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Phase Separation and Crystallization in soda-lime borosilicate glass enriched in MoO₃ studied by *in situ* Raman spectroscopy at high temperature

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Abstract – Phase separation and crystallisation processes may arise in molten glass when the MoO₃ content exceeds its solubility limit. Molybdenum combined with other elements such as alkali and alkaline-earth may form crystalline molybdates, known as “yellow phases” in nuclear glasses. In order to establish the sequence of phase separation and crystallization processes occurring during the cooling of the melt, a non-radioactive simplified glass composition was chosen in the SiO₂–B₂O₃–Na₂O–CaO system, with 2mol.% MoO₃. Various cooling scenarios were tested: cooling by air blowing, quenching between two copper plates and cooling on metallic plate. The resulting glass specimens were then characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and Raman spectroscopy in temperature. These observations made it possible to determine the sequence and the appearance temperature of phenomena upon cooling: first, a phase separation occurs, (small droplets dispersed in the molten glass) followed by molybdates crystallization inside the droplets.

INTRODUCTION

In order to confine the high level wastes (HLW) such as fission product solutions, arising from reprocessing of high burn-up UOX-type nuclear spent fuels, a new glass composition is being optimized [1]. The studies conducted to date on this borosilicate glass revealed that above about for more than 3 wt%, molybdenum oxide can lead (for glasses fabricated at 1200°C), to a glass-in-glass phase separation, followed by crystallization upon cooling. Concerning the structural role of molybdenum in silicate and borosilicate glasses, X-ray absorption spectroscopy showed that hexavalent molybdenum cations are located in unconnected tetrahedral MoO₄²⁻ entities within alkali and alkaline-earth rich depolymerised regions outside the silicate or borosilicate network (i.e., the oxygen atoms of MoO₄²⁻ units are not bounded to Si or B) [2-5]. The same kind of isolated molybdate tetrahedral entities are present in the Na₂MoO₄ and CaMoO₄ phases that can form in some nuclear borosilicate glasses. On account of

the solubility of alkali molybdates in water, this phase separation may decrease the chemical durability of the vitrified nuclear waste material [6]. The similarity between the local environment of MoO₄²⁻ entities in glasses and in molybdate crystalline phases may explain the low solubility of molybdenum in glasses and their tendency to crystallize during slow cooling of melts or heat treatment of glasses.

The present work was performed to identify the different steps of the transformation from the melt to the glass of a borosilicate glass rich in MoO₃ with Raman spectroscopy in temperature. A composition containing 2mol.% MoO₃ was chosen because depending on the type of cooling applied it allows to obtain an homogenous or partially crystallized glass.

EXPERIMENTAL PROCEDURE

Glass Preparation

For this study, a non-radioactive simplified glass composition was chosen in the $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O-CaO}$ system derived from that of a HLW glass keeping the same oxides ratio as in this complex composition. Two glass compositions (Table I) were prepared for this study: one with 2 mol.% of MoO_3 (M2) and another without MoO_3 (M0). For all samples, 0.15 mol.% Nd_2O_3 was introduced to facilitate ^{29}Si and ^{95}Mo nuclei relaxation during MAS NMR experiments and to perform optical studies not presented in this paper.

TABLE I. Nominal Glass Compositions (oxide mol.%).

	M0	M2
% SiO_2	66.40	65.07
% B_2O_3	10.75	10.54
% Na_2O	14.05	13.76
% CaO	8.65	8.48
% Nd_2O_3	0.15	0.15
% MoO_3	0	2.00

All glasses (~ 50 g batch) were prepared using reagent grade SiO_2 , CaCO_3 , Na_2CO_3 , H_3BO_3 , MoO_3 , and Nd_2O_3 powders and melted under air in platinum/gold crucibles at 1300°C for 3 h.

