Optimization of the nucleation of CaMO₄ powellite in molybdenum-rich aluminoborosilicate glass

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ABSTRACT/RESUME

Abstract: The In order to protect the humans and environment from radioactive materials dissemination during radioactive waste storage, ceramics materials offer a safe and secure solution for selected isotopes, as molybdenum. Aluminoborosilicates glass-ceramics are suitable materials for this purpose. In this study, a ceramic for Mo confinement was synthesized in Al_2O_3-Na_2O-B_2O_3-SiO_2-MoO_3alumino-borosilicate system. The material is synthesized by double melting at 1380°C for 3 h, followed by a nucleation stage at 530°C for 2 h, and a crystallization stage at 615°C. The crystallization duration is a crucial factor for the good sequestration of Mo, issued from the radioactive waste, and thus the crystallization time should be optimized. This parameter was optimized in the range from 2 to 72 h, with the aim of maximizing the occurrence of $CaMoO_4$powellite phase in the glass, and thus ensuring a suitable double confinement of Mo in the crystalline phase embedded in the glass. The phases' identification performed by X-ray diffraction (XRD) analysis shows that up to 24 h of crystallization, powellite is the main formed phase in the glass, with more than 65%. Beyond 24 h, the powellite re-dissolves in the glass with a small amount crystallized in the form of phosphate. The scanning electron microscope (SEM) analysis made it possible to observe the formation of the powellite crystalline phase. Fourier transform infrared spectroscopy (FTIR)analysis of the materials shows the similarity of chemical composition between the different glass-ceramics obtained for the whole of crystallization times. The main vibrations evidenced by FTIR are those of Si-O-Si and B-O-B bonds of SiO_4 and BO_4 structural units, respectively; and O-Mo-O of MoO_4 tetrahedrons. Raman spectroscopy analysis highlights the formation of powellite crystals in the glass, by the internal vibrations v1(2A1) and v2(2E) of MoO_4in $CaMoO_4$.

I. Introduction

The Radioactive waste solutions from research laboratories, medical sector or nuclear industry must be confined in appropriate matrix to reduce their volume before waste disposal. Powellite-based glass ceramics are the most appropriate matrices for confining radioactive molybdenum. This is justified by the fact that borosilicate glasses are known to be effective in the immobilization of radioactive waste, for their high loading capacity in radioactive elements, their high chemical durability and

resistance to self-irradiation. Moreover, when there are ceramics embedded in their structure they can ensure radioisotopes' double confinement.

The choice of ceramics to be embedded in the glassis based on the knowledge that there are many resistant naturally occurring minerals containing radioactive and non-radioactive species very similar to the radionuclide's contained in many radioactive waste solutions [1].

Powellite ($CaMoO_4$) is a naturally occurring mineral that forms as a product of alteration of molybdenite in geological conditions.

Thus, powellite (CaMoO4) is isostructural molybdate mineral widely considered as a continuous, binary solid solution serie, the powellite-scheelite series, in which Mo^{6+}substitute for one another. Together with the analogue Pb-molybdate and tungstate mineral wulfenite, Pb(MoO4) are make up the scheelite group. The observed geochemical and petrographic features can be reconciled with a redox model involving prograde deposition of a scheelite + molybdenite assemblage, followed by interaction with low-T fluids, leading to molybdenite dissolution and reprecipitation of Mo as powellite-rich domains [2]. It can also be formed as a secondary phase during the corrosion of borosilicate glasses containing radioactive elements of high activity [3]. The powellite crystallizes in the tetragonal scheelite-type structure with the space group I41/ a, and the lattice parameters a = 5.224 Å and c = 11.43 Å,Z=4 Å; V = 312.92at room temperature, in which the central Ca^{2+} ion is coordinated by eight molybdate groups by simple links.The dipyramidal crystalline structure symmetry is 4/M, calculated density = 4.25 and Axial ratio: a:c = 1:2.18738.

Molybdenum is present as MoO_4^{2-} (Figure 1) [4].

Radionuclides can form thermodynamically stable solid solutions with powellite.

