The Korean Journal of Ceramics, 5[4] 375-378 (1999)

Physicochemical Properties of ZrF_4-Based Fluoride Glasses Containing Rare-Earth Ions

Noriyuki Ishioka, Kouji Ogawa and Tsuyoshi Arakawa

Department of Industrial Chemistry, Faculty of Engineering
Kinki University in Kyushu, Iizuka, Fukuoka 820-8555, Japan
(Received September 23, 1998)

In the XRD study of $56ZrF_4 \cdot 34BaF_2 \cdot 4AlF_3 \cdot (6\text{-}x)LaF_3 \cdot xLnF_3$ glasses(Ln=Ce, Nd, Gd, Tb), halo pattern characteristic of an amorphous sample appeared. When the halo peak angle (θ_p) was converted into a wavenumber with $Qp=4\pi\sin\theta_p/\lambda$($\lambda$ is the wavelength of the radiation used), it was found that the Qp values varied almost linearly with the concentration of LnF_3. The emission spectra of Ce^{3+}-containing fluoride glasses under 273 nm excitation had a peak maximum at ca. 300 nm (Ce^{3+} 5d-4f transition). The maximal intensity of the fluorescence was observed when the CeF_3 content was extremely low (ca. 1 mol%). DTA measurement revealed that these fluoride glasses had two crystallization temperatures. In $56ZrF_4 \cdot 34BaF_2 \cdot 4AlF_3 \cdot (6\text{-}x)LaF_3 \cdot xNdF_3$ glasses, the activation energies of crystallization obtained from a Kissinger plot were 1.7 and 5.0 eV for the glass with x=2, and 1.9 and 5.6 eV for the glass with x=4.

Key words: Fluoride glass, Rare-larth ion, Fluorescence, Kissinger plot

I. Introduction

Fluorozirconate glasses (ZrF_4-based glasses) prepared by Poulain et al.[1] have attracted much interest because of the high optical transparency in the visible to infrared (IR) region. Since ZrF_4 cannot be a network former by itself, the formation of glass samples becomes feasible when ZrF_4 is melted with other fluorides, e.g, BaF_2. Lucas[2] described that the introduction of AlF_3 into ZrF_4-based glasses was favorable for the glass formation. Also, small amounts of rare earth ions proved to be effective for stabilizing the glassy phase.[2]

Especially, the ZrF_4-based fluoride glasses containing rare earth ions are attractive when developing rare erath-doped fiber amplifiers for use in optical communication system. The present study was carried out in order to obtain some physicochemical properties of $ZrF_4 \cdot BaF_2 \cdot AlF_3 \cdot LaF_3 \cdot LnF_3$(Ln=Ce, Nd, Gd, Tb).

II. Experimental

The fluoride glasses, $56ZrF_4 \cdot 34BaF_2 \cdot 4AlF_3 \cdot (6\text{-}x)LaF_3 \cdot xLnF_3$ glasses(Ln=Ce, Nd, Gd, Tb), were prepared by melting the desired mixture of the starting materials of analytical reagent grade under a dry nitrogen atmosphere. The melt was kept at 1123 K for 5 min and quenched by use of cold copper plate under in air. The formation of homogeneous glass samples was confirmed by X-ray diffraction (Rigaku Denki RAD2B) patterns. Fluorescence spectra were recorded on a Hitachi Fluorescence Spectrophotometer (F-4500). Glass transition temperature (T_g) and crystallization peak temperature (T_c) were determined by DTA (Shimadzu DTA-50).

III. Results and Discussion

1. Formation of glasses

Fig. 1. shows typical examples of X-ray diffraction patterns recorded for $56ZrF_4 \cdot 34BaF_2 \cdot 4AlF_3 \cdot (6\text{-}x)LaF_3 \cdot xCeF_3$

