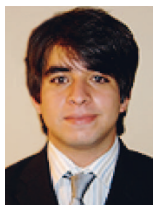## BUILDING MATERIALS

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# Effect of Fluxing Additives in Iron-rich Frits and Glazes in the Fe$_2$O$_3$–SiO$_2$–CaO–Al$_2$O$_3$ System

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## ABSTRACT

Glasses in the Fe$_2$O$_3$–SiO$_2$–CaO system are potential candidates for many technological applications due to their ferrimagnetic and semiconductive properties, which have been extensively studied; in this sense, the effect of adding different melting additives like Li$_2$O, B$_2$O$_3$, in this glass system on frits and glazes with 30–40 mass-% of Fe$_2$O$_3$ was studied. Ceramic frits were melted at different temperatures with subsequent cooling in water. Samples were characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM), differential thermal analysis and thermogravimetry (DTA, TG) and by heating microscopy. Finally, frits were applied as glazes on ceramic tiles to evaluate their capacity to adapt to the tile productive process. The frits showed low to high homogeneity (depending on the fusion temperature) and oxidation phenomena. High temperature fusion led to the crystallization of magnetite during cooling. Glaze porosity was observed after heat treatment with the presence of anorthite and hematite as crystalline phases in glazes.

## KEYWORDS

## 1 Introduction

Transition metal glasses, such as iron-rich glasses, are of considerable interest in medicine, electro-ceramics, optical ceramics, structural ceramics, waste sectors, as well as in geology and basic sciences. These glasses are well known for their interesting properties, which depend strongly on composition, synthesis method and thermal treatments [1–10]. In the floor and wall tile manufacturing industry, iron oxide-rich glasses have been used for the development of glazes with metallic and aventurine effect, using compositions rich in P$_2$O$_5$ and Fe$_2$O$_3$ [11–12]. The wide range of properties that such glasses display provides them with great potential for the development of numerous technological applications like semiconducting glazes for antistatic or radiant flooring and for electrical insulators [13–17]. The semiconducting properties in these glasses are a result of a mechanism known as polaron hopping, caused by the transfer of electrons between the same metallic ion in different oxidation states (e.g. from Fe$^{2+}$ to Fe$^{+3}$). This conduction mechanism is known to be present in iron-rich glasses and in crystalline phases like magnetite [18]. In this sense, the SiO$_2$–CaO–Fe$_2$O$_3$ glass system was initially studied for its magnetic properties, which are useful for biomedical and electronic applications. In numerous studies this system has shown the ability to vitrify or form high-temperature eutectics and to crystallize phases such as β-CaO·SiO$_2$ (wollastonite), zinc ferrites, magnesium ferrites, apatite in magnetic clusters, magnetite (Fe$_3$O$_4$) and γ-Fe$_2$O$_3$, hematite (α-Fe$_2$O$_3$) and cristobalite [1, 2, 7–10]. Taking advantage of magnetite's ease of crystallization in iron-rich oxide glass systems, previous

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## BUILDING MATERIALS

studies developed glazes in the chemical system $SiO_2$–$CaO$–$Fe_2O_3$, which could be adapted to the ceramic floor and wall tile production process [19]. However, the magnetic and conductive properties could be enhanced. The addition of fluxing oxides to these systems would allow the melting temperatures of these materials to be lowered and at the same time still help to the crystallization of ferromagnetic phases. Additives such as $Li_2O$ and $B_2O_3$ are good candidates for the improvement of these frits [20–23]. On the other hand, the effect of the fusion temperature on the $Fe^{2+}/Fe^{3+}$ proportion could influence magnetite conductivity and quantity. It is also known that these glasses undergo oxidation phenomena which are strongly related to the specific surface and surrounding atmosphere [24–25]. On the basis of interesting results obtained previously [20], the objectives of this research are:

- To synthesize ferrimagnetic frits in the $Fe_2O_3$–$SiO_2$–$CaO$ system, at the same time evaluating the effect of additives such as $Li_2O$ and $B_2O_3$
- To investigate the effect of additives on the melting temperature

- To study the adaptability of frits to the floor tile production process, which may have potential technological applications.

## 2 Experimental

### 2.1 Synthesis of frits and glazes

The frits were synthesized using previous research compositions [1, 2, 19] which were based on the $SiO_2$–$CaO$–$Fe_2O_3$ ternary phase diagram. The frits were melted in silico-aluminous crucibles at 1300 °C/1 h and 1400 °C/1h using a gas furnace and a laboratory electric furnace, respectively and industrial grade $SiO_2$, $CaCO_3$, $Fe_2O_3$, $Li_2CO_3$ and $H_3BO_3$. The compositions of the frits are shown in detail in Table 1.

