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Glass formation in the MoO_3-La_2O_3-Nd_2O_3 system

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Abstract. Novel low melting glasses in the MoO_3-La_2O_3-Nd_2O_3 system were obtained at different cooling rates (10^2 K/s and 10^4-10^5 K/s). Characterization of the amorphous samples was made by differential thermal analysis (DTA) and X-ray absorption fine structure (XAFS) method. According to DTA data of the glass samples, the glass transition temperatures are at 325-330 ^{0}C, the crystallization started above 410 ^{0}C and the melting temperatures are at 660-720 ^{0}C. A structural model of glasses was suggested on the basis of XAFS and IR investigations. It was shown that the predominant structural units in the amorphous network of glasses containing 90 -80 mol% MoO_3 are MoO_6 groups. The appearance of MoO_4 groups deteriorates the glass formation ability.

Introduction

The molybdate glasses are part of so-called non-traditional oxide glasses. MoO_3 as a conditional network former is not able to form glass itself at slow cooling rates. Many binary and more complex molybdate glasses can be obtained by introducing modifiers or other glass network formers. A survey on the results obtained by many authors was published elsewhere [1]. Rare earth molybdenum-oxide glasses have been obtained recently [1,2]. The glass regions are situated near the MoO_3 corner up to 25 mol% Ln_2O_3. It has been found by IR spectroscopy that MoO_6 units are main polyhedra building the amorphous network. More information is necessary to be collected to verify this statement. The purpose of the study is to determine the parameters of the short range order of the glasses in the MoO_3-La_2O_3-Nd_2O_3 system using X-ray absorption fine structure (XAFS) method. As was claimed by Purans et al. [3], XAFS method provides complimentary to XRD information on the short-range lattice distortion of MoO_3.

Experimental

Representative glasses with nominal compositions $90MoO_3.10La_2O_3$, $90MoO_3.10Nd_2O_3$ and $80MoO_3.10La_2O_3.10Nd_2O_3$ were chosen. All batches (10 g.) were prepared using reagent grade MoO_3 (Merck, p.a), La_2O_3 (Fluka, puriss) and Nd_2O_3 (Fluka, puriss) as starting materials. The batches were melted for 20 min. in air atmosphere in platinum crucibles at 1000 ^{0}C. Binary glasses were obtained by pouring of the melts on a copper plate (cooling rate 10^2 K/s) ternary glasses were obtained at high cooling rates 10^4-10^5 K/s using a roller quenching technique. The thermal stability of glasses was examined by differential thermal analysis (DTA Stanton Redcroft) at a heating rate of 10 K/min. The XAFS measurements were made at two beamline at Synchrotron Radiation

Center of Ritsumeikan University. Mo K-edge XAS measurements were done at BL-10B, by transmission mode. The double crystals monochromator with Si(311) crystals were used for monochromatic X-ray. La and Nd L_{III}-edge XAS measurements were done by transmission mode at BL-4 (monochromatic spectroscopy beamline). The double crystals monochromator with Ge (220) crystals were used for monochromatic X-ray. The EXAFS oscillation was extracted from the absorption spectrum using the standard procedure [4,5]. Radial structural functions (RSF) were obtained by Fourier transformation of the extracted EXAFS oscillations.

3. Results and Discussion

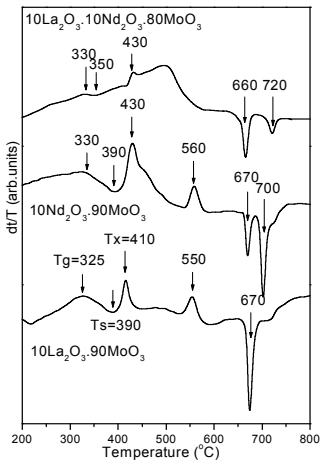

Fig. 1. DTA curves of glasses

DTA curves of the glasses are shown in Fig. 1. The glass transition temperatures, T_g, are at 325-330±5 ^{0}C. There are two exothermic effects at 410-430±5 ^{0}C and 550-560±5 ^{0}C as a result of crystallization of two phases during the heating: orthorhombic-MoO_3 (JCPDS 35-0609) and $Ln_2Mo_4O_{15}$ (JCPDS 23-1146). The strong endothermic effect at 670^{0}C of $90MoO_3.10La_2O_3$ glass corresponds to the eutectic temperature pointed in the phase diagram of the binary system [6]. For the other compositions two endothermic effects are observed that correspond to the solidus (660-670^{0}C) and liquidus (700-720^{0}C) temperature. Low temperature MoO_3-La_2O_3-B_2O_3 glasses with similar MoO_3 content crystallized in the same temperature region but increasing of B_2O_3 instead of MoO_3 shifts the crystallization temperature up to 800 ^{0}C [7].