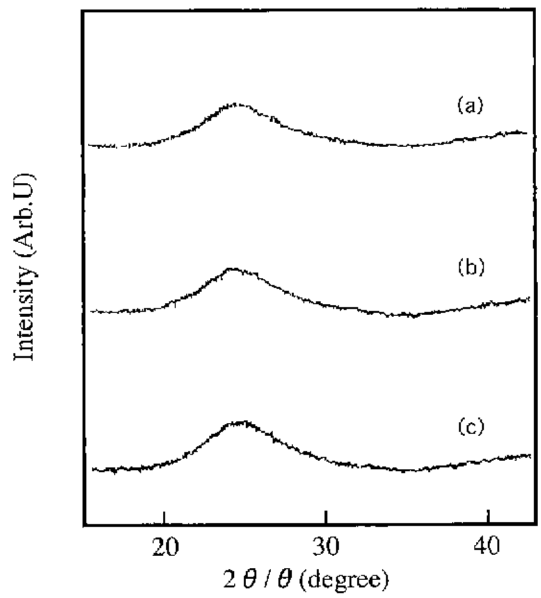

Fig. 1. X-Ray diffraction patterns of $56ZrF_4 \cdot 34BaF_2 \cdot 4AlF_3 \cdot (6\text{-}x)LaF_3 \cdot xCeF_3$ glasses. (a) x=1.8, (b) x=2.4, (c) x=3.0.

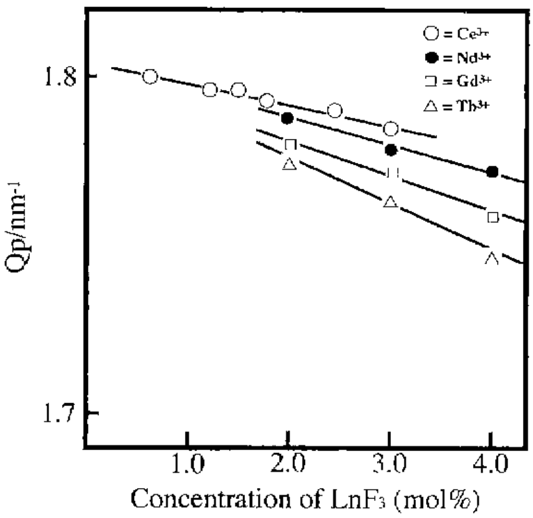

Fig. 2. Plot of the wavenumber, Qp/nm^{-1}, vs. LnF_3 concentration in $56ZrF_4 \cdot 34BaF_2 \cdot 4AlF_3 \cdot (6\text{-}x)LaF_3 \cdot xLnF_3$ glasses.

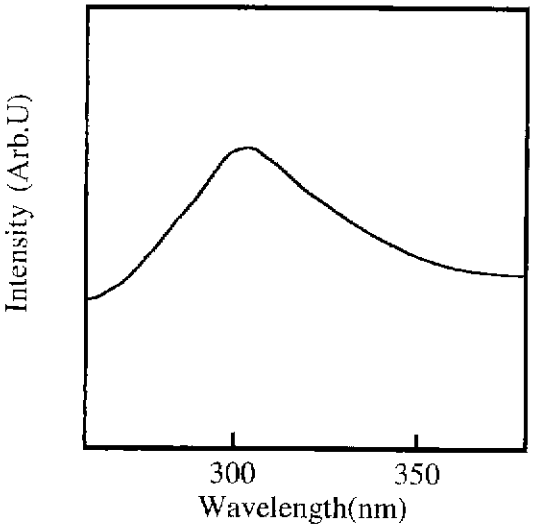

Fig. 3. Emission spectra of $56ZrF_4 \cdot 34BaF_2 \cdot 4AlF_3 \cdot 4LaF_3 \cdot 2CeF_3$ glass excited with the UV light with the wavelength of 273 nm.

glasses. A broad diffuse diffraction peak which is attributed to an amorphous sample is observed at around 20-30 degrees. The peak maximum of these halo patterns shifts to a lower angle with the increase of "x". Halo patterns were also obtained in the ZrF_4-based fluoride glasses containing other rate earth ions. After the halo peak angle (Qp) was converted into a wavenumber with $Qp=4\pi\sin\theta_p/\lambda$($\lambda$ is the wavelength of the radiation used), Qp values are plotted against the concentration of LnF_3. as shown in Fig. 2. It was found that the Qp values varied almost linearly with the concentration of Ln, while it diminished with the decrease of the ionic radius of Ln^{3+}. ZrF_4-BaF_2 glasses with low BaF_2 contents are known to have a layer structure composed of zigzag chains of ZrF_6 units, whereas they have a pseudo-chain structure composed of ZrF_7 units when the BaF_2/ZrF_4 ratio is close to unity.[3] Ba^{2+} ions occupy so-called "interstitial" sites, as a network modifier, surrounded by ZrF_6 and/or ZrF_7 units,[3] just like several alkali-and alkaline earth-metal ions in several oxide glasses. Thus, it can be considered that the relationship between Qp values and the concentration of Ln^{3+} is attributed to a gradual in-crease in the nearest-neighbour distance of the plane in-cluding Ln^{3+} ions. The Qp values decrease linearly with increase of concentration.