For the glazes, all the raw materials were mixed manually in the appropriate proportions, fused and then quenched in water according to the conventional fritting process. The chemical analysis of frits showed a high $Al_2O_3$ content that came from the silico-aluminous crucibles which were highly corroded. The glazes were then obtained by mixing the resulting frits with carboxymethyl cellulose (CMC), sodium tripolyphosphate (TPP), kaolin (10 mass-%) and sufficient water to obtain a fluid suspension. The sus-

pensions were applied on porcelain tile substrates using the doctor blade method and then fired in a pilot natural gas industrial kiln at 1200 °C using a typical porcelanic tile firing schedule.

### 2.2 Characterization techniques

The frits synthesized at 1400 °C were characterized by:
- XRF (Bruker AXS S4 Pioneer)
- Heating microscopy (Misura 3.32 hot stage microscope, from 600 to 1400 °C, 20 ˚C/min)
- XRD (Bruker D4 ENDEAVOR with copper anode, 20mA, 40 KV, 0.05 °/s, 2θ: 10–80 °)
- SEM (JEOL JSM 6390 and HITACHI S-2400)
- DTA-TG (Mettler Toledo TGA/SDTA851, 10 °C/min, from 25 to 1200 °C).

The frits melted at 1300 °C were characterized by: XRF, XRD, DTA-TG and by SEM. Finally, the fired glazes were characterized by XRD and SEM.

## 3 Results and discussion

### 3.1 Characterization of the frits

Tables 2–3 show the chemical analyses by XRF of the frits melted at in a gas furnace at 1300 °C and in an electric furnace at 1400 °C, respectively.

It can be seen that for both frits melting gives place to a deviation in the composition which is more severe in the case of frits melted at 1400 °C. The biggest change is observed in the amount of $Al_2O_3$, which can be as high as 16 mass-% in the case of the samples melted at 1400 °C (10 times as high as at 1300 °C). The effect of the fusion temperature on the corrosive capability of the melts on the walls of the crucibles is evident. The highly corrosive power of these frits has been reported previously by different authors [4, 19]. It was not possible to determine the content of $Li_2O$ and $B_2O_3$ because of the impossibility to measure the presence of these oxides in glass with the XRF technique. No significant association was found between the type of additive and the amount of $Al_2O_3$ introduced in the glass; it was more related to the melting temperature. Figure 1 shows the XRD spectra of the synthesized frits.

The frits obtained at 1300 °C showed crystalline phases in most of the sample; hematite $\alpha$-$Fe_2O_3$ being the primary crystalline phase for the samples with 30 mass-% of $Fe_2O_3$, with anorthite in sample 1 (without additives). Results obtained by SEM, which are not shown in this article, confirmed the presence of crystallized hematite, dendrites and $SiO_2$ not observed in the XRD spectra, which revealed a low homogeneity of the glasses due

### Table 1 • Frits composition in mass-%

| Sample | $SiO_2$ | CaO | $Li_2O$ | $B_2O_3$ | $Fe_2O_3$ |
|---|---|---|---|---|---|
| 1 | 45 | 25 | – | – | 30 |
| 2 | 40 | 20 | – | – | 40 |
| 3Li | 45 | 21 | 4 | – | 30 |
| 4Li | 40 | 16.8 | 3.2 | – | 40 |
| 5B | 40 | 25 | – | 5 | 30 |
| 6B | 35.6 | 20 | – | 4.4 | 40 |

### Table 2 • Chemical analysis by XRF of the frits melted at 1300 °C in mass-%

| Sample | $SiO_2$ | CaO | $Fe_2O_3$ | $Al_2O_3$ | $P_2O_5$ | $K_2O$ | MgO |
|---|---|---|---|---|---|---|---|
| 1 | 44.1 | 25.9 | 30 | 0.8 | – | – | 0.2 |
| 2 | 39.75 | 21.1 | 37.8 | 1.1 | – | 0.1 | 0.1 |
| 3Li | 44.35 | 21.75 | 29.15 | 1.5 | 0.1 | 0.1 | 0.1 |
| 4Li | 40.50 | 17.90 | 37.8 | 1.2 | 0.1 | 0.1 | 0.1 |
| 5B | 40.65 | 26.15 | 29.05 | 1.4 | – | 0.1 | 0.2 |
| 6B | 36.25 | 21.25 | 38 | 0.9 | – | – | 0.1 |

