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Influence of rare-earth ions on fluorogallate glass formation and properties

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Abstract

Various rare earths have been incorporated in a lead fluorogallate glass with the following chemical composition: $30PbF_2$–$20GaF_3$–$15InF_3$–$20CdF_2$–$15ZnF_2$ (PGICZ). Selected rare earths are La, Ce, Pr, Nd, Gd, Er, Yb and Lu, and the doping level varies between 1 and 10 mol%. The influence of rare earth fluorides on glass forming ability and on physical properties is investigated. At low concentration (<3 mol%) lanthanide incorporation increases glass stability. While large amounts of rare earths may enter glass composition, thick samples are difficult to obtain with this glass composition. Larger samples containing 9 mol% NdF_3 in a modified PGCIZ glass have been cast. Experimental results suggest that rare earths act as modifiers rather than vitrifiers in this fluorogallate system. The effect of rare earths on the values of glass transition temperature, refractive index, density and thermal expansion is reported. © 1998 Elsevier Science S.A.

Keywords: Rare-earth fluoride; Fluorogallate glass; Glass formation; Physical properties

1. Introduction

Glass formation in fluoride systems has been extensively studied for the last 20 years [1]. While most compositions still remain of pure academic interest, some standard fluoride glasses now make the basis of industrial optical fibers for a variety of applications, ranging from infrared technologies to fiber lasers and medicine [2] [3]. An increasing interest is devoted to active fibers which could be used for new laser lines and for optical amplification [4]. In both cases, rare earths play a major role and their specific spectroscopic properties determine to a large extent the characteristics of the final device. By comparison with classical oxide glasses, fluoride glasses have some advantages. First, rare earths enter fluoride glass composition as basic components rather than dopants [1], for example, early works described ternary glasses in the ZrF4–BaF_2–LnF_3 systems. Therefore their concentration may be higher, and clustering should not occur. Besides, phonon energy is smaller in fluoride glasses, which often reduces non-radiative decay from active levels. These features are also found in other non-oxide glasses such as Ga–La–S [5], but fluoride glass fibers offer the decisive advantage of low background losses, smaller than 20 dB km^{-1} between 1 and 2 μm [2].

Apart from practical applications, the study of the rare earths in fluoride glasses may help to understand the mechanisms of glass formation. While lanthanides are not reported to be glass progenitors in fluoride systems, the question is still pending. Some recent results in the InF_3–BaF_2–YF_3 [6] suggest that yttrium—and possibly small rare earths—could be vitrifiers insofar as YF_3 is the major component. However, from their field strength, rare earth cations rather appear as intermediate between glass progenitors such as Zr^{4+} or Al^{3+} and modifying cations such as Na^+ or Ba^{2+}. Their actual effect on glass formation may depend on the other cations entering glass composition. In fluorogallate and fluoroindate systems chemical bonds are weaker than in fluorozirconate and fluoroaluminate glasses, which results in lower phonon energy. As a consequence, they are promising hosts for Pr^{3+}-doped fiber amplifiers (PDFA) [5]. Considering that Ga^{3+} and In^{3+} field strengths are close to those of Ln^{3+}, one could expect that the incorporation of LnF_3 is easier in GaF_3/InF_3-based glasses. This paper reports some experiments implemented.

2. Experimental

Ideally, starting materials should be pure and anhydrous fluorides. However, it may advantageous in practice to use pure oxides from which fluorides may be synthesized, either separately or in situ, in order to obtain homogeneous glasses. Rare earth oxides, 3 or 4 N, are from Rhone

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Poulenc Chimie Fine, gallium and indium oxides, 3 N, are provided by Preussag, and other fluorides by Merck. Ammonium bifluoride is from Prolabo.

Fluorogallate glasses are prepared using ammonium bifluoride processing with special adjustment of processing time and temperature, in order to ensure the complete fluorination of Ga_2O_3. Fining, casting and annealing are carried out with temperatures and times close to those used for fluorozirconate glasses [1]. Samples of a few millimeters in thickness are obtained by casting the melt into a preheated brass mold.