2. *Fluorescence spectra*

A typical emission spectrum for $56ZrF_4 \cdot 34BaF_2 \cdot 4AlF_3 \cdot 5.4LaF_3 \cdot 0.6CeF_3$ glass under 273 nm excitation is shown in Fig. 3. This photoluminescence can be assigned to the electron transition in the $4f^1 \rightarrow 4f^05d^1$.[4] Generally, the wavelength of the emission peak for Ce^3 in may compounds is located at ca. 350~360 nm.[4] Hence, it is assumed that the Ce^{3+} ions in these fluoride glasses occupy distorted sites; the peak position of this emission band has shifted to a lower wavelength region.

It is well known that the emission intensity in various phosphors is affected by the concentration of Ce^{3+}. The effect of Ce^{3+} ion concentration on the emission band is presented in Fig. 4. The photoluminescence outputs (PL) of the samples were compared with that of $CaWO_4$: Pb (NBS 1026). The intensity of PL showed a specific pattern; initially, there was a sharp increase in the intensity along with the increase in the Ce^{3+} ions and then it reached a maximum at ca. 1 mol% of CeF_3. This effect is ascribed to the well-known "concentration quench-ing effect".

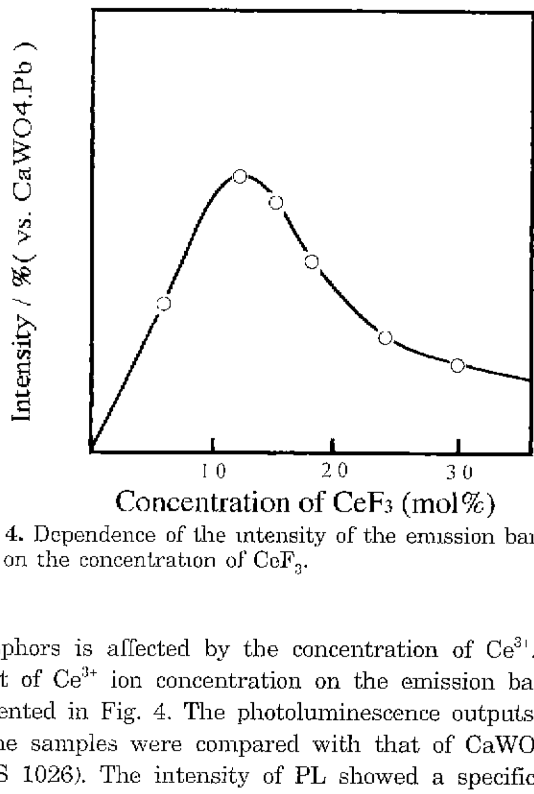

Fig. 4. Dependence of the intensity of the emission band for Ce^{3+} on the concentration of CeF_3.

Thus, because the peak position of the Ce^{3+} emission band for $56ZrF_4 \cdot 34BaF_2 \cdot 4AlF_3 \cdot (6\text{-}x)LaF_3 \cdot xCeF_3$ was located at a lower wavelength and the quenching effect of the emission intensity was observed at lower Ce^{3+} concentration, the rare earth ions in $56ZrF_4 \cdot 34BaF_2 \cdot 4AlF_3 \cdot (6\text{-}x)LaF_3 \cdot xLnF_3$ are considered to be located at "interstitial

