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CRYSTALLIZATION OF $3Ln_2O_3 \cdot 5Ga_2O_3$ GLASSES

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The oxide glasses of $3Ln_2O_3 \cdot 5Ga_2O_3$ were prepared, using Pr, Nd, Sm, Eu or Gd as a lanthanoid element. Crystallization of the glasses was studied by DTA and X-ray diffraction. A metastable phase was found on the way of the crystallization process of $3Pr_2O_3 \cdot 5Ga_2O_3$ and $3Nd_2O_3 \cdot 5Ga_2O_3$ glasses terminating in the transition into garnet. However, the phase transition transforming the amorphous phase directly into garnet not through a metastable phase was observed in case of $3Ln_2O_3 \cdot 5Ga_2O_3$ glasses (Ln=Sm, Eu or Gd).

Some glasses based on lanthanoid oxides have been previously found in the Ln-Al-O$^{1-2)}$ and La-Nb-O$^{3)}$ systems (with Ln=a lanthanoid element). The present investigation has been carried out in order to obtain the glassy state of $3Ln_2O_3 \cdot 5Ga_2O_3$, lanthanoid-gallium garnet composition, by the same method as that published in the previous paper$^{1)}$ and to examine the transformation from the amorphous to the crystalline phase by DTA and X-ray diffraction.

A batch was prepared with molar ratio Ln_2O_3:Ga_2O_3=3:5, using the pure oxides (99.9%). Glasses were obtained by an impact quenching apparatus. A detailed description about the glass preparation and the experimental techniques has been given in this journal previously published.$^{1-3)}$ When Pr, Nd, Sm, Eu or Gd was used as a Ln, a completely glassy state was obtained from the melt with the composition corresponding to $3Ln_2O_3 \cdot 5Ga_2O_3$. When La, Tb, Dy, Er, Tm, Yb or Lu was used, however, the resulted substance was put out of discussion because a considerable amount of crystalline phase was included in it. Devitrification of the glass was examined by DTA. Powdered sample (10 mg) in a platinum cell was heated or cooled at 10°C/min. in the range of a room temperature to 1200°C in argon atmosphere. The DTA curves in process of heating and cooling are shown in Fig. 1; in which exothermic peaks due to crystallization are observed. The curves obtained by cooling those glasses show there was no reaction.

For $3Pr_2O_3 \cdot 5Ga_2O_3$ glass, two distinct exothermic peaks are shown at 771°C and 900°C, respectively. The sample was heated for one hour at 800°C above the first peak (771°C), and cooled down to a room temperature. X-ray diffraction pattern of the sample was taken with CuKα-radiation at a room temperature. The results are shown in Table 1. The existence of a new phase having a tetragonal cell is indicated; of which the lattice constants are a=12.99±0.01Å, c=4.000±0.006Å and a/c=3.25. However, when heated for one hour at 1200°C, the X-ray diffraction pattern of the cooled sample showed the presence of the compound, $3Pr_2O_3 \cdot 5Ga_2O_3$ (garnet phase).

