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Structure and thermal stability of novel fluorophosphate glasses

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Abstract

A systematic investigation on glass formation in the PbF₂–InF₃–BaHPO₄ ternary system has been carried out. These glasses have characterized by IR spectra, Raman spectra and differential thermal analysis. The results show that the structure of these glasses is mainly affected by BaHPO₄ and InF₃ contents. With decreasing BaHPO₄ content, the glass structure gradually transforms from metaphosphate to polyphosphate. When InF₃ content is low, it mainly acts as network modifier, when its content is high; it enters glass matrix and forms In(O,F)₆ groups connecting the polymerized phosphorus oxygen species. PbF₂ mainly acts as network modifier in this system. Systematic variations of the glass transition temperature and the thermal stability index agree well with these results. The most stable glass with $\Delta T = 230$ °C and S = 21.79 K is obtained.

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1. Introduction

Fluorophosphate glasses have received great attention and are the subject of intense research mainly because of their wide transmission range from the ultraviolet to the infrared regions, possible doping levels with rare earth ions exceeding 10^{21} /cm³, low linear and non-linear refractive index, and high damage threshold as desirable for laser host materials [1,2]. The technological importance of fluorophosphate glasses make it in increasing demand for the development of new glasses with specific characteristics. In this paper, we develop a novel fluorophosphate glass in the PbF₂–InF₃–BaHPO₄ system. We investigate the structure of these glasses by IR spectra and Raman spectra, and report glass formation ability in this system in order to define glass compositions stable enough to give bulk samples, preforms and hopefully optical fiber.

2. Experimental

The starting materials used for preparation of the glasses were In₂O₃ (99.99%), PbF₂ (AR) and BaHPO₄ (AR). InF₃ was synthesized from corresponding oxide, In₂O₃, with ammonium bifluoride NH4HF2 as fluorinating agent, as described elsewhere [2]. The typical batch compositions (mol%) listed in Table 1 were prepared by conventional melting and quenching method. About 20 g batches of the well mixed raw materials were melted at 1000–1100 °C for 15 min in covered aluminium oxide crucibles in an electronic furnace. Then the melt was cast into a preheated stainless steel mould and annealed at the glass transition temperature. Samples were divided according to their appearance into three types: glasses, partially crystalline samples, and crystalline samples. Differential thermal analysis (DTA) was carried out to determine the glass transition temperature (T_g) , the crystallization onset temperature (T_x) , and the maximum of exotherm (T_p) of the glasses. The accurate temperature is ± 2 °C and the heating rate was 10 °C/min. Thermal stability factors ΔT and S were calculated from the temperatures $T_{\rm g}$,

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 Table 1

 Batch composition, *F/P* ratios^a, and appearance of melted samples

Sample	Batch composition (mol%)			F/P ratios ^a	Appearance	
	BaHPO ₄	PbF ₂	InF ₃			
P ₆₅ Pb ₃₅	65	35	0	1.08	Brown	
P65Pb30In5	65	30	5	1.16	Colorless	
P ₆₅ Pb ₂₅ In ₁₀	65	25	10	1.24	Colorless	
P65Pb20In15	65	20	15	1.3	Colorless	
P65Pb15In20	65	15	20	1.38	Colorless	
$P_{60}Pb_{40}$	60	40	0	1.34	Brown	
P60Pb35In5	60	35	5	1.42	Colorless	
$P_{60}Pb_{30}In_{10}$	60	30	10	1.5	Colorless	
P60Pb27In13	60	27	13	1.56	Colorless	
$P_{60}Pb_{25}In_{15}$	60	25	15	1.58	Colorless	
$P_{60}Pb_{20}In_{20}$	60	20	20	1.66	Colorless	
P50Pb50	50	50	0	2	Colorless	
P50Pb45In5	50	45	5	2.1	Colorless	
$P_{50}Pb_{40}In_{10}$	50	40	10	2.2	Colorless	
$P_{50}Pb_{30}In_{20}$	50	30	20	2.4	Colorless	

^a Ratios calculated from nominal compositions.

 T_x , and T_p according to the following relations: $\Delta T = T_x - T_g$ and $S = (T_x - T_g) (T_p - T_x)/T_g$ [3]. A Thermo Nicolet NEXU FT-IR spectrophotometer was used for IR spectra by using pressed KBr pellets containing 4 wt% of powdered glass samples. Raman measurements on samples were performed on a Labram-1B Raman spectrometer using a He–Ne laser (632.8 nm) for excitation.

3. Results and discussion

3.1. Glass-forming region

Systematic investigations have been implemented in the PbF_2 -InF₃-BaHPO₄ system. Fig. 1 shows the glass-forming region, which is broad and near to the PbF_2 -BaHPO₄ binary side. The clear glasses can be obtained in the limits of the glass-forming region. Some glasses are transparent and colorless in appearance, while others have brown color as described in Table 1.