Various cooling scenarios were tested for each composition: quenching between two copper plates (speed cooling about $10^4^\circ\text{C}/\text{min}$), cooling on metallic plate (speed cooling about $10^3^\circ\text{C}/\text{min}$). Moreover, M2 glass was also cooled by air blowing according to the method described by Schuller *et al* [7]: the sample were taken directly in the platinum crucible at 1100°C using a ring-tipped platinum rod then blown with compressed air through a nozzle. After blowing the samples were very thin films of glass about $10\ \mu\text{m}$ thick formed by bursting of glass bubbles, and constitute the very fast-quenched specimens. This method of cooling permitted to quench the molten glass at higher temperature than the two other methods (with a speed cooling higher than $10^4^\circ\text{C}/\text{min}$).

Samples Characterization

M2 samples quenched between copper plates or cooled on metallic plate were characterized by XRD on a Philips X'Pert Pro theta-theta X-ray diffractometer using monochromatised $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406\ \text{nm}$). Crystalline phases were identified by comparison of XRD powder

patterns with the crystallographic data base of the International Center of Diffraction data. The M2 sample cooled on metallic plate (opalescent) was studied by SEM and energy dispersive X-ray analysis (EDX).

Very fast-quenched M2 samples prepared by air blowing or quenched between two copper plates were analyzed by TEM and EDX.

In order to establish the phase separation and crystallisation sequence occurring during the cooling, the Raman spectra of the M2 glass quenched between two copper plates were recorded in the temperature range $1100\text{-}25^\circ\text{C}$ (after melting again at 1100°C).

Raman spectra of crystalline phases Na_2MoO_4 (commercial sample) and CaMoO_4 (ceramic sample prepared in our laboratory) was also recorded in the same range of temperature for comparison with our partially crystallized samples and for temperature calibration.

For this Raman experiment, an Aramis Jobin-Yvon confocal microRaman spectrometer equipped with a CCD detector was used. The 325 nm line of a Coherent He-Cd laser was the excitation source. High-temperature Raman observations were carried out in a Linkam T1500 heated stage for the collection of in-situ Raman spectra. Samples were put into the Pt crucible of heated stage and directly melted at 1100°C . Then, samples were cooled at the rate of $100^\circ\text{C}/\text{min}$.

All Raman spectra were corrected for temperature and frequency-dependent scattering intensity as described by Long [8] and then normalized to the data point of highest intensity.

RESULTS

Microstructural Characterization of M2 glass quenched at different rates

As shown in Fig. 1, the M2 glasses obtained after quenching between two copper plates or blowing by air were transparent and totally amorphous according to XRD and TEM. However, the M2 sample cooled on metallic plate glass was opalescent and the back-scattered SEM image showed white spherical micrometer size particles homogeneously dispersed in the bulk (Fig. 1c). XRD pattern of this sample revealed the presence of CaMoO_4 (powellite) and $\gamma\text{-Na}_2\text{MoO}_4$ crystals (Fig. 1e). Powellite has the same tetragonal structure as scheelite (CaWO_4) with

nearly regular isolated MoO_4^{2-} tetrahedra and one site for Ca^{2+} ions in which these cations are surrounded by eight close oxygen atoms.

According to literature [9, 10], $\gamma\text{-Na}_2\text{MoO}_4$ is an orthorhombic phase stable only at high temperature (between 592 and 637°C)[10].

The apparent spherical shape of the Mo-rich particles tends to indicate that molybdate crystallized in spherical shape particles previously formed by liquid-liquid phase separation in the melt during cooling. These liquid spherical particles would concentrate Mo and would then facilitate molybdate crystallization [11].

Study of M2 Glass During Cooling

In order to determine the appearance temperature of phase separation and crystallization phenomenon, the M2 glass obtained after quenching between two copper plates was selected and studied by Raman spectroscopy in temperature during the cooling (from 1100°C to room temperature).

For each temperature, the Raman spectra of M2 sample were compared with those of molybdate crystalline phases (CaMoO_4 and Na_2MoO_4) recorded separately in the same temperature range.

For this high temperature study, Raman spectra were recorded from 100 to 1200 cm^{-1} . Consequently, the principal vibration bands (internal modes) of MoO_4^{2-} entities which are in crystallized (as CaMoO_4 or Na_2MoO_4) or in amorphous environment were observed.

From 1100°C To 950°C

The image (Fig. 1a) of M2 sample cooled by air blowing from 1100°C showed that this glass was homogeneous at the TEM scale (no crystalline phase was detected). It is supposed that molybdenum is totally located inside the glassy network at this temperature.