### Table 3 • Chemical analysis by XRF of the frits melted at 1400 °C in mass-%

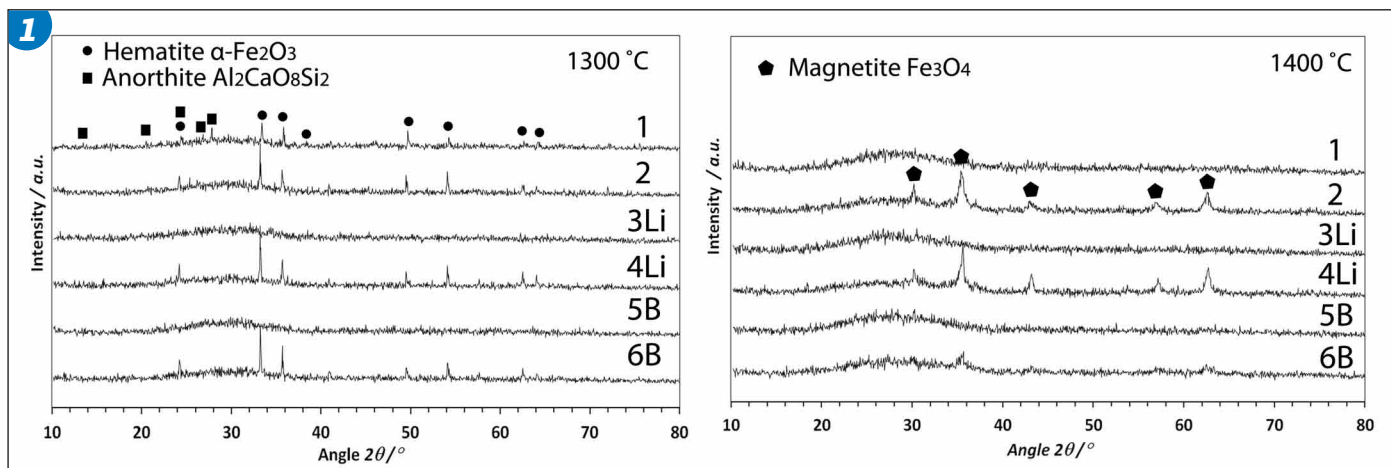| Sample | $SiO_2$ | CaO | $Fe_2O_3$ | $Al_2O_3$ | $TiO_2$ | MgO | $K_2O$ | $P_2O_5$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 43.35 | 20.00 | 23.35 | 13.70 | 0.18 | 0.13 | 0.27 | 0.01 |
| 2 | 39.45 | 15.65 | 30.80 | 14.45 | 0.23 | 0.10 | 0.29 | 0.02 |
| 3Li | 43.40 | 17.35 | 25.15 | 11.75 | 0.18 | 0.11 | 0.26 | 0.01 |
| 4Li | 39.80 | 13.70 | 33.10 | 11.35 | 0.23 | 0.10 | 0.25 | 0.01 |
| 5B | 39.55 | 18.75 | 22.25 | 16.25 | 0.19 | 0.12 | 0.33 | 0.01 |
| 6B | 37.65 | 15.80 | 30.15 | 13.20 | 0.22 | 0.10 | 0.27 | 0.01 |

## BUILDING MATERIALS



**Fig. 1** • XRD spectra of the frits fused in a gas crucible kiln at 1300 °C (left); XRD spectrum of the frits fused in the electric crucible kiln at 1400 °C (right)
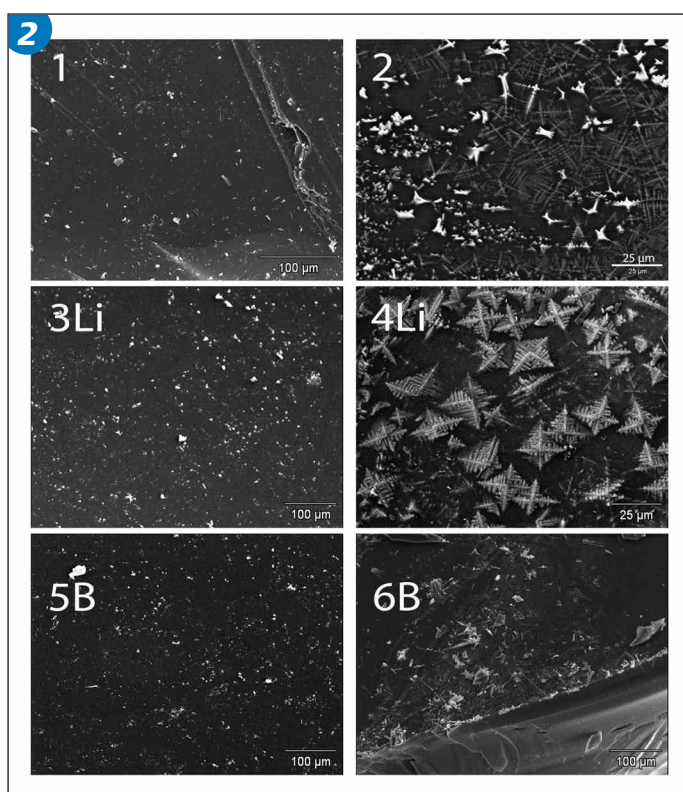


