Promising Immobilization of Cadmium and Lead inside Ca-rich Glass-ceramics

A. Karnis and L. Gautron

Abstract**—**Considering toxicity of heavy metals and their accumulation in domestic wastes, immobilization of lead and cadmium is envisaged inside glass-ceramics. We particularly focused this work on calcium-rich phases embedded in a glassy matrix.

Glass-ceramics were synthesized from glasses doped with 12 wt% and 16 wt% of PbO or CdO. They were observed and analyzed by Electron MicroProbe Analysis (EMPA) and Analytical Scanning Electron Microscopy (ASEM). Structural characterization of the samples was performed by powder X-Ray Diffraction.

Diopside crystals of $CaMgSi_2O_6$ composition are shown to incorporate significant amounts of cadmium (up to 9 wt% of CdO). Two new crystalline phases are observed with very high Cd or Pb contents: about 40 wt% CdO for the cadmium-rich phase and near 60 wt% PbO for the lead-rich phase. We present complete chemical and structural characterization of these phases. They represent a promising way for the immobilization of toxic elements like Cd or Pb since glass ceramics are known to propose a “double barrier” protection (metal-rich crystals embedded in a glass matrix) against metal release in the environment.

Keywords**—**Cadmium, Calcium-rich phases, Diopside, Domestic wastes, Fly ashes, Glass-ceramics, Lead, Municipal Solid Waste Incineration.

I. INTRODUCTION

HEAVY Metals like lead or cadmium are widely used in our domestic activities and they are found in significant quantities in domestic wastes. For example, in France in 2004, 795 and 4 milligrams of Pb and Cd respectively were found per kilogram of domestic waste [1].

In occidental countries, incineration is the major treatment of domestic waste [2] (43 wt% of domestic waste in France). This technique offers a great reduction of waste volume and generates thermal or electrical energy. However, Municipal Solid Waste Incineration (MSWI) produces further ultimate wastes: bottom and fly ashes. Bottom ashes are found be used as road and railway filling materials. Up to present, fly ashes are only stored in class1-type landfills for hazardous wastes, because of their contents of toxic elements (up to 0.02 wt% of PbO or CdO [3]). Note also that about 1.2 million of tones of fly ashes are produced each year in Western Europe [4]. Then it appears that land storage is not a long-term solution for the treatment of municipal wastes, because of increasing wastes production throughout the world due to demographic expansion, and economic development of many emerging countries. A promising way could then be a valorization through a stable immobilization of toxic elements in matrices which allow a further use as new materials.

Several matrices had been studied for immobilization of toxic element, such as glasses, ceramics and cements. Glass-ceramics are also envisaged because of their high chemical flexibility or lower diffusion coefficient. Moreover, their high density of grain boundary makes them very resistive to brutal crack [5]-[7]. In glass-ceramics, when toxic elements are incorporated in specific sites inside crystals (embedded by a glassy matrix), we can consider that this process corresponds to a double barrier protection from any release of these hazardous elements into the environment.

Calcium-rich glass-ceramics appears as good candidates to immobilize cadmium and lead because calcium has a large ionic radius and then calcium crystal sites are expected to host voluminous cations like those of Cd and Pb. Note that such Ca sites (in silicate perovskite) were shown to host large amounts of voluminous cations U^{4+} [8], [9].

In this study, diopside crystals ($CaMgSi_2O_6$ composition) were targeted for their expected capacity to incorporate large cations, especially in the 8-fold coordinated M2 site. Diopside was found to accept uranium in this typical site [10]. We can expect similar behaviour for Cd and Pb since Ca^{2+} is known to display a ionic radius of 1.12 Å when 8-fold coordinated while Cd and Pb display ionic radius of 1.10 Å and 1.29 Å respectively when in the same coordination [11]. In previous studies [12], [13], the immobilization of elements like Cd, Cr or Pb (present in fly ashes), was tested in diopside-based glass- ceramics. But it appears that these studies did not clearly quantify and demonstrate the incorporation of these toxic elements inside diopside crystals.

II. METHOD

Starting glasses were synthesized from oxides mix in the

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system SiO_2-MgO-CaO-Al_20_3. They were doped with relatively large amounts of CdO or PbO, as presented in Table 1. We chose excess of doping elements in order to better constrain the insertion mechanisms of Cd and Pb. Oxides mixes (typically 2 grams in weight) were finely crushed in ethanol so as to get relatively homogeneous starting materials. To minimize the volatilization of lead or cadmium during synthesis of parent glasses, pellets of our samples were prepared. We observed maximum 3-4 wt% difference between Cd or Pb contents before and after glass synthesis at high temperature.