In figures 2-10 are shown the Mo K-edge, La L_{III}-edge and Nd L_{III}-edge spectra (XAFS spectra, EXAFS oscillation spectra and radial structure functions RSF) for all glasses. Structural parameters obtained from curve-fitting procedure are listed in Tables 1, 2. The average Mo-O distance in the first coordination shell is at 1.75 Å in all investigated glasses. The coordination number against the oxygen varies between 6 and 5 depending on the composition. The La-O distance is in the range 2.47 Å and 2.55 Å. The average coordination number of La is 7. The distances Nd-O are longer, 2.73 Å, and the coordination number is near 7. The XAS investigation of orthorhombic MoO_3 has been performed by Ressler et al. [8]. On the Fourier transform function peaks below 2.0 Å were assigned to Mo-O coordination shells, while peaks that correspond to Mo-Mo scattering paths via MoO_6 octahedron edges and corners are above 2.6 Å. For the perfect edge shared MoO_6 with Mo-O distances of 1.94 Å Mo-Mo distances should be at 2.74 Å which is close to the Mo-Mo distances in the metal molybdenum [9]. In the presented spectra (Fig. 4) Mo-Mo distances in the Mo-foil and crystalline $CaMoO_4$ are well resolved. In the F.T. spectra of the glasses these regions are not well resolved that may be connected with the increasing of the disorder in the second coordination shell (middle range order). It is seen that the peaks between 1.6-2.0 Å in the glass spectra are not sharp that is an indication for the distortion of the polyhedra in the glass network.

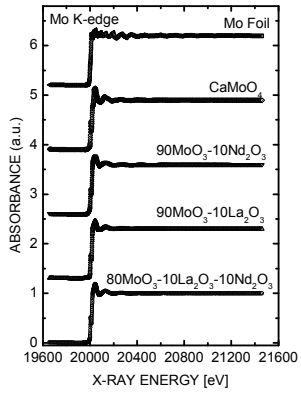

Fig. 2. Mo K-edge XAFS Spectra

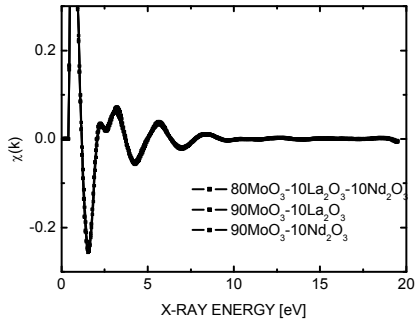

Fig. 3. EXAFS Oscillation Spectra

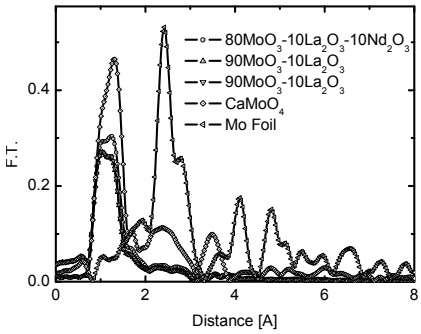

Fig. 4. Radial Structure Function

According our previous IR spectral data the glass network of the same glasses is build up mainly of MoO_6 octahedra (strong band at 880 cm^{-1}) [1,2]. Partial $MoO_6 \rightarrow MoO_4$ transformation (weak band at 720 cm^{-1}) is observed. The calculated coordination number of Mo between 5 and 6 (Table 1) we interpret with the presence of distorted MoO_6 octahedra and small amounts of MoO_4 tetrahedra. Our hypothesis is that Ln ions break some Mo-O-Mo bridges and Mo_{short}-O-$_{long}$Ln bonds are formed (Ln-O = 2.47–2.73 Å). This process actually leads to the formation of weak bonded MoO_4 tetrahedra.

