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Glass-ceramic crystallization from tailings of the Morille tungsten deposit, Spain

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ABSTRACT

The potential of the tailings from the Morille scheelite-bearing calc-silicate deposit as a commercial raw material for inert glass–ceramic was determined. Nucleation and crystal growth temperatures of glass were studied. The temperatures of maximum nucleation rate of the parent glass are 612 °C and 660 °C and crystal growth is at 776 °C and 1047 °C. At 776 °C a glass–ceramic of nepheline, wollastonite and akermanite is formed. In glasses treated at higher temperature nepheline becomes unstable and at 1047 °C a wollastonite-akermanite glass ceramic was obtained. The leaching tests show that the potentially toxic elements are effectively bound in the structure of the glass–ceramic, which can be considered inert.

1. Introduction

Mine tailings represent the deposition of great volumes of wastes susceptible of causing a high environmental pollution due to the release of potentially toxic elements (PTE). The use of tailings as raw materials for glass and glass–ceramic production is an environmentally friendly solution to the disposal of mining wastes [1,2]. In the framework of circular economy, this use complies with four of the five areas established for a sustainable mining [3]: safety, economy, resource efficiency and environment.

Tungsten is considered a strategic raw material for the European Union [4]. The stratabound-stratiform Morille deposit (Salamanca, Spain) belongs to the Sn–W metallogenic province of the Variscan European Belt. The ore is scheelite hosted in calcsilicate rocks. This deposit was mined until 1986, when the low price of metals forced its closure. Morille is currently under evaluation for to be exploited again.

The present work aims to determine the potential of the tailings from the Morille tungsten mine to be used as raw materials for glass–ceramic production. The use of these residues to produce glass was previously investigated [5]. Glass-ceramics were obtained in other tungsten tailings [6–10]. This application could contribute to reduce the wastes during a future reopening.

2. Experimental

The parental glass was prepared using 85% of wastes sampled at the Morille tungsten mines as raw materials using a procedure detailed in Alfonso et al. [5]. Several glass fragments of 1.2x1.2x0.8 cm, were used for the experiments.

Glasses were treated at the nucleation and crystallization temperatures. The temperature of maximum nucleation rate (T_{NMR}) was obtained from the Differential Thermal Analysis (DTA) of the parent glass as described by Tarragó et al. [11].

To obtain the glass-ceramics, several thermal treatments were carried out as listed: (1) glass was treated at 15 °C/min up to the T_{MNR}, 612 °C, for 6 h (2) the same treatment followed by another step up to the T_{MNR} of 665 °C, for 6 h. (3) glass directly treated at 665 °C, for 6 h. (4) nucleated glass treated at 776 °C for 4 h, (5) nucleated glass treated at 776 °C followed by step of 1047 °C for 4 h.

For the mineralogical characterization the newly-formed minerals were analysed by X-ray powder diffraction (XRD) in a Bragg–Brentano PAN Analytical X'Pert Diffractometer.

Raman spectrum of the parent glass was obtained with a T64000 Jobin-Yvon Raman spectrometer equipped with a CCD detector. The light source was an Ar^+ laser operating at 488 nm with an output of 100 mW on the sample. The integration time was 120 s and the spectral range 20 – 1500 cm^{-1}.

