oxidized by oxygen in the open atmosphere at high temperatures, so a special platinum crucible instead of ceramic crucible was selected in the measurement. Polycrystals of PbFCl (1:1 mol ratio) was ground into a fine powder in an agate mortar and put into the platinum crucible. After sealing the crucible, it was heated at a rate of 10°C/h from room temperature to 650°C. As shown in Fig. 1, a sharp endothermic peak is observed at 608°C in DTA curve. The melting point of PbFCl thus we obtained is a little bit higher than that reported before (601°C) [11].

3. Crystal growth

PbFCl crystals were grown by modified Bridgman method developed in Shanghai Institute of Ceramics, Chinese Academy of Sciences (SIC-CAS). PbF₂ (99.999%) and PbCl₂ (99.5%) powders were used as starting materials. They were first dried at 150°C for 3 h and thoroughly mixed in vacuum in according to the 53:47, 1:1 and 47:53 molar ratios, respectively. In order to eliminate the oxygen contamination brought by the air, the powder of raw materials was compressed as tight as possible and put into the capillary platinum

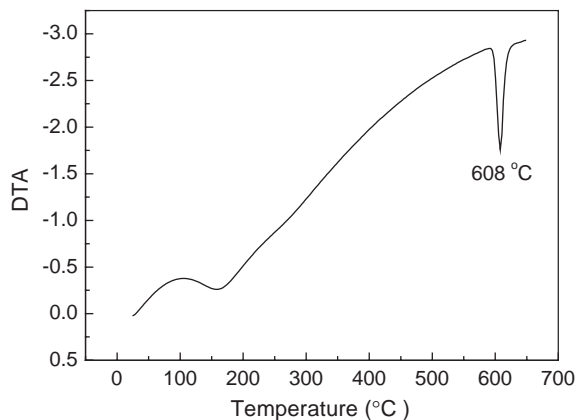


Fig. 1. DTA curves for PbFCl crystal (1:1 mol ratio).

Table 1

Dependence of PbFCl crystal quality on the ratio of F/Cl

ID	F ⁻ /Cl ⁻ ratio	Transparency	Cleavage
PFC-1	53:47	Opaque	Weak
PFC-2	50:50	Translucent	Strong
PFC-3	47:53	Transparent	Strong

crucible. After the crucible was sealed, it was placed into a modified Bridgman furnace, which was heated at a rate of 30°C/h. The temperature was regulated with a proportional integral differential (PID) controller. After the charge was completely molten, the crucible was descended through the temperature gradient zone at a rate of 1 mm/h till all the melt was crystallized. Then the furnace was cooled at a rate of 20°C/h down to room temperature. The platinum crucible was stripped off and PbFCl crystal was obtained. The ID number and compositions of three samples are summarized in Table 1.

4. Experimental results and discussion

4.1. Crystal growth

There are two adjacent planes composed of chloride ions perpendicular to the C-axis in PbFCl structure, which causes it to cleave easily along the (001) plane, so it is very difficult to grow thick samples. So far the maximum thickness of transparent plate sample we got is 4 mm. The description on these PbFCl samples is given in Table 1. PbF₂ or PbCl₂ has high solubility in PbFCl ingot. We have spent a lot of time on growing 1:1 compounds at first, but usually the as grown crystals are translucent. The excess of PbF₂ will degrade the transparency and prohibit the cleavage of the crystal. The transparency of PbFCl is improved with the increase of PbCl₂ content, but further increase of PbCl₂ will aggravate the cleavage of the crystal. When F⁻/Cl⁻ reaches 42.5:57.5, only very thin slice of PbFCl can be obtained. Fig. 2 shows the picture of PFC-3. It is the largest PbFCl plate in all the samples we obtained with the thickness of 3 mm.

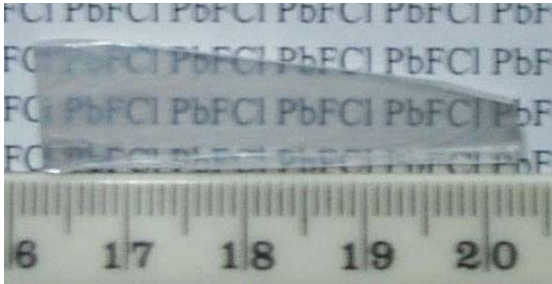


Fig. 2. PbFCl crystal grown by modified Bridgman method.