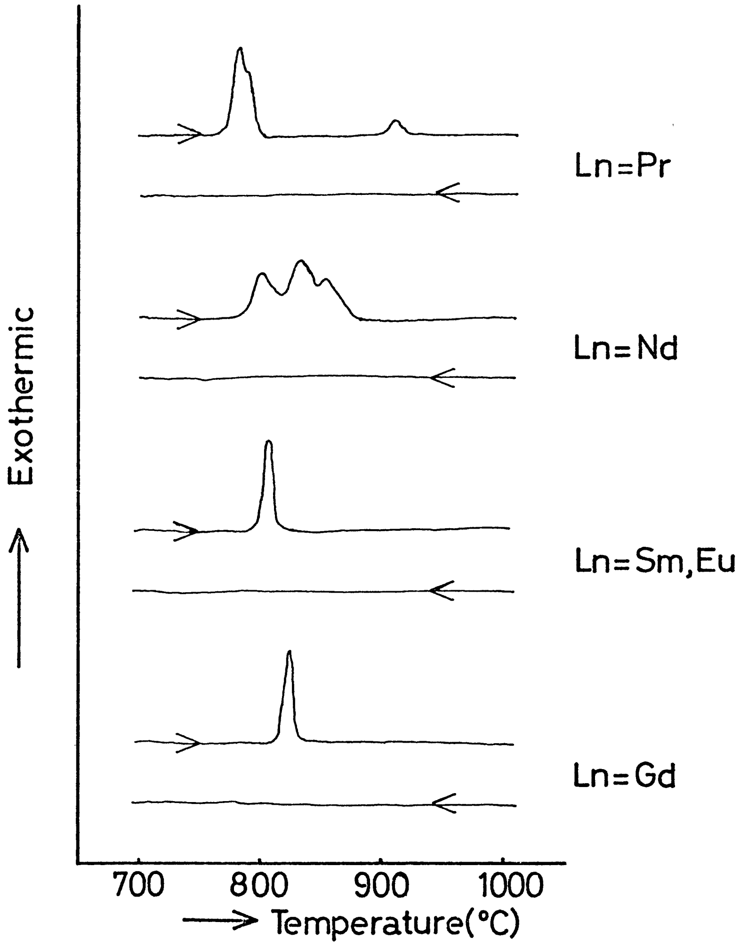

Fig.1. DTA curves of the $3Ln_2O_3 \cdot 5Ga_2O_3$ glass during heating and cooling.

Table 1.
Results of the X-ray diffraction analysis of the $3Pr_2O_3 \cdot 5Ga_2O_3$ glass after heating at 800°C for one hour.

h k l	$d_{cal.}$ (Å)	$d_{obs.}$ (Å)	$I_{obs.}$
1 0 1	3.818	3.823	vw
4 1 0	3.151	3.150	w
3 0 1	2.938	2.940	vs
4 2 0	2.907	2.912	vs
4 3 0	2.598	2.589	w
4 0 1	2.521	2.522	w
0 0 2	2.000	1.993	vw
7 0 0	1.856	1.855	vw
4 6 0	1.801	1.803	vw
2 5 2	1.540	1.548	m

Hence it is considered that these two kinds of phases exist not only at a room temperature but also at 800°C and 1200°C, respectively, because no peak or dip in the DTA curve was observed on cooling. The first and the second exothermic peaks are attributed to crystallization of the new phase as a metastable state and to appearence of the garnet phase, respectively.

For $3Nd_2O_3 \cdot 5Ga_2O_3$ glass, somewhat overlapping three exothermic peaks were observed. The initial crystallization temperature was 789°C. No diffraction peak was obtained for the sample cooled after heating up to 800°C, that is, a temperature between the first (789°C) and the second peak (825°C). The diffraction pattern of the sample cooled after heating up to 835°C somewhat higher than that of the second peak showed the existence of a mixture of a new phase having a tetragonal cell and the stable phase of $3Nd_2O_3 \cdot 5Ga_2O_3$. The crystalline phase formed after heating for one hour at 1200°C and followed by cooling was identified to be a garnet alone. The former is considered to be the metastable phase the same as that in case of $3Pr_2O_3 \cdot 5Ga_2O_3$ glass. Though the cause of overlapping of three exothermic peaks has not been elucidated, these peaks may be attributed to crystallization leading to formation of the new metastable phase and $3Nd_2O_3 \cdot 5Ga_2O_3$ garnet.

For $3Sm_2O_3 \cdot 5Ga_2O_3$, $3Eu_2O_3 \cdot 5Ga_2O_3$ and $3Gd_2O_3 \cdot 5Ga_2O_3$, their exothermic peaks are found at 801°C, 801°C and 810°C, respectively. These peaks are attributed to crystallization leading to formation of the garnet phase.

Table 2 gives the thermochemical properties regarding the crystallization of $3Ln_2O_3 \cdot 5Ga_2O_3$ glasses prepared by making use of Pr, Nd, Sm, Eu or Gd as a Ln.

Table 2

Thermochemical properties of the $3Ln_2O_3 \cdot 5Ga_2O_3$ glasses.

Glass	Initial Crystallization, T_C °C	Heat of Crystallization, ΔH_C Kcal/mol
$Pr_3Ga_5O_{12}$	771	41.5 (2.04)
$Nd_3Ga_5O_{12}$	789	— —
$Sm_3Ga_5O_{12}$	801	61.0 (3.05)
$Eu_3Ga_5O_{12}$	801	68.0 (3.40)
$Gd_3Ga_5O_{12}$	810	60.5 (3.02)

The values in parentheses inserted in the right-end column of the table are heat of crystallization calculated for $Ln_{3/20}Ga_{5/20}O_{12/20}$. Crystallization temperature increases to some extent with increasing atomic number of lanthanoid. The heat of crystallization, ΔHc, was determined from the exothermic peak area, which, according to Speil et al[4)] and Kerr,[5)] is equal to $(\Delta Hc \cdot M)/(g \cdot \lambda)$; M is the mass of the reactive sample, λ is the thermal conductivity of sample and g is a constant dependent on the furnace and sample-holder geometry. The constants, λ and g, were obtained making use of the thermal reactions of the known compounds, i.e., $BaCO_3$, $SrCO_3$, Na_2MnO_4 and Na_2SO_4.

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