Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Crystallization of sodium molybdate-phosphate and tungstate-phosphate glasses

Ladislav Koudelka[a,*], Oksana Kupetska[a], Petr Kalenda[a], Petr Mošner[a], Lionel Montagne[b], Bertrand Revel[b]

[a] Department of General and Inorganic Chemistry, University of Pardubice, 532 10 Pardubice, Czech Republic
[b] University of Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181, UCCS, Unité de Catalyse et Chimie du Solide, F-59000 Lille, France

ARTICLE INFO

Keywords:
Phosphate glasses
Crystallization
Raman spectra
NMR spectra
Tungsten oxide
Molybdenum oxide

ABSTRACT

The glass to crystal transformation was studied for two glasses with composition $25Na_2O{\cdot}50MoO_3.25P_2O_5$ and $25Na_2O{\cdot}50WO_3.25P_2O_5$. During the heat treatment process, two crystalline compounds were formed, $NaMoO_2PO_4$ and $NaWO_2PO_4$, respectively. Physico-chemical properties of the corresponding glasses and crystals were compared, as well as their Raman and ^{31}P MAS NMR spectra. Differential thermal analysis revealed crystallization peaks at 483 °C for the Mo-containing glass and at 624 °C for the W-containing glass; melting points of crystalline compounds were determined as 695 ± 2 °C for $NaMoO_2PO_4$ and 858 ± 2 °C for $NaMoO_2PO_4$. Sodium tungstate-phosphate glass has lower solubility in comparison with the sodium molybdate-phosphate glass. The study of the crystallization mechanism showed a prevailing surface nucleation. ^{31}P MAS NMR spectra of the two glasses revealed the same shape and almost the same width, which reflects a similar local environment for P in these glasses. The position of the resonance for W-containing glass at a more negative chemical shift than the Mo-containing one is attributed to the different electrical field strength of W atoms than Mo atoms. ^{31}P MAS NMR spectra of crystals revealed two resonances at +17 and − 0.5 ppm for the Mo glass and at −0.1 and − 1.9 ppm for the W glass, reflecting the presence of two different phosphorus short range environments, in agreement with their crystal structure. Raman spectra showed similarity in structural features for Mo and W glasses and their isomorphic compounds. Splitting of the dominant Raman bands in the crystal spectra reflects a distortion of MoO_6 and WO_6 octahedra. Raman spectra also suggested the breaking of Mo-O-Mo and W-O-W linkages during crystallization.

1. Introduction

WO_3 and MoO_3 are two transition metal oxides, which form glasses with phosphorus pentoxide P_2O_5 over a wide range of composition [1–4]. In these glasses, MoO_3 and WO_3 easily change their valence state from W^{6+} and Mo^{6+} to W^{5+} and Mo^{5+}, respectively [5,6], so that both states are present in the glasses. Such glasses reveal interesting electrical properties due to the transfer of an unpaired d-electron of a transition metal ion in a lower oxidation state (Me^{5+}) to the upper oxidation state (Me^{6+}) [5,6].

Study of crystallization of various ternary glasses with MoO_3 or WO_3 revealed that in several ternary systems a crystalline compound is formed at the $25MO(M_2O){\cdot}50MoO_3(WO_3){\cdot}25P_2O_5$ composition. In the ternary system $PbO\text{-}MoO_3\text{-}P_2O_5$, Masse et al. [7] prepared such a compound by the reaction of lead tetraphosphate $Pb_2P_4O_{12}$ with molybdenum oxide at 650 °C and described its composition as Pb $(MoO_2)_2(PO_4)_2$. From XRD analysis of single crystals, the authors [7] solved its structure consisting of chains of inter-connected PO_4 tetrahedra and MoO_6 octahedra linked via Mo-O-P bridges between their corners. We have prepared this compound by crystallization of the glass composition $25PbO\text{-}50MoO_3\text{-}25P_2O_5$ [8] by annealing the glass powder at 600 °C for 2 h and studied glass to crystal transformation at this glass composition [9]. Based on the similarity of basic spectral features of both spectra, we assumed that the short-range order in the glass is similar to that in the crystal $Pb(MoO_2)_2(PO_4)_2$ and the basic structural units in both phases are probably the same. Santagneli et al. studied glass to crystal transformation in the $AgPO_3\text{-}MoO_3$ glasses, where the similar compound of the composition of $AgMoO_2PO_4$ was described [10,11].