According to K. B. Patel [5], the durability of powellite at irradiation with 7 Mev Au^{3+} ion did not cause significant changes in the residual amorphous network and did not induce priming of $CaMoO_4$ based on variations in particle size and density.

Meng and all obtained the durability of the powellite Ca0.5Li0.25Gd0.25MoO4 composition exhibits the great retention of Gd and Mo, 7-day NLMoare found to be in the order of 10^{-4}g m^{-2}. The leaching behaviors of minor actinide surrogate Mo in the powellite ceramic are attributed to the interfacial dissolution–reprecipitation mechanism [6].

They remain immobilized after the initial failure e of the technological barrier of storage facilities [7].

The aim of this study is the formation of $CaMoO_4$ powellite phase in a Mo-rich alumino-borosilicate glass, in order to obtain a powellite-rich glass-ceramic material. The phase identification is carried out by different analysis methods: X-ray diffraction (XRD), and both Fourier transform infrared (FTIR) and RAMAN spectroscopies. Both techniques will illustrate the microstructural modifications in the synthesized glass-ceramic.

II. Materials and methods

II.1. Glass-ceramic synthesis

The reagents used for the preparation of the glass ceramic matrice are as follows:

Al_2O_3 (Fluka), B_2O_3 (BDH), CaO (Merck), Fe_2O_3 (Merck), Li_2O (Merck)), MoO_3 (Merck), Nd_2O_3 (Fluka), P_2O_5 (Merck), SiO_2 (SupelcoAnalytica), ZrO_2 (Aldrich), Na_2O (Merck), ZnO (Labosi), Cs_2CO_3(Fluka), $Sr(NO_3)_2$ (BDH Chemicals), et Co_3CO_4 (Fluka).

The glass is synthesized by a double melting under air at 1380°C with a step of 6°/ min for 3 hours in a Carbolite BLF1800 furnace. Glass slices of 1 to 2 mm thick are obtained by cutting the pellets in a chainsaw.
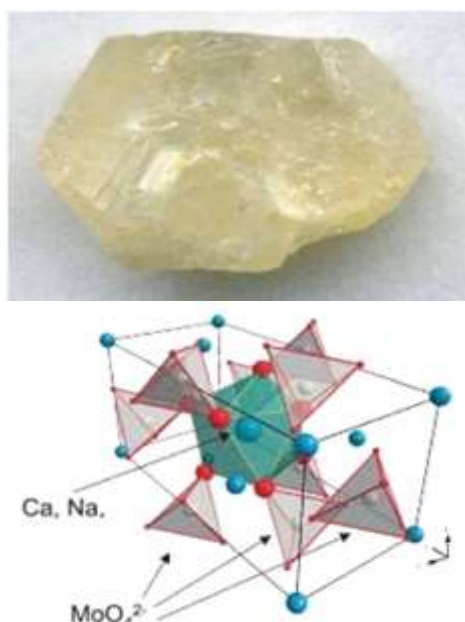
Figure 1. Monocrystal and crystalline structure of the powellite (Schmidt. M (2013)).

The pellets undergo a heat treatment carried out by two stages: a nucleation at Tn=530°C for 2 h, and a crystallization at Tc=615°C, with variation of the crystallization time, from 2 to 72 h.

The crystalline phases formed in the glass ceramic are identified by X-ray analysis using a Philips X'Pert Pro diffractometer equipped with a Cu anticathode. The phases' identification is carried out by the X' Pert High Score plussoftware [8].

The SEM observations are performed by a Zeiss supra 40 SEM microscope in BSE mode. Such mode is employed when dealing with less

conducting conducting materials. The observations are made on transversal cross sections.

The FTIR spectroscopy analysis is carried out using a NICOLT 380 apparatus in the range 3500-450 cm^{-1}. The samples are crushed, then a small amount of powder is mixed with KBr (Fluka) and pressed into a very fine pellet. The spectra obtained are processed by the OMNIC software (2001) [9].