The Raman spectrum of M2 sample (melt) recorded at 1100°C (Fig. 2a) reveals the presence of a main band at 901 cm^{-1} . The Raman spectrum (recorded at room temperature) of the glass M0 without molybdenum (Fig. 2b) shows that this band is not present without molybdenum. Thus, this band may be associated with a vibration band of MoO_4^{2-} entities in a glassy environment.

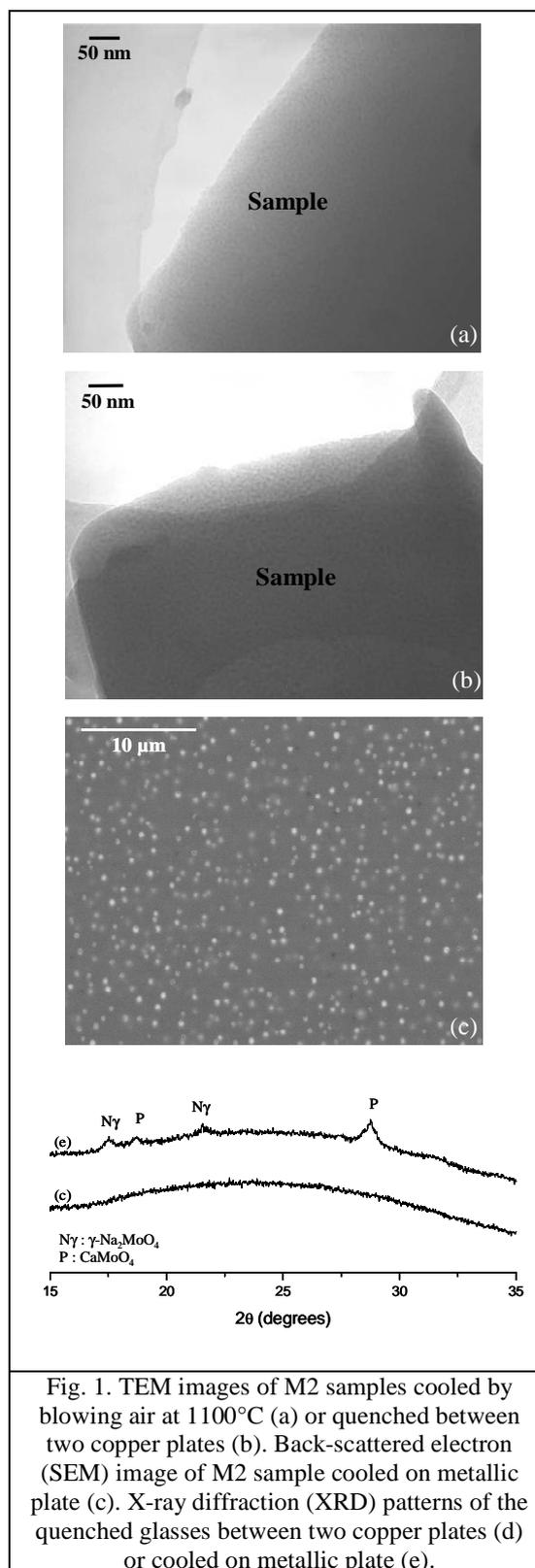


Fig. 1. TEM images of M2 samples cooled by blowing air at 1100°C (a) or quenched between two copper plates (b). Back-scattered electron (SEM) image of M2 sample cooled on metallic plate (c). X-ray diffraction (XRD) patterns of the quenched glasses between two copper plates (d) or cooled on metallic plate (e).

The fact that the Raman spectrum of glass M2 could not be correlated with the spectrum of crystalline CaMoO_4 whose main band is narrower and is located at 885 cm^{-1} ($T = 1100^\circ\text{C}$) confirms that molybdenum is not located in molybdate crystals. According to Sarantopoulou *et al* [12] the band at 885 cm^{-1} is associated to the symmetric stretching vibration band of MoO_4^{2-} entities in the crystalline phase CaMoO_4 at 1100°C .