Characteristic temperatures are T_g for glass transition, T_x for onset of crystallization and T_p for the maximum of the exothermic peak. They are measured using a Seiko 220 DSC at 10 K min^{-1} heating rate. Assessment of glass stability is made from the value of the stability range $\Delta T = T_x - T_g$ or from the S factor $((T_x - T_g)(T_p - T_x)/T_g)$ [7]. Refractive index is measured using an Abbe refractometer and thermal expansion from a Seiko TMA/SS 120. Estimated accuracy is ± 1°C for temperatures, ± 0.0005 for refractive index and $\pm 5 \times 10^{-7}$ K^{-1} for thermal expansion. The Archimedean method used for density is expected to lead to an error margin of ± 0.01.

3. Results

3.1. Effect of rare earth ions on glass formation

For this study we have used a multicomponent glass (PGICZ) developed in our group and stable enough against devitrification to produce thick samples. Glass composition is based on the fluorides of Ga, In and Pb as major components, that is, in mol%: $30PbF_2–20GaF_3–15InF_3–20CdF_2–15ZnF_2$.

Rare earth fluorides LnF_3 have been incorporated in this base glass as additives: x mol% LnF_3 was added to 1 mol PGICZ. Various samples were synthesized with a concentration varying between 1 and 5 mol% in fluorides of La, Ce, Pr, Nd, Gd, Er, Yb and Lu. Thermal measurements have been made on these samples and the corresponding results are displayed in Table 1.

Fig. 1 shows that glass transition temperature increases with the LnF_3 concentration. This could be correlated to the high melting point temperature of the rare earth fluorides. It is widely admitted that there is a 2/3 ratio between glass transition and liquidus temperatures. Additives with a high melting point increase liquidus temperature, which in turn increases T_g. The conclusions drawn from the values of the stability criteria are contrasted: by comparison with based glass, the ΔT value is larger only for samples doped with 1% Pr and Nd, as exemplified by Fig. 2. However, the value of the S factor rather suggests that glasses are more stable even at 2 or 3 mol% doping level (Fig. 3). This last conclusion is rather consistent with experimental observations: doped samples are usually easier to synthesize than undoped glass. Reduced cooling rate may be applied to the melt, allowing thick samples to be cast, as shown in Fig. 4.

Table 1
Characteristic temperatures of rare earth-doped glasses

Ln-doped sample	T_g (°C)	T_x (°C)	T_p (°C)	ΔT (°C)	S (K)
Basic glass	243	354	374	111	9.1
5 mol% LaF_3	253	321	334	68	3.5
10 mol% LaF_3	not a good glass				
5 mol% CeF_3	257	326	341	69	4.1
1 mol% PrF_3	245	358	385	113	12.5
2 mol% PrF_3	248	353	383	106	12.7
5 mol% PrF_3	254	331	349	77	5.4
10 mol% PrF_3	253	331	354	78	7.0
1 mol% NdF_3	245	359	384	114	11.7
2 mol% NdF_3	246	354	385	108	13.3
3 mol% NdF_3	249	348	377	99	11.3
1 mol% GdF_3	245	355	380	110	11.3
2 mol% GdF_3	248	359	387	111	12.7
3 mol% GdF_3	250	356	383	106	11.5
5 mol% GdF_3	254	334	380	80	5.4
2 mol% ErF_3	248	355	382	107	11.6
5 mol% ErF_3	255	324	341	69	4.5
5 mol% TmF_3	255	326	342	71	4.4
2 mol% YbF_3	247	352	377	105	10.5
5 mol% YbF_3	253	327	344	74	4.9
2 mol% LuF_3	247	350	370	103	8.4

From the compositions shown in Table 1, it can be seen that up to 10 mol% LnF_3 had been incorporated in the base glass. However, quenching is required in order to obtain vitreous samples. From our experience, glass compositions should be adjusted to obtain thick glass samples with higher rare earth concentration. Various experimental attempts have shown that more stable glasses are obtained when rare earths substitute Pb, Cd and Zn instead of Ga or In. As an example, we have successfully introduced 9 mol% NdF_3 in the modified PGICZ composition: $26PbF_2–20GaF_3–15InF_3–17CdF_2–13ZnF_2–9NdF_3$. Samples were cast with the usual cooling rate into a preheated mold.

3.2. Effect of rare earths on glass properties

Some physical properties have been measured on doped glass samples. Density evolution versus the nature of the rare earth is reported in Fig. 5. As one could expect, density increases as atomic number increases. The incorporation of lanthanides lighter than Gd rather decreases density, except for cerium. The deviation from the average evolution which is observed for cerium may be explained if we assume that a part of cerium is at oxidation state IV, with a smaller ionic radius. This assumption is consistent with the behavior of the cerium-doped fluoride glasses under irradiation, which emphasizes the part of cerium IV in the scintillation mechanism [8].

