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$In(PO_3)_3$ stabilised fluoroindate glasses

Y. Messaddeq[a,*], D. Grando[a], P. Melnikov[a], S.J.L. Ribeiro[a], L.F.C. Oliveira[b]

[a] *Instituto de Quimica, UNESP, PO Box 355, Araraquara, 14801-970-SP, Brazil*
[b] *Dept. de Química, Universidade Federal de Juiz de Fora, Juiz de Fora, MG, Brazil*

Abstract

Results on thermal and optical characterization of new lanthanide containing fluoroindate glasses in the system InF_3–BaF_2–$In(PO_3)_3$ are presented. Good optical quality and very stable glasses presenting up to 5 mm in thickness could be prepared in this system. Thermal analysis, Raman scattering and Eu^{3+} luminescence were the techniques utilized. A novel method for $In(PO_3)_3$ synthesis is proposed and the dependence of physical properties and structural features on the polyphosphate content is stressed. © 1998 Elsevier Science S.A.

Keywords: Indium polyphosphate; Fluoride glasses; Europium

1. Introduction

Fluoroindate glasses have received great attention and are the subject of intense research mainly because of their characteristic low phonon energies and their large resistance to atmospheric moisture [1–3]. The development of new glass compositions with specific characteristics are in increasing demand. In parallel, phosphate glasses are very stable against crystallization and many different compositions may be prepared for different applications [4]. Preparing mixed glasses, adding together the appropriate physical and chemical properties of fluoroindate and phosphate glasses would be very interesting.

We present, in this work, new fluoroindate glasses stabilized by $In(PO_3)_3$. Characterization includes thermal analysis, Raman scattering and spectroscopy of Eu^{3+} added as structural probe. Since reproducibility of physicochemical properties strongly depends on purity grade of indium polyphosphate, much attention has been paid to the elaboration of an experimental technique allowing the preparation of a product containing neither In_2O_3 nor $InPO_4$ in detectable amounts.

2. Experimental

2.1. $In(PO_3)_3$ preparation

Phosphoric acid (85%, a Merck product, analytical grade purity) was frizzed in a mortar by addition of liquid nitrogen and ground with a calculated amount of In_2O_3 (a Preussag product, 99.99% purity). The resulting fine powder, after reaching room temperature during 4 h, turned out to be a perfectly homogeneous and stable suspension of indium oxide in H_3PO_4. It was heated at 180°C until the crystallization of dihydrophosphate $In(H_2PO_4)_3$ was completed after ≈8 h. Dihydrophosphate was ground and heated step-wise, stopping at 300 and 500°C for 1 h, then fired at 900°C for 3 h. The X-ray pattern (Siemens Kristalloflex diffractometer, Cu Kα radiation) was identical to the monoclinic long chain indium polyphosphate, $[In(PO_3)_3]$ [5].

2.2. Glass preparation

Stoichiometric amounts of InF_3, BaF_2 and $In(PO_3)_3$ were well mixed and the batches were melted in platinum tubes 10 cm high, 1 cm in diameter in a vertical furnace at 800°C for 1 h in air. Fining, casting and annealing were carried out in a way similar to the standard treatment of fluoride glasses. Good optical quality glasses, amorphous to X-rays, could be obtained with up to 5 mm thickness, with compositions $0.6(1-x)InF_3$–$xIn(PO_3)_3$–$0.4BaF_2$ ($x=0.05, 0.1, 0.15$). One mol % Eu^{3+} containing glasses were also prepared for spectroscopic measurements.

2.3. Optical and thermal measurements

Room temperature Raman spectra were obtained for

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[*] Corresponding author. Tel.: +55 16 2322022 ext. 127; fax: +55 16 2227932; e-mail: younes@iq.unesp.br

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polished samples in the classical 90° geometry. Parallel (VV) and perpendicular (VH) spectra were obtained with a Jobyn-Yvon U-100 spectrometer and the 5145 Å line from a Coherent Ar laser as excitation source. Liquid nitrogen Eu^{3+} emission and excitation spectra were obtained with a SPEX F121I fluorimeter equipped with both continuous (450 W) and pulsed (5 J per pulse, 3 μs bandwidth) Xe lamps. Decay times were treated with the Spex 1930 phosphorimeter. Characteristic temperatures of glass samples were obtained by differential scanning calorimetry using TA 2910 equipment. Powder samples were analyzed in aluminum pans under N_2 atmosphere at a heating rate of 10°C min^{-1}.

