Evidence for the Coordination Number Change of Rare Earth Ions in Rare Earth Phosphate Glasses

Hitoshi Kanno and Yoshifumi Akama†
Department of Chemistry, National Defense Academy, Yokosuka 239
†Department of Chemistry, Meisei University, Hino, Tokyo 191

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Rare earth phosphate glasses of the composition $Ln(PO_3)_3 \cdot KPO_3$ (Ln : rare earth ion) were prepared and their glass transition temperatures (T_g's) were measured. From the T_g variation across the series, it is shown that the coordination number of rare earth ions changes, probably from nine to eight, in the middle of the series.

It is now well established that the inner-sphere hydration number of rare earth ions in aqueous rare earth electrolyte solutions changes from nine for the light rare earth members to eight for the heavy ones in the middle of the series[1-5] although a few groups are still arguing against the hydration number change. The coordination number change takes place due to the large difference between the ionic size of a rare earth ion and the hydration sphere of water molecules. In aqueous rare earth electrolyte solution systems the hydration number change is the major cause for various irregularities observed in thermodynamic and transport properties.[6,7]

In recent years, much attention has been paid to glasses containing rare earth ions for their potential uses for optical applications and display devices.[8-10] The optical properties of doped rare earth ions are greatly dependent on the environments around the doped ions. In view of these observations, it is very interesting to see if the same, i.e., coordination number change, would take place in glass systems. In this paper, we report the DTA results of the rare earth phosphate glasses.

As starting materials for making phosphate glasses, the mixtures of $NH_4H_2PO_4 \cdot KH_2PO_4$ and rare earth oxide (Ln_2O_3) were used. The molar ratios of $NH_4H_2PO_4 : KH_2PO_4 : Ln_2O_3$ were 6 : 2 : 1 in most starting materials (in the cases of preparing Pr- and Tb- glasses, different molar ratios were adopted so as to give the same composition as other glasses in the product glasses). After grinding well the mixture in an agate mortar, it was put in an alumina crucible and was heated in an electric furnace with step-wise temperature rises up to 1400 ℃. The melt was stirred several times and then poured out on a Cu-plate and cooled down quickly by pressing the melt with another Cu-plate. Although the exact cooling rate was rather difficult to determine, it was estimated to be around 10^3 ℃ /min. The chemical composition of the obtained glasses were determined by the EDTA titration of rare earth ions and is found to be expressed approximately by the formula $Ln(PO_3)_3 \cdot KPO_3$. The DTA trace was measured with a Rigaku 8100 type DTA spectrometer by use of Al_2O_3 as the reference material. The heating rate was 5 ℃ /min in the glass transition temperature region. Reproducibility of the T_g measurements was better than ±3 ℃.

A typical DTA trace of the $La(PO_3)_3 \cdot KPO_3$ glass is shown in Figure 1. It is important to note that all the DTA traces give the similar patterns: one glass transition and two crystallization peaks (one at 610 - 710 ℃ and the other at 720 - 800 ℃), each of which rises with the decrease in ionic radius of rare earth ion.

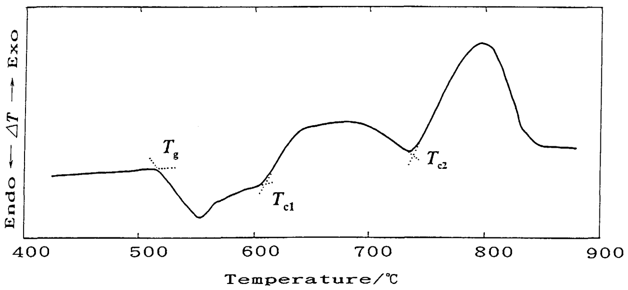

Figure 1. A typical DTA trace of a $Ln(PO_3)_3 \cdot KPO_3$ glass. Two crystallization peaks (T_{c1}: 610 ℃, T_{c2} : 735 ℃) are observed.