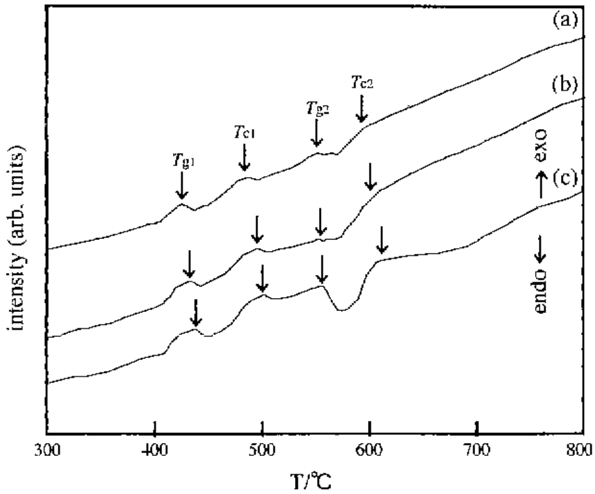

Fig. 5. DTA curves of $56ZrF_4 \cdot 34BaF_2 \cdot 4AlF_3 \cdot 4LaF_3 \cdot 2CeF_3$ glass recorded at heating rates of (a) 20, (b) 25 and (c) 30 K/min.

sites" which a surrounded by ZrF_6 octa field, as will be described later.

3. Crystallization energy

The short-range structure of ZrF_4-based fluoride glasses doped with rare erath ions was discussed with the values of activation energy (E_a) of crystallization. A Kissinger plot in the differential thermal analysis (DTA) is generally used for estimating the E_a of crystallization. The Kissinger equation[5] is expressed by

$$\ln(T_c^2/\alpha)E_a/RT_c + \text{const} \quad (1)$$

in which T_c, α and R are the crystallization peak temperature (in K), heating rate of the sample, and the gas constant, respectively. DTA measurements were carried out for the Ce^{3+}-and Nd^{3+}-doped fluoride glasses. Fig. 5 shows a DTA curve of $56ZrF_4 \cdot 34BaF_2 \cdot 4AlF_3 \cdot (6\text{-}x)LaF_3 \cdot xNdF_3$ glass recorded at heating rates of 20, 25 and 30 K. This fluoride glass had two crystallization temperatures.

And the peak temperatures of the crystallization increased with an elevating of the heating rates. Two crystallization temperatures were observed for $56ZrF_4 \cdot 34 BaF_2 \cdot 4AlF_3 \cdot (6\text{-}x)LaF_3 \cdot xNdF_3$ glasses. The slope of the straight line in the Kissinger plot of $56ZrF_4 \cdot 34BaF_2 \cdot 4AlF_3 \cdot (6\text{-}x)LaF_3 \cdot xCeF_3$ (Fig. 6) yielded the E_a values of 1.4 and 4.0 eV for the glass with x=2, and 1.6 and 4.8 eV for the glass with x=3. A Kissinger plot for $56ZrF_4 \cdot 34BaF_2 \cdot 4AlF_3 \cdot (6\text{-}x)LaF_3 \cdot xNdF_3$ is shown in Fig. 7 for comparison, which yielded E_a values of 1.7 and 5.0 eV for the glass with x=2, and 1.9 and 5.6 eV for the glass with x=4.

If a rare earth ion is cross-liked to a F^- ion coordinating to a Zr^{4+} ion in layer structure of composed of zigzag chains of ZrF_6 units, the average binding energy is estimated as follows; 1/8 ($\Delta H_{Nd-F}+\Delta H_{Zr-F}$)=4.7 and 1/8 ($\Delta H_{Ce-F}+\Delta H_{Zr-F}$)=4.7 eV.

Since 4~5 eV of the activation energy of crystallization was ranged in this average binding energy, it was considered that cleavage Ln-F and Zr-F bonds triggered the crystallization.

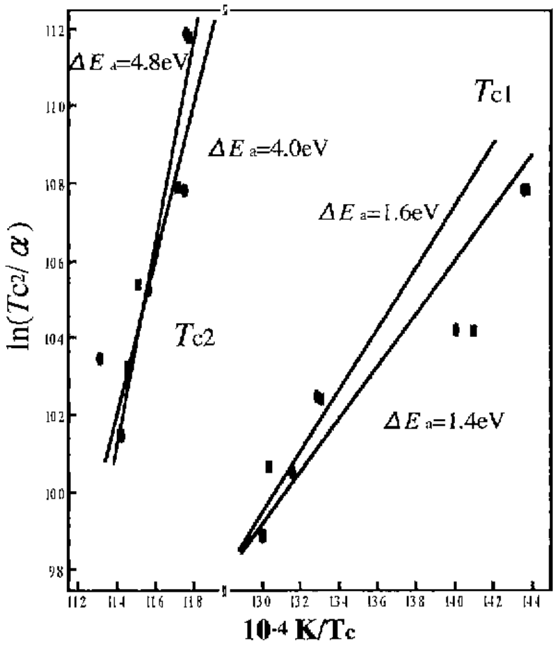

Fig. 6. Kissinger plot for (●)$56ZrF_4 \cdot 34BaF_2 \cdot 4AlF_3 \cdot 4LaF_3 \cdot 2CeF$ and (■)$56ZrF_4 \cdot 34BaF_2 \cdot 4AlF_3 \cdot 3LaF_3 \cdot 3CeF_3$ glasses.