3. Results and discussion

The usual methods employed for the synthesis of tripositive metal polyphosphates comprise the heating of metal sesquioxides with $NH_4H_2PO_4$. As a first step it implies the formation of ammonia and phosphoric acid. The latter reacts with the oxide giving dihydrophosphates $Me(H_2PO_4)_3$ which after condensation would form the corresponding $[Me(PO_3)_3]_n$. However, this method presents serious disadvantages since the quality of polyphosphates is considerably influenced by the availability of side products, mainly of ammonium polyphosphate $(NH_4PO_3)_n$. Its polymorphic varieties contain chains with an average length from 10 to 50–200 tetrahedral units PO_4 [5]. With increasing temperature, these chains may twist into various configurations which would persist in random proportions within the structural network of final polyphosphates. Another difficulty is due to the poor diffusion within the mixture. Metal oxide reacts actively only on the surface of the oxide aggregates producing polyphosphate slots contaminated with starting and intermediate materials, which are difficult to remove. Such impurities are unsuitable for glass preparations.

Presuming that indium polyphosphate might be formed in the dehydration sequence similar to scandium polyphosphate, $Sc(PO_3)_3$ [6], we developed the appropriate cryo-technique applied here for $In(PO_3)_3$ synthesis.

Videau et al. [7] were the first to demonstrate glass formation in the binary system InF_3–BaF_2. These glasses present low thermal stability and we have observed that polyphosphates are particularly indicated as stabilizers for various fluoride systems. In this way a systematic study has been implemented on the ternary system InF_3–BaF_2–$In(PO_3)_3$. Glass compositions along with their characteristic temperatures are shown in Table 1, where T_g refers to glass transition temperature, and T_x and T_c refer to the onset and the maximum of the crystallization peak. $(T_x - T_g)$ values indicate that samples containing a higher concentration of $In(PO_3)_3$ present good thermal stability.

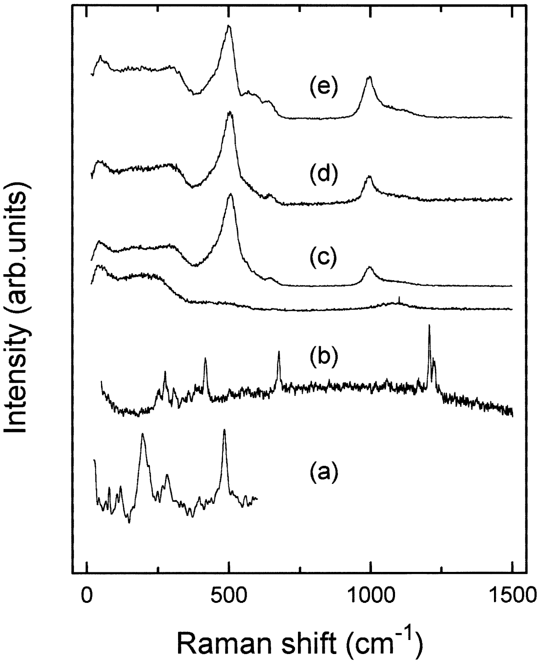

Fig. 1. Raman scattering spectra. (a) InF_3 (polycrystalline); (b) $In(PO_3)_3$ (polycrystalline); (c) VV and VH spectra. Glass $0.55InF_3$–$0.05In(PO_3)_3$–$0.4BaF_2$; (d) VV spectrum. Glass $0.50InF_3$–$0.10In(PO_3)_3$–$0.40BaF_2$; (e) VV spectrum. Glass $0.45InF_3$–$0.15In(PO_3)_3$–$0.40BaF_2$.

3.1. Raman spectra

In Fig. 1(b) Raman spectrum for the monoclinic $In(PO_3)_3$ is shown. Two strong bands at 1206 and 1224 cm^{-1} and two relatively weaker bands at 1180 and 1080 cm^{-1} are observed for the high frequency region of the spectrum. In the medium frequency region there is one band at 676 cm^{-1} and in the low frequency region a group of six bands is observed between 250 and 420 cm^{-1}. Assignments may be done by comparison with the work performed by Nga et al. [8] on $Gd(PO_3)_3$. It is also monoclinic and the spectrum presented by the authors is

