Journal of Alloys and Compounds 275–277 (1998) 733–737

Cerium-containing glasses for fast scintillators

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Abstract

Electromagnetic calorimetry requires fast and dense scintillators, such as CeF_3. Glasses offer an attractive alternative because their synthesis is easier. Glass formation has been investigated in $NaPO_3$–CeF_3–MF_2 (M=Zn, Cd, Ba, Pb) ternary systems. CeF_3 concentration could reach 35 mol.%, but this content should be smaller to obtain large bulk samples free of crystals. The influence of composition on glass stability to devitrification was systematically investigated. Composition adjustments have been implemented in order to increase the stability of glasses containing 35 mol.% CeF_3. Scintillation emission wavelength is 370 nm and the scintillation lifetime is 30 ns. Light yield of a 25 mol.% CeF_3-containing glass (e.g. 45 $NaPO_3$–30 BaF_2–25 CeF_3) reaches 60% of that of crystalline CeF_3. © 1998 Elsevier Science S.A.

Keywords: Cerium fluoride; Fast scintillator; Fluorophosphate glass; Physical properties

1. Introduction

Since the early 1990s, the cerium fluoride crystal has attracted an increasing interest as a fast scintillator material which could be used for high energy physics, nuclear medicine and other aspects [1,2]. Meanwhile various studies were undertaken on cerium-doped glass scintillators in order to take advantage of the specific features of the vitreous materials: good optical transmission, extended variety of shapes and forms, and hopefully low cost. Most of these studies were devoted to fluoride glasses including fluorozirconates, fluorohafnates and fluoroaluminates [3–6]. First results showed a good fluorescence and a short decay time in a CeF_3-doped fluorohafnate glass. But the output luminescence light yield was relatively low. This behavior led some researchers to consider that the lack of long-range ordering of the glass structure makes the main reason limiting light yield [7,8]. The ionizing energy may be absorbed by all ions of host material, including active centers and defects. Most of this energy is lost in the migrating processes which take place before excitation reaches active ions. As a consequence, light yield is limited by the small number of active ions which have been excited directly. A possible solution for overcoming this problem is to increase the concentration of the active elements, for example Ce^{3+} cations. In this way, exciting energy absorbed by the active element is favored. In addition, a short-range ordering is kept in the glass structure, and the decrease in the mean distance between active ions will minimize the disordered path during excitation transfer. The aim of this study is the synthesis of fluorophosphate glasses containing a much higher concentration in CeF_3 than standard fluorohafnate glasses studied previously. This paper will report new glass composition and some physical properties, including scintillation.

2. Experimental

Glass synthesis was carried out using two different methods. In the first one, batches of raw materials, around 10 g in weight, were mixed and introduced into a platinum crucible, then melted at fusion temperature. The second method includes two steps. First phosphates are melted until the resulting liquid has no more bubbles. After a short cooling, the other starting materials are dropped into the platinum crucible and then the mixture is reheated. After fining for several minutes, the melt is poured into a brass mold preheated at a temperature slightly below the glass transition temperature and annealed at this temperature for about 15 h. All glasses are processed in reducing conditions.

Characteristic temperatures, T_g, T_x and T_p, are the glass transition temperature, and the onset and peak temperatures of the crystallization. They were measured using Seiko DSC 220. The experimental uncertainties are

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PII: S0925-8388(98)00431-9

<±1°C. Glass-forming ability was estimated using the criteria ($\Delta T = T_g - T_x$) and $S = ((T_x - T_g)(T_p - T_x)/T_g)$ [9]. The glass density was obtained by Archimedean method with an uncertainty 0.02.

The scintillation properties, fluorescence emission wavelength, decay time and light yield, were measured under Co^{60} exposure at LPCML in Lyon and Le Verre Fluoré SA in Rennes.

3. Results

3.1. Glass formation in ternary systems

New vitreous compositions have been investigated in fluorophosphate systems in order to introduce a large amount of rare earth fluoride. A first set of experiments was implemented in the $NaPO_3$–MF_2–CeF_3 (M=Pb, Zn, Cd, Ba) ternary systems. The corresponding vitreous areas are shown in Fig. 1. The shady domains correspond to more stable glasses which could be cast as samples thicker than 3 mm. From this figure, we observe that the vitreous zone in the $NaPO_3$–PbF_2–CeF_3 system is very limited. But it increases significantly when BaF_2 replaces PbF_2. While binary glasses may be obtained in a very limited composition range between $NaPO_3$ and CeF_3, the binary range is much more important for $NaPO_3$–ZnF_2, and remains significant for $NaPO_3$–BaF_2 and for $NaPO_3$–CdF_2. When BaF_2 content is increased, CeF_3 can be incorporated into glass up to 30–35 mol.%. Thus, BaF_2 appears as a component favorable to the formation of CeF_3-doped fluorophosphate glasses. In addition, it does not have a negative effect on the scintillating properties of Ce^{3+} ions.