Fig. 1. Glass-forming region in the PbF_2 -In F_3 -BaHPO₄ system. Compositions are expressed in mol%.



Fig. 2. IR absorption spectra from the $P_{65}Pb_{35-x}In_x$ (x = 0, 5, 10, 15) glasses.

3.2. IR spectra

The IR spectra of samples containing 65 mol% BaHPO₄ are shown in Fig. 2. The IR spectra of the P₆₅Pb₃₅ glass is characterized by bands at \sim 1269, 1087, 887, 728, and $519 \,\mathrm{cm}^{-1}$. The bands have been assigned based on previous work [4–6] as follows: $\sim 1269 \,\mathrm{cm}^{-1}$ band is thought to be attributable to the asymmetric stretching of P=O groups and/or the asymmetric stretching vibrations of O-P-O groups, $\sim 1087 \,\mathrm{cm}^{-1}$ band to stretching of ionic P–O⁻ groups, $\sim 887 \,\mathrm{cm}^{-1}$ band to asymmetric stretching of linear metaphosphate chains (P–O–P), \sim 728 cm⁻¹ band to symmetric stretching of P-O-P groups of small metaphosphate rings and \sim 519 cm⁻¹ band to bending vibration of P-O bonds. Glass consisting of metaphosphate has bands at \sim 1295, 1110, 910, and 520 cm⁻¹; pyrophosphate has bands at ~ 1110 , 910, and 520 cm⁻¹; orthophosphate has bands at ~ 1075 and 520 cm^{-1} [7].

With the increase of InF3 content, the band intensity at $\sim 1269 \,\mathrm{cm}^{-1}$ gradually decreases and disappears in $P_{65}Pb_{25}In_{10}$ glass, whereas the $\sim 1087 \,\mathrm{cm}^{-1}$ band intensity increases and it also shifts towards higher wavenumber. These two bands gradually form a new band at $\sim 1134 \text{ cm}^{-1}$. These facts clearly indicate that the glass structure gradually transforms from metaphosphate to pyrophosphate structure. The large broadening and shifting of the $\sim 1087 \,\mathrm{cm}^{-1}$ band also indicates the formation of fluorophosphate unit of $P_2(O,F)_7$ since it has been found to be caused by the overlapping of stretching vibration of O–P–F bond (appears at \sim 1140 cm⁻¹) with the \sim 1112 cm⁻¹ band of P–O⁻ group [7]. Gradual shifting of $\sim 887 \,\mathrm{cm}^{-1}$ band, with the increase of InF3 content, towards higher wavenumber indicates the formation of F-P-F bonds as a result of breaking of linear metaphosphate chains (P–O–P), because the F–P–F stretching vibrations have been found in the $750-1050 \text{ cm}^{-1}$ range [8]. This agrees well with the results reported by Fuxi and Haiyan [9] and Wasylak and Czerwosz [10]. The slight shifting of \sim 728 cm⁻¹ band to higher wavenumber with increasing InF₃ content also indicates the decrease of chain length, because it has been previously observed in phosphate



Fig. 3. IR absorption spectra from the $P_{60}Pb_{40-x}In_x$ (x = 0, 5, 10, 15) glasses.

glasses that as chain length decreases, the symmetric stretching P–O–P band increases in frequency [11]. It is interesting that, with the increase of InF_3 content, the $\sim 519 \text{ cm}^{-1}$ band intensity increases and slightly shifts to higher wavenumber. This might be the result of the overlapping of In-F stretching vibration (appears at \sim 509 cm⁻¹) [12] with the bending vibration of P–O [13]. On the other hand, it could be tentatively assigned to the formation of $In(O,F)_6$ vibrational mode when InF_3 content is high, suggesting that the In^{3+} acts as a network forming cation to form a structure similar to Al(O,F)₆ in the aluminium fluorophosphate glasses [4]. Those small fragments, such as $P_2(O,F)_7$ groups and F-P-F, may be linked up to a greater extent by the $In(O,F)_6$ polyhedral, which leads to strengthening of the glass network. Compared with Fig. 2, the glasses with 60 mol% BaHPO₄ in Fig. 3 have the similar bands and transformation tendency with the increase of InF3 content, except for the band intensity.

Fig. 4 shows IR spectra of $P_{50}Pb_{45}In_5$ and $P_{50}Pb_{30}In_{20}$ glasses, characterized by bands at ~1115, 909, 729, 529 cm⁻¹. Compared with Fig. 2 and Fig. 3, the most noticeable change as decreasing BaHPO₄ content from 60



Fig. 4. IR absorption spectra from the $P_{50}Pb_{50-x}In_x$ (x = 5, 20) glasses.