Figure 2 shows the T_g values plotted against the reciprocal of ionic radius of rare earth ions. An important aspect is that they show an extended z-shaped variation across the series although the ionic radius of rare earth ions decreases smoothly from La^{3+} to Lu^{3+}. The extended s- or z-shaped behavior is a common feature for the viscosity and partial molar volume variations of aqueous solutions of simple rare earth electrolytes and the s-shaped series behavior is more common than the z-shaped one.[6,7,11,12] The origin of the irregular series behavior of this type (s- or z-shaped variation) is attributed to the coordination number change of rare earth ions in the middle of the series.[6,7] In the cases of aqueous rare earth electrolyte solutions, the inner-sphere coordination number of light rare earth ions (La^{3+}- Pm^{3+}) is nine, that of the heavy ones is eight (Ho^{3+}- Lu^{3+}) and that of the middle members (Sm^{3+}- Dy^{3+}) is the value between nine and eight, due to the coexistence of two types of coordination numbers.[1,2] Therefore, the extended z-shaped behavior of the T_g values can be ascribed to the coordination number change although more direct experimental evidence such as x-ray diffraction datum is not available at present. As the inner-coordination sphere consists of oxygen atoms of PO_3^- ions, the coordination number change in these phosphate glasses is expected to be the same as that in aqueous solutions (namely, nine to eight).

Recently, Medda et al.[13] have examined the local environment of Eu^{3+} ions in a $0.9Zn(PO_3)_2 \cdot 0.1Eu(PO_3)_3$ glass by x-ray diffraction method and have shown that the Eu^{3+} ion is surrounded on average by a polyhedron of about 7.4 oxygens at 236 pm and about 1.6 oxygens at 268 pm. Although the direct inference from their x-ray results to the present phosphate glasses can not be made, it is plausible that the existence of the 1.6 oxygens at 268 pm is the indication of two types of the coordination numbers, i.e., eight and nine. Obviously, this point should be clarified by a x-ray diffraction study of the $Ln(PO_3)_3 \cdot$

KPO_3 glasses in the future.

A notable feature about the coordination number change in the Ln-phosphate glasses is that the T_g rise slows down a little in the transition region. This T_g slow-down is just the opposite of the rapid T_g rise observed in the aqueous solution systems. It is a general phenomenon that a rather abrupt T_g rise is observed in the region where the hydration number change takes place in aqueous rare earth electrolyte solutions.[3] The T_g rise in aqueous solution is the reflection of the increase of the total hydration sphere and of the thermal stability of the glass.

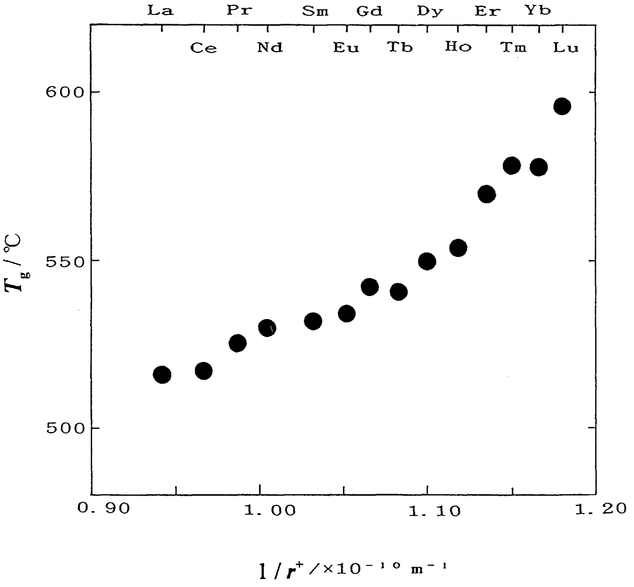

Figure 2. The T_g variation across the rare earth series.

The downward T_g shift, although only a slight one, indicates that the thermal stability of the phosphate glass decreases a little due to the coordination number decrease which arises from the geometrical origin. In other words, as the ionic size of rare earth ions decreases, the number of oxygen atoms coordinating to a rare earth ion can not exceed eight due to the insufficient size of the ion. In aqueous solution systems, a clear hydration sphere around a rare earth ion is formed by rearrangements of water molecules in the second and third coordination spheres which are expected to contribute to the stabilization of the whole system.

On the other hand, no formation of a distinct solvation sphere outside of the first one is expected in the phosphate melt due to the strong interaction of interconnecting PO_3^- units. Therefore, the coordination number change might invite a weak destabilization of the glass although the interpretation is rather speculative.

The significance of the present results is the manifestation that the coordination number change across the rare earth series takes place even in the $Ln(PO_3)_3 \cdot KPO_3$ glass system.

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