3.2. Glass characteristic temperatures

Main characteristic temperatures for a glass are T_g, T_x and T_p, for glass transition, onset of crystallization and maximum of crystallization exotherm, respectively. Table 1 reports these temperatures for glasses containing 30% of BaF_2 or CdF_2. Glass stability may be estimated from the value of the two criteria, ΔT and S. These glasses exhibit a good resistance against devitrification in the 0–10% CeF_3 range. When CeF_3 concentration is further increased up to 20% for the BaF_2 system and 15% for the CdF_2 system, a smaller peak of crystallization emerges before the major crystallization exotherm. Fig. 2 displays a typical DSC curve of the high CeF_3 content fluorophosphate glass. Table 1 reports the measured values. In this table, T_x^1, T_x^2 and T_p^1, T_p^2 correspond to the first and the second crystallization peaks, respectively. ΔT and S values were calculated using the parameters of the first peak. In practice the stability thermal range $\Delta T = T_x - T_g$ is reduced

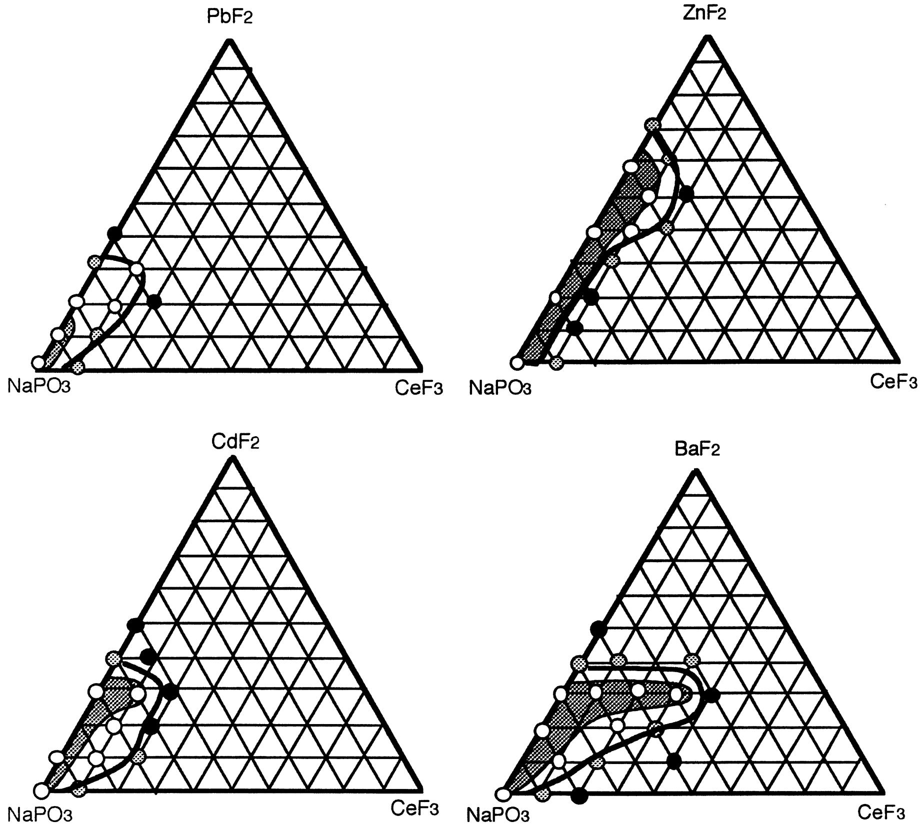

Fig. 1. Vitreous areas in the $NaPO_3$–MF_2–CeF_3 systems (M=Pb, Zn, Cd, Ba). The shady zones correspond to cast glasses more than 3 mm in thickness.

Table 1
Composition and characteristic temperatures in the $NaPO_3$–BaF_2(CdF_2)–CeF_3 system

Composition (mol.%)	T_g (°C)	T_x (°C)	T_p (°C)	T_x-T_g (°C)	S (K)
$70NaPO_3$–$30BaF_2$	255	419	435	164	5.0
$67NaPO_3$–$30BaF_2$–$3CeF_3$	265	421	471	156	14.5
$65NaPO_3$–$30BaF_2$–$5CeF_3$	270	432	476	162	13.1
$60NaPO_3$–$30BaF_2$–$10CeF_3$	285	450	508	169	16.8
$50NaPO_3$–$30BaF_2$–$20CeF_3$	306	377^1, 432^2	396^1, 438^2	71	
$45NaPO_3$–$30BaF_2$–$25CeF_3$	314	365^1, 435^2	374^1, 440^2	51	
$70NaPO_3$–$30CdF_2$	290	460	494	170	10.2
$67NaPO_3$–$30CdF_2$–$3CeF_3$	307	472	507	165	10.0
$65NaPO_3$–$30CdF_2$–$5CeF_3$	309	463	497	154	9.0
$60NaPO_3$–$30CdF_2$–$10CeF_3$	317	429	450	112	4.5
$55NaPO_3$–$30CdF_2$–$15CeF_3$	325	371^1, 444^2	380^1, 457^2	46	

in glasses exhibiting two crystallization peaks. This is consistent with the observed difficulty for casting thick samples free of crystal from such compositions.