Raman analysis is carried out with a LabRAM HR Evolution equipment with a CDD detector. The excitation source consists of a visible red laser at 633 nm. The measurements are made at ambient temperature, in the spectral range 2000-100 cm^{-1}. The samples are slices of 2 mm thickness placed on a transparent sample holder.

III. Results and discussion

III.1. *Microstructural characterization*

The X-ray spectra of glass ceramics synthesized at different crystallization times are shown in Figure 2.

For the whole, the phase identification shows the formation of a tetragonal $CaMoO_4$ phase, as a main phase (>65%- JCPDS 01-085-1267). After 24 h of crystallization, a secondary phosphate phase: $Cs_2Co(PO_3)_4$(JCPDS: 01-073-0076) appears, confining the cesium. After a longer time, powellite phase dissolves.

At 48 h, the dominant phase is a phosphate of formula $Cs_4(Mo_{10}P_{18}O_{66})$ (JCPDS: 01-084-1645), confining both Mo and Cs. Beyond 48 h, a silicate of Na, Al, and Ca: $(Ca_{0.89}Na_{0.11})(Al_{1.89}Si_{0.11})Si_2O_8$ (JCPDS: 01-089-1465)begins to form, and dominates at 72 h, with 62%.

One can conclude that the best crystallization time for powellite formation in borosilicate glass is between 24 and 48 h.
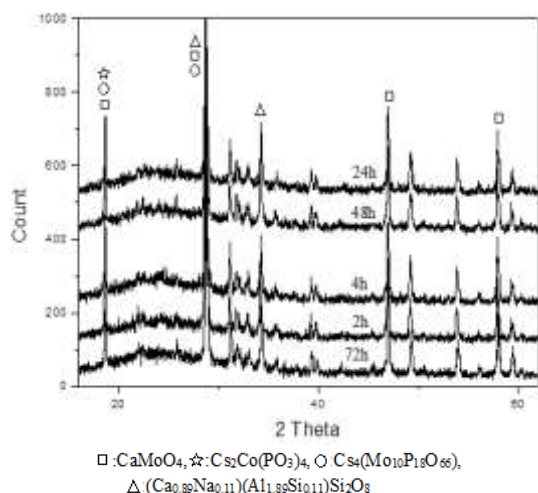

$\square$:$CaMoO_4$, ☆:$Cs_2Co(PO_3)_4$, ○ $Cs_4(Mo_{10}P_{18}O_{66})$,
△ $(Ca_{0.89}Na_{0.11})(Al_{1.89}Si_{0.11})Si_2O_8$

Figure 2. *DRX spectra of glass ceramics obtained at different crystallization times*

III.2. Scanning electron microscope analysis

Typical SEM micrographs of the glass-ceramic obtained at different crystallization times are given in figure 3.

The SEM micrographs show the presence of both glassy and crystalline phases.

The matrices' micrographs show the crystalline phases' formation on the cross section of the analyzed samples. The clearer phases represent the heaviest identified minerals.

The picture background in dark gray represents the glassy phase.

In general, there is a homogeneous repartition of the crystals in the glass host phase; which is a necessary condition to reach a homogeneous structure which can insure isotropic properties. There is no significant porosity in the observed zones.
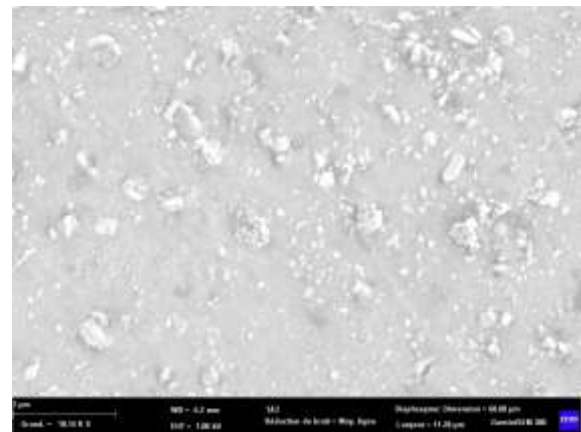

Figure 2. *A typical SEM micrograph of the synthesized glass-ceramics*

### III.3. *FTIR spectroscopic analysis*

The materials FTIR spectra for different crystallization times are given in figure 4.

