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GLASS FORMATION IN THE Ln-Al-O SYSTEM (Ln : LANTHANOID AND YTTRIUM ELEMENTS)

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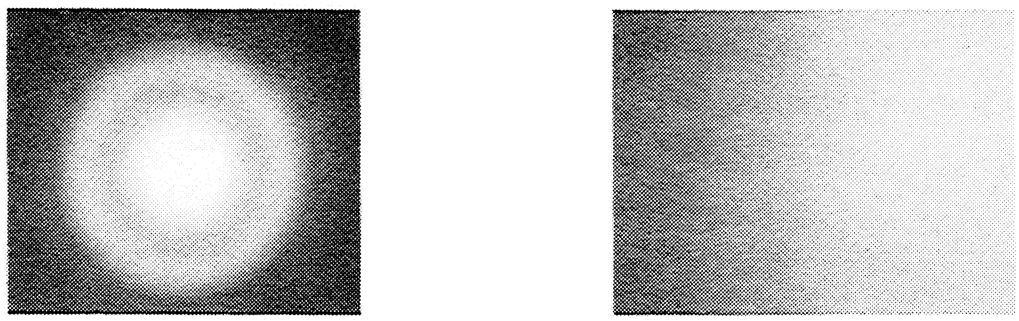
Oxide glasses in the Ln-Al-O system were prepared with the molar ratio of $Ln_2O_3:Al_2O_3$ of 10:1 to 1:10 for all the lanthanoids and yttrium by an impact quenching technique. Each quenched material was examined by polarizing microscope, X-ray diffraction and electron diffraction. The electron diffraction patterns show diffuse halos characteristic of an amorphous state.

Impact quenching apparatus was made to obtain glassy state of the Nd-Al-O system which is usually very difficult to obtain; this was reported previously[1]. Macroscopic measurement of the Nd-Al-O glass was made by polarizing microscope and X-ray diffraction techniques.

In the present experiment, attempts were made to obtain glassy state of the Ln-Al-O system in addition to the case of Ln=Nd, using the same apparatus.

Purities of the lanthanoid, yttrium and aluminium oxide (α-Al_2O_3) used are over 99.9%. The powders (325 mesh under) of Ln_2O_3[2] and Al_2O_3 were weighed in the nineteen different molar ratios of $Ln_2O_3:Al_2O_3$ of 1:x (and 1/x) where x is an integer ranging from 1 to 10, and mixed well by mortar grinding. The mixed powder was formed into a pellet, 5 mm in diameter and 1 mm in thickness, by pressing at 4 ton/cm^2. The pellet was then sintered at 1000°C for five hours in air. The sintered pellet was melted by arc plasma flame and quenched by impact quenching.

The specimens obtained were about 5 mm in diameter and about 1μ in thickness, and they were so transparent for visible light that they could be observed by polarizing transmission-microscope. Further, observations by X-ray diffraction, electron diffraction and microscope were carried out. No birefringence was exhibited under crossed Nicols in observation by polarizing transmission-microscope. Thus they revealed themselves to be of glassy state macroscopically. The specimens were examined with a JEM-200A type electron microscope. The electron diffraction patterns show diffuse halos characteristic of an amorphous state. As a typical example, $La_2O_3 \cdot 6Al_2O_3$ is shown in Fig. 1 (a). Line profiles of the diffraction patterns are given in Fig. 2, for $La_2O_3 \cdot 6Al_2O_3$, $Gd_2O_3 \cdot 6Al_2O_3$ and $Lu_2O_3 \cdot 6Al_2O_3$. Photometry of the line profiles was made by a self-balanced type densitometer. The diffraction rings of gold were used as standard of the s-values ($s=4\pi\sin\theta/\lambda$, where 2θ is the scattering angle and λ is the wavelength of electrons). Profiles of the halo patterns are the same for all the lanthanoids. However, s-values of peaks of the halo patterns shift somewhat to the higher angles as the lanthanoid in Ln-Al-O system turns from light to heavy element. This shift in line profiles indicates lanthanoid contraction. In X-ray diffraction, the halo patterns and also the lanthanoid contraction were observed.



(a) (b)
(62500 times magnification)

Fig. 1 Halo patterns (a) and Bright field photo-micrograph (b) of $La_2O_3 \cdot 6Al_2O_3$ glass taken by transmission electron microscope operating at 150KV.

