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Thermal stability of $SiO_2-B_2O_3-Al_2O_3-Na_2O-CaO$ glasses with high Nd_2O_3 and MoO_3 concentrations



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ABSTRACT

The incorporation of high MoO₃ amounts in borosilicate glasses developed for the immobilization of radioactive waste may lead to the crystallization of Mo-rich phases that may induce a decrease of the long term performances of glasses. It is thus essential to understand their crystallization mechanisms and the possible effect of other abundant fission products present in the wastes (such as rare earths) in order to control or to avoid their formation during glass preparation. This paper presents a study, performed by X-ray diffraction, scanning electron microscopy, Raman and optical absorption spectroscopies of the stability as a function of the thermal treatment temperature T_{C} of a simplified Mo-rich nuclear waste glass. The impact of the addition of a high amount of Nd₂O₃ on the thermal stability of this glass is studied. For comparison, the thermal stability of a Nd₂O₃-rich glass without Mo is also presented. The crystallization range of all phases formed in these glasses (CaMoO₄, Na₂MoO₄, Ca₂Nd₈(SiO₄)₆O₂ (apatite)) and the evolution of their structure and microstructure as a function of T_C are presented. The introduction of Nd₂O₃ in the MoO₃-rich glass inhibits the crystallization of molybdates (increase of Mo solubility), as long as apatite does not form which suggests that $[MoO_4]^{2-}$ entities and Nd³⁺ cations are close to each other in the glass structure. Besides, when a high density of apatite crystals form, for instance from glass surface, small Mo-rich partially crystallized globular heterogeneities are observed between these crystals that exacerbate the nucleation of new apatite crystals (nucleating effect).

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1. Introduction

Vitrification is the most widely used technology for the immobilization of high level radioactive wastes throughout the world [1–4]. The aim is to dissolve the radionuclides as homogeneously as possible at the atomic scale in the aperiodic structure of a glassy matrix for more than 10000 years [5]. After the reprocessing of spent nuclear fuel, the radioactive waste solutions are generally confined in borosilicate glasses that present very good characteristics (high glass transition temperature T_g , low crystallization tendency during melt cooling, high leaching resistance against

water, high self-irradiation resistance). Research is in progress in nuclear industry on new glass compositions to immobilize higher concentrations of nuclear waste (fission products + actinides) than today while keeping good physicochemical properties and long term performances [6-11]. This will enable to decrease the number of glass canisters and to reduce the cost of disposal.

Molybdenum is abundant in commercial HLW solutions (defense HLW does not contain much Mo) [12] and its incorporation in glassy waste forms is a big challenge as MoO_3 presents a limited solubility in silicate and borosilicate glasses [13–17]. Indeed, when these glasses are prepared under oxidizing or neutral atmosphere, the main and most stable oxidation state of molybdenum is +VI [15,18,19]. According to Mo EXAFS and XANES studies [13,18,20], Mo^{6+} cations are present in silicate and borosilicate glasses as molybdate tetrahedral entities $[MOO_4]^{2-}$ (oxoanions) that are not directly connected to the silicate network (absence of direct Mo–O–Si bondings). It has been proposed that these oxoanions are



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located in depolymerized regions of the glassy network (i.e. in regions rich in non-bridging oxygen atoms (NBOs)) where their negative charge is compensated by the alkali and alkaline-earth cations that are also located in these regions [13,21]. As a consequence, the presence of high contents of both molybdenum and alkali and alkaline-earth cations in the same depolymerized regions of the glass structure where these species are rather mobile because they are not strongly connected to the silicate network would favor the separation and the crystallization of alkali and alkaline-earth molybdate phases such as Na₂MoO₄ and CaMoO₄ (scheelite structure) during melt cooling which would explain the poor molybdenum solubility in these glasses [3,16,21–23]. Indeed, the structure molybdate phases such as CaMoO₄ and Na₂MoO₄ consists in the same kinds of isolated $[MoO_4]^{2-}$ entities charge compensated by Na^+ or Ca^{2+} cations [21]. The crystallization of Na_{0.5}Nd_{0.5}MoO₄ (scheelite structure) during the cooling of SiO₂-B₂O₃-Na₂O-ZnO-Nd₂O₃-MoO₃ glasses containing or not CaO has also been reported by Kashchieva et al. [24]. The same team also studied glass formation and crystallization of Mo- and rare earths-rich phases in simple B2O3-MoO3-RE2O3 systems (RE: La, Nd) [25–28]. Using a thermodynamic approach with the Calphad method, Gossé et al. [29] recently predict the separation of a MoO₃ and Na₂O rich-phase (that would then crystallize to form Na₂MoO₄) in the SiO₂-Na₂O-MoO₃ system in accordance with experimental results [30]. As alkali molybdate crystalline phases such as Na₂MoO₄ exhibits very poor chemical durability against water and that radioactive cesium can partially replace sodium in their structure, the crystallization of such phases must be avoided in nuclear waste glasses. In previous studies, we showed that it was possible to control the formation of Na₂MoO₄ in favor of CaMoO₄ in Mo-rich borosilicate glasses for instance by increasing B₂O₃ or CaO concentrations [21-23]. Nevertheless, even if the chemical durability of alkaline earth molybdate phases such as CaMoO₄ is relatively good, their potential crystallization during melt cooling or glass heating must be controlled because such phases may incorporate actinides (Np, Am, Cm present in waste) in their structure by partial substitution of alkaline-earth cations [31] that may then induce local swelling under the effect of α -self-irradiation followed by strains and glass cracking during waste forms disposal. Indeed, recent external Ar irradiation studies performed on RE-doped CaMoO₄ single crystals (RE = rare earths being used as actinide surrogates) to simulate the effects of α -decays showed that powellite may swell by more than 5% at saturation but this phase has a high radiation resistance because amorphization was not reached during these experiments [32].

The present work joins within the continuity of previous studies concerning the crystallization of Mo-rich phases in simplified nuclear borosilicate glasses [10,21-23,33-34]. Particularly, we present a study on the crystallization of molydbate phases as a function of temperature (650-1100 °C), in a simplified nuclear waste glass composition (Mo glass) belonging to the SiO₂-B₂O₃-Al₂O₃-Na₂O-CaO-MoO₃ system with 1.61 mol% (~3.6 wt%) MoO₃ (Table 1). Besides, as RE are also abundant fission products in high level radioactive waste [12], which may crystallize during melt cooling to form RE-rich silicate phases such as apatite $(Ca_2RE_8(SiO_4)_6O_2)$ [9,35,36], the complexity of the previous glass composition (Mo glass) was increased by adding a high amount of Nd₂O₃ (3.54 mol% i.e. ~ 16 wt%, Table 1) in order to become closer to a real nuclear waste glass with high waste loading (RE = Nd is the most abundant RE and simulates here all the RE and actinides present in wastes [3,36]). The thermal stability of this glass containing both Mo and Nd (MoNd glass) was studied and compared to that of the Mo glass. To complete this work, the crystallization as a function of temperature of a Nd₂O₃-rich glass (Nd glass) containing 3.6 mol% Nd₂O₃ (~16.5 wt%, Table 1) without molybdenum was also

Table 1

Nominal composition (in mol% (a) and wt% (b)) and glass transition temperature (T_g) determined by DTA [34] for Mo, Nd and MoNd glasses. The true glass compositions (c) as determined by chemical analysis (ICP-AES) are also given for comparison (in wt%).

Glass	SiO ₂	B_2O_3	Al_2O_3	Na ₂ O	CaO	MoO ₃	Nd_2O_3	$T_g(^{\circ}C)$
Mo (mol%) ^a	57.95	10.45	5.11	16.49	8.40	1.61	0.00	556
Mo (wt%) ^b	53.94	11.27	8.07	15.84	7.30	3.59	0.00	
Mo (wt%) ^c	53.72	10.98	8.47	15.57	7.46	3.55	0.00	
Nd (mol%) ^a	56.78	10.24	5.00	16.16	8.23	0.00	3.59	584
Nd (wt%) ^b	46.69	9.75	6.98	13.71	6.32	0.00	16.54	
Nd (wt%) ^c	46.64	9.66	6.65	13.57	6.17	0.00	16.83	
MoNd (mol%) ^a	55.90	10.08	4.93	15.91	8.10	1.55	3.54	580
MoNd (wt%) ^b	45.29	9.46	6.77	13.30	6.13	3.01	16.05	
MoNd (wt%) ^c	44.93	8.60	6.29	13.56	5.93	2.89	15.79	

studied and compared to that of the MoNd glass. In a previous paper [37], we presented the impact of the addition of increasing Nd₂O₃ contents (0–16 wt%) on the structure and the crystallization tendency of the melt at constant cooling rate (1 °C/min) to simulate natural cooling in metallic canisters after melt casting. Moreover, in another paper we compared the crystallization tendency during cooling from the melt or prolonged isothermal heating (750 °C) from the glassy state of Mo-, Nd- and Mo + Nd-rich glasses with or without ruthenium oxide, RuO2 representing in this study the platinoids present in waste solutions [33,34]. In the present paper, in order to study more precisely the tendency of the supercooled melts to crystallize as a function of the temperature, isochronal heat treatments above the glass transformation temperature T_g with a nucleation stage at a fixed temperature (T_N) followed by a growth stage during 6 h at increasing temperature (T_C) were performed. The quenched glasses and heat treated glass samples were then characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman and optical absorption spectroscopies.