During the study of the $PbO\text{-}WO_3\text{-}P_2O_5$ glasses, we observed that crystallization of the glass composition $25PbO{\cdot}50WO_3.25P_2O_5$ produces a new crystalline compound with XRD data similar to that in the ternary

* Corresponding author.
E-mail address: ladislav.koudelka@upce.cz (L. Koudelka).

https://doi.org/10.1016/j.jnoncrysol.2018.05.028
Received 4 April 2018; Received in revised form 15 May 2018; Accepted 19 May 2018

system with molybdenum, i.e. $Pb(WO_2)_2(PO_4)_2$ [12]. In the $BaO\text{-}MoO_3\text{-}P_2O_5$ ternary system, Masse et al. [7] described the formation of a similar compound. In previous studies we have observed during the crystallization of $25BaO{\cdot}50MoO_3.25P_2O_5$ glass the formation of a crystalline compound [13], but its diffraction pattern and unit cell parameters were different from the data provided by Masse et al. [7]. Considering the complexity of lead and barium containing compositions, we decided to investigate the equivalent sodium composition for which more crystallographic data are available.

We investigated the structure and properties of sodium molybdate-phosphate glasses $40Na_2O\text{-}xMoO_3\text{-}(60\text{-}x)P_2O_5$ and compared them with similar sodium tungstate-phosphate glasses $40Na_2O\text{-}yWO_3\text{-}(60\text{-}y)P_2O_5$ with 1D ^{31}P MAS NMR spectroscopy and Raman spectroscopy [14]. We were also able to prepare glasses within a broad concentration range of x(y) = 0–50 mol% of the modifying oxides MoO_3 and WO_3, respectively. We found in literature [15] that in these ternary systems similar compounds $NaMoO_2PO_4$ and $NaWO_2PO_4$ were prepared by the reaction of oxides WO_3 or MoO_3 with $NaPO_3$ and their structure was studied by Kierkegaard in 1961 [15].

Several papers have been published dealing with glasses of the $Na_2O\text{-}MoO_3\text{-}P_2O_5$ system. Glass-forming region in this ternary system was determined in [16], where the authors devoted their efforts namely to the study of the electrical conductivity of these glasses in three different compositional series corresponding to either a fixed Na_2O content or a constant Mo/P ratio.

Bih et al. [17] and Santagneli et al. [18] studied glasses in the compositional series $NaPO_3\text{-}MoO_3$. While the authors [17] only applied FTIR, DSC and EPR techniques for their study of glasses within the concentration span of 0–50 mol% MoO_3, in [18] advanced NMR techniques and Raman spectroscopy were used for glasses containing 0–70 mol% MoO_3. Structural studies of $NaPO_3\text{-}WO_3$ glasses with advanced NMR techniques and Raman spectroscopy were also reported by de Araujo [19].

The aim of this work was to compare structural information obtained by spectroscopic methods on the glasses and their crystalline phases from the $Na_2O\text{-}MoO_3\text{-}P_2O_5$ and $Na_2O\text{-}MoO_3\text{-}P_2O_5$ systems. We have also applied thermoanalytical methods for the study of glass to crystal transformation to complete the existing data on the crystallization of sodium molybdate-phosphate and tungstate-phosphate glasses.

2. Experimental

Glasses of the composition $25Na_2O{\cdot}50MoO_3.25P_2O_5$ and $25Na_2O{\cdot}50WO_3.25P_2O_5$ were prepared by melting Na_2CO_3 (99%; Penta), MoO_3 (99.5; Sigma-Aldrich), WO_3 (99.9; Fluka Analytical), and H_3PO_4 (85 wt%, p.a. Sigma-Aldrich) using a total batch weight of 30 g. The homogenized starting mixtures were slowly calcined up to 600 °C with the final calcination at the maximum temperature for 2 h in order to remove the water. The reaction mixtures were then melted at 900–1000 °C under ambient air, in a platinum crucible. The melt was subsequently poured into a preheated graphite mold ($T < T_g$) and the obtained glass was then cooled to room temperature. The amorphous character of the prepared glasses was checked by X-ray diffraction analysis.

