

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

O. Tomasa<sup>1</sup>, M. Garcia-Valles<sup>2</sup>, P. Alfonso<sup>1</sup>, M. Tarragó<sup>3</sup>, S. Martínez<sup>2</sup>

<sup>1</sup>Departament d'Enginyeria Minera, Industrial i TIC, Universitat Politècnica de Catalunya Barcelona Tech, Manresa 08242 maria.pura.alfonso@upc.edu

<sup>2</sup>Departament de Mineralogia, Petrologia i Geologia Aplicada, Universitat de Barcelona, Barcelona 08028

<sup>3</sup>Departament Institut de Physique du Globe de Paris, Paris, 750055



## Introduction

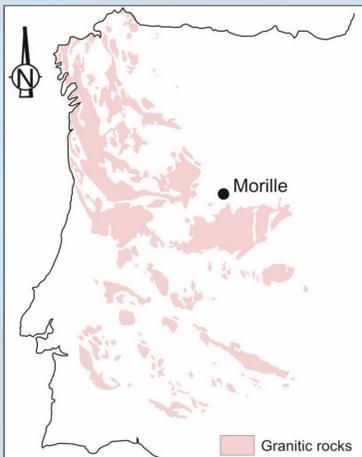


Figure 1. Location of Morille

The use of tailings as raw materials for glass and glass-ceramic production is an environmentally friendly solution to the disposal of mining waste. An advantage associated with the use of this raw material is that they were already industrially processed, hence, often have good homogeneity and fine particle size. Furthermore, the material extraction costs are minimal, due to the surface disposal. In addition, the mining activity income an additional application which promotes the circular economy by vitrification processes applying the mining waste reuse.

The aim of this study was to determine the potential as glass-ceramic raw material of the calco-silicate tailings from the Morille tungsten mine, Salamanca, Spain (Figure 1)) to be used as a commercial product. A representative sample from the waste of the ancient processing plant of Morille tungsten mine (Spain) was used. The experimental procedure is Figure 2.

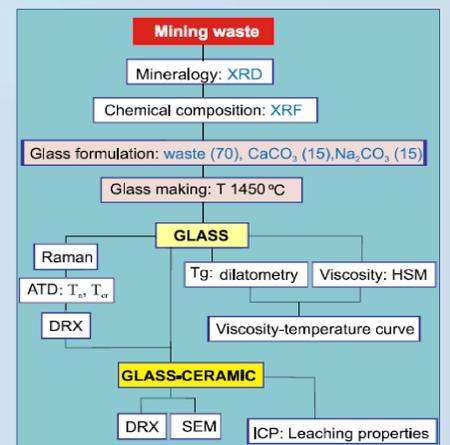


Figure 1. Experimental Methods

## Results & Discussion

The chemical composition of the Morille tailing is in Table 1. indicated that 15 wt.% of CaCO<sub>3</sub> and 15 wt.% of Na<sub>2</sub>CO<sub>3</sub> were added to make the glass.

Table 1. Chemical composition (wt.%).

Oxides, wt%	SiO	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	MgO	CaO	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	MnO	LOI
Raw material	62.5	13.35	0.55	3.76	1.99	1.63	9.60	1.03	1.18	0.18	4.23
Original glass	53.21	12.99	0.40	3.55	11.46	1.88	14.58	1.19	0.64	0.11	

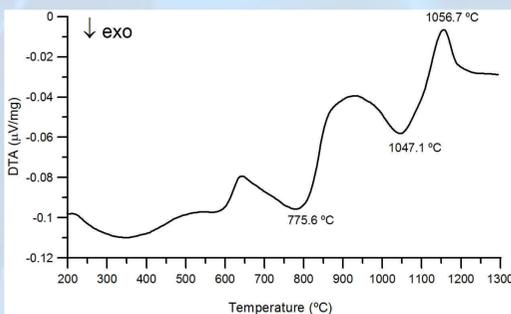


Figure 4. DTA diagram of the original glass.

Table 3. Temperatures of nucleation (T<sub>N</sub>) and cristal growth (T<sub>GR</sub>).

Phase	T <sub>N</sub> (°C)	T <sub>EX</sub> (°C)	T <sub>GR</sub> (°C)
A	612	776	786
B	665	1047	1054

To determine the mineralogy of the phases formed at T of the first exothermal peak (A), the glass was heated to its T<sub>N</sub> at 612 °C and after a holding time of 3 h, at the T<sub>GR</sub> (758.9 °C) and a holding time of 2 h.

For the phases formed at T of the second exothermal peak (B), the glass was heated at T<sub>N</sub> (665 °C) during 3 h followed by heating up to 1000 °C and a holding time of 2 h.

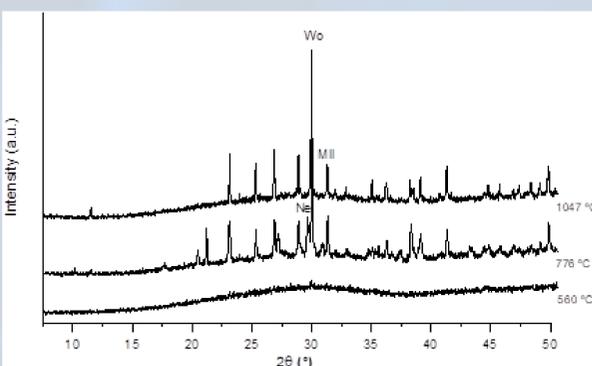


Figure 6. XRD diagram showing the mineral phases formed in glasses heated at the temperatures obtained from the DTA.