2. Experimental procedure

2.1. Samples preparation and thermal treatment

A Mo-rich glass composition (Mo glass) was chosen in the SiO₂-B₂O₃-Al₂O₃-Na₂O-CaO-MoO₃ system and derives from that of a more complex glass envisaged to immobilize highly concentrated waste. From Mo glass, another glass was prepared by adding Nd₂O₃ (MoNd glass). The nominal composition of these two glasses is given in Table 1. For comparison, a Nd-rich glass without molybdenum (Nd glass) was also prepared keeping constant the molar ratios of other oxides (Table 1). The composition of Nd glass derived from that of MoNd glass by removing molybdenum oxide from its composition. The true composition of the three glasses was analysed by inductively coupled plasma-atomic emission spectroscopy method (ICP-AES) at the Service Central d'Analyses (Vernaison, France) and the results obtained showed good agreement between experimental and nominal glass compositions (Table 1). Neodymium oxide was chosen here to simulate all the rare earths and actinides occurring in high-level waste solutions because neodymium is the most abundant rare earth in these waste solutions [12] and it is considered as a good surrogate for all trivalent rare earths and actinides [36].

Mo, MoNd and Nd glasses (50 g batch) were prepared using appropriate quantities of reagent grade SiO₂, H₃BO₃, Al₂O₃, Na₂CO₃, CaCO₃, MoO₃ and Nd₂O₃ powders and melted in air in an electrical furnace at 1300 °C for 3 h in Pt–Au (5 wt% Au) crucibles, and then cast. The glass obtained was then ground and melted again at 1300 °C for 2 h to ensure homogeneity before casting on a steel

plate at room temperature. The MoNd and Nd quenched glasses were transparent, macroscopically and microscopically homogeneous. The Mo quenched glass was lightly opalescent because of the existence of a phase separation phenomenon as detected by scanning electron and transmission microscopies. Indeed, Mo-rich globular particles (~50 nm size) homogeneously dispersed in the Mo sample were clearly observed by these techniques (images not shown) and are characteristic of a liquid–liquid phase separation occurring in the melt or in the supercooled melt. For Mo glass, phase separation (at least on the optical scale) can be avoided by rapidly quenching the melt between two metallic plates after casting. However, despite this little opalescence for the Mo glass, all quenched glasses were amorphous according to XRD and Raman spectroscopy [34].

After quenching, a two-step thermal treatment of nucleation and growth was performed on bulk samples for the three glass compositions in order to induce crystallization. The nucleation step was performed at $T_N = T_g + 20$ °C for 2 h (T_g is the glass transition temperature determined by differential thermal analysis (DTA) [34], Table 1) and followed by a growth step for 6 h at T_C between 650 and 1100 °C. The subscripts N and C for the heating temperatures T_N and T_C respectively refer to the Nucleation and Crystallization steps. For these thermal treatments, pieces of glass were put in Pt—Au crucibles and introduced successively in two preheated furnaces at the corresponding temperatures (T_N and T_C) and then quenched at room temperature.

For comparison with the partially crystallized samples obtained above, two ceramics (used in this paper as references for XRD and Raman spectroscopy) have also been synthesized: a powellite CaMoO₄ ceramic and an apatite Ca₂Nd₈(SiO₄)₆O₂ ceramic. The powellite ceramic was synthesized by solid state reaction with a first heat treatment during 6 h at 800 °C (heating and cooling at 5 °C/min) of a mixture of $CaCO_3 + MoO_3$ in stoichiometric proportions followed by a sintering during 3 h at 1150 °C (heating and cooling at 5 °C/min). The apatite ceramic was synthesized by solid state reaction with a first heat treatment during 24 h at 900 °C (heating and cooling at 5 °C/min) of a mixture of $SiO_2 + CaCO_3 + Nd_2O_3$ in stoichiometric proportions followed by a sintering during 100 h at 1500 °C (heating and cooling at 5 °C/min). According to XRD measurements, pure powellite and apatite phases were obtained (Fig. 1a). Besides, a Na₂MoO₄ crystalline commercial powder (Aldrich, AD2690) was also used as reference (α form, stable at room temperature and until 440–460 °C [38,39]).

2.2. Characterization methods

XRD patterns of the ceramics, guenched and heat treated glass samples were recorded at room temperature on an X'Pert PRO PANalytical instrument using Cu-K α radiation ($\lambda = 0.15406$ nm) in Bragg-Brentano $(\theta - 2\theta)$ geometry. For this analysis, the samples were crushed into powders with particle size <80 µm. XRD patterns were recorded for 2θ ranging from 10° to 80° with a step of $0.026^{\circ}(2\theta)$ and a time acquisition per step of 79s. Before performing the thermal treatment of nucleation at T_N (T_g + 20 °C), T_g was determined by DTA for all quenched glasses with a Netzsch Geratebau STA 409 apparatus with heating at 10 °C/min (Table 1). Field-emission gun scanning electron microscopy (FEG-SEM) observations were performed on quenched and heat treated glass samples using a Zeiss supra 55VP microscope with a tungsten wire of 200 nm operating at 25 kV with a working distance of 5 mm. Before SEM observation, the samples were cut, embedded in resin, polished with diamond paste at $1 \mu m$ (Fig. 2) and coated with a thin carbon layer to eliminate electrostatic effects. Transmission electron microscopy (TEM) observations were carried out on quenched glasses with a JEOL JEM 2010F electron microscope operating at



Fig. 1. (a) XRD patterns of the powellite (CaMoO₄) and apatite ($Ca_2Nd_8(SiO_4)_6O_2$) reference samples. The purity of the phases was verified by comparison with the files provided by the International Centre for Diffraction Data (ICDD): CaMoO₄ powellite (00-029-0351) and Ca₂Nd₈(SiO₄)₆O₂ apatite (04-007-5968). (b) Raman spectra of CaMoO₄, Na₂MoO₄ and Ca₂Nd₈(SiO₄)₆O₂ reference samples.

200 kV. In this last case the samples were prepared by finely crushing glasses in an agate mortar and ultrasonically stirring them in butanol. The smallest particles were then collected in the supernatant liquid using a holey carbone-coated copper grid.

Raman spectroscopy was conducted at room temperature on a Horiba Jobin-Yvon HR800 micro-Raman spectrometer equipped with a CCD detector. The 488 nm line of a coherent Ar⁺ laser was used as the exciting source. Experiments were carried out with a confocal $\times 100$ objective and a confocal hole of 300 μ m. Spectra were recorded between 700 and 1200 cm⁻¹ using a 1800 grooves per mm grating and a 100 μ m slit, and with a total acquisition time of 120s (60s acquisition time and 2 successive acquisitions to reduce spurious noise). All the spectra shown in this paper were corrected for temperature and frequency dependency of the scattering intensity using a correction factor of the form proposed by Long [40]. A polynomial baseline was fitted directly to the corrected Raman spectra which were then normalized. For comparison with the heat treated glass samples, the Raman spectra and XRD patterns of the crystalline references Ca₂Nd₈(SiO₄)₆O₂, CaMoO₄ and Na₂MoO₄ were also recorded (Fig. 1).

Optical absorption spectra were recorded in transmission at 10 K with a double-beam CARY-6000i spectrometer to follow the evolution of Nd^{3+} ions environment with T_C (Nd glass). Translucent



Fig. 2. Pictures of the heat treated Mo ($T_C = 700 \ ^{\circ}C(a)$, 750 $^{\circ}C(b)$), Nd ($T_C = 700 \ ^{\circ}C(c)$, 800 $^{\circ}C(d)$) and MoNd ($T_C = 700 \ ^{\circ}C(e)$, 750 $^{\circ}C(f)$) glasses after cutting, embedding in resin and polishing (samples size ~ 1 cm).

pellets were prepared from 25 mg of finely ground material mixed with KBr (125 mg), and spectra were collected in the 420–440 nm (22727–23810 cm⁻¹) region using a spectral band width of 0.6 nm, data interval of 0.2 nm, and 1 s acquisition time. This wavelength region corresponds to the ${}^{4}I_{9/2} \rightarrow {}^{2}P_{1/2}$ transition of the Nd³⁺ ion. At 10 K, only the lowest Stark level of the ${}^{4}I_{9/2}$ ground state of Nd³⁺ ions is populated. As the ${}^{2}P_{1/2}$ state is not split by the crystal field around Nd³⁺ ions, each kind of neodymium environment is characterized by a single ${}^{4}I_{9/2} \rightarrow {}^{2}P_{1/2}$ absorption band whose position depends on the degree of Nd–O bonds covalency (nephelauxetic effect) [41]. For the MoNd sample, the evolution with T_c of the ${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}$.²G_{7/2} transition occurring in the 550–610 nm (16400–18200 cm⁻¹) region was also to detect the possible presence of Nd³⁺ ions in the molybdate crystals. This last transition is known as hypersensitive transition as it is very sensitive to changes in the environment of Nd³⁺ ions such as the symmetry of the crystal field [41].