4.2. X-ray diffraction pattern

X-ray powder diffraction (XRD) analysis was used to determine the phases existed in the ingots. The samples were cut from the middle part of the ingots and ground into a fine powder. The results are shown in Fig. 3. In order to enlarge the weak diffraction peaks of impurity in the ingot, the intensity of the diffraction peak of (002) plane was reduced to half-size of its original. Only PbFCl phase exists in the sample of PFC-1, which is well accordant with the data of JCPDS card (No. 26-311). Besides PbFCl phase, the PbF_2 phase and PbCl_2 phase is found in the patterns of PFC-2 and of PFC-3, respectively. From the experiment results one can see that PbF_2 or PbCl_2 has high solubility in the PbFCl ingots during the process of crystal growth. The existence of PbF_2 or PbCl_2 in the ingots does not change the positions of the diffraction peaks of PbFCl.

4.3. Transmittance

Dependence of the absorption coefficient for PbFCl was derived by Kramers–Kronig analysis from the reflectance spectra at 84 K [7]. The absorption near 381 nm was found and was attributed to either oxide impurity or non-stoichiometric composition regarding F^- and Cl^- [14]. In our experiments each of three pieces of PbFCl crystal with different compositions was polished to a thickness of 0.4 mm. Transmittance was measured by a Shimadzu UV-2501 spectrophotometer. The results are shown in Fig. 4. No obvious absorption band is found from 270 to 800 nm in all of three samples. The results

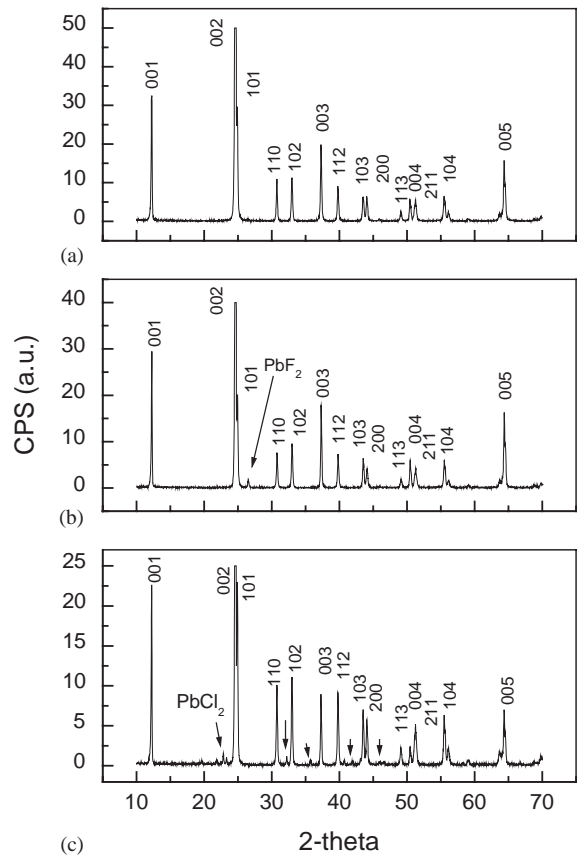


Fig. 3. X-ray powder diffraction patterns of PbFCl samples: (a) PFC-1; (b) PFC-2; (c) PFC-3.

illustrate that the excess of F^- or Cl^- in PbFCl does not cause the additional absorption. Whether the existing oxygen is the cause of the absorption at 381 nm is still under investigation. Although different ratios of F^-/Cl^- do not introduce new absorption band, it influences the transmittance of PbFCl to a large extent. The transmittance increment of three samples is in the order of: PFC-2 < PFC-1 < PFC-3.

4.4. X-ray excited luminescence

The X-ray excited luminescence was measured at room temperature. The instrument was designed and constructed in SICCAS. The scheme of the setup is given in Fig. 5. Its working conditions are 80 KV, 4 mA, and W target. The sample was wrapped with Teflon tape except a large face was

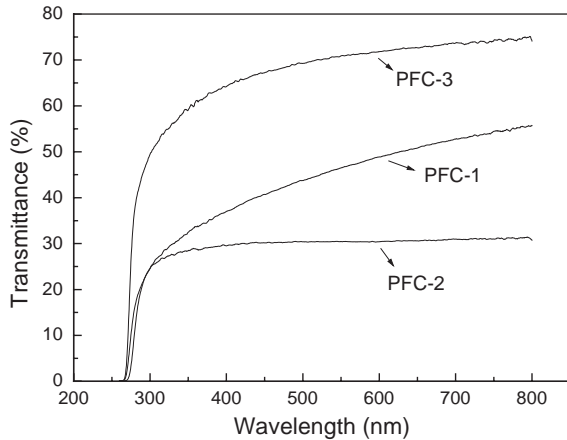


Fig. 4. Transmittance of PbFCl crystal in 0.4mm thickness.