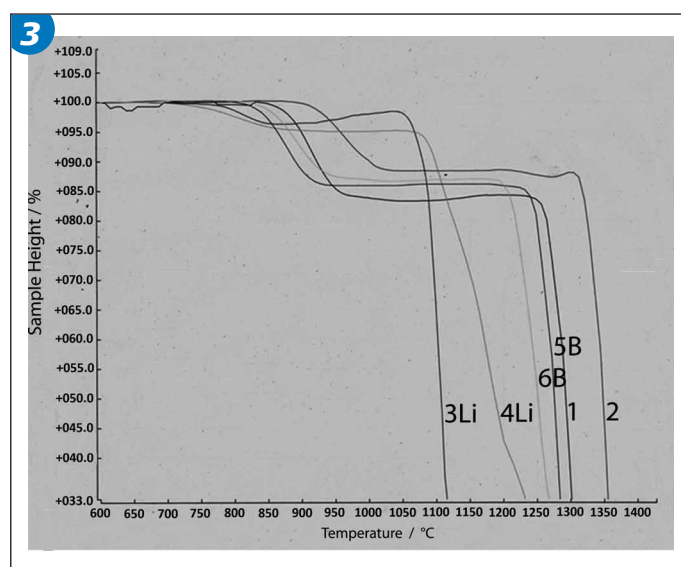**Fig. 2** • SEM micrographs in backscattered electron mode of the frits melted at 1400 °C



**Fig. 3** • Sintering curves of the frits melted at 1400 °C, determined by hot stage microscopy

to the low melting temperature and/or short melting time. It is widely known that iron-rich glasses undergo liquid phase separation at high temperatures, where one of the liquid phases is richer in iron and tends to crystallize during cooling as hematite or magnetite, depending on the $Fe^{2+}/Fe^{3+}$ ratio, which is temperature dependent) [2, 4, 19, 20, 25, 26]. Moreover, according to the $SiO_2$–$CaO$–$Fe_2O_3$ ternary diagram, the melting temperature is below the eutectic point ($\approx 1450$ °C). For the frits obtained at 1400 °C (Fig. 1, right-hand side), magnetite was developed for the frits with 40 mass-% of $Fe_2O_3$, samples 6B being the least crystalline.

This is understandable since $B_2O_3$ is a glass network former. On the other hand, the effect of the fusion temperature may be observed; higher temperatures favour the reduction of $Fe^{+3}$ to $Fe^{2+}$, as the Ellingham diagram suggests [2]. The partial reduction of $Fe^{3+}$ to $Fe^{2+}$ favours subsequent magnetite nucleation in the glass, which is a spinel type phase with simultaneous states of $Fe^{2+}$ and $Fe^{3+}$ ($FeO \cdot Fe_2O_3$). In the rest of the paper, only the results of the frits synthesized at 1400 °C are presented, owing to their ferrimagnetic properties observed after quenching. Figure 2 shows images of the frits synthesized at 1400 °C, obtained by SEM.