3. Results

3.1. XRD analysis

3.1.1. Crystallization of the Mo-rich glass

The XRD patterns of the Mo glass heat treated between 650 and 1100 °C and then quenched to room temperature are presented in Fig. 3a. According to the XRD pattern of the powellite ceramic (Fig. 1a), the presence of CaMoO₄ crystals is clearly put in evidence



Fig. 3. (a) XRD patterns of the heat treated Mo glass at T_C varying from 650 to 1100 °C. All the diffraction peaks can be attributed to powellite (Fig. 1a). (b) XRD patterns of the heat treated Nd glass at T_C varying from 650 to 1100 °C. All the diffraction peaks can be attributed to apatite crystals (Fig. 1a) except several small peaks for T_C = 800 °C (indicated by asterisks) that were not identified. (c) XRD patterns of the heat treated MoNd glass at T_C varying from 650 to 1100 °C. All the diffraction peaks detected on the patterns are attributed to apatite crystals (Fig. 1a).

in all the samples heat treated between 650 and 900 °C. No Na_2MoO_4 crystals or other crystalline phases were detected by this method. For the sample heat treated at 950 °C, it is still possible to



Fig. 4. Evolution of the intensity (integration) of the XRD line located at $2\theta = 47.1^{\circ}$ of the powellite (CaMoO₄) phase formed in the heat treated Mo and MoNd glasses as a function of T_C. This diffraction line was selected because in the case of both apatite and powellite crystallization, it remains isolated and not hidden by one of the diffraction lines of apatite (as it would have been the case for instance for the most intense XRD line of powellite, located at $2\theta = 28.8^{\circ}$ (Figs. 1 and 3)).



Fig. 5. Unit cell parameters a = b and c, determined from the XRD patterns (Fig. 3a), of the powellite crystals ($I4_{1/a}$ space group) formed in the heat treated Mo glass as a function of T_c. (a) a = b parameter, (b) c parameter. For comparison, the lattice parameters of the powellite ceramic sample synthesized at 1150 °C (\bigcirc) are also reported on figure (a = b = 5.2267 Å, c = 11.4363 Å).



Fig. 6. Unit cell parameters a = b and c, determined from the XRD patterns (Fig. 3b), of the apatite crystals (space group P6₃/m) formed in the heat treated Nd glass as a function of T_C. (a) a = b parameter, (b) c parameter. For comparison, the lattice parameters of the Ca₂Nd₈(SiO₄)₆O₂ ceramic sample synthesized at 1500 °C are also reported on figure (a = b = 9.529 Å, c = 7.022 Å).

observe the most intense diffraction peak of the powellite phase but its intensity is very weak, which means that powellite crystallization rate is very low at this temperature. Then, beyond 1000 °C, no more crystallization is observed according to XRD measurements (Fig. 4). Thus, in Mo glass, powellite crystals are not stable above 950 °C. This result is in good agreement with the high temperature in situ Raman spectroscopy study of Magnin et al. [42,43] performed between 1100 and 25 °C by cooling from the melt a soda lime borosilicate composition with 2 mol% MoO₃. Indeed these authors showed, by comparing their Raman spectra with those of pure crystalline CaMoO₄ and Na₂MoO₄ at the same temperatures, that the crystallization of CaMoO₄ in their system (close to the one studied in the present paper) only occurred below 950 °C whereas Na₂MoO₄ crystallization was detected near 650 °C. In our work, quenching from $T > 950 \degree C$ probably enabled to avoid the crystallization of CaMoO₄ during cooling.

The *a* and *c* lattice parameters of the powellite crystals (scheelite structure, $I4_{1/a}$ space group) [44] formed in the Mo glass have been determined by full pattern profile fitting for the samples heat treated between 700 and 900 °C. These parameters do not evolve significantly with T_C (Fig. 5a,b) which means that by increasing T_C there is no effect of thermally activated rearrangement within the structure of powellite and that the composition of the crystals probably does not change. The *a* parameter of the crystals formed in Mo glass is consistent with the value obtained for the powellite



Fig. 7. Back-scattered SEM images of the heat treated Mo glass at T_c varying from 650 to 1100 °C, (a) 650 °C, (b) 700 °C, (c) 750 °C, (d) 850 °C, (e) 900 °C, (f) 950 °C, (g) 1000 °C, (h) 1100 °C. In several globular heterogeneities (see (f) for instance) white spots can be observed that have been identified by EDX as gold particles originating from the corrosion of the Pt–Au crucible by the melt. By comparison, melting performed in pure Pt crucibles followed by glass heat treatment has shown that the gold particles observed here have not any impact on phase separation and molybdate crystallization.



Fig. 8. Back-scattered SEM images of the heat treated Nd glass at T_C varying from 650 to 1100 °C. (a) 650 °C, (b) 750 °C, (c) 800 °C, (d) 850 °C, (e) 900 °C, (f) 950 °C, (g) 1050 °C, (h) 1100 °C.

ceramic synthesized for this study (a = 5.227 Å, Fig. 5a) and with values reported in literature (a = 5.2261 Å) [44]. However, the *c* parameter of these crystals is quite different (~0.03 Å higher, Fig. 5b) from that of the synthesized powellite ceramic (c = 11.436 Å) and from values reported in literature (11.4329 Å) [44]. The origin of this difference concerning the *c* parameter is unclear but several explanations may be proposed. The composition of the powellite crystals grown in the supercooled borosilicate melt may deviate from the CaMoO₄ stoichiometry of the ceramic, but this would be in contradiction with the lack of important difference for the *a* parameter (Fig. 5a). Nevertheless, because of their too small size (<1 µm, see Fig. 7 in Section 3.2.1), it was not possible to determine their composition by energy dispersive X-ray analysis

(EDX) or electron probe micro-analysis (EPMA). A more plausible explanation may arise from the fact that powellite is known to exhibit an important anisotropic behavior of its average lattice thermal expansion coefficient α along *a*- and *c*-axis between 25 and 1000 °C: $\alpha_a = 13.5.10^{-6}$ °C and $\alpha_b = 22.8.10^{-6}$ °C [44]. Thus, the powellite crystals formed in the supercooled melt and quenched to room temperature may have retained a slight length excess along *c*-axis after samples quenching which could explain the lattice parameters difference observed at room temperature (Fig. 5b).

3.1.2. Crystallization of the Nd-rich glass

The XRD patterns of the Nd glass heat treated between $T_C = 650$ and 1100 °C and then quenched to room temperature are presented

in Fig. 3b. According to the XRD pattern of the apatite ceramic (Fig. 1a), the presence of apatite crystals is clearly put in evidence in all the samples heat treated between 800 and 1100 °C. For $T_C = 750 \ ^{\circ}C$ only very weak intensity lines due to apatite crystallization from the surface are detected (see Fig. 8b in Section 3.2.2). From Fig. 3b it also appears that the intensity of the pattern is maximal at about 850 °C which indicates that after increasing until 850 °C, the amount of apatite crystals formed decreases with T_c. Moreover, several low intensity peaks, only detected for $T_C = 800 \degree C$ (indicated by asterisks), were not identified. By comparison with the results concerning the Mo glass presented above (Fig. 3a), it appears that the crystallization of the Nd glass occurs at higher T_C. Nd glass is thus more stable than Mo glass. This is consistent with our previous DTA results [34] that showed that the difference ΔT between the maximum of the exothermic peak T_p associated with the crystallization of apatite or powellite and $T_g (\Delta T = T_p - T_g)$ was significantly higher for Nd glass (398 °C) than for Mo glass (192 °C). This lower stability of Mo glass can be explained structurally by the higher mobility of $[MoO_4]$ entities that, unlike Nd³⁺ ions, are not directly connected to NBOs. This difference would be at the origin of the highest phase separation tendency and preferential crystallization of powellite in the bulk of Mo glass (see Fig. 7 in Section 3.2.1).