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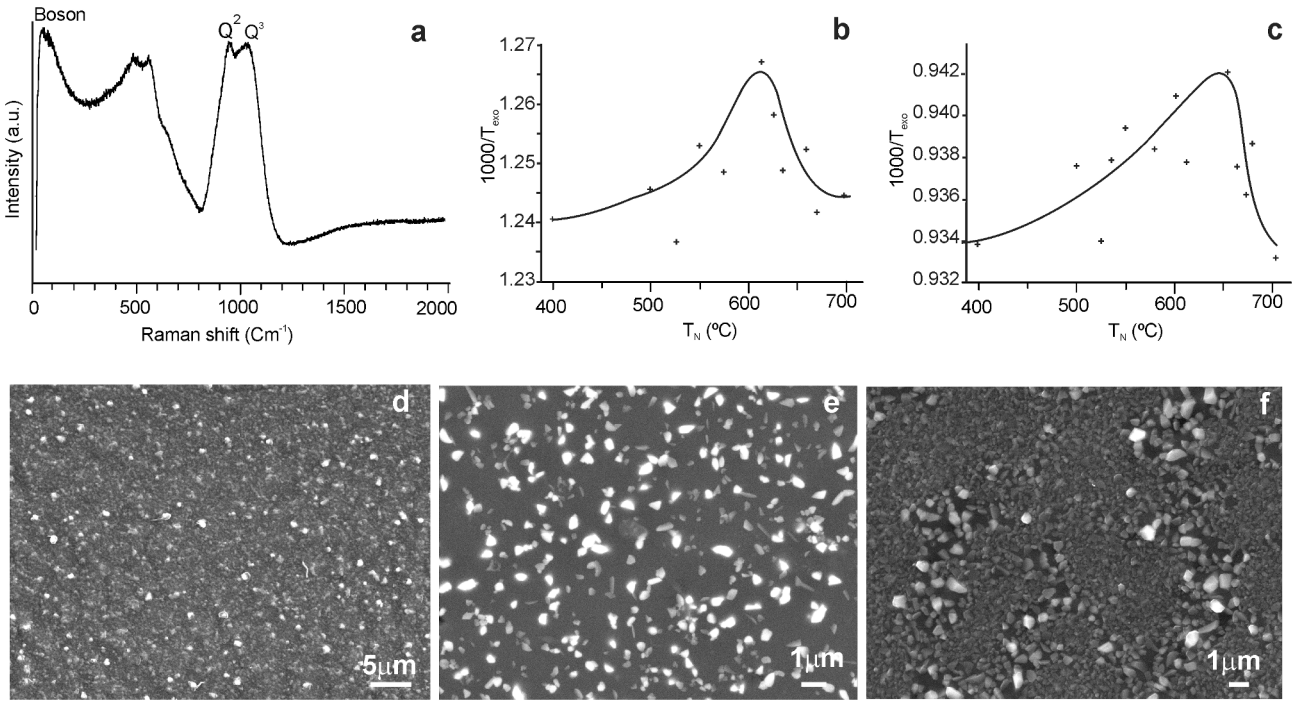

Fig. 1. a) Raman spectrum of the parent glass, b) shift of the temperature of the exothermic peak at the nucleation temperature at 612 °C, c) shift of the temperature of the exothermic peak at the nucleation temperature at 665 °C, d) glass treated at a T_{MNR} of 612 °C, e) glass treated at T_{MNR} of 612 °C and 665, f) glass treated directly at a T_{MNR} of 665 °C.

Microtextures were observed by scanning electron microscopy (SEM), using a JEOL J-7100F field emission scanning electron microscope with EDS detector INCA 250.

The leachability of the glass-ceramics was evaluated to determine their ability to be a binder for PTE according to the DIN 38414-S4 standard [12]. The leachates were analysed by inductively coupled plasma optical emission spectrometry and inductively coupled plasma mass spectroscopy. The PTE content of the glass was determined by X-ray fluorescence.

3. Results and discussion

The main characteristics of the parental glass were presented in [5]. In addition to this study a Raman analysis was carried out in the present research. In the Raman spectrum (Fig. 1a), the boson region, between 20 and 200 cm^{-1}, is characteristic of glasses and represents the distortion of the silicate network. The bands in low frequency zone, between 250 and 800 cm^{-1}, are associated with the motions of bridging oxygen in T–O–T linkages (T = Si, Al) [13,14]). The high frequency zone (800 – 1250