The comparison between the fluorophosphate glasses containing BaF_2 and CdF_2 show that stability decreases with CeF_3 content with CdF_2, while it remains rather good with BaF_2 (see Fig. 3). There may be a size effect, from a structural viewpoint, as the presence of large cations such as Ba^{2+} may help cerium cations to find a site energetically favorable in the glass structure.

3.3. Stabilization of high CeF_3 content glass by adjustment of Na/P in composition

In order to solve this problem and to obtain some more stable glasses with high cerium concentration, we tried to adjust the Na_2O/P_2O_5 ratio in a glass containing 35% CeF_3. For this purpose, different contents of $(NH_4)_2HPO_4$ and Na_2HPO_4 were introduced for the same relative composition in P, Ba and Ce. From the thermal properties listed in Table 2, it seems that glass stability increases when the Na/P ratio rises from 0.71 to 1.47. But an excess of Na^+ may have the reverse effect: the value of ΔT is

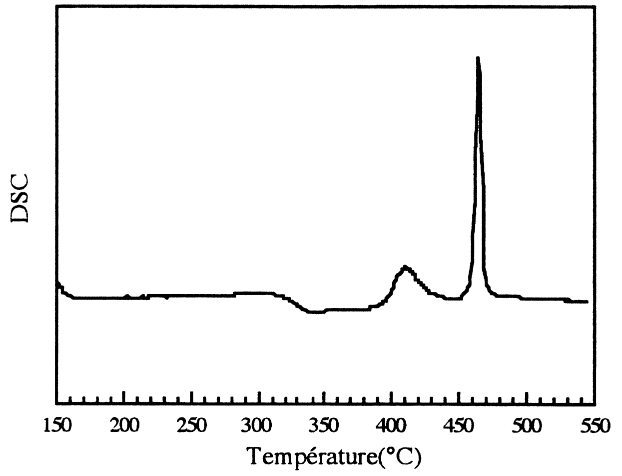

Fig. 2. Typical DSC curve of a fluorophosphate glass with high CeF_3 content (more than 20 mol.%).

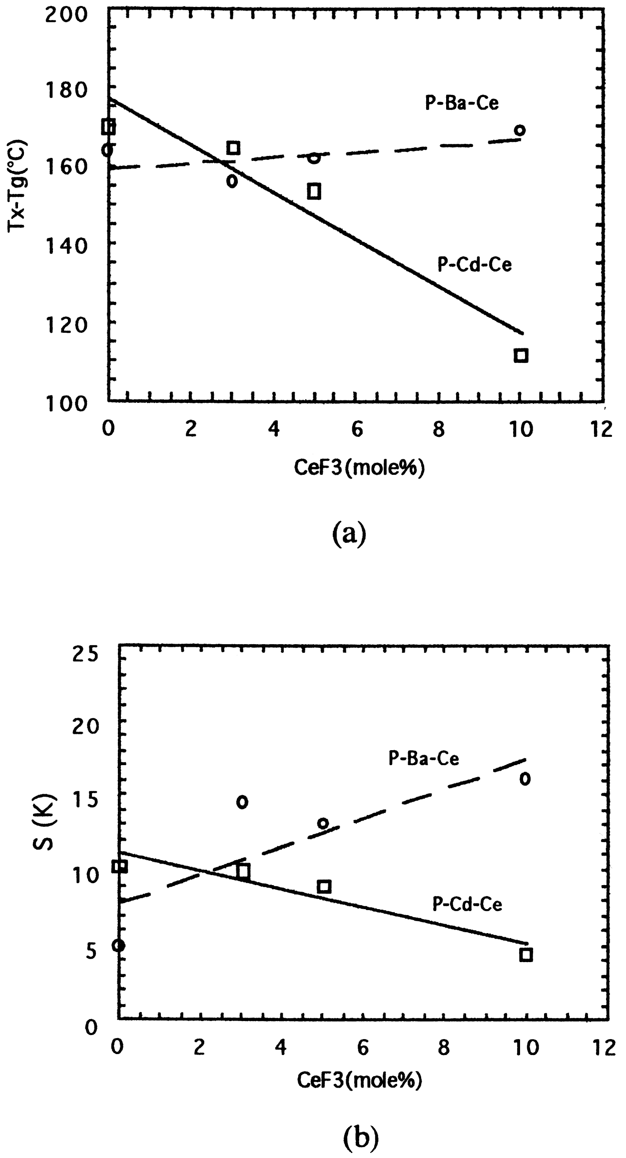

Fig. 3. Evolution of the stability criteria T_x-T_g (a) and S (b) versus CeF_3 concentration in $(70-x)NaPO_3$–$30CdF_2$–$xCeF_3$ and $(70-x)NaPO_3$–$30BaF_2$–$xCeF_3$ glasses.