The *a* and *c* lattice parameters of the apatite crystals (hexagonal structure, space group $P6_3/m$) formed in the Nd glass have been determined by full pattern profile fitting for the samples heat treated between 850 and 1100 °C. It appears that a and c increase significantly with T_C (Fig. 6a,b) and become closer to the lattice parameters of the apatite ceramic prepared at 1500 °C (a = 9.529 Å, c = 7.022 Å). Different explanations can be proposed to explain the variation with T_C of the apatite crystals lattice parameters (Fig. 6). For instance, the composition of the apatite crystals may deviate from the stoichiometric $Ca_2Nd_8(SiO_4)_6O_2$ composition. Indeed, in a previous study performed on Nd-rich partially crystallized glasses with composition close to that of the Nd glass, we showed that the lattice parameters of the apatite crystals $(Ca_{2+x}Nd_{8-x}(SiO_4)_6O_{2-0.5x})$ decrease with the non-stoichiometry [45]. Thus, in the present study, this would mean that at low heating temperature $(T_C = 850 \circ C)$ the non-stoichiometry x of the apatite crystals would be important (x ~ 0.4 at 850 °C according to the data given by Quintas et al. [45]) and would then decrease with T_c to reach a value close to x = 0 (stoichiometric apatite ceramic composition, Fig. 6). Nevertheless, it is important to note that in Ref. [45] the decrease of x was observed by increasing the CaO/Na2O concentration ratio while keeping the same thermal treatment (slow cooling from the melt or nucleation + growth). As in the present case the composition of the glass remained the same for all the heat treatment temperatures, it is possible that the increase of lattice parameters with T_C has a different origin. It is probably due to the evolution with T_C of the ordering of Ca^{2+} and Nd^{3+} ions in the 6 h and 4f sites of the apatite structure as discussed below from the optical results of the partially crystallized samples.

3.1.3. Crystallization of the Mo and Nd-rich glass

For the heat treated MoNd glass, the XRD patterns presented in Fig. 3c bring to light the crystallization of apatite $Ca_2Nd_8(SiO_4)_6O_2$ apparently as unique phase. Apatite crystallization is always observed beyond $T_C = 750$ °C, with a maximum crystallization rate in the range $T_C = 850-900$ °C (Fig. 3c). An evolution with T_C of the XRD patterns and apatite crystals lattice parameters very similar to that of Nd glass was observed (Figs. 3 and 6). Whatever T_C , no molybdate crystalline phase was detected by XRD (Fig. 3c). The effect of neodymium oxide addition on powellite crystallization is detected by XRD in the heat treated MoNd glass contrary to the heat treated

Mo glass (Fig. 3a), this puts in evidence that adding neodymium oxide to the glass composition inhibits the crystallization of molybdate phases. This observation is consistent with the results of our previous works [33,34,37] and with the SEM observations on the quenched Mo and MoNd glasses presented in this paper, where it appeared that Nd₂O₃ addition suppressed the formation of the globular Mo-rich phase detected in Mo glass. By comparison with the results concerning Mo glass presented above (Fig. 3a), it appears that the crystallization of MoNd glass occurs at higher T_C, MoNd glass is thus more stable than Mo glass. This is consistent with our previous DTA results [34] that showed that the difference Δ T between the maximum of the exothermic peak T_p associated with the crystallization of apatite or powellite and T_g was significantly higher for MoNd glass (360 °C) than for Mo glass (192 °C).

3.2. SEM analysis

3.2.1. Crystallization of the Mo-rich glass

SEM shows that powellite crystallization (facetted crystals with pyramidal shape) is uniform within the bulk of the Mo glass heat treated between 650 and 900 °C (Fig. 7a-e). The crystal size is very small for all the samples (<1 µm) but increases with T_C. Besides, it appears that the number of crystals per unit volume decreases when the temperature increases. These two observations are consistent with an Oswald ripening. When $T_C > 950$ °C, despite the fact that no crystalline phase is detected by XRD, the glass is not homogeneous. Indeed, Mo-rich globular heterogeneities (as analysed qualitatively by EDX) with a size of about 1 μ m can be observed for the heat treated Mo glass (Fig. 7g-h). Similar globular heterogeneities were also observed in the sample heat treated at 950 °C (Fig. 7f) for which only weak CaMoO₄ crystallization was put in evidence by XRD (Fig. 3a). This globular morphology, associated with the absence of diffraction peaks on the XRD patterns between 950 and 1100 °C, indicates that a phase separation phenomenon occurs at these temperatures and that the Mo-rich heterogeneities are amorphous. This is consistent with the study performed by Magnin et al. [42,43] on a Mo-rich soda lime borosilicate composition that showed that liquid-liquid phase separation of Mo-rich droplets occurred in the melt below 1100 °C. For the Mo glass sample heat treated at 950 °C, it seems that the very small diffraction peaks observed on the XRD pattern (Fig. 3a) correspond to crystals that did not appear during the thermal treatment of growth but only after, when the heat treated sample was quenched from 950 °C to room temperature. In this case, a small amount of powellite crystals was probably formed inside the separated Morich globular heterogeneities and the crystallization mechanism is consequently different from the one observed in the Mo glass heat treated between 650 and 900 °C. Indeed, the geometrical morphology of the CaMoO₄ crystals formed in this temperature range (Fig. 7a-e) indicates that they have grown within the bulk of the melt and not within globular heterogeneities. Nevertheless, the very small and homogeneously dispersed globular Mo-rich heterogeneities (~50 nm) present in the quenched Mo glass and originating from a small scale phase separation in the melt during quenching, probably act as nucleation sites in the bulk for the crystallization of the facetted CaMoO₄ particles during thermal treatment below 950 °C. During growth, these crystals probably consume the molybdenum initially present in the small globular Mo-rich heterogeneities, so that after 6 h heating, there are no traces of the initial small scale phase separation (Fig. 7b-e).

Macroscopic observations show that the heat treated Mo samples are totally opaque when $T_C < 950$ °C (the samples corresponding to $T_C = 700$ and 750 °C are shown in Fig. 2a,b) and become slightly translucent when $T_C \ge 950$ °C. According to the SEM results, the presence of a high density of crystalline particles dispersed



Fig. 9. Back-scattered SEM images of the heat treated MoNd glass at T_C varying from 650 to 1100 °C: (a) 650 °C, (b) 700 °C, (c and i) 750 °C, (d) 850 °C, (e) 900 °C, (f) 950 °C, (g) 1000 °C, (h) 1100 °C, (j) 800 °C. A: apatite Ca₂Nd₈(SiO₄)₆O₂; M: Mo-rich globular heterogeneities.

everywhere in the bulk with size higher than 100 nm in the glass heated below 950 °C (Fig. 7) enables to explain why these samples appear totally opaque (Fig. 2a,b) whereas the samples heated at $T_C \geq 950$ °C are slightly opalescent due to the lower density of particles (Fig. 7).

3.2.2. Crystallization of the Nd-rich glass

SEM images show that the microstructure and the distribution of the apatite crystals formed in the Nd glass strongly depend on T_C (Fig. 8). At $T_C = 650$ °C, in accordance with XRD (Fig. 3c) no crystals are detected neither in the bulk nor on the surface of the sample (Fig. 8a). For $T_C = 750 \ ^{\circ}C$ (Fig. 8b), apatite crystallization (heterogeneous) is almost only detected from the glass surface (layer thickness ~ 30 μm). For 800 $^\circ C$ \leq T_C \leq 950 $^\circ C$ (Fig. 8d–f), the amount of crystals has strongly increased in accordance with XRD (Fig. 3c) and apatite crystallization is detected both from the surface and in the bulk. As observed by XRD, the maximal density of crystals occurs at $T_C = 850$ °C. Below 900 °C the crystals exhibit a dendritic shape that can be explained by the high viscosity of the supercooled melt in this temperature range. Above $T_C = 950 \ ^{\circ}C$ (Fig. 8g,h), the density of crystals has significantly decreased. Crystals are still formed in the bulk but their microstructure is no more dendritic due to the decrease of the viscosity of the supercooled melt in this temperature range. All these SEM results are in agreement with macroscopic observations showing that the heat treated Nd samples remain transparent in the bulk when $T_C \leq 750$ °C but become opaque when $T_C \geq 800$ °C (the samples corresponding to $T_C = 700$ and 800 °C are shown in Fig. 2c,d).