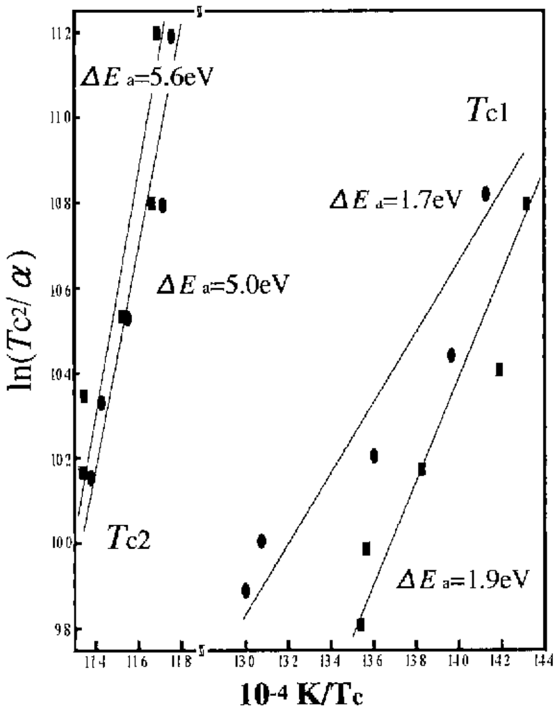

Fig. 7. Kissinger plot for (●)$56ZrF_4 \cdot 34BaF_2 \cdot 4AlF_3 \cdot 4LaF_3 \cdot 2NdF$ and (■)$56ZrF_4 \cdot 34BaF_2 \cdot 4AlF_3 \cdot 2LaF_3 \cdot 4NdF_3$ glasses.

IV. Summary

We have studied some physicochemical properties of rare earth doped ZrF_4-based fluoride glasses. From $Qp = 4\pi\sin\theta_p/\lambda$($\theta_p$: a 1/2 of halo peak angle in the XRD $56ZF_4 \cdot 34BarF_2 \cdot 4AlF_3 \cdot (6\text{-}x)LaF_3 \cdot xLnF_3$ glasses (Ln=Ce, Nd, Gd, Tb), λ: wavelength of the radiation used), it was found that the θ_p values varied almost linearly with the concentration of LnF_3. In the photoluminescence of Ce^{3+} containing fluoride glasses, the wavelength of emission peak was smaller than that of normal phosphors and the concentration quenching effect was observed at extreme low concentration of CeF_3. 2~5 eV of the activation energy of crystallization obtained from a Kissinger plot was ranged in the average binding energy which was due to the bridged rare earth ion.

Reference

1. Mi. Poulain, Ma. Poulain and J. Lucas, "Verres fluores au tetrafluorure de zirconium proprietes optiques d'un verre dope au Nd^{3+}," *Mater. Res. Bull.*, **10**, 243-246 (1975).
2. D. Leroy, J. Luca, Ma. Poulain and D. Ravaine, "Etude de la conduction la conduction ionique de verres a base de ZrF_4," *Mater. Re Bull*, **13**, 1125-1133 (1978).
3. R. M. Almeida and J. D. Mackenzie, "Vibrational spectra and structure of fluorozirconate glasses," *J. Chem. Phys.*, **74**(11), 5954-5961 (1981).
4. G. Blasse and A. Bril, "Study of energy trnasfer from Sb^{3+}, Bi^{3-}, Ce^{3+}, to Sm3+, Eu^{3+}, Tb^{3+}, Dy^{3+}", *J. Chem. Phys.*, **47**(6), 1920-1926 (1967).
5. H. E. Kissinger, "Reaction kinetics in differential thermal analysis," *Anal. Chem.*, **29**(11), 1702-1706 (1957).