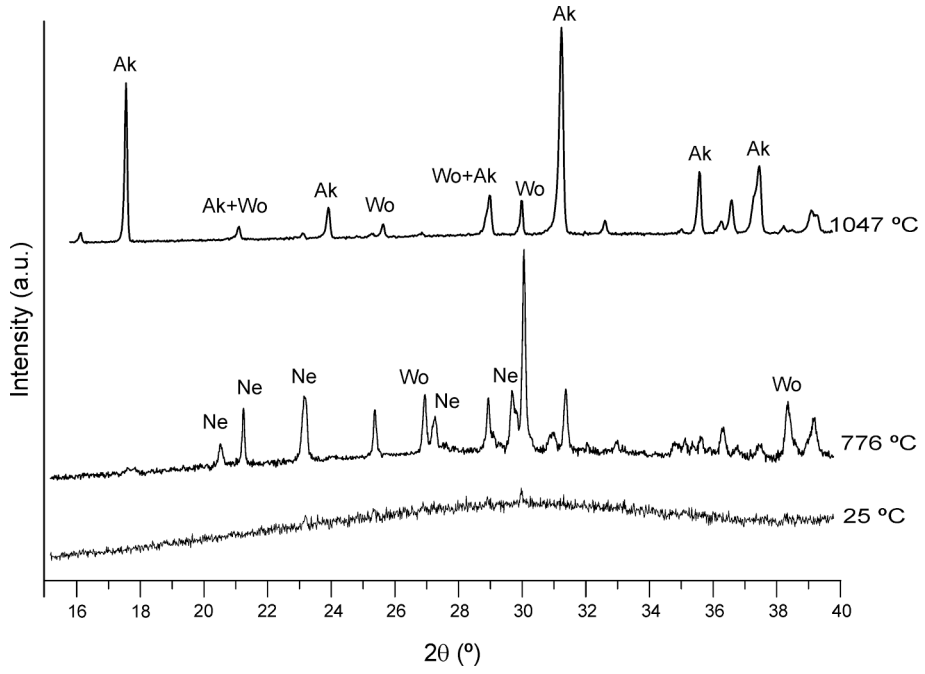

Fig. 2. XRD patterns of the parental glass and glass treated at 776 °C and 1047 °C.

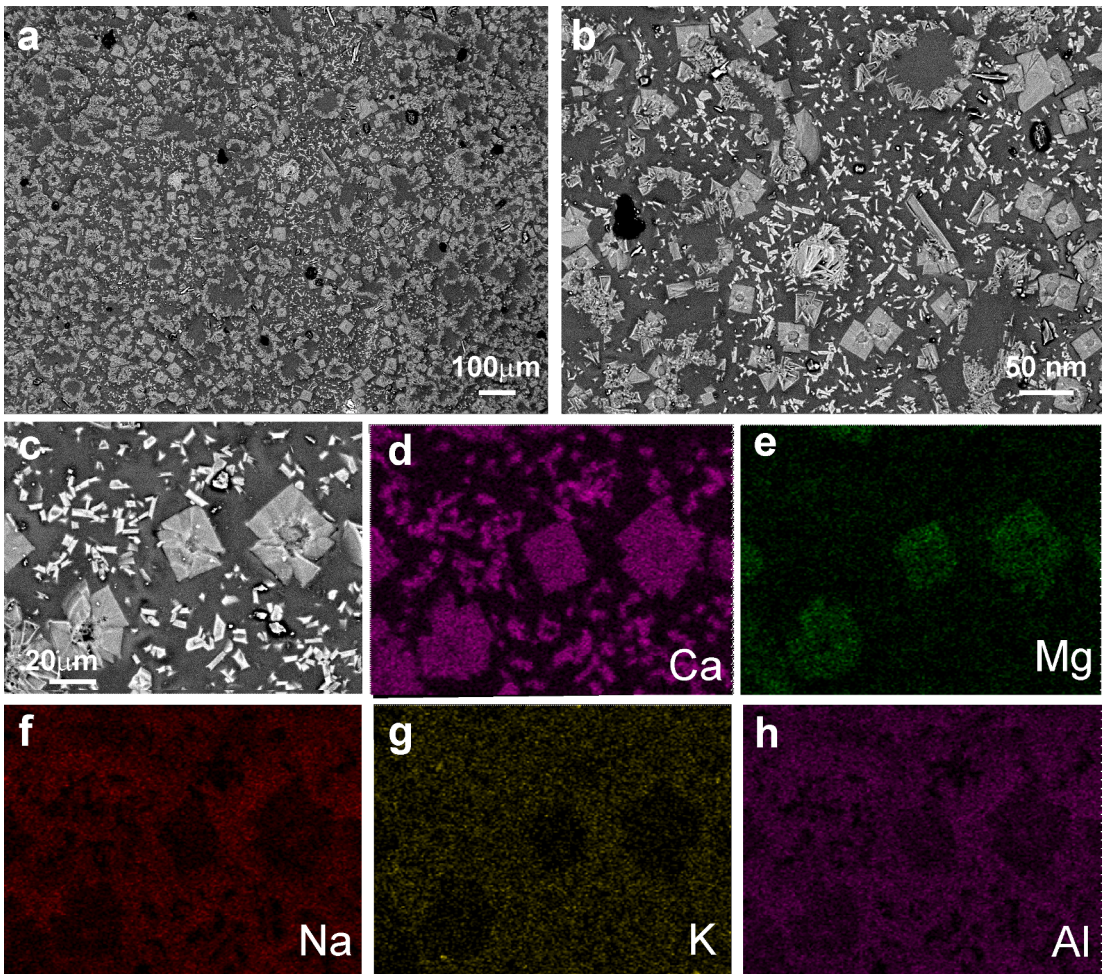

Fig. 3. SEM images of microtexture of the glass–ceramic. a) general view, b) detailed view, c) detail of the area of compositional maps presented in d-h.

cm^{-1}) corresponds to the T-O stretching motion of Q^n species (Q, TO_4 units; n, number of bridging oxygens) mainly to the vibrations of the aluminosilicate groups. The band centred at 950 cm^{-1} can be linked to Q^2 groups, representing chains and the band at 1040 cm^{-1} can be related to the vibration of Q^3 groups corresponding to such as Q^3 groups consisting of sheets or layers, and Q^2 groups representing chains [15–16].