The SEM micrographs show that magnetite dendrites were only observed in the frits with 40 mass-% of $Fe_2O_3$ (2 and 4Li). Even though frit 6B contained magnetite, as the XRD patterns suggested, it was not possible to observe it by SEM. This could be related to the low crystallinity observed by XRD and the glass forming effect of the $B_2O_3$. The magnetite in iron-rich glasses usually crystallizes with dendritic morphology when rapidly cooled, forming a 90 ° angle between the crystalline axes in the dendrites [4, 27]. However, different magnetite crystal morphologies were observed in SEM, including round crystals and thin dendrites. Compared to the frits synthesized at 1300 °C, these frits showed more homogeneity. It may be noted that samples 2, 4, and 6 responded strongly to the presence of a magnet. The sintering curves of the frits studied are shown in Fig. 3.
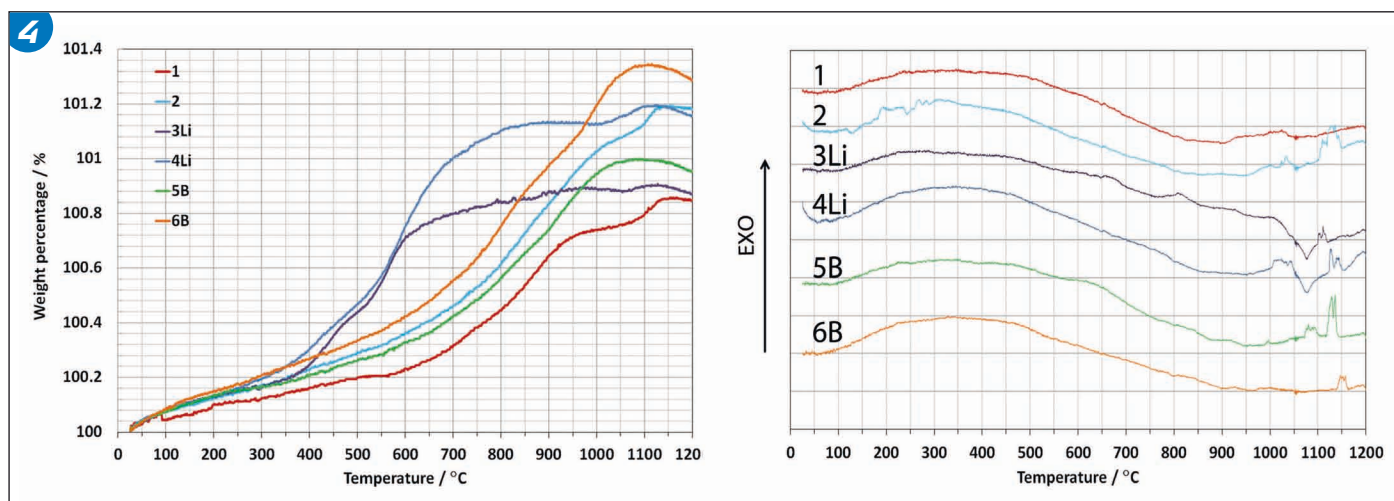
## BUILDING MATERIALS



**Fig. 4 • Differential thermal analysis (right) and thermogravimetric analysis (left) curves of the frits melted at 1400 °C in air**

The sintering curves of the samples reveal the fluxing effect of the additives in the samples, being more important in the case of the $Li_2O$ as it would be expected. Also, it is observed with at higher $Fe_2O_3$ content, the melting temperature of the material is increased. This effect was reversed in the case of the samples with $B_2O_3$, albeit with very little difference. On the other hand, it was observed that in all the samples, the sintering process started between 700 and 900 °C and fully sintered fully between about 850 and 1100 °C. It can be seen that in the sample with $Li_2O$ the fusion temperature is lower compared to the other samples and approximately lower than the maximum temperature in the porcelanic tiles firing process (1200 °C). Figure 4 shows the DTA-TG curves of the frits fused at 1400 °C.

According to the DTA curves, all samples (powder samples) with grain size between 30 μm and 150 μm exhibited crystallization peaks. A pronounced fusion endothermic peak was observed for the frits with $Li_2O$ at about 1080 °C, which is correlated with the melting results obtained in Fig. 3. Most crystallization phenomena appear to be complex in nature due to the number and morphology of the crystallization peaks above 1050 °C (including frits with $B_2O_3$) and their associated oxidation, which could alter the magnetite phase. The TG curves indicated that all compositions underwent oxidation. The oxidation was more severe in the case of samples with higher iron oxide content (40 mass-% $Fe_2O_3$). At low temperatures (below 300 °C) the mass gain seems to be related due to oxygen adsorption. Then (above 400 °C), it was observed that samples 3Li and 4Li oxidized more rapidly than the other frits. This is reasonable, considering that the glass with $Li_2O$ has a more open
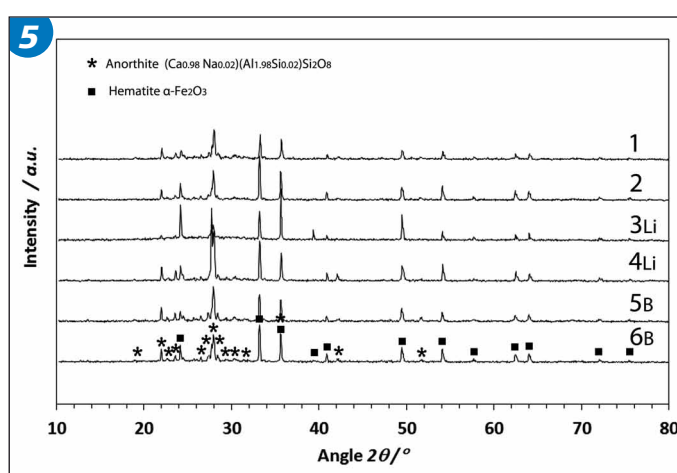
structure, which is more susceptible to atomic diffusion. The oxidation process above 400 °C in these glasses has been reported previously and it is caused by the oxidation of $Fe^{2+}$ species in the surface [20, 25, 26, 28]. It is important to highlight that in previous research, photoelectron X-ray spectroscopy (XPS) studies on these glasses without additives revealed the presence of many iron oxides in the surface, which may be available for oxidation upon heating [20]. Above 1100 °C most of the samples start to lose mass, which is possibly related to the evaporation of some of the liquid phase formed. Samples with additives tend to oxidate more that those without additives.