The absorption bands obtained are as follows:

The weak bands around 1480 and 1653-1620 cm^{-1}, shift slightly with the increase in crystallization time, indicate the asymmetric relaxation of the B-O bond of trigonal BO_3 units [10].

The asymmetric stretching relaxation of the B-O bond of trigonal BO_3 units with NBO, reported in the literature in the region of 1360 to 1240 cm^{-1}, is absent, indicating a strong polymerization of the network [11].

The bands between 430 and 470 cm^{-1} are assigned to theflexion of the O-B-O bonds [12].
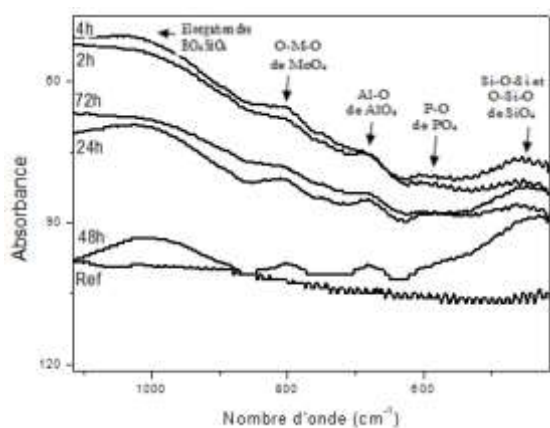
4. a. From 1100 to 400 cm^{-1}
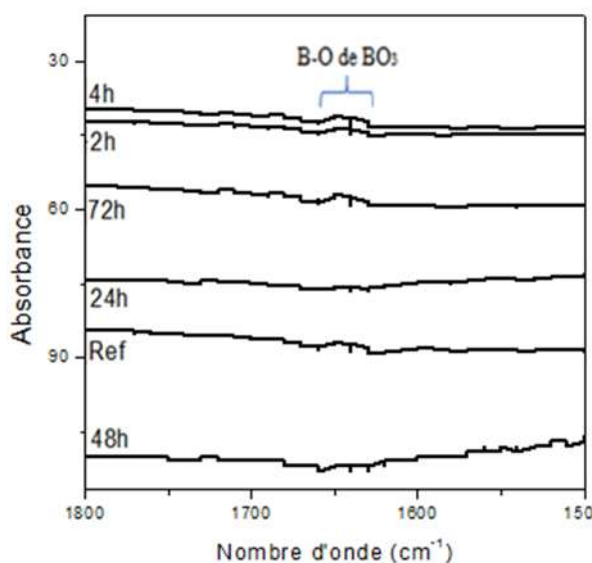
4.b. From 1800 to 1500 cm^{-1}

Figure 4. *FTIR spectra of the glass-ceramics obtained for different crystallization times.*

The In the region 900-1200 cm^{-1} appears a very broad peak reflecting the combined elongation vibrations of the borate BO_4 and silicate SiO_4 structural units. This peak is centered at 1036 cm^{-1}. It shifts from 1016 cm^{-1} to 1036 cm^{-1} when the crystallization time increases [13]. This reflects the displacement of the combined Si-O-Si and BOB elongation vibration of the SiO_4 and BO_4 structural units [14]. Moreover, in the region of 457-470 cm^{-1}

the extensional vibrations of Si-O-Si and O-Si-O of SiO_4 units are also observed [15].

A band is observed at about 811cm^{-1} due to the O-M-O elongation vibration of the MoO_4 tetrahedron of powellite. Itshifts from 850 cm^{-1} to lower wavelengths because of the influence of the glassy phase [16].

The bands appearing around 770 cm^{-1} are attributed to the vibrations of the Al-O bonds of AlO_4 units. It can shift till 700 cm^{-1} [17].

The weak peaks in the region of 595-615 cm^{-1} are attributed to the P-O bonds of PO_4 indicating the formation of apatite [18].