Leaching properties were determined in glass-ceramics. Chemical composition of leachates, according to the method DIN 38414-S4, indicates that the metals are fixed in the structure of the glass-ceramics.

Table 5. Chemical composition of leachates according to the DIN 38414-S4 test

Elements, ppm	Zn	Cd	Pb	As	Cu	Cr	Ni	W	Sn
Original glass	66.2	3.3	6.4	93.2	18.0	100	27.6	340	181
GC-867	8.22	0.23	0.92	0.00	13.29	0.74	4.64	0.19	0.09
GC-980	6.00	1.77	0.65	0.34	11.58	1.02	4.55	2.64	0.24

In the Raman spectrum of the original glass (Figure 3) the boson represents the distortion of the silicate network. The high frequency zone shows bands correspondig to Q3 groups (structure in sheets or layers), and Q2 groups represent chains.

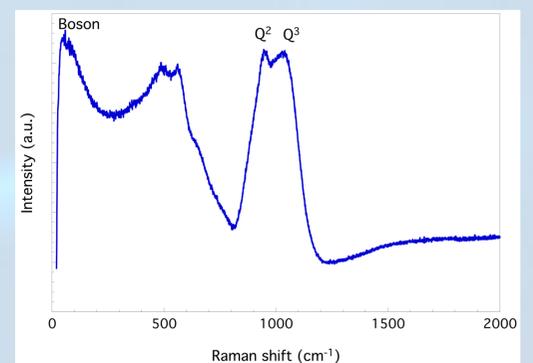


Figure 3. Raman diagram of the original glass.

Based on the method proposed by (Xu et al 1991) the temperature of maximum nucleation rate (TMNR) was determined from a sequence of DTA. Two events have been defined with peaks at 612 and 650 °C (Figure 4) corresponding at TC (crystallization temperature) of 776 and 1047 °C, respectively (Table 3).

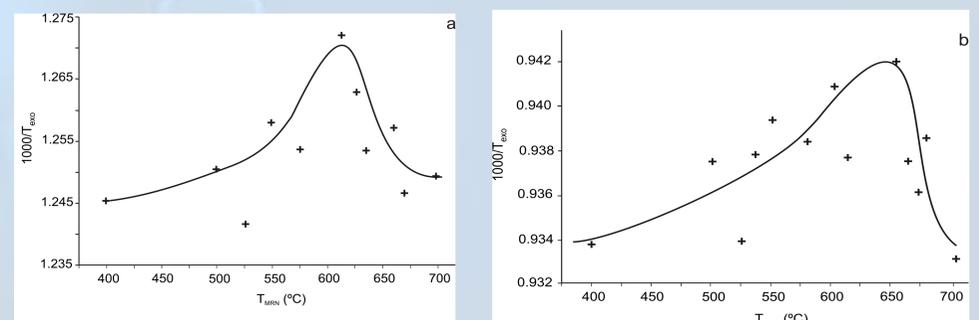


Figure 4. Relation between the inverse of the exothermic peak temperature as a function of temperature corresponding to the exothermic events.

The mineral phases of the produced glass-ceramic were wollastonite, melilite-group minerals and nepheline hosted in a glassy matrix.

The presence of Q2 and Q3 units in the glass (Figure 1) could be interpreted as preceding the simultaneous nucleation of wollastonite and nepheline, which begin to crystallize at the TMNR of 612 and 650 °C, respectively.

Table 4. Mineralogy of the glass-ceramic

Mineral	Formule	A	B
Wollastonite	Ca(SiO <sub>3</sub> )	67	83
Nepheline	Na <sub>3</sub> (Na,K)(Al <sub>4</sub> Si <sub>4</sub> O <sub>16</sub> )	26	-
Ghelenite	Ca <sub>2</sub> (Al <sub>2</sub> SiO <sub>7</sub> )	7	-
Akermanite	Ca <sub>2</sub> Mg(Si <sub>2</sub> O <sub>7</sub> )	-	17

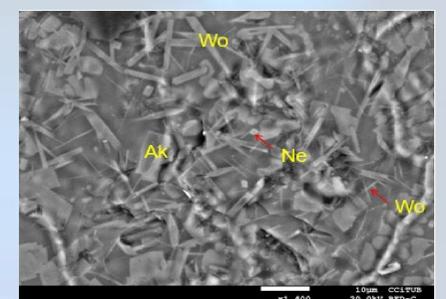


Figure 7. SEM image of the glass ceramic

## Conclusions

A glass-ceramic from calc-silicate waste materials from tungsten mining was obtained. The contents in potentially toxic elements leached from the obtained glass-ceramic were below the limits established by the European legislation. Then the production of glass ceramics using these wastes can be useful to prevent pollution of tailings after processing these tungsten ores.