3.2.3. Crystallization of the Mo- and Nd-rich glass

The SEM images of the heat treated MoNd glass bring additional information (Fig. 9). Firstly, they confirm the XRD results as it is possible to observe the dendritic-shape and then hexagonal-shape apatite crystals for T_C ranging from 750 to 1100 °C. The evolution with T_C of the shape and distribution (surface/bulk) of apatite crystals is globally similar to that of the Nd sample (Fig. 8). Nevertheless, a careful examination of the apatite crystals growing from the surface shows significant differences between the Nd and MoNd samples. Indeed, the thickness of the crystallized layer significantly increases when MoO₃ is added to the glass composition, for instance it grows from 30 to 200 μm for T_C = 750 $^\circ C$ (Figs. 8b and 9i) and from 170 to 700 μ m for T_C = 800 °C (Figs. 8c and 9j). The layer microstructure is also different between the Nd and MoNd samples. Whereas the crystals constituting the layer of the heat treated Nd glass almost all originate from the surface (Fig. 8), the crystallized layer of the heat treated MoNd glass is made of a succession of apatite crystals that have nucleated at different distances from the surface (Fig. 9i-j). Besides, by comparing the SEM images obtained for the heat treated Mo and MoNd glasses, the strong effect of neodymium oxide on the crystallization of molybdate phases put in evidence by XRD can be described more precisely. Indeed, at 650 and 700 °C, no crystals are observed in the bulk of the heat treated MoNd glass (Fig. 9a-b), whereas powellite clearly appeared in the bulk of the heat treated Mo glass for the same T_C (Fig. 7a-b). Macroscopic observation confirms that in this temperature range the MoNd samples - unlike the heat treated Mo samples (Fig. 2a) – remain transparent in the



Fig. 10. Evolution of the normalized Raman spectra (in the region 700-1200 cm⁻¹) of the heat treated Mo (a) and MoNd (b) glasses at T_c varying from 650 to 1100 °C. The spectra have been corrected for temperature and frequency dependent scattering intensity. The black circles (\bullet) correspond to the vibration bands of [MoO₄]²⁻ tetrahedral entities in the powellite phase, the white square (\Box) corresponds to a vibration band of [MoO₄]²⁻ tetrahedral entities in the Na₂MoO₄ crystalline phase and the star (*) corresponds to the symmetric stretching vibration of [MoO₄]²⁻ tetrahedral entities in the glassy phase. The broad band located around 1070 cm⁻¹ is due to the symmetric stretching vibration of the [SiO₄]⁴⁻ (Q_n) tetrahedral entities in the glass (the dotted line is a guide for the eyes), it is difficult to detect this band for the Mo glass heat treated between 650 and 900 °C because of the presence of the intense bands due to the vibration of [MoO₄]²⁻ tetrahedral entities in the glast (SiO₄)₆O₂ phase. In accordance with XRD, no crystalline phases were detected by Raman spectroscopy (spectra not shown) for the quenched Mo and MoNd glasses [34].

bulk (Fig. 2e). Thus, in agreement with the XRD results (Fig. 3a and c), it is clearly shown that Nd₂O₃ addition inhibits the crystallization of the powellite phase in the bulk when $T_C < 750$ °C. In this temperature range only a very thin partially crystallized layer (10–15 µm) - probably constituted of apatite crystals - is formed from the surface (not shown in Fig. 9). When $T_C \ge 750$ °C, apatite crystallizes both from the surface and the bulk of MoNd glass (Figs. 2f and 9c–j) as in Nd glass (Fig. 8). Nevertheless, contrary to Nd glass, it is here possible to observe small (<1 µm) globular heterogeneities (Mo-rich, as analysed qualitatively by EDX) between and close to the apatite crystals (Fig. 9c–g). According to the study of the heat treated Mo glass presented above, these globular heterogeneities probably originate from a phase separation phenomenon in the neighborhood of the apatite crystals where the

residual glass has been neodymium depleted (as shown in Ref. [37] by electron microprobe analysis of Nd close to the apatite crystals formed during slow cooling from the melt in MoNd glass). In the next section, it is shown by Raman spectroscopy that these heterogeneities are not totally amorphous. The presence of such Morich particles in the neighborhood of apatite crystals was already observed after slow cooling from the melt in a previous paper [34].

3.3. Raman spectroscopy

3.3.1. Crystallization of the Mo-rich glass

Raman spectra of the Mo glass heat treated between 650 and 1100 °C are presented in Fig. 10a. They are consistent with the results obtained by XRD and SEM (Figs. 3a and 7). Indeed, for the Mo glass heat treated between 650 and 900 °C, the symmetric stretching vibration bands of the [MoO₄]²⁻ tetrahedral entities in CaMoO₄ crystals clearly appear with very high intensities. These bands can be associated with this crystalline phase thanks to the Raman spectrum of the pure powellite ceramic (Fig. 1b). Besides, these vibration bands are so intense that it is very difficult to observe the vibration bands of $[MoO_4]^{2-}$ tetrahedral entities and $[SiO_4]^{4-}$ (Q_n) units that are present in the residual glass. It is also interesting to note that the vibration bands of $[MoO_4]^{2-}$ tetrahedral entities in Na₂MoO₄ crystals are not observed for T_C varying from 650 to 900 °C (the spectrum of the Na₂MoO₄ reference is given Fig. 1b), which confirms that the only molybdate phase that crystallizes in the heat treated Mo glass is powellite. Even for a prolonged heat treatment (30 h) at $T_c = 750 \,^{\circ}C$ followed by quenching to room temperature, we showed in Ref. [34] by Raman spectroscopy that CaMoO₄ was the only crystalline molybdate phase crystallizing in Mo glass whereas both Na₂MoO₄ and CaMoO₄ crystals were detected after controlled cooling from the melt. This difference of crystallization tendency of Na₂MoO₄ during melt cooling and glass heating was explained from structural considerations by taking into account the temperature dependence of the amount of Na⁺ ions available for the charge compensation of molybdate entities [34]. Moreover, the fact that sodium molybdate crystals were not formed in our samples (all heat treated at $T_C \ge 650$ °C and then quenched to room temperature) is in agreement both with the low melting point of Na₂MoO₄ (~690 °C) [38,39] and with the in-situ high temperature Raman spectroscopy study performed by Magnin et al. [42,43] on a Mo-rich soda lime borosilicate glass that showed that Na₂MoO₄ crystallization only occurred below around 650 °C during melt cooling. Then, for T_C varying from 950 to 1000 °C, no more vibration bands associated with the crystallization of molybdate phases are observed and the vibration bands of $[MoO_4]^{2-}$ tetrahedral entities and $[SiO_4]^{4-}(Q_n)$ units in the glass are then clearly visible. The fact that no vibration bands associated with powellite crystals are detected for $T_C = 950$ °C in Fig. 10a whereas low intensity lines due to powellite are detected on the XRD pattern (Fig. 3a) is unclear but could be due to a sampling problem during Raman or XRD characterization. Anyway, we can conclude from these results that the Mo-rich globular heterogeneities observed by SEM when $T_C = 950-1000 \circ C$ (Fig. 7f-g) are essentially amorphous. However, it is important to note the slight crystallization observed for the Mo glass heat treated at 1100 °C. Indeed, for this sample, the Raman spectrum shows the presence of vibration bands associated with the crystallization of a small amount of both CaMoO₄ and Na₂MoO₄ phases (Fig. 10a). As we explained above, these crystalline phases are no more stable at this temperature according to the in situ high temperature Raman study of Magnin et al. [42,43]. As a consequence, it seems that these crystals were not formed during the thermal treatment at T_C, but only after, when the heat treated sample has been quenched from 1100 °C to room temperature. In this case, a small quantity of CaMoO₄ and Na₂MoO₄ crystals was formed inside the separated globular particles during cooling of the melt probably because the time that the sample reaches room temperature was longer than at 950 and 1000 °C. Nevertheless, the intensity of these vibration bands remains very low compared to the intensity of the vibration bands associated with powellite crystals in the Mo glass heat treated between 650 and 900 °C. This indicates that the crystallization detected in the Mo glass heat treated at 1100 °C is very weak and explains why CaMoO₄ and Na₂MoO₄ were not observed by XRD. Thus, this little crystallization artefact occurring during sample cooling will be not considered for the explanation of crystallization mechanisms of molybdate phases versus temperature.

3.3.2. Crystallization of the Mo and Nd-rich glass

The Raman spectra of the heat treated MoNd glass are presented in Fig. 10b. For the MoNd glass heat treated at 650 and 700 °C, the only vibration bands observed are those attributed to the symmetric stretching vibration of $[MoO_4]^{2-}$ and $[SiO_4]^{4-}(Q_n)$ entities in the glass which is consistent with the XRD and SEM results (Figs. 3c and 9). At 750 °C, a new band is observed at about 860 cm⁻¹, which is associated with the beginning of the crystallization of the apatite Ca₂Nd₈(SiO₄)₆O₂ phase (Fig. 1b) [33,37]. In accordance with XRD (Fig. 3c), the intensity of this band decreases for high T_C (1100 °C) due to the decreasing amount of apatite crystals formed in the glass. It is also interesting to note that the vibration band at about 912 cm⁻¹ of the [MoO₄]²⁻ tetrahedral entities in the glass significantly shifts toward lower frequencies (~900 cm⁻¹) as soon as apatite crystallizes. This phenomenon, linked to the evolution of the concentration of neodymium - and probably also of calcium - in the residual glass depleted in Nd₂O₃ and CaO because of apatite crystallization, has already been observed and explained in detail elsewhere [37]. It is linked to the evolution of the average field strength of the charge compensator cations (Na^+, Ca^{2+}, Nd^{3+}) in the neighborhood of $[MoO_4]^{2-}$ entities in the glass. Consequently, the shift observed for the vibration band of the [MoO₄]²⁻ entities in the glass for the heat treated MoNd glass depends on the amount of apatite formed. Moreover, it has also been observed that this shift depends on the glassy regions of the sample that are probed by the exciting laser beam during Raman experiments: the closer to the apatite crystals, the more depleted in neodymium and calcium is the residual glass and the lower is the frequency of the vibration band of $[MoO_4]^{2-}$ entities. From $T_C = 800-950$ °C, new vibration bands associated with the crystallization of CaMoO₄ and Na₂MoO₄ are detected (compare Fig. 10b with Fig. 1b), whereas these crystalline phases were not observed by XRD (Fig. 3c). As the SEM images show the presence of Mo-rich globular heterogeneities between the apatite crystals (Fig. 9), it seems that these particles are not totally amorphous but contain molybdate crystals, at least when $T_C > 750$ °C. However, the amount of crystalline molybdates is probably too low to be detected by XRD. Finally, beyond 950 °C, no crystallized molybdate phases can be detected on the Raman spectra which can be explained by the fact that such phases are no more stable in this T_C range as indicated above [42,43]. Thus, molybdates would not crystallize within the Mo-rich globular heterogeneities which would remain amorphous after quenching when $T_C > 950$ °C. Indeed, for these high T_C , Raman spectra only show the vibration bands associated with the apatite crystalline phase, and with the $[MoO_4]^{2-}$ and $[SiO_4]^{4-}$ (Q_n) entities in the residual glass.