The elemental analysis of the bulk glasses was carried out by scanning electron microscope LYRA 3 (Tescan) equipped with EDS analyzer AZtec X-Max 20 (Oxford Instruments). The EDS measurement was performed at 20 kV acceleration voltage on two 400 × 400 μm spots.

The glass density, ρ, was determined with bulk samples with the Archimedes method using toluene as the immersion liquid. The molar volume, V_M, was calculated using the expression:

$$V_M = \acute{M}/\rho,$$

where $\acute{M}$ is the average molar weight of the glass composition a.M(Na_2O) + b.M(MoO_3/WO_3) + c.M(P_2O_5) calculated for $a + b + c = 1$. Density of polycrystalline samples was determined using a helium gas pycnometer AccuPyc II 1340, where the volume of the sample was measured by measuring the volume of the helium gas displaced by the sample. Molar volume was then calculated from the equation above.

The chemical durability of the glasses was evaluated from the measurement of the dissolution rate, DR, at 25 °C on glass cubes with a dimension of ~5 × 5 × 5 mm. The glass cubes were shaken in 100 cm^3 of distilled water for 24 h. The dissolution rate was calculated from the expression:

$$DR = \Delta\omega/St,$$

where $\Delta\omega$ is the weight loss (g), S is the sample area (cm^2) before the dissolution test and t is the dissolution time (min).

The thermal behaviour of the glasses was studied with a DTA 404 PC (Netzsch) operating in the DSC mode at a heating rate of 10 °C min^{-1} over the temperature interval 30–1000 °C. The measurements were carried out with finely crushed bulk samples in a silica crucible in an inert N_2 atmosphere. The thermal expansion coefficient, α, the glass transition temperature, T_g, and the dilatometric softening temperature, T_d, were measured using a dilatometer DIL 402 PC (Netzsch). Bulk samples, with dimensions of 20 × 5 × 5 mm^3, were cut out from a larger piece with a diamond saw. From the obtained dilatometric curves, the coefficient of thermal expansion, α, was determined as the mean value in the temperature range of 150–250 °C. The glass transition temperature, T_g, was determined from the change in the slope of the elongation vs. temperature plot and dilatometric softening temperature, T_d, was determined as the maximum of the expansion trace corresponding to the onset of viscous deformation. The dilatometric measurements were carried out in air at a heating rate of 5 °C min^{-1}.

IR spectra were recorded at spectral resolution of 2 cm^{-1} using a Nicolet Protege 460 FT-IR spectrometer in the 400–4000 cm^{-1} range, with 32 scans. Powdered samples were mixed and homogenized with spectroscopically pure KBr and pressed into pellets.

Raman spectra in the range 1400–200 cm^{-1} were measured on bulk and powder samples at room temperature using a DXR Raman spectrometer Thermo Scientific DXR SmartRaman with a 532 nm solid state (Nd:YAG) diode pumped laser.

^{31}P MAS NMR spectra were measured at 9.4 T on a BRUKER Avance 400 spectrometer with a 4 mm probe. The spinning speed was 12.5 kHz and relaxation (recycling) delay was 180 s. The chemical shifts of ^{31}P nuclei are given relative to H_3PO_4 at 0 ppm.

A Bruker D8 Advance diffractometer with CuK_α radiation was used for the study of heat treated glass powders. A database of inorganic compounds from the International Center of Diffraction Data [20] was used for the phase identification.

3. Results and discussion

For the study of glass to crystal transformation, we have prepared $25Na_2O{\cdot}50MoO_3.25P_2O_5$ and $25Na_2O{\cdot}50WO_3.25P_2O_5$ glasses by the procedure described above. It was determined, that the compositions of the glasses correspond to $24.7Na_2O.49.5MoO_3.25.8P_2O_5$ and $24.8Na_2O.50.3WO_3.24.9P_2O_5$. The analyzed composition is also given in Table 1. Due to small deviations from the batch composition, the nominal composition will be used in the following discussion.

Both glassy samples were of dark blue color due to the presence of Mo^{5+} and W^{5+} ions, respectively, in the prepared glasses. The values of the density and molar volume of both glasses are given in Table 1.

Thermal behavior of both glasses was studied by differential thermal analysis and dilatometry. The curves from DTA measurements are shown in Fig. 1. We can see exothermic crystallization peaks and sharp endothermic melting peaks on the obtained DTA curves. Both curves also reveal a small step before the crystallization peak