Fig. 5. Raman spectra from the $P_{65}Pb_{35-x}In_x$ (x = 5, 15) glasses.

to 50 mol% is the complete disappearance of the bands at ~1269 and 1254 cm⁻¹. As mentioned previously the bands at ~1115, 909, 729 cm⁻¹ may be attributed to fluorophosphate unit of P₂(O,F)₇ groups, F–P–F stretching vibrations, symmetric stretching of P–O–P groups, respectively. The ~529 cm⁻¹ band may be caused by the overlapping of In–F stretching vibration with bending vibration of P–O, and/or In(O,F)₆ vibration. All these facts clearly indicate that these glasses have pyrophosphate-like structure. With the increase of InF₃ content or *F/P* ratio, the intensity of bands at ~1115, 909, 729, 529 cm⁻¹ increases, which indicates that the addition of fluorides leads to rupturing of long metaphosphate chains and more formation of short structure fragments of P₂(O,F)₇ and F–P–F.

3.3. Raman spectra

The Raman spectra of glasses containing 65, 60, 50 mol% BaHPO₄ are shown in Figs. 5–7. The Raman spectra of the $P_{65}Pb_{30}In_5$ glass is characterized by a band at ~1160 cm⁻¹, two weak shoulders at ~1229 and 1054 cm⁻¹, a strong band at ~691 cm⁻¹, a broad band at ~493 cm⁻¹, and a medium band at ~322 cm⁻¹. The shoulders at ~1229 and



Fig. 6. Raman spectra from the $P_{60}Pb_{40-x}In_x$ (x = 5, 15) glasses.



Fig. 7. Raman spectra from the $P_{50}Pb_{50-x}In_x$ (x = 5, 20) glasses.

 1054 cm^{-1} are attributable to asymmetric stretch of the PO₂ unit and the isolated P (O,F)₄ monomers, respectively [14]. The $\sim 1160 \,\mathrm{cm}^{-1}$ band is the dominant feature of the spectra, which has been assigned to the symmetrical stretching mode of the PO₂ [14]. The \sim 691 cm⁻¹ band is attributed to the in-chain symmetric stretching modes along the P-O-P chains, while the $\sim 493 \text{ cm}^{-1}$ band could be tentatively assigned to InOF vibrational modes [14,15]. The 322 cm^{-1} band is due to PO_2 group deformation vibrations [16]. With the increase of InF3 content, a decrease occurs in the intensity of Raman bands at ~ 1160 and $691 \, \text{cm}^{-1}$, at the same time, the $\sim 1160 \,\mathrm{cm}^{-1}$ band shifts to lower frequency while the $\sim 691 \text{ cm}^{-1}$ band shifts to higher frequency. These facts indicate a breaking of the P–O–P bond in the metaphosphate chain structure and the consequent decrease in the number of the P–O–P [11]. With the increase of InF₃ content, the gradual disappearance of the $\sim 1229 \text{ cm}^{-1}$ shoulder also indicates the rupture of P–O–P chains, and the slight increase in the intensity of the ~ 493 cm⁻¹ band indicates that the In³⁺ acts as a network forming cation and leads to strengthening of the glass network.

Compared with Fig. 5, the Raman spectra of glasses containing 60 mol% BaHPO₄ in Fig. 6 change significantly with increasing InF₃ content. The Raman spectra of the $P_{60}Pb_{35}In_5$ glass, which is characterized by bands at ~1154, 689, 505, 341, 156 cm^{-1} and shoulders at ~1213 and $1067 \,\mathrm{cm}^{-1}$, is similar to that of 65 mol% BaHPO₄ glasses except for the $\sim 156 \,\mathrm{cm}^{-1}$ band attributable to Pb–O bond [17]. The Raman spectra of the $P_{60}Pb_{25}In_{15}$ glass is characterized by weak shoulders at \sim 1227, 1053 cm⁻¹, bands at \sim 1111, 738, 510, and 341 cm⁻¹. Videau et al. [18] suggested that the symmetric stretching of O-P-O in $P_2(O,F)_7$ dimers has a band at ~ 1080 cm⁻¹, then the band at ~ 1111 cm⁻¹ can be tentatively assigned to the symmetric stretching of O-P-O in $P_2(O,F)_7$ dimers. With increasing InF_3 content, the band at \sim 689 cm⁻¹ shifting to 738 cm⁻¹ indicates that the glass network is ruptured heavily, and this is consistent with the results of the IR spectra. The other bands are essentially unaffected by the increasing InF₃ content.