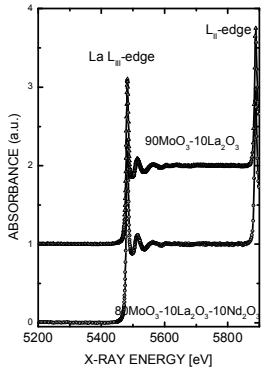

Fig. 5. La L_{III}-edge XAFS Spectra

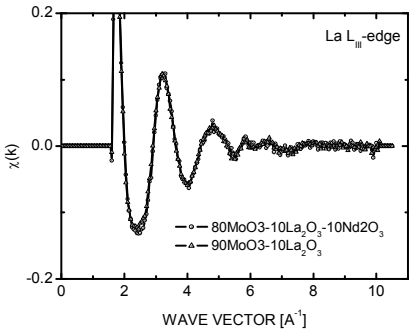

Fig. 6. EXAFS Oscillation Spectra

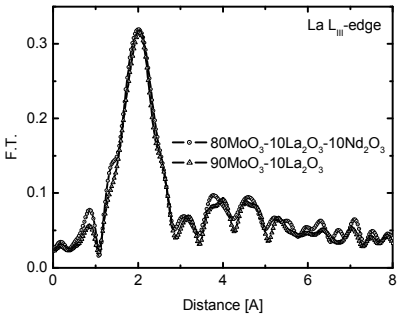

Fig. 7. Radial Structure Function

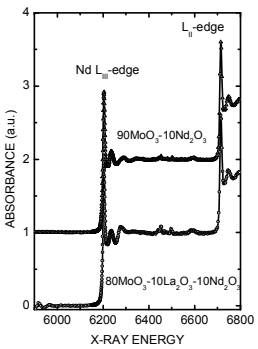

Fig.8. Nd L_{III}-edge XAFS Spectra

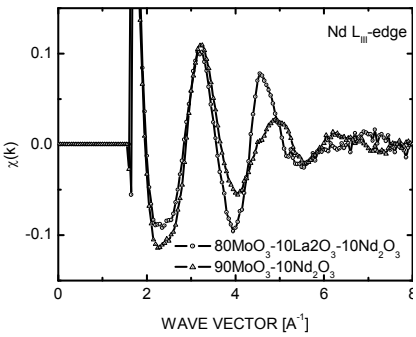

Fig.9. EXAFS Oscillation Spectra

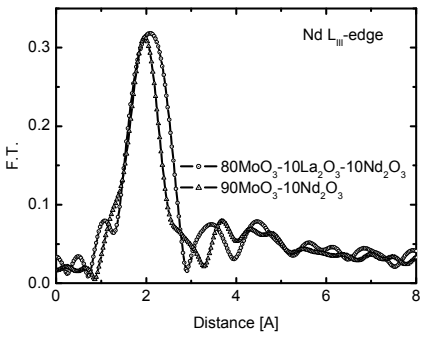

Fig.10. Radial Structure Function

Table 1. Structural parameters obtained from curve-fitting procedure

Sample (mol. %)	**Coordination number**	**Mo-O distance**	D-W Factor
90MoO3.10La2O3	5.0 (4)	1.75 (3)	0.056
80MoO3.10La2O3.10Nd2O3	5.8 (8)	1.76 (6)	0.063
90MoO3.10Nd2O3	5.2 (2)	1.75 (5)	0.060
CaMoO4	4.0 (0)	1.79 (7)	0.044

Table 2. Structural parameters obtained from curve-fitting procedure

Sample (mol. %)	**Coordination number**	**La-O distance**	**Nd-O distance**	**D-W Factor**
90MoO3.10La2O3	6.8 (7)	2.55 (9)		0.061
80MoO3.10La2O3.10Nd2O3	6.9 (3)	2.47 (3)		0.048
90MoO3.10Nd2O3	7.2 (14.0)		2.51 (5)	0.039
80MoO3.10La2O3.10Nd2O3	7(13.8)		2.73 (7)	0.040

Conclusion

The obtained glasses are low melting and thermally stable up to 400 ^{0}C. The average coordination number of Mo against the oxygen varies between 6 and 5 depending on the composition. The present study confirms our previous suggestion [1,2,10] that the amorphous network of non-traditional molybdate glasses does not satisfy one of the Zachariazen's criteria for favourable role of the polyhedra with low (4) coordination number to stabilize the glass network.

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