Table 1
Glass compositions with their characteristic temperatures

Glass composition in (mol %)	T_g (°C)	T_x (°C)	Tp (°C)	$T_x - T_g$ (°C)
$55InF_3$–$5In(PO_3)_3$–$40BaF_2$	339	417	427	78
$50InF_3$–$10In(PO_3)_3$–$40BaF_2$	358	451	462	93
$54.35InF_3$–$4.95In(PO_3)_3$–$39.6BaF_2$ $1EuF_3$	330	409	416	79
$39.6InF_3$–$9.9In(PO_3)_3$–$49.5BaF_2$–$1EuF_3$	396	485	492	89
$44.55InF_3$–$14.85In(PO_3)_3$–$39.6BaF_2$–$1EuF_3$	418	539	546	121

very similar to the one for $In(PO_3)_3$ shown here. The strongest line at 1206 cm^{-1} in Fig. 1(b) may be assigned to symmetric stretching vibration (ν_s) for non-bridging PO. It appears at 1203 cm^{-1} for $Gd(PO_3)_3$. The other three bands in the high frequency region of Fig. 1(a) are assigned to PO asymmetric stretching vibrations (ν_{as}), while four bands at 1236, 1165, 1126 and 1057 cm^{-1} are mentioned in [8]. The band at 676 cm^{-1} is assigned to symmetric vibration ν_s for bridging PO (it appears at 681 cm^{-1} for the $Gd(PO_3)_3$) and the group of bands appearing in the region between 250–500 cm^{-1} are assigned to the PO_2 group deformation vibrations (δ).

In Fig. 1(a) the spectrum obtained for the InF_3 polycrystalline compound is shown. The band appearing at 483 cm^{-1} is assigned to the ν_1 (A_{1g}) symmetric vibration of the octahedral [InF_6] group. The bands at 282 and 196 cm^{-1} can be assigned to the split ν_5 (T_{2g}) mode of the same group [9,10].

In Fig. 1(c)–(e) the VV (parallel) Raman spectra obtained for the glasses are shown. Only one VH (perpendicular) spectrum is presented in Fig. 1(c) for the sake of clarity. A broad depolarized band centered at 1083 cm^{-1} and a relatively narrower completely polarized band centered at 994 cm^{-1} are observed in the high frequency part of the spectra. In the medium frequency region there are three polarized bands. Two weak ones at 649 and 588 cm^{-1} and one stronger at 506 cm^{-1}. In the low frequency region at least three broad bands may be observed: one polarized at 300 cm^{-1}, one depolarized at 220 cm^{-1} and the third one depolarized at 40 cm^{-1}; these last low frequency bands being characteristic of the glassy state and known as Boson peaks [9,10]. With the increase in the polyphosphate concentration there is a relative increase in intensity for the high frequency bands and also for the bands appearing at 649 and 588 cm^{-1}. A red shift for the strong band in the 500–510 cm^{-1} region is also observed.

Comparing the spectra obtained for the glasses and the crystalline phases, tentative assignments may be done. In this way the high frequency bands are assigned to the symmetric (polarized band) and asymmetric (depolarized band) vibrations of the tetrahedral phosphate groups. There is a red shift of ≈200 cm^{-1} between glasses and the crystalline phase. We could assign the band appearing for the glass to the ν_1 (A_1) stretching mode of the orthophosphate group usually appearing around 980 cm^{-1}. However, we have to consider that our compositions present a high F/O ratio and therefore the assignments may be done comparing our results with data obtained for other fluorophosphate glasses studied before. It is most probable that in our glasses we deal with fluorinated tetrahedral phosphate groups like the [$-OPOF_2$] one identified by the authors in [11]. Following the same reasoning the bands at 649 and 588 cm^{-1}, also red shifted when comparing with crystalline $In(PO_3)_3$, may be assigned to POP symmetric stretching vibrations in these fluorinated phosphate groups. These bridging group bands would not exist for orthophosphate groups.

The strong polarized band appearing at 506 cm^{-1} is the same one observed for InF_3–MF_2 (M=Ba, Sr) glasses studied before [9,10]. It is well assigned to the symmetric vibration of the octahedral [InF_6] group supposed to exist isolated in vitreous structure [10], in close resemblance with the crystalline InF_3. The red shift observed with the increase in phosphate concentration may be understood as the contribution of the phosphate groups, bridging octahedral [InF_6] groups, in the same way as proposed for aluminum fluorophosphate glasses [11]. This bridging would increase the effective reduced mass of the vibrating group, shifting the frequencies to lower frequencies. These structural features also could account for the enhanced stability of these mixed glasses against crystallization.