The evolution of refractive index versus the rare earth is shown in Fig. 6. By comparison with base glass, refractive index is decreased, which is explained by the decrease in

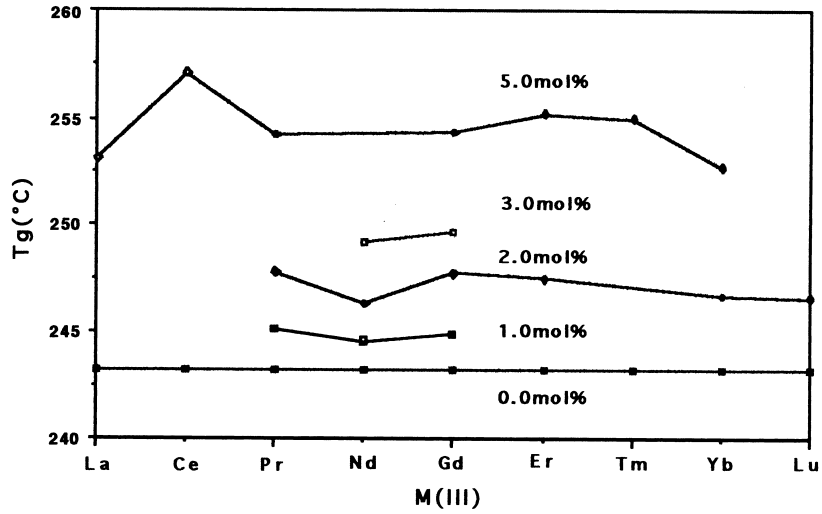

Fig. 1. Evolution of glass transition temperature T_g versus the nature and the concentration of the rare earth. Lines are drawn as guides for the eye.

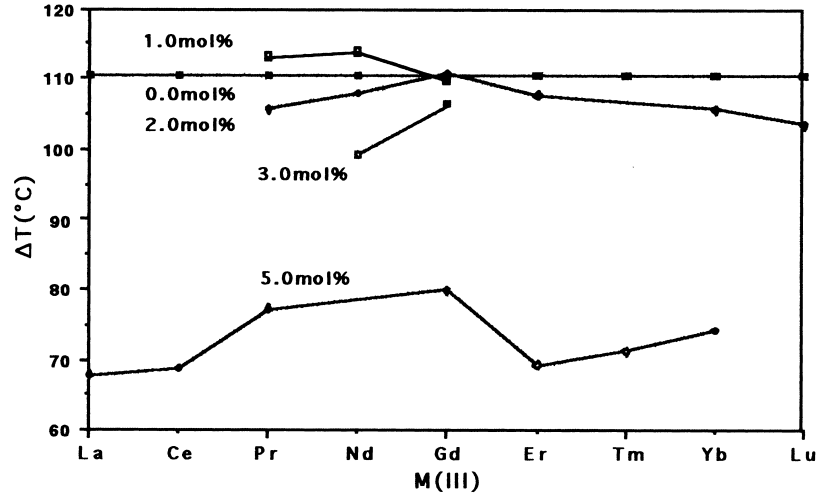

Fig. 2. Evolution of thermal stability range ΔT versus the nature and the concentration of the rare earth. Lines are drawn as guides for the eye.

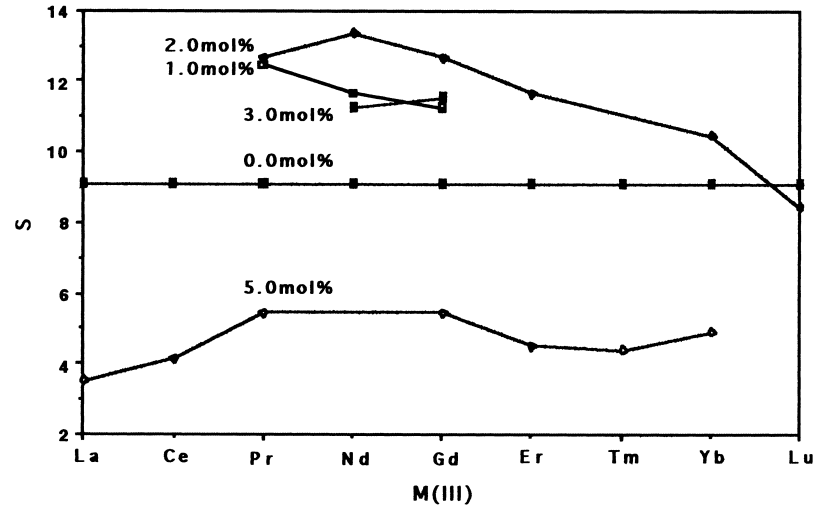

Fig. 3. Evolution of stability factor S versus the nature and the concentration of the rare earth. Lines are drawn as guides for the eye.