Upon cooling from 1000 to 950°C there are not modifications of the vibration band associated with the elongation of MoO_4^{2-} entities. Thus it appears that in this temperature range, tetrahedral MoO_4^{2-} entities are only located in a glassy environment. The absence of stretching vibration bands characteristics of MoO_4^{2-} inside crystallized environment indicates that the melt is not crystallized in the temperature range from 1100 to 950°C .

From 950°C to room temperature

Below 950°C , a strong evolution of the bands associated with MoO_4^{2-} entities vibration is observed.

Indeed, the Raman spectrum of M2 sample recorded at 900°C shows now a main vibration band at 867 cm^{-1} (Fig. 3a). This wave number is associated with vibration bands of tetrahedral MoO_4^{2-} entities in a crystallized environment of CaMoO_4 type. The new band at 780 cm^{-1} (Fig. 3a) also corresponds to a vibration band of tetrahedral MoO_4^{2-} entities in CaMoO_4 crystals. Moreover a weak shoulder is observed near 900 cm^{-1} which is characteristic of the MoO_4^{2-} vibration band in the glass as shown in Fig. 2a. This shoulder appears in all Raman spectra recorded for each temperature.

Between 800 and 700°C , Raman spectra of M2 (Fig. 3b,c) remained similar; the elongation vibration band of MoO_4^{2-} tetrahedra in CaMoO_4 is always observed.

Starting from 650°C , a low-intensity shoulder appeared at 890 cm^{-1} in the M2 Raman spectrum (Fig. 3d). The intensity of this shoulder increased in the Raman spectrum recorded at 550°C (Fig. 3e). When comparing this spectrum with that of Na_2MoO_4 recorded at the same temperature, we can see that this band may be associated with a vibration band of tetrahedral MoO_4^{2-} entities in

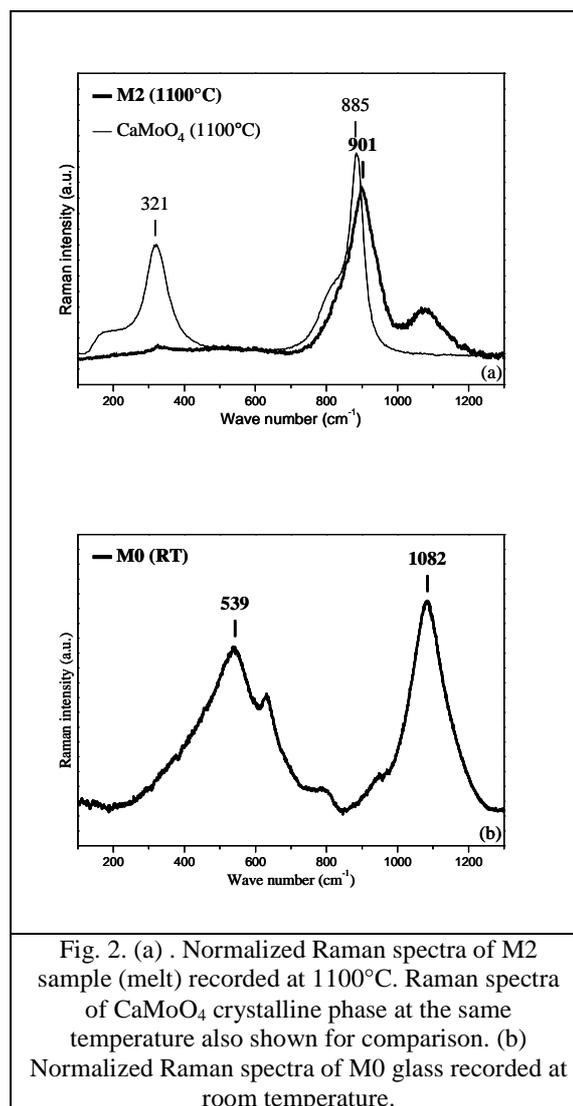


Fig. 2. (a) . Normalized Raman spectra of M2 sample (melt) recorded at 1100°C . Raman spectra of CaMoO_4 crystalline phase at the same temperature also shown for comparison. (b) Normalized Raman spectra of M0 glass recorded at room temperature.

the crystalline phase Na_2MoO_4 . But we cannot determine its allotropic form.