3.2. Eu^{3+} luminescence

In Fig. 2 the overall LNT Eu^{3+} emission spectra under 394 nm excitation are shown. Spectra for the glasses containing increasing amounts of $In(PO_3)_3$ (Fig. 2(b)–(d)) and also for the binary $0.6InF_3$–$0.4BaF_2$ are presented for comparison purposes. Emission is observed from the ^5D_J ($J=0$,1, 2 and 3) excited states to the $^7F_{J'}$ ($J'=0$, 1, 2, 3 and 4) lower levels. It is to be noted that enhanced intensity is observed for the lower wavelength lines. Blue

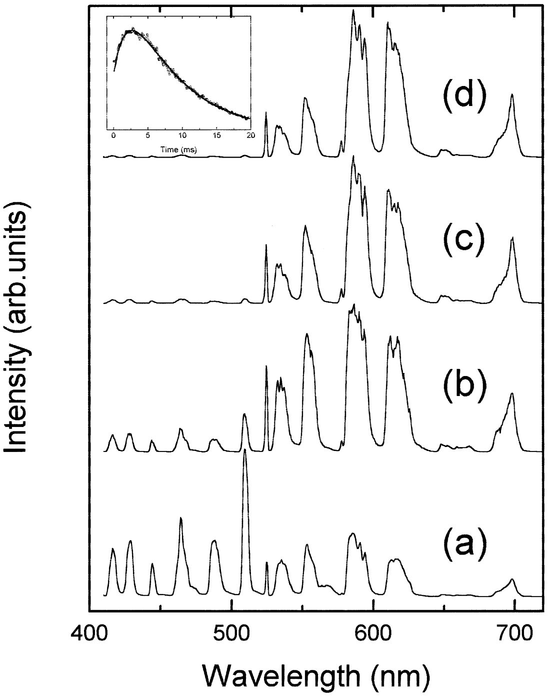

Fig. 2. Emission spectra for 77 K Eu^{3+} ^5D_J ($J=0$,1,2 and 3) obtained under 394 nm excitation. (a) $0.6InF_3$–$0.4BaF_2$; (b) $0.55InF_3$–$0.05In(PO_3)_3$–$0.4BaF_2$; (c) $0.50InF_3$–$0.10In(PO_3)_3$–$0.40BaF_2$; (d) $0.45InF_3$–$0.15In(PO_3)_3$–$0.40BaF_2$. Inset: $^5D_0$ decay time for the sample containing 5 mol% $In(PO_3)_3$. Circles: experimental data; line: fit ($e^{-t/\tau(D)} - e^{-t/\tau(R)}$).

and green emission is as important as the orange and red ones in spectrum (a) for the binary InF_3–BaF_2. One can even observe emission from higher states of the $4f^6$ configuration of Eu^{3+}. Dejneka et al. [12] reported UV emission from $^5H_3$ level under 318 nm excitation in some low phonon fluoride glasses. With the phosphate introduction, higher level emissions are quenched by the well known multiphonon processes. In Fig. 2(b)–(d) this effect is clearly observed. Quenching is also reflected in the measured lifetimes. Under 394 nm emission decay curves from ^5D_J levels are characterized by rise and decay times. These two processes have been considered in the fit by $(e^{-t/\tau(D)} - e^{-t/\tau(R)})$ type functions where $\tau(R)$ and $\tau(D)$ are rise and decay lifetimes respectively. The inset in Fig. 2 shows one decay curve as an example. In Table 2 the results obtained for $\tau(R)$ and $\tau(D)$ in this way are shown. there is evidence for multiphonon quenching processes by the fall in both lifetimes for ^5D_J levels with $J=3$, 2 and 1. Lowering for $^5D_0$ level lifetime can not be explained by multiphonon processes, mainly due to the large gap between $^5D_0$ and $^7F_6$ levels, while changes in the local environment for Eu^{3+} ions could well account for this. These changes are clear from the ratio η_{12} between relative intensities for the magnetic dipolar $^5D_0 \rightarrow {}^7F_1$ (≈590 nm) and the electric dipolar $^5D_0 \rightarrow {}^7F_2$ (≈615 nm) transitions. As is well known, the higher the value of η, the closer to an inversion center is the local symmetry for Eu^{3+}. η values vary from 1.5 for the glass not containing phosphate, to 1.1 for the glass containing 15 mol % $In(PO_3)_3$.