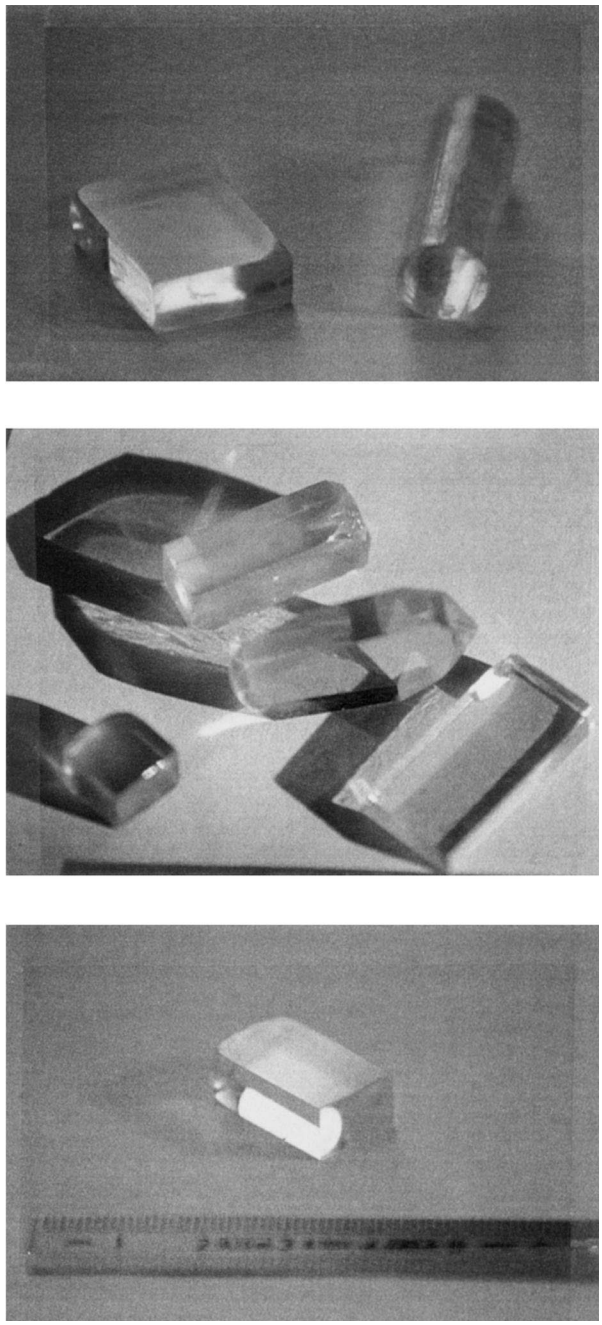

Fig. 4. Photographs of glass samples stabilized by 2 mol% (1) PrF_3, (2) NdF_3 and (3) GdF_3.

the number of polarisable elements per unit volume. It may also be understood by reference to the refractive index of the rare earth fluorides which are below 1.6.

Fig. 7 shows that rare earth fluoride incorporation leads to the decrease of the thermal expansion coefficient by comparison with the base glass. The highest value is observed for cerium-doped glass, while the smallest value corresponds to the Gd-containing glass. With small rare earths, thermal expansion is close to that of lanthanum-doped glass. The correlation between T_g and thermal expansion makes a first explanation for the general trend. However, the evolution is not monotonous. Also there must be some correlation between thermal expansion and structure. The crystal chemistry of the lanthanides emphasizes differences between ceric and yttric rare earths which are often correlated to changes in coordination number induced by the decrease of the ionic radius. It may be assumed that this is the case in these glasses. Finally, several factors are likely to influence the value of the thermal expansion coefficient.