Table 2
Influence of Na/P proportion on the characteristic temperatures of the glasses: $x(NH_4)_2HPO_4-(35-x)Na_2HPO_4-30BaF_2-35CeF_3$

	x	Na/P	T_g (°C)	T_x (°C)	T_p (°C)	T_x-T_g (°C)
PBC16	22.5	0.71	369	475	485	106
PBC9	20.0	0.86	346	465	473	119
PBC10	17.5	1.00	330	454	465	124
PBC11	15.0	1.14	318	446	456	128
PBC12	12.5	1.28	317	445	460	128
PBC13	10.0	1.43	301	443	457	142
PBC14	5.0	1.71	297	369	382	72
PBC15	0	2.00	292	391	403	99

dramatically reduced when Na/P ratio reaches 1.7 or more. This provides guidelines for the preparation of stable compositions for scintillation studies.

3.4. Scintillating properties

Some optical measurements have been implemented in order to make a comparison between these fluorophosphate glasses and other Ce-doped glasses. Table 3 summarizes the scintillating properties of various fluoride and oxide glasses. For convenience, light yield is expressed by comparison with CeF_3 crystals. The GS1 silicate glass, based on the SiO_2–MgO–Li_2O system, shows the highest luminescent output among the glass scintillators, but its weak density brings about some limitations. CeF_3-doped fluorohafnate glasses are always attractive because of their high density close to that of CeF_3 crystal. However, their luminescent light yield should be improved for practical applications. From the data in Table 2, it is only 38% of that of crystalline CeF_3, which is probably the largest value reported to-date for a fluorohafnate glass. By comparison, the high CeF_3 content fluorophosphate glasses appear as promising scintillator glasses, although their density is still inferior to fluorohafnate glass. Its luminescent light yield increases with the CeF_3 concentration [4] and reaches 60% when CeF_3 concentration is 25 mol.%.

4. Discussion

These results exemplify the potential of fluorophosphate glasses for scintillation. They also raise some questions about the scintillation mechanism. Obviously, there is a strong correlation between cerium concentration and light yield, which justifies the hypothesis underlying these experiments. However there are other factors influencing scintillation, for example the purity of the final material. In addition, the oxidation state of the cerium cations may be critical because Ce(IV) may act as a desactivator. For this reason, fluoride materials may be attractive materials because they favor the III oxidation state. In this respect, we did not observe a significant difference in the behavior of fluorohafnates and fluorophosphates. In practice it is necessary to prevent oxidation of Ce(III) during glass processing, which requires some compromise as glass fining usually implies an oxidation stage for the reduced species present in the melt.

The comparison between crystalline CeF_3 and cerium-doped scintillating glasses demonstrates that the lack of long-range ordering and the defects associated with vitreous structures do not account for the limitation of the light yield, as it may be higher in a glass (GS1) than in the pure crystal. However, there may also be some optimum concentration in cerium. While there is an obvious advantage in increasing this concentration in glasses, some deactivation processes may also occur in the pure CeF_3.

Vitreous materials appear as attractive materials for future scintillators, not only because they may be processed more easily than single crystals, but also because they offer very large compositional flexibility. It should be possible to obtain glasses more concentrated in cerium and also more dense.

5. Conclusion

Fluorophosphate glasses containing cerium fluoride as a basic glass component have been synthesized and characterized. Cerium fluoride concentration may reach 35 mol.%. Their stability against devitrification is large enough to allow bulk samples to be cast without crystallization. Their density is close to 4 g cm^{-3} and their light yield under scintillation reaches 60% of that of crystalline CeF_3. These characteristics could be improved by further work on compositions.

Acknowledgements

Authors are grateful to the Human Capital and Mobility European network for financial support, contract CHRX-

Table 3
Scintillation properties of CeF_3 crystal and some Ce-doped glasses

Samples	Density (g cm^{-3})	Emission wavelength (nm)	Scintillation lifetime (ns)	Light yield % CeF_3
CeF_3 [2]	6.2	310, 340	~5, 30	100
GS1 [10]	~2.6	395	~60	140
HFG [4]	5.7	320	~20–25	38
FPG	4.0	370	30	60

GS1 is a silicate glass, HFG is a fluorohafnate and FPG a fluorophosphate from this study.

CT93-0108. They also thank the LPCML of Lyon and Le Verre Fluoré SA for optical measurements.

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