Several samples with different amounts of doping element were synthesized for a systematic analysis (12 and 16 wt% of CdO or PbO). In this paper, we present the results obtained from two glass-ceramics representative of all samples studied in this work. The composition of the corresponding parent glasses is given in Table I.

For synthesis of parent glasses, pellets of oxides mix were placed in a platinum crucible and carried at 300°C during 30 minutes (ethanol volatilization) then brought at 900°C for 60 minutes (decarbonatation) and then brought to 1500°C during 20 minutes, to get homogeneous glasses with limited cadmium and lead loss by volatilization.

TABLE I
COMPOSITION OF PARENT GLASS FOR GLASS-CERAMICS DOPED WITH CADMIUM OR LEAD OXIDES

Oxide	GD16Cd *	GD12Pb *
SiO_2	44.52 wt%	46.64 wt%
MgO	20.16 wt%	21.12 wt%
CaO	11.76 wt%	12.32 wt%
Al_2O_3	7.56 wt%	7.92 wt%
Doped element	CdO: 16 wt%	PbO: 12 wt%

* G for Glass and D for diopside. 16Cd for glass doped with 16 wt% of CdO. 12Pb for glass doped with 12 wt% of PbO

Glasses samples were splitted in two parts. One was resin-embedded, polished and carbon-coated for microanalysis. And the other was used as parent glass for glass-ceramics synthesis.

Diopside-based glass-ceramics were synthesized by a two-stage thermal treatment: a nucleation stage at 750°C during 90 minutes and a crystal growth stage at 1000°C during 90 minutes. Temperatures and duration of these stages were chosen in order to maximize number and size of crystallites.

Glass-ceramics were characterized by X-Ray Diffraction (XRD) with a Bruker-AXS D8-Discover diffractometer using CuKα wavelength ($\lambda = 1.5418$ Å). Glasses and glass-ceramics were studied by Electron MicroProbe Analysis (EMPA, CAMECA SX50) and by using an Analytical Scanning Electron Microscope (ASEM, LEICA S440) equipped with a TRACOR-NORAN Energy Dispersive X-ray (EDX) spectrometer. We observed a very good agreement between analyses obtained from these two latter techniques (with less than 1 wt% difference).

III. RESULTS

Both glass-ceramics display the same characteristics (Fig. 1) with a glassy matrix in clear grey, diopside crystals in dark grey and in each case a new phase which appears in white (backscattered electron contrast corresponding to dense material). Anorthite crystals (in black) are also present but they are known to be generated by surface corrosion processes.

In all samples, many diopside crystals are present whereas the volume of the glassy matrix appears to be quite small. Unlike previous studies [12], [13], the diopside crystals observed in the present work are slightly bigger (about 5 micrometers compared to 3 micrometers) due to higher temperatures of crystal growth stage.

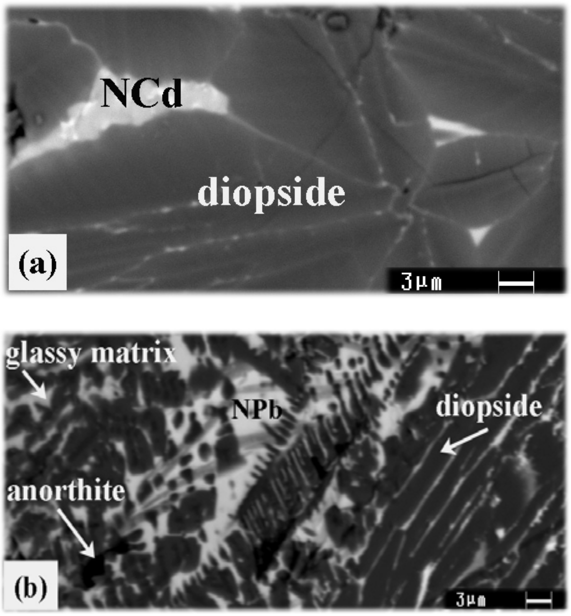

Fig. 1 Scanning Electron Microscope pictures of (a) GD16Cd (Glass-ceramic doped with 16 wt% of CdO) and (b) GD12Pb (Glass-ceramic doped with 12 wt% of PbO)