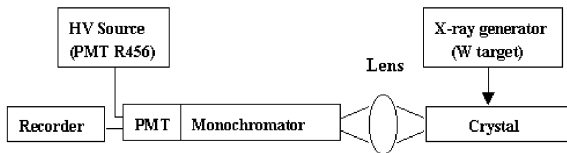


Fig. 5. Scheme of the setup for measuring the X-ray excited luminescence spectrum.

left to lead the emission light out of the sample. The light was detected by photomultiplier tube Model R456. The luminescence spectra were recorded by an x - y recorder.

PbFCl has violet, blue and red emission bands at room temperature. The relation between compositions and emission bands was not discussed [5,13]. In this article, we concentrated on the two strong emission bands (i.e. violet and blue). XEL spectra of three samples are shown in Fig. 6. We can see that PbFC-1 has a violet and a blue emission band with the peaks at 388 and 423 nm, respectively when it is excited by X-ray. PFC-2 also gives out two emission bands, but they shift to long wavelengths, with the peaks at 396 and 441 nm. In PFC-3 XEL spectrum, the violet emission band disappears and a strong blue emission band with its peak shifts to 448 nm is observed. The PbF₂ in PbFCl ingot depresses the intensity of violet and blue emissions and varies the position of emission peaks, while the presence

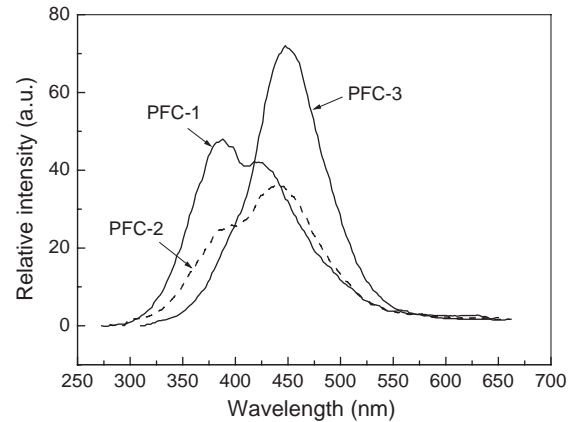


Fig. 6. X-ray excited luminescence spectra of PbFCl crystals ($T = 300$ K).

of PbCl₂ depresses the violet emission and enhances the blue emission. Energy transfer may occur between two kinds of emission centers.

5. Conclusions

Three samples of PbFCl crystal with different F/Cl ratios were grown by modified Bridgman method. The excess of PbF₂ will degrade the transparency and depress the cleavage of the crystal. On the contrary, the transparency of PbFCl is improved and the cleavage is aggravated with the increase of the content of PbCl₂. X-ray powder diffraction analysis indicates that PbF₂ or PbCl₂ will remain in the ingots of PbFCl when the mixed starting materials deviate from stoichiometric composition. The presence of PbF₂ or PbCl₂ does not introduce new absorption band and the excess of PbCl₂ will improve the transmittance of PbFCl. The number of emission bands and their peak positions in X-ray excited luminescence spectra mainly depend on the F/Cl ratio.

References

- [1] H.P. Beck, J. Solid State Chem. 17 (1976) 275.
- [2] A.M. Gurvich, C. Hall, I.A. Kamenskikh, J.S. Worgan, J. X-ray Sci. Tech. 6 (1996) 48.

- [3] H. Li, P. Hackenschmeied, M. Batentschuk, *Mater. Sci. Eng. B* 94 (2002) 32.
- [4] G. Starck, *Z. Anorg. Allg. Chem.* 70 (1911) 144.
- [5] A.J.H. Eijkelenkamp, *J. Solid State Chem.* 19 (1976) 313.
- [6] A.J.H. Eijkelenkamp, *Solid State Commun.* 18 (1976) 295.
- [7] A.J.H. Eijkelenkamp, K. Vos, *Phys. Stat. Sol. B* 76 (1976) 153.
- [8] A.F. Halff, G. Blasse, *Solid State Commun.* 13 (1973) 677.
- [9] A.F. Halff, *J. Solid State Chem.* 27 (1979) 397.
- [10] V.Ya. Anosov, N.N. Patsukova, *Russ. J. Inorg. Chem.* 1 (1956) 104.
- [11] J. Schoonman, G.J. Dirksen, G. Blasse, *J. Solid State Chem.* 7 (1973) 245.
- [12] A.F. Corsmit, G.J. Dirksen, *J. Crystal Growth* 37 (1977) 187.
- [13] J.M. Chen, D.Z. Shen, R.M. Mao, G.H. Ren, Z.W. Yin, *J. Crystal Growth* 250 (2003) 393.
- [14] A.J.H. Eijkelenkamp, *Phys. Stat. Sol. B* 76 (1976) 153.