3.4. Optical absorption

3.4.1. Crystallization of the Nd-rich glass

As strong structural and microstructural evolutions with T_C have been reported in the previous sections, a study has been conducted



Fig. 11. (a) Optical absorption spectra of Nd³⁺ ions (${}^{4}I_{9/2} \rightarrow {}^{2}P_{1/2}$ transition) recorded at T = 10 K of the quenched and heat treated (T_C = 650–1100 °C) Nd glass. The spectrum of apatite Ca₂Nd₈(SiO₄)₆O₂ ceramic is given at the top. For the ceramic, the two intense bands correspond to Nd³⁺ ions located in the 6 h and 4f sites. The small band indicated by an asterisk (*) on the ceramic spectrum is probably due to Nd³⁺ ions also located in the 4f site of apatite crystals but that are slightly different to that of the most intense band (this small band was not considered for the spectra simulation used in Fig. 12). (b) Optical absorption spectra of Nd³⁺ ions (${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}$, ${}^{2}C_{7/2}$ hypersensitive transition) recorded at T = 10 K of the heat treated (T_C = 650–950 °C) MoNd glass. The spectrum of apatite Ca₂Nd₈(SiO₄)₆O₂ ceramic is shown at the top Nd³⁺ ions located in the 6 h and 4f sites of apatite crystals. P: bands due to Nd³⁺ ions in powellite crystals [22,37].

by optical absorption spectroscopy on the guenched and heat treated Nd glass to follow the incorporation of Nd³⁺ ions in apatite crystals. The evolution with T_C of the spectra corresponding to the ${}^{4}I_{9/2} \rightarrow {}^{2}P_{1/2}$ transition is shown in Fig. 11a. For comparison, the optical absorption spectrum of the apatite Ca₂Nd₈(SiO₄)₆O₂ ceramic is also given. Between $T_C = 650$ and 750 °C, only one broadband (~100 cm⁻¹ width) with maximum at 23217 cm⁻¹ is detected. This band is similar to that of neodymium in the guenched Nd glass which shows (bottom spectrum in Fig. 11a) that, for this T_C range, the great majority of Nd³⁺ ions remained in the glassy phase (for $T_C = 750 \ ^\circ C$ only a very small amount of apatite crystals formed on glass surface was detected by XRD and SEM (Figs. 3b and 8b)). From 800 °C, two new narrower bands are detected on the spectra at about 23143 and 23245 cm⁻¹. By comparison with the spectrum of the apatite Ca₂Nd₈(SiO₄)₆O₂ ceramic (top spectrum in Fig. 11a), these two new contributions can be attributed to the absorption of



Fig. 12. Evolution with T_C of the position of the optical absorption bands (${}^{4}I_{9/2} \rightarrow {}^{2}P_{1/2}$ transition) of Nd³⁺ ions in the heat treated Nd glass: (a) 4f site, (b) 6 h site, (c) residual glass. The position of the bands associated with Nd in the 6 h and 4f sites of the apatite Ca₂Nd₈(SiO₄)₆O₂ ceramic (AC) is also shown (\bigcirc).

Nd³⁺ ions in the 6 h and 4f sites respectively. All spectra were simulated with three Gaussian bands: one for Nd³⁺ ions in the residual glass and one for each of the sites (6 h, 4f) occupied by Nd³⁺ ions in apatite crystals. The evolution of the position of these three bands with T_C is shown in Fig. 12. Firstly, concerning the evolution of the position of the band associated with Nd³⁺ ions in the glassy phase (Fig. 12c), for T_C < 800 °C no significant evolution is observed, but as soon as apatite crystallized in the bulk, a significant shift towards low energies is put in evidence (the shift maximum (17.7 cm⁻¹) is observed for T_C = 850 °C). When T_C ≥ 900 °C, a shift in the opposite direction, towards higher energies, is observed to reach a value (23215 cm⁻¹) for T_C = 1100 °C only slightly lower than that of the quenched Nd glass. Concerning

now the evolution with T_C of the bands associated with Nd^{3+} ions in the apatite crystals (4f and 6 h sites), a significant shift with T_C of their position (Fig. 12a,b) and an evolution of their relative intensities (increase of the intensity of the 6 h band, Fig. 11a) towards that of the $Ca_2Nd_8(SiO_4)_6O_2$ ceramic are put in evidence.

The variation with T_C of the position of the ${}^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition associated with the neodymium ions remaining in the glassy phase (Fig. 12c) indicates that the environment of these ions is significantly modified after crystallization. This is related to a variation of the average Nd–O bond covalence linked to an evolution of the average Nd–O bond length in the glass surrounding the crystals (nephelauxetic effect) [41,46]. For instance, a band shift towards lower energies indicates an increase of the Nd–O bond



Fig. 13. Schematic representation proposed for the structure of peralkaline aluminoborosilicate glasses containing sodium, calcium and neodymium according to previous works [3,47]. In peralkaline glass compositions, as it is the case of the Nd glass of the present study, the amount of charge compensator cations (here Na⁺ and Ca²⁺) available is higher than the amount of AlO₄ entities. In this figure are shown: bridging oxygen atoms (BOs), non-bridging oxygen atoms (NBOs), SiO₄ tetrahedra with or without NBOs, AlO₄ and BO₄ tetrahedra charge compensated by Na⁺ or Ca²⁺ cations, BO₃ triangles and Nd³⁺ cations with their nearest neighbor oxygen atoms. According to both molecular dynamics simulation results [51–53] and bond valence-bond length considerations [3] reported on RE-bearing silicate and aluminosilicate glasses, the nearest neighbor oxygen atoms of neodymium would be mainly NBOs. Nd³⁺ ions would be preferentially located in Na⁺, Ca²⁺ and NBO-rich regions of the network (depolymerized regions indicated by PR). In DR, Na⁺ or Ca²⁺ cations would both contribute to the formation of NBOs and to compensate the negative charge excess of the NBOs present in the neighborhood of Nd³⁺ ions. The dotted lines separate DR and PR regions.

covalence and a decrease of the Nd–O distance [46]. Thus, the band shift towards lower energies for 750 $^{\circ}C < T_C < 900 \,^{\circ}C$ indicates that the average Nd-O distance in the residual glass has decreased in comparison with the average Nd-O distance in the quenched glass and in the samples heat treated at $T_C \leq 750$ °C. Then, for $900 \circ C < T_C < 1100 \circ C$, the average Nd–O distance increases again to finally reach an average Nd-O distance close to that of the quenched glass. This evolution of the Nd–O distance in the glassy phase with T_c can be explained by the variation of the total amount of apatite crystals formed (Figs. 3b and 8) and by the consecutive evolution of the relative proportions of Na^+ and Ca^{2+} cations available in the glassy phase for local charge compensation in the neighborhood of the non-bridging oxygen atoms (NBOs) surrounding Nd³⁺ ions (see the structural scheme shown Fig. 13 proposing that Nd^{3+} ions are located in the (Na^+, Ca^{2+}) -rich depolymerized regions of the glass structure) [3,47]. Indeed, the crystallization of apatite, that contains two calcium atoms by formula unit, induces a depletion of Ca^{2+} ions - and thus a relative enrichment in Na⁺ cations - in the residual glass. Thus, using bond valence - bond length considerations [46], it can be shown that the Na^+/Ca^{2+} concentration ratio increase in the surrounding of Nd^{3+} ions induces a decrease of the average Nd-O distance. The opposite tendency (Nd–O increase) observed when $T_C \geq$ 900 °C, can be explained by the progressive decrease with T_C of the amount of apatite crystals - and thus by the decrease of the Na^+/Ca^{2+} concentration ratio in the residual glass - as shown by XRD and SEM (Figs. 3b and 8).