III.4. *RAMAN spectroscopy analysis*

The Raman spectroscopy analysis of the glass-ceramic crystallized 48 h is given in figure 5.

The vibration bands of the external modes of tetrahedral MoO_2^{-4} units and Ca^{2+} cations are at 114 and 146 cm^{-1}, respectively [19].

At 201 cm^{-1} appears a vibration band of the free rotation mode in CaMoO4, $v_{f.r}$ (2F1). The internal vibration mode v1(2A1) of MoO_4 appears in a strong band at 878 cm^{-1}.

Peaks below 201 cm^{-1} are external vibrations, indicating a high degree of crystallinity in powellite. We also observe the vibration of the MoO_4 v_2(2E) mode at 323 cm^{-1}, and that of the MoO_4 v_4(2F2) mode at 397 cm^{-1} [19]. This last band indicates the internal vibrations of MoO_4 in the structure [20].

In the 770-795 cm^{-1} region, the vibration bands are associated with the six units' rings of BO_4 vibrating with one or two BO_4 tetrahedrons [21].

Edukondalu. A (2014)) and Gaffar. MS (2009) [22] assign this peak to the formation of six-member rings containing a BO_4 tetrahedron. The displacement of these peaks towards the low frequencies indicates the vibration of these rings with six members with two BO_4 tetrahedrons in the same time.

The six-member rings vibrating with BO_4 appears in the networks: triborate, tetraborate or pentaborate; and those with six members vibrating with two BO_4 appear in the networks: diborate, di-triborate or di-pentaborate.

One can conclude to the identification of CaMoO4 phase and the incorporation of Mo in this phase, thus ensuring thedouble confinement of Mo in the synthesized glass ceramic.
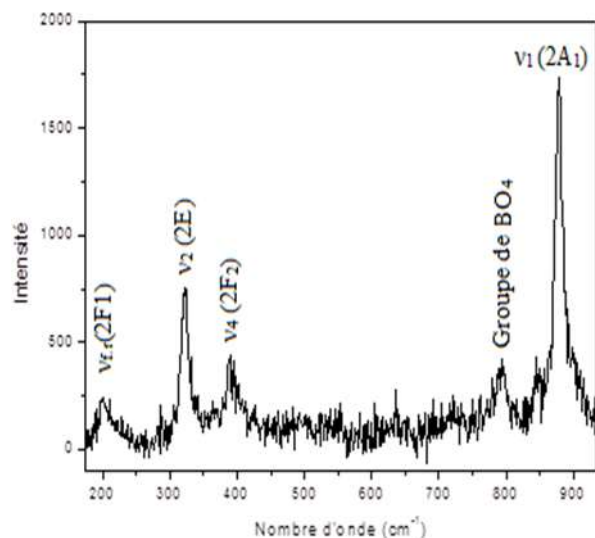
Figure 5. *RAMAN spectrum of the glass-ceramic crystallized 48 h*

IV. Conclusion

In this study, a Mo confinement glass-ceramicis synthesized in the Al_2O_3-Na_2O-B_2O_3-SiO_2-MoO_3aluminoborosilicate system. The synthesis is conducted by a double melting at 1380°C for 3 h, followed by a germination at 530°C for 2 h, and a crystallization at 615°C, the crystallization times ranging from 2 to 72 h.

The XRD analysis confirms the formation of CaMoO4 phase in the aluminoborosilicate glass, for an optimum crystallization time ranging from 24 to 48 h.

The SEM micrograph shows the presence of both glassy and crystalline phases.

The FTIR analysis of the materials shows the similarity of the chemical compositions between the different glass-ceramics obtained at different crystallization times. The main vibrations evidenced are those of Si-O-Si and B-O-B bonds of the SiO_4 and BO_4 structural units, and O-Mo-O of MoO_4 tetrahedron.

Raman spectroscopy confirms the formation of CaMoO4 crystals in the glass, by CaMoO4vibration modes: $\nu_{f.r}(2F1)$, ν_1 (2A$_1$), ν_2 (2E) et ν_4 (2F$_2$).

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