After cooling down to room temperature we can see the three elongation band contributions of tetrahedral MoO_4^{2-} entities following if they are located in the glass, in CaMoO_4 or Na_2MoO_4 crystallized phases (Fig. 3f).

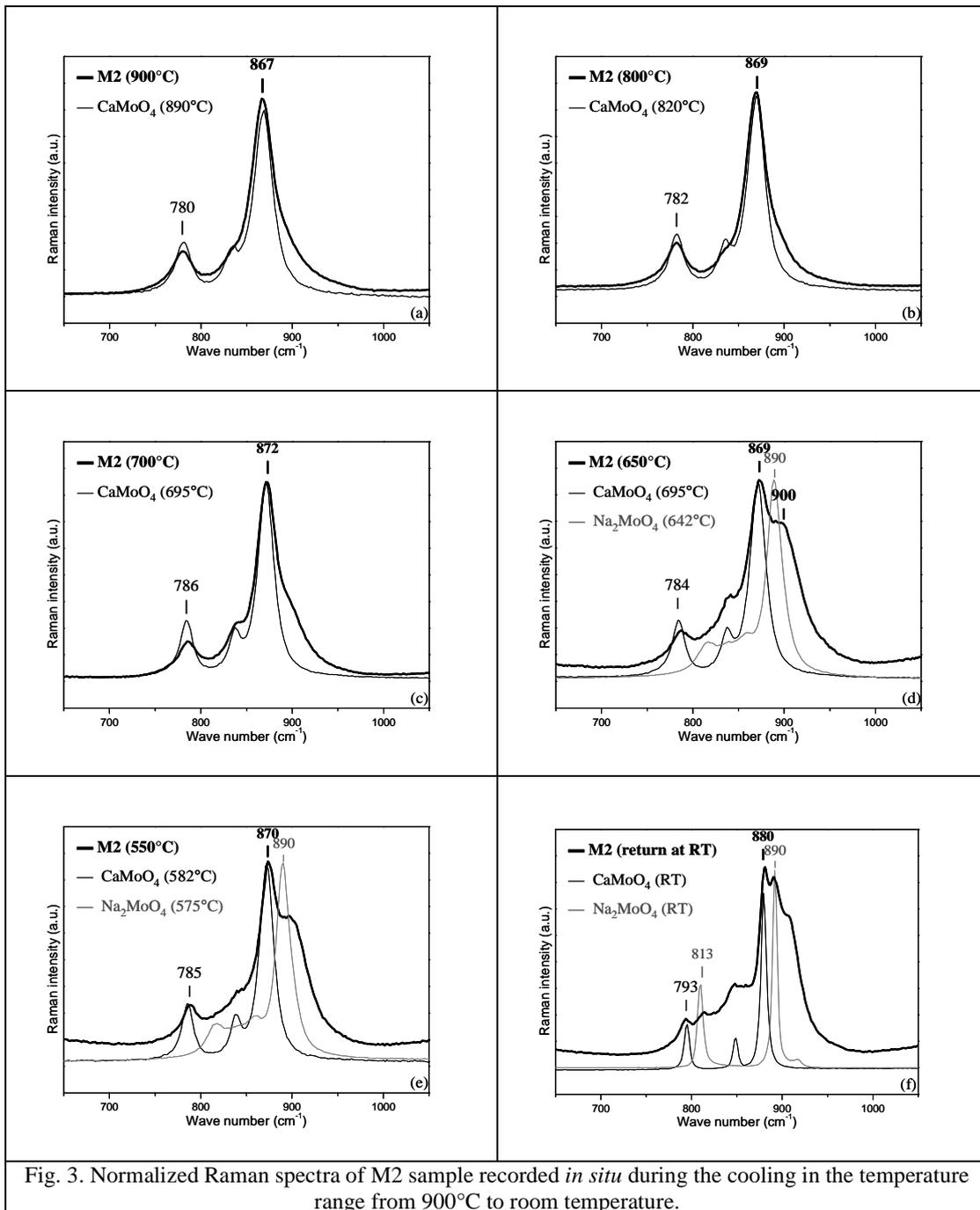
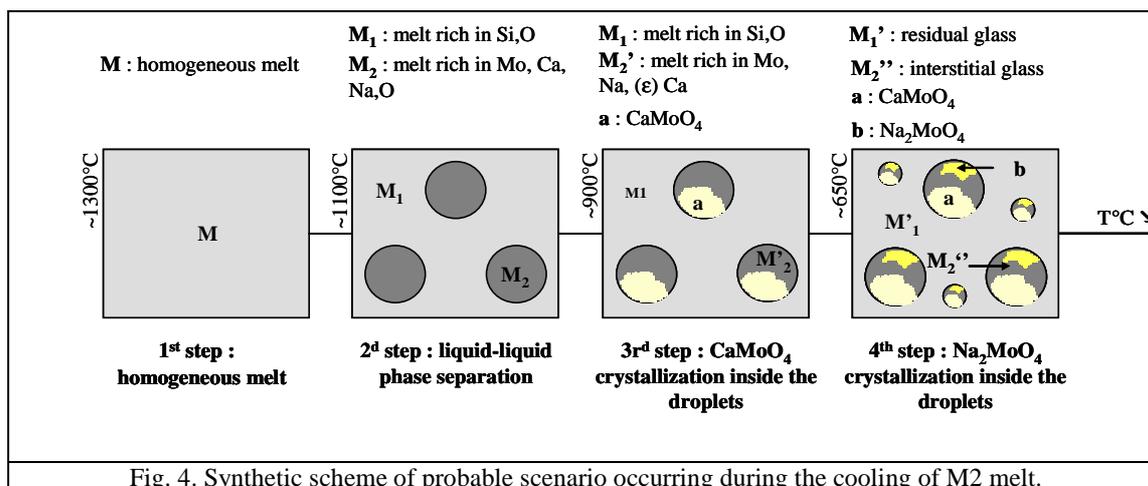