The Raman spectra of glasses containing 50 mol% BaHPO₄ are characterized by bands or shoulders at ~1095 and 1118, 1040 and 1059, 967 and 994, 741 and 736, 516 and 529, 336 and 341 cm⁻¹. Compared with Figs. 6 and 7, the shoulders appearing in Fig. 6 disappear completely in Fig. 7 and a new shoulder which is tentatively associated with symmetric stretching vibration of [PO₄] with three non-bridging oxygen atom [11,14] appears at ~967 and 994 cm⁻¹. The sources of other bands have been already discussed above and they have no apparent changes with increasing InF₃ content. All these facts indicate that these glasses have pyrophosphate-like structure.

Some literatures have mentioned the structural role of Pb^{2+} in glass network by Raman spectra. Unfortunately, the ways to interpret as well as the results are quite distinct and even contradictory from one another. Liu and Chin [17] suggest that the covalent Pb–O bond is indeed present in the metaphosphate as well as the polyphosphate structure. However, it seems to be not a peak characteristic of the Pb–O bond in Figs. 5, 6 and 7, except a weak absorption band at ~156 cm⁻¹. Then we can suggest that Pb²⁺ mainly occupies the modifier sites in the PbF₂–InF₃–BaHPO₄ glasses.

3.4. Characteristic temperature and glass stability

The properties of the glasses can be understood on the basis of the structure discussed above. The glass transition temperature (T_g) and the onset crystallization temperature (T_x) were clearly observed in all the glasses indicated by the open circles in Fig. 1. The characteristic temperature and stability indices of some glasses are given in Table 2. The selection of good glass compositions can be done on the basis of the thermal stability indices, which are important factors for fiber drawing [19]. In our glasses, the largest ΔT value of 230 °C and the highest *S* value of 21.79 K have been obtained. With the substitution of InF₃ for PbF₂, it is observed that the T_g values increase dramatically, while the evolution of ΔT and

 Table 2

 The characteristic temperatures and stability indices

Sample	$T_{\rm g}$ (°C) ± 2	$T_{\rm X}$ (°C) ± 2	T_p (°C) ± 2	$\Delta T (^{\circ}C)$	S (K)
P ₆₅ Pb ₃₅	300	440	480	140	18.67
P65Pb30In5	362	482	526	120	14.59
P65Pb25In10	465	595	632	130	10.34
P65Pb20In15	468	660	700	192	16.41
P65Pb15In20	486	680	732	194	20.76
$P_{60}Pb_{40}$	278	438	475	160	21.29
$P_{60}Pb_{35}In_5$	350	465	510	115	14.79
P60Pb30In10	415	540	580	125	12.05
P60Pb27In13	470	608	642	138	9.98
P60Pb25In15	475	705	750	230	21.79
$P_{60}Pb_{20}In_{20}$	478	660	702	182	16
P50Pb50	308	412	455	104	14.52
$P_{50}Pb_{45}In_5$	440	570	588	130	5.32
P50Pb40In10	445	568	595	123	7.46
$P_{50}Pb_{30}In_{20}$	490	655	688	165	11.11

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S values is not monotonous. The evolution of T_g for the In/Pb substitution can be easily explained since the glass transition involves the breaking of the chemical bonds. The bond energy of the In-F is much larger than that of Pb-F because the charge densities of $\ln^{3+} (z/a^2 = 469 \text{ nm}^{-2})$ is larger than that of Pb²⁺ ($z/a^2 = 139 \text{ nm}^{-2}$), then the substitution of InF₃ for PbF_2 leads to the increase of the T_g values. At the same time, the obvious increase of $T_{\rm g}$ also indicates a restructuring of the network. The evolution of the ΔT and S values may be explained on the basis of the structural evolution. The initial decrease of the ΔT and S values, with the substitution of InF₃ for PbF₂, may be due to the weakening PbF₂–BaHPO₄ glass network ruptured by fluorine ions. With the increase of InF₃ content, the ΔT and S values increase notably. This may be explained by the formation of $In(O,F)_6$ groups, which is believed to increase the structural cross linkage of the glass network and enhance the glass formation. All these facts are consistent with the results of IR spectra and Raman spectra.

4. Conclusions

Novel fluorophosphate glasses were developed in the PbF₂–InF₃–BaHPO₄ system. From the IR spectra and Raman spectra, it is known that the structure of these glasses is mainly affected by BaHPO₄ and InF₃ contents. With decreasing BaHPO₄ content, the glass structure gradually transforms from metaphosphate to polyphosphate. When the InF₃ content is low, it mainly acts as network modifiers, when its content is high; it enters glass matrix and forms In(O,F)₆ groups connecting the polymerized phosphorus oxygen species. Systematic evolution of glass stability indices confirms these results. The most stable glass, P₆₀Pb₂₅In₁₅, with $\Delta T = 230$ °C and S = 21.79 K, is obtained, which is a promising material for fiber drawing and laser glasses doped with RE ions.

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