### 3.2 Characterization of the glazes obtained
The XRD spectra of the glazes obtained after the porcelanic tile firing schedule (Fig. 5) show that the predominant crystalline phases in the glazes were hematite and anorthite. Hematite had already been encountered in previous studies with similar compositions, and its formation seemed to arise by

two means: with the gain in weight seen in TG above 400 °C (surface oxidation), by phase separation at 1100 °C, as previously reported or by the oxidation of magnetite present in the glass [29]. The oxidation of magnetite in the frits probably took place in the gas kiln in which the oxygen partial pressure during firing is usually between 0.13 and 0.17 atm. of $O_2$ [28]. Unfortunately, the addition of $Li_2O$ or $B_2O_3$ to the frit did not avoid these phenomena. The presence of anorthite is explained by the high amounts of alumina (up to 16 mass-%) originating from the fusion crucible and the kaolin from the glaze composition. The micrographs of the cross-sections and surfaces of the glazes are shown in Fig. 6. Therein an image is also presented of the surface of sample 4, which clearly shows anorthite and hematite crystals.

Most of the coatings exhibited high porosity in the engobe and in the glaze, which is unfavourable for ceramic products. The largest surface pores were observed in the samples containing $Li_2O$ as additive, which usually



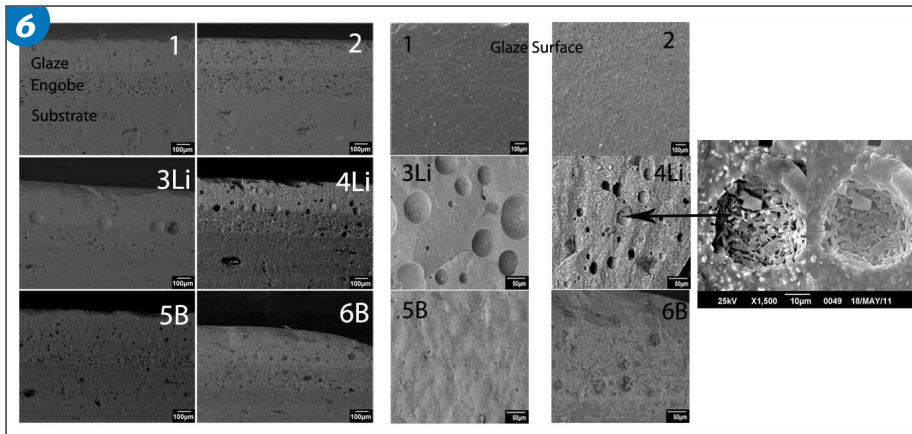**Fig. 5 • XRD spectra of the glazes obtained by fusion at 1400 °C**

**Fig. 6 •** SEM micrographs of cross-sections and surfaces of the glazes. (Right) anorthite crystals (angular grey crystals) and hematite crystals (white crystals)

suggests greater flowability of the molten glazes. These glazes could be improved by the modification of the firing schedule making a short heating dwell near the sintering temperature determined by heating microscopy, in order to prevent the trapping of gas inside the glaze. Therefore, the glaze would be free of porosity or less defective. Finally, the obtained frits may be useful as fillers used in structures for electromagnetic shielding due to their ferrimagnetic properties [30].

## Acknowledgments

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