(1) The mean cationic charge. This is increased by the addition of lanthanide trifluoride to the base glass in which it is only 2.35.

(2) The decrease of the ionic radius of the rare earth, insofar as coordination number does not vary.

(3) Change in the coordination numbers of the cations.

(4) Change in oxidation state, for example Ce^{4+} instead of Ce^{3+}, which also modifies both coordination polyhedron and ionic radius.

In this respect, our observations would be consistent with a change in the lanthanide site between large and small rare earth, and also with a partial oxidation of the cerium trifluoride. However, more accurate and more systematic studies should be implemented to support these hypothesis.

4. Discussion

These results show that rare earths can be incorporated in these fluorogallate glasses in fairly large amounts. By comparison with the base glass, devitrification rate could be reduced in a optimized doping concentration range (2–4 mol%). This means that LnF_3 dopants should not increase scattering losses in active fibers made from these materials at the usual doping level. In a more extensive way, it should be possible to make glass samples with higher rare earth content for special optoelectronic devices, either when co-doping is necessary or for high gain and short path components.

By comparison with fluorozirconate glasses, rare earth incorporation appears easier. This is probably related to differences in glass structure. Standard fluorozirconate glasses derive from the ZrF_4–BaF_2 binary glass and lanthanum replaces barium, acting as a modifier, according to the classical network model. In these fluorogallate glasses, lanthanide cations are close to Pb^{2+} from their ionic radius and to Ga^{3+} and In^{3+} from their ionic charge. Consequently their insertion should require only minor structural change by comparison with the base glass. In addition, binary glass may be formed between GaF_3 and YF_3 [9], which supports the idea that small rare earths are favorable to glass formation when associated to gallium. However, in PGICZ glass devitrification rate increases when lanthanides replace Ga and In, while it does not change significantly with the Ln/Pb or Cd substitution. As the content of the glass progenitors (GaF_3, InF_3) in PGICZ

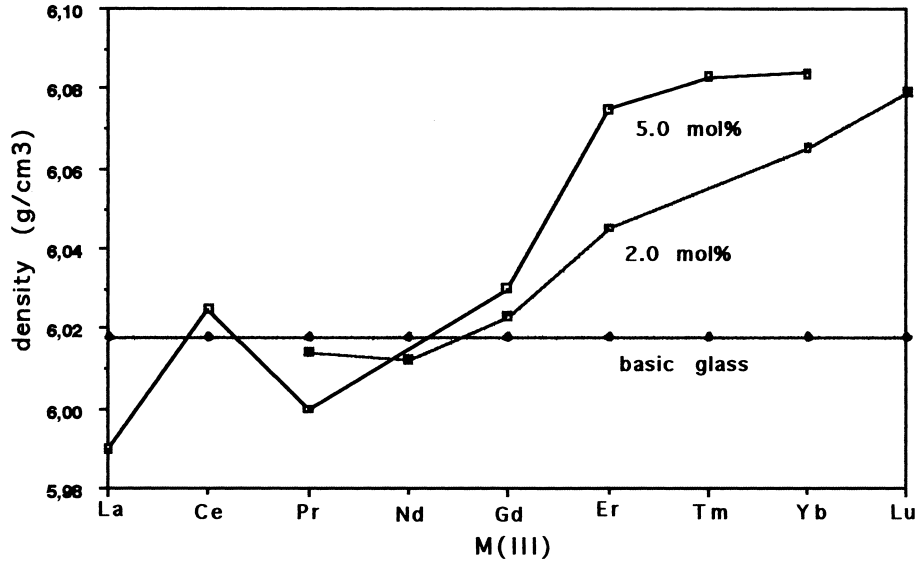

Fig. 5. Evolution of glass density versus the nature and the concentration of the rare earth. Lines are drawn as guides for the eye.

glass is low, a further decrease is detrimental to glass formation, which is not compensated by LnF_3 incorporation. In this respect, LnF_3 does not act as a glass network former and appears rather as a modifier.

More systematic studies would be useful to investigate the possibilities for stable fluorogallate glasses with high rare earth content. One may expect different behaviors for the large and the small lanthanides.

5. Conclusion

Rare earth fluorides have been incorporated in a multicomponent lead fluorogallate glass ($30PbF_2$–$20GaF_3$–$15InF_3$–$20CdF_2$–$15ZnF_2$). Glass-forming ability has been assessed from the value of the stability factors ΔT and S. It is increased when LnF_3 content remains below 3 mol%. When rare earth content is increased, samples must be cooled more rapidly to obtain a glass. However, cast glasses containing 9 mol% NdF_3 have been obtained. Further composition adjustments are needed to obtain stable glasses with higher lanthanide concentration.