The variation with T_C of the intensity and position of the ${}^{4}I_{9/}_{2} \rightarrow {}^{2}P_{1/2}$ transitions associated with Nd³⁺ ions in the 4f and 6 h sites of apatite crystals (Figs. 11a and 12a,b) can be explained by a strong evolution with T_C of the distribution of Ca²⁺ and Nd³⁺ ions

between the 6 h and 4f sites from a random occupancy of Nd^{3+} ions between the 6 h and 4f sites for the lowest temperature to an occupancy closer to that existing in the $Ca_2Nd_8(SiO_4)_6O_2$ ceramic apatite prepared at 1500 °C (preferential occupancy of 6 h sites by TR^{3+} ions [48,49]) for the highest temperature. A similar evolution of ions occupancy was already observed and discussed in Ref. [50] about the effect of the heating temperature on the structure of the apatite crystals formed in a Nd-rich soda-lime aluminoborosilicate glass. The lower thermal energy available at low T_C for cations diffusion is probably not sufficient to enable cationic organization inside apatite crystals during heat treatment to minimize their free energy which would explained the evolution observed.

3.4.2. Crystallization of the Mo and Nd-rich glass

The evolution with T_C of the spectra corresponding to the ${}^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition of Nd^{3+} in MoNd glass (not shown) is very similar to that of the heat treated Nd glass (Fig. 11a). The bands associated with Nd^{3+} ions in the 6 h and 4f sites of the apatite crystals are detected above 700 °C and present a similar evolution with T_C towards the spectra of the Ca_2Nd_8(SiO_4)_6O_2 ceramic. This confirms the XRD results presented above that have shown that the presence of MoO_3 does not strongly disturb apatite crystallization. Nevertheless, following only this transition, the presence of a fraction of Nd^{3+} ions in the molybdate crystals (detected by Raman spectroscopy in the MoNd heat treated glass, Fig. 10b) cannot be excluded. Indeed, in a previous work [37], we showed that the position of the ${}^4I_{9/2} \rightarrow {}^2P_{1/2}$ band associated with Nd^{3+} in the 6 h site of apatite crystals occurs at the same position as the band associated with Nd^{3+} in powellite crystals. However, the study of the evolution with T_C of the ${}^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition clearly demonstrates that a small fraction of Nd^{3+} ions is detected in the



Fig. 14. Schematic representation of phase separation and crystallization phenomena of molybdates in a soda-lime aluminoborosilicate glass as a function of both Nd₂O₃ addition and T_C, according to this work. (a) crystallization of Mo glass at low T_C (<750 °C) \rightarrow formation of facetted powellite crystals throughout the sample; (b) effect of the addition of Nd₂O₃ to Mo glass (MoNd glass) at low T_C (<750 °C) \rightarrow suppression of molybdate crystallization; (c) effect of increasing T_C (\geq 750 °C) \rightarrow crystallization of apatite from the surface and in the bulk; (d) phase separation and crystallization (CaMO₄ + Na₂MOO₄) at T_C of a globular Mo-rich phase (in yellow) in the neighborhood of the apatite crystals formed at T_C \geq 750 °C (when T_C \geq 1000 °C, molybdate crystallization is not observed, Fig. 10b). P: powellite facetted crystals, RG: residual glass remaining between the crystal, HG: homogeneous glass without any phase separation and crystallization, A: Apatite Ca₂Nd₈(SiO₄)₆O₂ crystals (pink). The evolution of the residual glass shown in the figure between (b) and (c) indicates that this one is depleted in Nd after apatite crystallization. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

powellite crystals when $750 \le T_C \le 900$ °C (Fig. 11b) which is close to the T_C range where powellite is detected by Raman spectroscopy (Fig. 10b).

4. Discussion

4.1. Effect of neodymium addition on the crystallization of molybdate phases

According to the results presented above, the comparison between the quenched and heat treated Mo and MoNd glasses allows putting in evidence compositional effects on the phase separation and crystallization tendency of molybdate phases in these glasses:

- According to SEM, Nd₂O₃ addition to the glass composition inhibits the phase separation of molybdates in the quenched glasses.
- According to XRD measurements (Figs. 3b and 4), Nd₂O₃ addition also inhibits the crystallization of molybdates in the heat treated glass samples when T_C < 750 °C. This observation is confirmed by SEM for T_C = 650 and 700 °C (compare Fig. 7a–b to Fig. 9a–b). However, for the MoNd glass heated at T_C ≥ 750 °C, Mo-rich globular heterogeneities are observed between the apatite crystals formed in the bulk or from the surface (Fig. 9c–h). Because of their characteristic morphology and their location only in the neighborhood of the apatite crystals, it seems that these Mo-rich particles come from a phase separation phenomenon in the Nd-depleted supercooled melt close to the apatite crystals formed at T_C. According to Raman spectra (Fig. 10b), these globular particles contain CaMoO₄ and Na₂MoO₄ crystals, but in a concentration too low to be detected by XRD (Fig. 3c).

All these observations can be summarized by a simple scheme (Fig. 14) that can be described as follows. When glass composition does not contain Nd₂O₃ (Mo glass), a Mo-rich phase is formed throughout the sample during the thermal treatment, either as facetted powellite crystals (T_C < 950 °C, Fig. 14a) or as globular amorphous particles (T_C ≥ 950 °C, Fig. 7). When Nd₂O₃ is added to the glass composition (MoNd glass), the crystallization of the powellite phase disappears for thermal treatments at T_C < 750 °C (Figs. 9a–b and 14b), which means that neodymium addition improves the solubility of molybdenum in the glass in accordance

with our previous works [34,37]. We proposed that it is the close relationship existing between Nd³⁺ cations and [MoO₄]²⁻ tetrahedral entities in the glassy network [37] that is at the origin of the increase of molybdenum solubility and of the disappearance of the phase separation and crystallization of powellite when neodymium is added to the glass composition. However, in accordance with the results concerning the glass composition with only Nd₂O₃ (Nd glass, Figs. 3b and 8), when $T_C > 750$ °C apatite crystallizes firstly only from the surface of the MoNd glass and then also in the bulk (Figs. 3c and 9). Consequently, the Mo-rich residual glass remaining between and close to the apatite crystals is depleted in neodymium (Fig. 14c). As a matter of fact, the composition of this residual glass becomes closer to that of the Mo glass that does not contain Nd₂O₃ and for which Mo-rich phase separation or powellite crystallization may occur during heat treatment (Fig. 7). In these conditions, the solubility of molybdenum is affected which can explain the formation of Mo-rich globular particles containing CaMoO4 and Na₂MoO₄ crystals between apatite crystals (Fig. 14d). The fact that the formation of Na₂MoO₄ is almost never observed in the heat treated Mo glass (Fig. 10a) whereas it is detected along with CaMoO₄ in the heat treated MoNd glass (Fig. 10b) can be explained by the increase of the Na/Ca ratio in the residual glass close to the apatite crystals (Ca depletion).

Thus, this study of thermal stability versus temperature confirms that neodymium addition to a Mo-rich glass inhibits the separation and crystallization of molybdate phases as long as apatite crystallization is avoided (T_C < 750 $^{\circ}$ C). Otherwise, the separation of a Mo-rich phase followed by molybdates crystallization appears again in the Nd-depleted regions of the residual glass (i.e. close to apatite crystals). In particular, it is important to avoid the crystallization of Na₂MoO₄ that could incorporate radioactive Cs and is poorly durable, and consequently prohibited for the nuclear application envisaged here. As during the interim storage and geological disposal of nuclear waste glasses their temperature is expected to always remain about 100 °C lower than Tg (Tg ~ 580 °C for the simplified nuclear waste MoNd glass studied in this work), no apatite crystallization is expected during storage (T < 750 °C, Fig. 10b) and all the RE present could help the incorporation of Mo⁶⁺ cations in the glass structure, thus preventing molybdates separation and crystallization. Nevertheless, it is important to underline that during nuclear glass production the melt (at 1150-1300 °C) is not rapidly quenched below 750 °C but it is poured in a metallic canister and undergo natural cooling



Fig. 15. Schematic representation of crystallization and phase separation phenomena close to the surface of Nd (top) and MoNd (bottom) glasses as a function of time at a given temperature T_{C} . (a) quenched Nd glass; (b,c) apatite crystallization from the surface of the Nd glass with increasing the duration of heat treatment; (d) quenched MoNd glass; (e) apatite crystallization from the surface of the MoNd glass followed by the separation of Mo-rich particles between apatite crystals during heat treatment; (f) nucleation and growth of new apatite crystals from the region containing Mo-rich particles with increasing the duration of heat treatment of MoNd glass. To simplify the figure, apatite crystals nucleating directly in the bulk (observed in Figs. 8 and 9) have not been represented. G: glass; A: Apatite $Ca_2Nd_8(SiO_4)_6O_2$ crystals (in pink); M; Mo-rich globular partially crystallized particles (in yellow). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(~1 °C min⁻¹). During this cooling (several hours), partial crystallization of the melt could occur. In a previous paper performed on similar glass compositions containing both MoO₃ and Nd₂O₃ [37] we showed that if the amount of Nd₂O₃ remains lower than 14 wt% (i.e. 3.0 mol%) and higher than 8 wt% (i.e. 1.65 mol%) no crystallization (apatite or molybdates) occurs during controlled cooling of the melt from 1300 °C to room temperature at 1 °C min⁻¹. However, for the MoNd glass studied in the present paper which is slightly above the upper limit - because it contains 16 wt% Nd₂O₃ (Table 1) - we showed in Ref. [37] that during cooling at 1 °C min⁻¹ the melt partially crystallized in apatite followed by phase separation and crystallization of Mo-rich particles. Therefore, to benefit from the positive effect of the presence of rare earths on the solubility of molybdenum both during nuclear glass synthesis and storage, it is very important to introduce a controlled amount of rare earths in the composition (enough to prevent molybdates crystallization but not too much to remain below rare earths solubility limit in the system).