EDX analysis reveals that diopside does not incorporate lead, probably due to ionic radius differences (as described above). However, the picture is different for cadmium: diopside is shown to accept cadmium up to about 9 wt% CdO (then about 1.5 at% Cd), probably in the Ca sites. After these results, we can propose the chemical formulae for the diopside crystals doped with cadmium as in equation (1) with the hypothesis of cadmium inserted in the calcium site.

$$(Ca_{0.59},Cd_{0.15},Al_{0.26})Mg(Si_{0.87},Al_{0.13})_2O_6 \quad (1)$$

Based upon stoichiometric considerations, we see that aluminum can be distributed over both calcium and silicon sites: this can only be achieved with a charge compensation as seen in a previous study [14]. XRD reveals that the cadmium insertion does not induce a significant distortion of the diopside crystal structure, since the Bragg peaks positions are almost exactly those expected from Analytical Standard for Testing Materials files (see XRD pattern in Fig. 2).

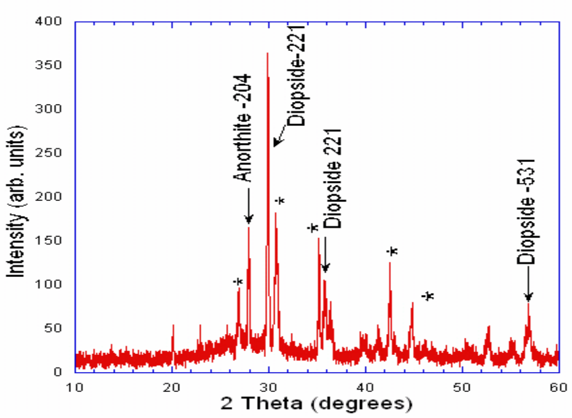

Fig. 2 XRD pattern of glass-ceramics GD12Pb. Stars (*) represent Bragg's peaks of the New Pb-rich phase (NPb), while main peaks for diopside and anorthite are assigned with *hkl* Miller indices. Note the coarse background at 2ϑ around 30° witch is a signature of the glass-matrix.

In both glass-ceramics samples, new Cd- or Pb-rich phases are observed. They appear with a light contrast (relative to heavy metal insertion, as pictured in Fig. 1). The new Pb-rich phase (named NPb) contains up to 57 wt% of PbO (about 9.8 at% of Pb). The new Cd-rich (named NCd) displays CdO content up to 41 wt% (then nearly 9 at% of Cd). Both phases are observed throughout the whole sample. After EMPA and EDX analysis, we can write a chemical formula as in equation (2) for NPb and equation (3) for NCd if we assume that cadmium is inserted into calcium site.

$$PbAl_{0.62}Si_{1.45}O_{4.83} \quad (2)$$

$$(Ca_{0.19},Cd_{0.81})_{1.2}Si_{1.5}Mg_{1.47}Al_{0.22}O_6 \quad (3)$$

Bragg peaks of these new phases were identified, but no indexation from related possible crystal structures could be found for both NPb and NCd XRD patterns. XRD details of both phases are listed in Table II.

In both cases, the glassy matrix also contains cadmium or lead. We can assume that these new phases display solubility limits of Cd and Pb, since the Cd or Pb excess is found in the glass matrix.

IV. CONCLUSION

This study shows that diopside-based glass-ceramics incorporate up to about 9 wt% of CdO (or 1.5 at% of Cd) inside diopside crystals without significant structural change.

TABLE II
X-RAY POWDER DIFFRACTION DATA OF THE NEW CD-AND PB-RICH PHASES

NPb		NCd	
$2\vartheta(°)$	I/I_0	$2\vartheta(°)$	I/I_0
26.9	61	20.19	53
30.75	100	26.91	59
35.17	95	36.11	100
42.5	64	39.62	53
44.77	43	41.29	47

NPb is a new Pb-rich phase and NCd is a new Cd-rich phase observed in the glass-ceramics studied in this works

Lead is not incorporated into diopside, probably due to ionic radius differences.

In these glass-ceramics, two new phases are observed and can be envisaged as good candidates for Cd or Pb immobilization. The new Cd-rich phase contains up to 41 wt% of CdO (then 9 at% of Cd) while the new Pb-rich phase contains about 57 wt% of PbO (9.8 at% of Pb).

In order to determine the capacity of these new phases to retain heavy metals, leaching experiments need to be done to determine their long-term behaviour in terms of Cd and/or Pb release into the environment.

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