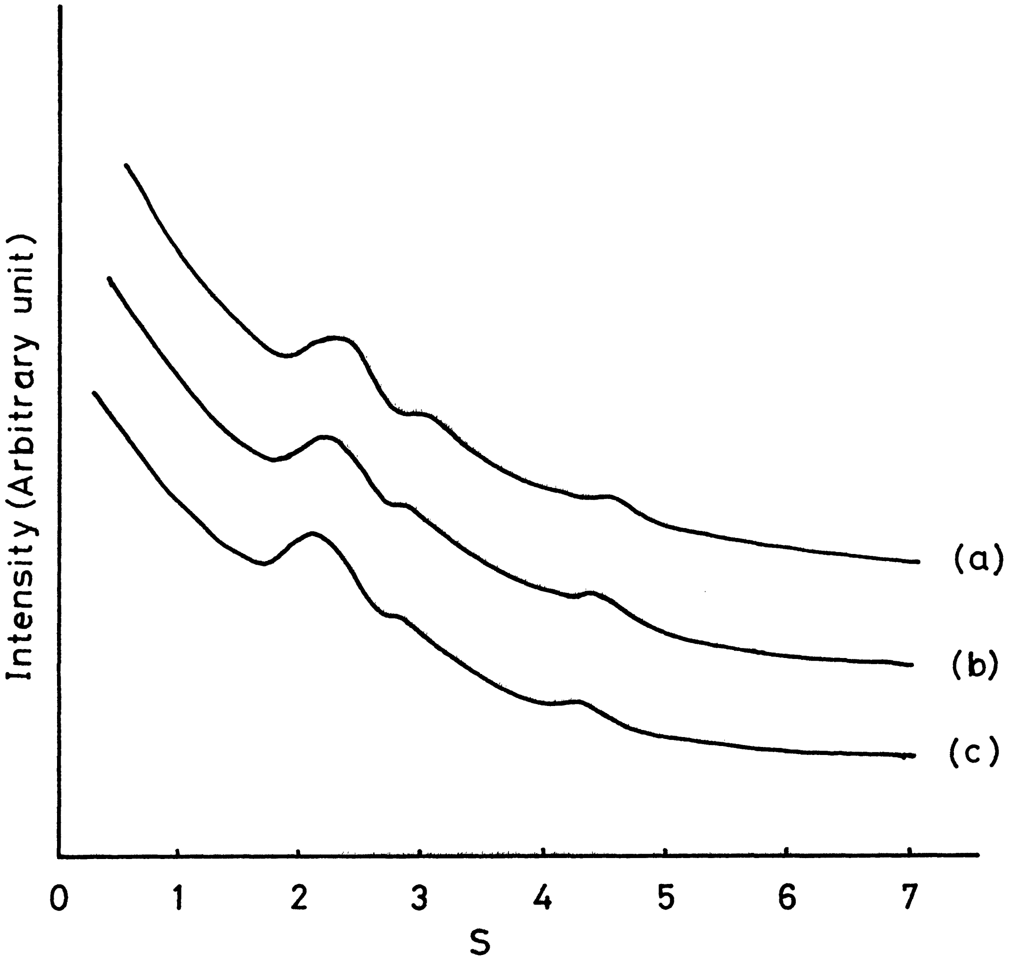


Fig. 2 Line profiles of electron diffraction patterns for $La_2O_3 \cdot 6Al_2O_3$(c), $Gd_2O_3 \cdot 6Al_2O_3$(b) and $Lu_2O_3 \cdot 6Al_2O_3$(a).

Transmission electron photomicrographs of the specimens were obtained; the photograph of $La_2O_3 \cdot 6Al_2O_3$ as a typical example is shown in Fig. 1 (b). No inclusion nor grain boundary is seen in the photograph. The specimens of Ln-Al-O system were found to be glass microscopically. Glassy state was obtained in the Ln-Al-O system with all the lanthanoids and yttrium in the whole range of x. It is, however, the most easily attained at the molar ratio of $Ln_2O_3:Al_2O_3=1:6$. The glassy specimens ($Ln_2O_3 \cdot 6Al_2O_3$) are shown in Table 1 with their original colors and those developing after heat treatment at 1200°C for ten hours in air, and also the phases appearing after the same heat treatment.

Table 1. Glasses of the Ln-Al-O System

Ln-Al-O	Color	Color after Heat Treatment	Phases after Heat Treatment
La-Al-O	colorless	opal	P + α
Ce-Al-O	colorless	opaque, pale brown	CeO_2 + α
Pr-Al-O	pale green	opaque, pale green	↑
Nd-Al-O	pale blue	opaque, pale blue	│
Sm-Al-O	pale brown	opal	P + α
Eu-Al-O	straw yellow	opal	│
Gd-Al-O	colorless	opal	↓
Tb-Al-O	colorless	opal	↑
Dy-Al-O	colorless	opal	│
Ho-Al-O	colorless	opal	│
Er-Al-O	pale pink	opaque, pale pink	│
Tm-Al-O	colorless	opal	G + α
Yb-Al-O	pale orange	opal	│
Lu-Al-O	colorless	opal	│
Y-Al-O	colorless	opal	↓

Crystallization of the glass specimens ($Ln_2O_3 \cdot 6Al_2O_3$) was observed preliminarily by differential thermal analysis. The observed crystallization temperature was about 900°C. Hence the specimens were treated for various times at 1200°C and then they were observed by X-ray diffraction. By heat treatment for ten hours, the broad diffraction pattern changed into that with many peaks, in La-Al-O and Pr-Al-O to Gd-Al-O systems, indicating the existence of a mixture of $LnAlO_3$ (p) and α-Al_2O_3 (α), as Table 1. Ce-Al-O glass changed into a mixture of CeO_2 and α-Al_2O_3. In Tb-Al-O to Lu-Al-O and Y-Al-O systems, on the other hand, the glassy material changed into a mixture of $3Ln_2O_3 \cdot 5Al_2O_3$ (G) and α-Al_2O_3. All the specimens after the heat treatment were opaque for visible light. By the heat treatment, the specimens changed their colors, i.e. from colorless to pale brown for Ce-Al-O glass, from pale brown to opal for Sm-Al-O glass, from straw yellow to opal for Eu-Al-O glass and from pale orange to opal for Yb-Al-O glass.

References

1) S. Yajima, K. Okamura, and T. Shishido, Chem. Letters, 7, 741 (1973).

2) CeO_2, Pr_6O_{11} and Tb_4O_7 were used in the case of Ln=Ce, Pr and Tb, respectively.

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