Fig. 3. Normalized Raman spectra of M2 sample recorded *in situ* during the cooling in the temperature range from 900°C to room temperature.



DISCUSSION

The TEM image of M2 sample quenched by air blowing from 1100°C argues that the melt is homogeneous at this temperature. The Raman spectrum recorded at 1100°C confirms that the tetrahedral MoO₄²⁻ entities are in a glassy environment (absence of crystallization).

During melt cooling of M2 sample from 1100°C to 950°C, there is no evolution of Raman spectra. However, the microstructure of M2 cooled on metallic plate suggests that the phenomenon of phase separation appears before crystallization. Therefore, it is expected to observe the liquid-liquid phase separation phenomenon in this temperature range.

The first CaMoO₄ crystals appear between 950 and 900°C, and this crystalline phase remains up to room temperature.

Between 700 and 650°C, two low-intensity shoulders appear which can be correlated with stretching elongation bands of MoO₄²⁻ entities in the crystalline phase Na₂MoO₄ type and in the glass.

The probable scenario of the different phenomenon occurring during M2 melt cooling deduced from all our results is reported in Fig. 4.

CONCLUSIONS

The aim of this work was to study a glass belonging to the SiO₂-B₂O₃-Na₂O-CaO system rich in MoO₃. The glass quickly cooled at 10⁴°C/min is homogenous. But when it is cooled more slowly (about 10³°C/min) CaMoO₄ and

Na₂MoO₄ crystallization occurs in the bulk. By Raman spectroscopy investigations from the melt temperature (1100°C) to room temperature, CaMoO₄ crystallization occurs near 900°C while the Na₂MoO₄ crystallization appears at lower-temperature (near 650°C).

Thus we identified the occurrence temperatures of crystalline phase CaMoO₄ and Na₂MoO₄ in borosilicate glass rich in MoO₃ during slow cooling. In order to quantify the thermal stability areas of these crystalline phases, a study on glass heating is under progress.

Further studies will be carried out in order to determine the appearance temperature of the phase separation phenomenon, and to describe the microstructural evolution of glass M2. In addition, the composition effects will be studied with the aim of increasing the solubility of MoO₃ in borosilicate glasses.

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