GLASS FORMATION IN THE MoO$_3$-Nd$_2$O$_3$-Me$_x$O$_m$ SYSTEM, (Me=Ba, Bi) OF NON-FIRED REFRACTORIES

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ABSTRACT

Novel low melting glasses in the MoO$_3$-Nd$_2$O$_3$-Me$_x$O$_m$ Me=Ba, Bi systems were obtained at slow (10$^5$-10$^7$ K s$^{-1}$) and high cooling rates (10$^8$-10$^9$ K s$^{-1}$). The amorphous state of the samples was proved by X-ray diffraction. Comparative analysis of infrared spectra of obtained glasses and other available data was carried out. The structure of glasses with a high MoO$_3$ content was found to consist of corner shared MoO$_3$ units. The introduction of Nd$_2$O$_3$ and Me$_x$O$_m$ (Me = Mg, Bi) led to partial transformation of MoO$_3$ to MoO$_2$ units, as a result of which the number of bridging bonds was decreased and the glass forming ability was deteriorated.

Keywords: Glass formation, non-traditional glasses, infrared spectroscopy.

INTRODUCTION

MoO$_3$ is well-known as a conditional network former and it is not able to form a glass itself at slow cooling rates. The main problems of the preparation of glasses without participation of classical network formers are related to the high crystallization tendency of the components. Many binary and more complex molybdate glasses can be obtained by introducing modifiers or other glass network formers [1-4]. The aim of this investigation was to obtain new molybdate glasses containing the rare earth oxide Nd$_2$O$_3$ and to make conclusions on the glass structure.

EXPERIMENTAL

All batches were prepared using reagent grade MoO$_3$, Nd$_2$O$_3$, Bi$_2$O$_3$ and BaCO$_3$ as starting materials. The homogenized batches (10 g) were melted for 20 min in air in platinum crucibles within the temperature range of 900-1200°C, depending on the melting temperatures of the compositions. The glass formation was achieved at high cooling rates (10$^4$-10$^5$ K s$^{-1}$) using a roller-quenching technique. Fragmented 1-3 mm flat pieces, about 50-100 µm thick, were produced. Compositions in which the vitreous pieces were prevalent (above 70%) were assumed to determine the glass formation range. The amorphous state of the samples was established by X-ray phase analysis (Philips APT-15 diffractometer, Cu K$_\alpha$ radiation). The obtained glasses were investigated by infrared spectroscopy (Nicolet-320 FTIR spectrometer) using the KBr pellet technique.

RESULTS AND DISCUSSION

In MoO$_3$-Nd$_2$O$_3$-MeO$_x$ (Me=Ba, Bi) systems glasses with high MoO$_3$ content (90-75 mol%) are obtained at lower cooling rates (10$^4$-10$^5$ K s$^{-1}$). High cooling rates (10$^5$-10$^9$ K s$^{-1}$) shift the border of the glass formation area up to 70 mol % MoO$_3$ (Fig. 1 a, b). The
Table 1. Infrared absorption bands of different MoO₆ polyhedra.

<table>
<thead>
<tr>
<th>Polyhedra</th>
<th>Absorption frequency, (cm⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO₆ condensed</td>
<td>985, ν(Mo=O) 870, 813, ν(Mo-O-Mo) 590, 490 (δ)</td>
<td>7, 8</td>
</tr>
<tr>
<td></td>
<td>990, ν(Mo=O) 876, 818, ν(OMO₂) 600-400 ν(OMO₃)</td>
<td></td>
</tr>
<tr>
<td>MoO₆ isolated</td>
<td>680-590, 400-360 ν₃(Mo-O) ν₄(Mo-O)</td>
<td>9, 10</td>
</tr>
<tr>
<td>Mo₂O₈</td>
<td>950, 900 ν₄(MoO₂), ν₃(MoO₂)</td>
<td>11, 12</td>
</tr>
<tr>
<td>Mo₂O₇</td>
<td>990-910, 890-780, 600-530, 500-450 ν₃(MoO₃) ν₃(Mo-O-Mo), ν₄(Mo-O-Mo)</td>
<td>10</td>
</tr>
<tr>
<td>MoO₄ (with T₄ symmetry)</td>
<td>840 – 780 ν₃ (Mo-O) 320 ν₄ (Mo-O)</td>
<td>5, 13, 14</td>
</tr>
<tr>
<td>MoO₄ (with low symmetry)</td>
<td>900–870, 860–760, below 450 ν₁(Mo-O) ν₂(Mo-O), ν₂ and ν₄</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>960-900 850-700 below 410 ν₁(Mo-O) ν₂(Mo-O) ν₂ and ν₄</td>
<td></td>
</tr>
<tr>
<td></td>
<td>980-960 930-680 below 400 ν₅ ν₃(Mo-O-Mo)</td>
<td></td>
</tr>
<tr>
<td>linked MoO₆ and MoO₄</td>
<td>875 785 600 450 ν₁(MoO₄) ν₃(MoO₄) δMO₂(oct.) vMo-O (oct.)</td>
<td>16</td>
</tr>
</tbody>
</table>

Fig. 1. Glass formation regions in the a) MoO₃-Nd₂O₃-BaO, b) MoO₃-Nd₂O₃-Bi₂O₃ systems.

typical X-ray diffraction pattern of a glass sample, which is X-ray amorphous, is shown in Fig.2. The IR spectra of the selected key glasses in the MoO₃-Nd₂O₃-MeOₓ (Me=Ba, Bi) systems are presented in Fig. 3 (a, b). The assignment of the infrared bands in the glass spectra is made in the framework of the local point symmetry approach [5, 6]. The spectral data obtained are compared with those on the respective crystalline phases.
and with data on their crystal structure which are summarized in Table 1. The previous spectral results on the molybdate glasses have also been taken into account [2, 4]. On this basis, the strong band at 880 cm\(^{-1}\) present in the spectrum of binary 90MoO\(_3\)-10Nd\(_2\)O\(_3\) glass (Fig. 3a) can be connected with the stretching vibration of a Mo-O-Mo bridge associated with MoO\(_6\) octahedra without terminal a Mo=O bond (Table 1). Probably the glass formation is achieved by breaking of edge bonds between MoO\(_6\) units (absence of a band below 600 cm\(^{-1}\)). The appearance of a shoulder at 930-920 cm\(^{-1}\) in the spectra of three component MoO\(_3\)-Nd\(_2\)O\(_3\)-Me\(_2\)O\(_3\) glasses (Fig. 3a,b) and the displacement of the bands in the 880-840 cm\(^{-1}\) range are due to distortion of MoO\(_4\) polyhedra. On the other hand, the vibrations at 930-880 (\(\nu_1\)), 880-840 cm\(^{-1}\) (\(\nu_2\)) together with the weak band at about 720 cm\(^{-1}\) (\(\nu_3\)) detected in all glass spectra may be connected to the formation of isolated MoO\(_4\) units (see Table 1), as a result of partial transformation of octahedra to tetrahedra.

**CONCLUSIONS**

Novel molybdate glasses with participation of rare earth oxide-Nd\(_2\)O\(_3\) are obtained. The glass network is built up by MoO\(_6\) and MoO\(_4\) units. The glass formation tendency of the compositions depends on the ratio between the different types of polyhedra and the degree of the of network polymerization.

**REFERENCES**

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