The evolution of characteristic temperatures, density, refractive index and thermal expansion has been studied according to the nature and the concentration of the rare earth fluoride incorporated into the glass composition. In cerium-doped samples a part of the Ce^{3+} cations is oxidized as Ce^{4+}. The experimental results suggest that

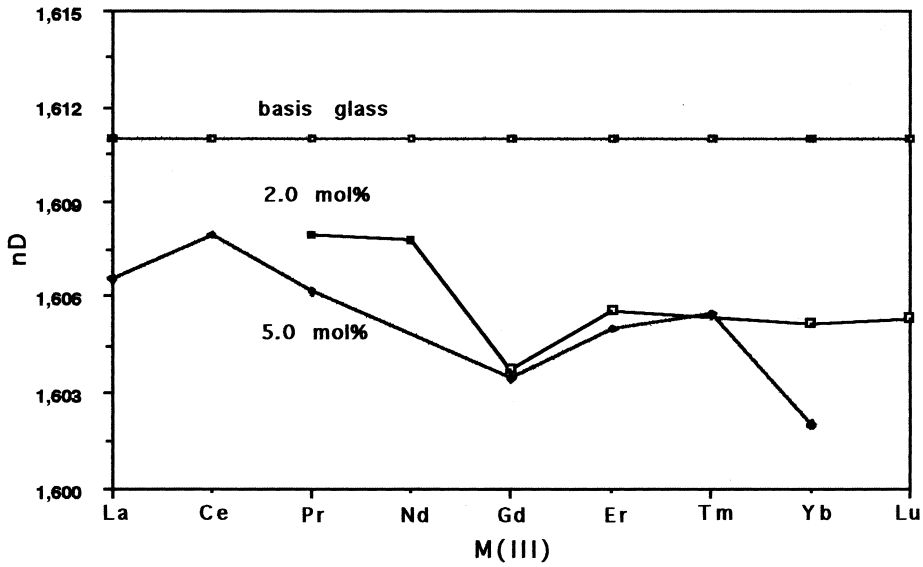

Fig. 6. Evolution of refractive index versus the nature and the concentration of the rare earth. Lines are drawn as guides for the eye.

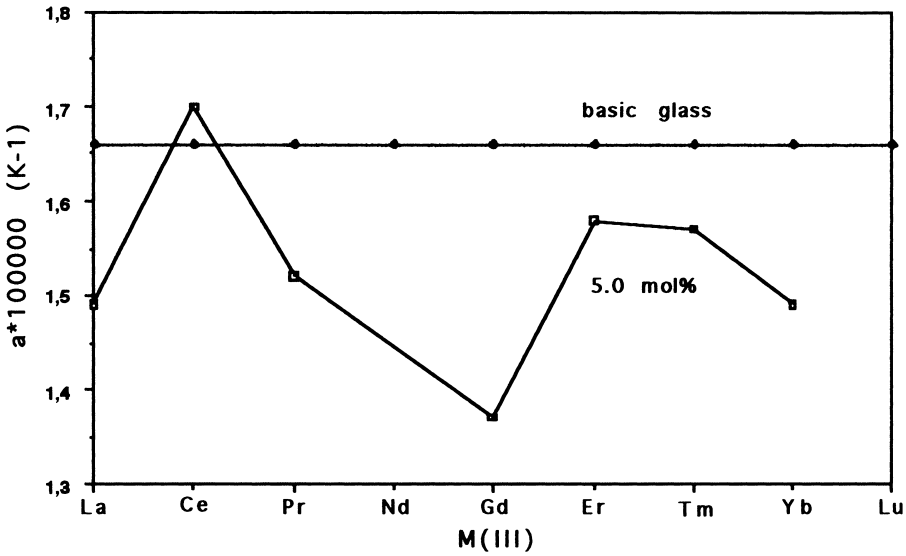

Fig. 7. Evolution of thermal expansion coefficient versus the nature and the concentration of the rare earth.

rare earths rather act as glass modifiers in this fluorogallate system. These data provide a basis for the development of low phonon energy glasses for optoelectronic applications.

Acknowledgements

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