Interestingly enough, spectra and lifetime values obtained for the sample containing 5 mol % $In(PO_3)_3$ (Fig. 2(b)) are in close resemblance with the data obtained for multicomponent fluoroindate glasses studied before, containing only fluorides [14]. Some InF_3 based glasses have also been studied [13]. This feature suggests that the compromise existing between the enhanced stability against crystallization and the quenching processes for some high energy levels, both observed with phosphate addition, may be optimized depending on some specific application.

Emission excitation spectra, not shown here, also show the well known absorption transitions easily assigned to Eu^{3+} configuration [14]. In Fig. 3(c) a selected part of the excitation spectra of the sample containing 15% of $In(PO_3)_3$ is shown. It contains the side band observed for the $^7F_0 \rightarrow {}^5D_2$ transition. In the Figure, the position of the electronic line (21 598 cm^{-1}) is brought to zero showing that the side band is located 1000 cm^{-1} apart from it. Therefore this band can be assigned to vibronic transitions involving phosphate stretching modes. The relative intensity of the vibronic line increases with the increase in polyphosphate concentration.

Table 2
Results for the fits on Eu^{3+} $^5D_{0,1,2,3}$ decay curves

Level	Sample (%$In(PO_3)_3$)							
	0		5		10		15	
	τ(R)	τ(D)	τ(R)	τ(D)	τ(R)	τ(D)	τ(R)	τ(D)
$^5D_0$	3.6	12.0	2.04	7.34	0.77	7.54	0.51	6.44
$^5D_1$	1.55	4.71	0.2	3.36	–	2.68	–	2.07
$^5D_2$	0.41	3.25	–	0.58	–	0.20	–	0.10
$^5D_3$	–	1.64	–	0.33	–	0.15	–	0.10

τ(R): Rise times and τ(D): decay times in ms.

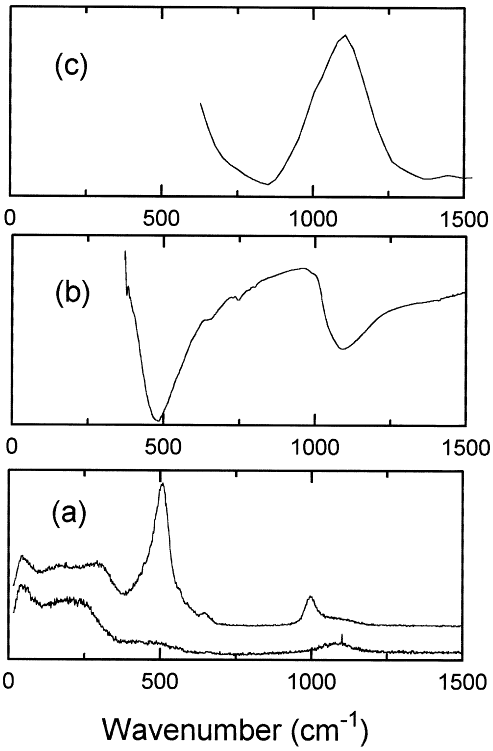

Fig. 3. $0.45InF_3$–$0.15In(PO_3)_3$–$0.40BaF_2$. (a) VV and VH Raman scattering spectra; (b) IR transmission spectrum (CsI pellet); (c) selected part of the Eu^{3+} excitation spectrum showing the vibronic band. $^7F_0 \rightarrow {}^5D_2$ electronic line brought to zero.

In Fig. 3(a) and (b) Raman Scattering and Infrared transmission spectra are shown respectively. It is clear that the vibronic spectra displays asymmetric PO stretching vibration modes.

4. Conclusion

Appropriate cryo-techniques have been applied for $In(PO_3)_3$ synthesis. This compound has been used for the exploitation of the new glass forming system InF_3–BaF_2–$In(PO_3)_3$. Good optical quality and very stable glass compositions presenting up to 5 mm in thickness have been prepared in this system. From Raman spectra [InF_6] and [–$OPOF_2$] groups were identified. Eu^{3+} containing samples were also prepared with spectroscopic characteristics being put forward. It was shown that the polyphosphate content can be optimized so as to obtain stable glasses with low multiphonon decay rate for upper excited states. Vibronic bands assigned to the coupling of PO asymmetric stretching modes with the electronic $^7F_0 \rightarrow {}^5D_2$ transitions are easily assigned from the comparison between the vibronic spectrum and the Raman and IR transmission spectra.

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