CHEMISTRY LETTERS, pp. 221-222, 1974. Published by the Chemical Society of Japan

CRYSTALLIZATION OF AN AMORPHOUS OXIDE IN La-Nb-O SYSTEM

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An amorphous oxide of which composition corresponds to $La_2O_3 \cdot 5Nb_2O_5$ was prepared by making use of an impact quenching technique. The phase transformation from an amorphous to an equilibrium crystalline state was studied by means of differential thermal analysis (DTA) and X-ray diffraction. From the experimental results, the crystallization process was characterized mainly by the two successive transitions, i.e., glassy phase → a new metastable phase → stable phase of $La_2O_3 \cdot 5Nb_2O_5$.

It was previously reported[1-2] that a glassy state was obtained in the Ln-Al-O system by making use of an impact quenching apparatus.

The purpose of the present study is to obtain the glassy state in the La-Nb-O system using the same apparatus and to examine the crystallization of the glass.

An oxide mixture was prepared from La_2O_3 (99.9%) and Nb_2O_5 (99.9%) powders. The powders, which were weighed in the molar ratio of La_2O_3:Nb_2O_5=1:5, were thoroughly mixed and formed into pellets of 5mm in diameter and 1mm in thickness at a pressure of 4 ton/cm^2. The molar ratio corresponds to the lowest eutectic temperature in the La_2O_3-Nb_2O_5 system[3].

The pellets were sintered at 1000°C for five hours in air. The sintered pellets were melted by an arc plasma flame and quenched by impact quenching. The specimens were obtained in a form of thin film, 1μ in thickness and 5mm in diameter. The samples were examined by polarizing transmission-microscope and X-ray diffraction at room temperature. They were confirmed to be in vitreous state. The crystallization process of the glass, devitrification, was examined by differential thermal analysis. The glassy sample (10 mg) was pulverized and subsequently submitted to DTA (micro Rigaku Denki equipment). Alumina powder was used as an inert reference material. The powdered sample placed into a platinum cell was heated or cooled at 10°C/min. in the range of room temperature to 1200°C in both of air and argon atmosphere. DTA data for the glass are given in Fig. 1, which shows there are three exothermic peaks during heating. Those peaks were observed at 714°C, 771°C and 922°C, resulting from crystallization of the glass. On cooling from any temperature, no peak or dip was observed. The results obtained in air and argon atmosphere were almost identical.

In the first place, the powdered sample was heated for an hour at 728°C somewhat higher than the temperature of the first peak (714°C), and was cooled down to room temperature. The X-ray diffraction pattern of the sample was taken by X-ray powder

diffractometer with CuKα radiation at room temperature. The result shown in Table 1 indicates the presence of a new phase with a hexagonal cell of which lattice constants are a=7.400Å and c=4.240Å. The X-ray diffraction pattern of the sample cooled after heating for an hour at 825°C shows the existence of a mixture of the new phase and the stable phase, $La_2O_3 \cdot 5Nb_2O_5$[4], with an orthorhombic structure. The phase of the sample cooled after heating for an hour at 1150°C can be identified as $La_2O_3 \cdot 5Nb_2O_5$ only. Each of the above-mentioned crystalline phases is to be virtually in existence at the respective temperature (728°C, 825°C and 1150°C), because no peaks or dips in the DTA-curve were observed on cooling. The first, the second and the third exothermic peak, respectively, are due to the crystallization of the new phase, the appearence of $La_2O_3 \cdot 5Nb_2O_5$, and the complete transition of the new phase to $La_2O_3 \cdot 5Nb_2O_5$. Hence, the new phase is considered to be a metastable phase of the system.

Further experiments to obtain the glassy state were carried out over a wide range of compositions in the La_2O_3-Nb_2O_5 system and the glassy state was obtained in the range of the molar ratios of La_2O_3:Nb_2O_5=1:1 to 1:7. The details will be reported elsewhere.

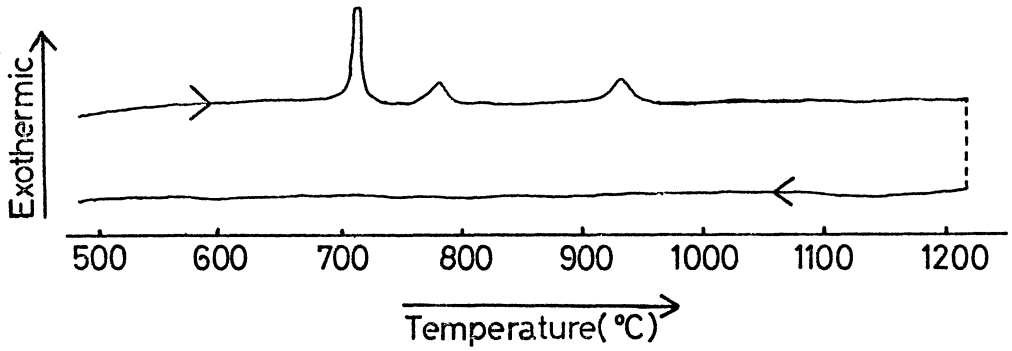

Fig. 1 DTA curve of the $La_2O_3 \cdot 5Nb_2O_5$ glass during heating and cooling.

Table 1. Results of X-ray diffraction analysis of the sample after heating at 728°C for an hour.

hkl	$d_{obs.}$ (Å)	$d_{cal.}$ (Å)	I/I_1
110	3.705	3.700	60
200	3.195	3.204	100
111	2.777	2.788	20
002	2.120	2.120	20
220	1.850	1.850	50
400	1.601	1.602	30
320	1.470	1.470	20
420	1.212	1.211	20

Acknowledgement: The authors are indebted deeply to Dr. H. Takei for his valuable discussion.

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(Received December 7, 1973)