The presence of Q^2 and Q^3 units in the Raman spectrum of the glass (Fig. 1a) could be interpreted as preceding the simultaneous nucleation of wollastonite ($CaSiO_3$) and nepheline, which nucleate in the glass and start forming at similar temperatures corresponding to the T_{MNR} of 612 °C (Fig. 1b). At 665 °C is the T_{MNR} of akermanite (Fig. 1c).

At 612 °C nepheline and wollastonite crystals of nanometric size are formed (Fig. 1d). In glasses treated directly at the T_{NMR}, at 665 °C, only the presence of a single phase is observed, with larger crystals than those treated at 612 °C and more abundant glassy phase (Fig. 1e). Nepheline, akermanite and wollastonite form in the glass treated at both T_{NMR} (Fig. 1f).

At 776 °C, the main phases formed are nepheline ($Na_3(Na,K)Al_4Si_4O_{16}$) and wollastonite together with minor contents of akermanite, whereas at 1047 °C only the two last phases remain. The rise of temperature promotes an increase in the crystallization rate of wollastonite and a decrease in the rate of nepheline crystallization. (Fig. 2).

SEM observations of the glass–ceramic show a regular microtexture constituted by two crystalline phases embedded in a glassy matrix (Fig. 3). Akermanite occurs as tabular idimorphic crystals of about 20 μm and with a dissolved center. Semiquantitative EDS analyses indicate that its composition is closer to the akermanite end member of the akermanite-gehlenite series ($Ca_2MgSi_2O_7$ – $Ca_2AlAlSiO_7$). The EDS compositional maps indicate that during crystallization Ca and Mg are preferentially locate in this phase rather than in the glassy matrix (Fig. 3). The other phase is constituted by prismatic wollastonite crystals, of about 10 μm in length.

Table 1
Potentially toxic elements (ppb) of glass and leachates from the glass–ceramic. TL: thresold limits for each PTE according to [12].

Element	Zn	Cd	Pb	As	Cu	Cr	Ni
Parent glass (x10^4)	66.2	3.3	6.4	93.2	18.0	100	27.6
GC-1047	2.6	0.01	0.81	1.12	0.33	0.32	1.49
TL	4000	40	500	500	2000	500	400

The glassy phase is enriched in Na, K and Al compared to the crystalline phases and constitutes the matrix in which the crystals are arranged. Some unconnected pores also appear.

The crystalline evolution with temperature can be attributed to the fact that initially, the glass has a relatively low SiO_2 content, so the most stable phase will be a feldspathoid, in this case nepheline. The concentration of Si in the residual glass increases up to the point where nepheline becomes unstable and only wollastonite and akermanite remain.

3.1. Leaching behaviour

The leaching test in the glass–ceramic evaluated the efficiency of the vitrification method in the inertization of hazardous metals, showing that the PTE content in the leachate was low (Table 1), always under the threshold values indicated in DIN 38414-S4 [12]. In the present study,

the potentially toxic elements present in the mining waste were bound in the structure of the glass-ceramics in agreement to previous studies of glass ceramics obtained from tailings [17].

4. Conclusions

Calc-silicate waste originated in tungsten mining are appropriate to produce glass–ceramic materials. The parent glass had T_{MRN} at 612 °C and 665 °C and crystallization temperatures at 776 °C and 1047 °C.

Nepheline, wollastonite and akermanite crystallised from the treatment at 776 °C. Nepheline formed simultaneously with wollastonite but this became unstable at higher temperatures, hence, the glass–ceramic obtained at 1047 °C contains wollastonite and akermanite.

The contents in potentially toxic elements leached from the obtained glass–ceramic were below the limits established by the European legislation. In consequence, Morille mine tailings can be used as raw materials in glass–ceramic production following the principles of circular economy (reducing both environmental pollution and waste volume).

CRediT authorship contribution statement

Pura Alfonso: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Oriol Tomasa:** Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Maite Garcia-Valles:** Methodology, Software, Validation, Formal analysis, Investigation, Resources, Writing – original draft, Writing – review & editing. **Mariona Tarrago:** Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Salvador Martínez:** Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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