4.2. Effect of molybdenum addition on the crystallization of the apatite phase

XRD results have shown that the evolution of the patterns (Fig. 3b and c) and lattice parameters (Fig. 6) were very similar for the Nd-rich glasses without (Nd glass) or with molybdenum (MoNd glass). Independently of the presence of MoO₃, apatite crystallization is not detected below $T_C = 750$ °C. Moreover, the optical absorption results have shown that the presence of MoO₃ in the glass composition had no impact on the evolution of the environment of Nd³⁺ ions in the apatite crystals formed during heat treatment (same evolution of spectra with T_C for Nd and MoNd glasses). All these results demonstrate that the addition of molybdenum to the Nd glass has no effect on the temperature above which apatite crystallization is detected ($T_C \ge 750$ °C) and on the structure of the

apatite crystals formed during heat treatment. Nevertheless, SEM observations have put in evidence that the thickness of the crystallized layer (mainly constituted of apatite crystals) and growing from the surface was significantly higher when MoO₃ was present in glass composition (Figs. 8 and 9). Important microstructural differences were also observed by SEM between the crystallized layers formed in Nd and MoNd glasses. Indeed, Fig. 9i-j shows that, during the heat treatment of MoNd glass, numerous new apatite crystals nucleate and grow between the apatite crystals that are growing from the surface. Such a phenomenon, which was not observed for Nd glass (Fig. 8), may explain the higher thickness of the crystallized layer in MoNd glass. As numerous Mo-rich globular heterogeneities appear between apatite crystals during their growth in the MoNd glass (Fig. 9c), we propose in accordance with a previous paper [34] that these Mo-rich particles are at the origin of the nucleation of the new apatite crystals in the crystallized layer and act as nucleating agent. Nevertheless, the fact that these apatite crystals nucleate directly or not from the surface of these Mo-rich particles remains to be checked by direct observation by TEM for instance. A scheme is proposed in Fig. 15 that compares the processes of crystallization from the surface in Nd and MoNd glasses, with the Mo-rich globular particles acting as nucleating agent for apatite and leading to an increase of the density of apatite crystals in the crystallized layer and of its thickness. The same processes also occur in the neighborhood of the apatite crystals formed in the bulk of glass samples (Fig. 9). The following sequence explains the formation of the complex crystallized layer in MoNd glass (Fig. 15d–f): (1) heterogeneous crystallization of apatite from glass surface and growth towards the bulk; (2) neodymium depletion in the residual glass between the apatite crystals in the layer; (3) decrease of molybdenum solubility in this residual glass; (4) separation of Mo-rich globular particles followed by molybdates crystallization within them; (5) nucleation of new apatite crystals from the Mo-rich particles (nucleating agent) and growth toward

the bulk. In comparison, in Nd glass, the apatite crystals forming the layer have mainly grown from the surface (Fig. 15a–c).

5. Conclusions

Mo and Nd are abundant fission products in nuclear wastes. The wish to increase in the future the amount of waste in nuclear glasses may be problematic because of the risk of separation and crystallization of Mo-rich and Nd-rich phases due to the high field strength of Mo^{6+} and Nd^{3+} cations. In order to evaluate independently the effect of the introduction of high amounts of MoO_3 or Nd_2O_3 on the thermal stability of a simplified nuclear glass and then to study the consequence of the simultaneous presence of these two oxides in this glass, three soda-lime aluminoborosilicate glasses containing only MoO_3 or Nd_2O_3 or both MoO_3 and Nd_2O_3 have been prepared and heat treated above T_g between 650 and 1100 °C. The effect of the heating temperature on the phase separation and crystallization phenomena has been investigated for these glasses and comparison has been made with crystalline reference Mo-rich or Nd-rich phases.

In the glass with only Mo, CaMoO₄ (powellite) crystallization (facetted crystals) has been detected between 650 and 900 °C and is uniform throughout the bulk of the samples (Fig. 14a). The evolution with heating temperature of the structure of CaMoO₄ crystals has been followed. In this temperature range, the small Mo-rich phase separated amorphous globular particles (~50 nm size) that are present in the quenched glass act as heterogeneous nucleation sites for the crystallization of CaMoO₄ (but not Na₂MoO₄ as shown by XRD and Raman spectroscopy). Above 950 °C, CaMoO₄ is no more stable and does not crystallize anymore, but Mo-rich amorphous globular particles (~1 μ m size) are formed by a phase separation phenomenon (Fig. 7).

In the glass with only Nd, no phase separation or crystallization has been observed below 750 °C, this glass is thus more stable than the glass with only Mo. Above this temperature, $Ca_2Nd_8(SiO_4)_6O_2$ (apatite) crystals are firstly detected only close to the glass surface (heterogeneous nucleation, Fig. 15b) and then, at higher temperature, also in the bulk (Fig. 8). The evolution with heating temperature of the structure of apatite crystals, that has been followed by XRD and optical absorption spectroscopy, has shown an increase of their lattice parameters that may be explained by the evolution with temperature of the ordering of Ca^{2+} and Nd^{3+} ions in the 6 h and 4f sites of the apatite structure. The evolution with the heating temperature of the environment of the Nd^{3+} ions remaining in the residual glass has been also followed by optical absorption spectroscopy and correlated with the evolution of the amount of apatite crystals present in the glass.

In the glass with both Mo and Nd, it has been shown that, as long as Nd^{3+} ions remain solubilized in the glass structure (i.e. as long as the apatite phase does not crystallize in the glass composition studied here, which is the case when the heating temperature remains lower than 750 °C), the presence of Nd₂O₃ inhibits the Morich phase separation and the crystallization of powellite (Fig. 14a-b) in comparison with what is observed for the glass with only Mo. Consequently, neodymium addition improves the solubility of molybdenum in the glass in agreement with our previous studies [34,37] and increases its thermal stability. It is proposed that this beneficial effect is due to a close relationship existing between Nd^{3+} ions and $[MoO_4]^{2-}$ tetrahedral entities in the regions rich in non-bridging oxygen atoms of the glassy network. However, as soon as the apatite phase is formed either from the surface or in the bulk of the glass (i.e. when the heating temperature is higher than 750 °C), the separation of globular Mo-rich particles containing CaMoO₄ and Na₂MoO₄ crystals is observed close and between the apatite crystals (Figs. 14d and 15e) because the residual glass remaining between these crystals is depleted in Nd. In the regions of the samples where these Mo-rich particles are observed numerous new apatite crystals nucleate and grow between the previous apatite crystals. In comparison with the glass with only Nd the microstructure is thus significantly modified: increase of the thickness of the apatite layer growing from the surface and higher density of apatite crystals (Fig. 15f). It is proposed that the Mo-rich particles are at the origin of the nucleation of these new apatite crystals and act as nucleating agent. Nevertheless, in comparison with the glass with only Nd, the presence of MoO₃ in the composition has not effect on the structure of the apatite crystals formed during heat treatments and on the environment of Nd³⁺ ions in these crystals.

All the results presented in this work have thus shown that the simultaneous presence of Nd₂O₃ and MoO₃ in the simplified sodalime aluminoborosilicate nuclear glass increases the glass stability if the heating temperature remains lower than 750 °C which is significantly higher than the glass transformation temperature ($T_g \sim 580$ °C). This enables to avoid the crystallization of Na₂MoO₄ that is prohibited for the nuclear application envisaged here. Nevertheless, to benefit from the positive effect of the presence of rare earths on the solubility of molybdenum also during nuclear glass synthesis and more particularly to avoid partial crystallization of apatite and molybdates during natural cooling of the melt in canisters (~1 °C min⁻¹), it is very important to introduce a controlled amount of rare earths in the composition (enough to prevent molybdates crystallization but not too much to remain below rare earths solubility limit in the system) [37].

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