

SYNTHESIS OF FRITS WITH ZnO MADE FROM ZAMAK WASTE

S, Mestre⁽¹⁾, M.P. Gómez⁽¹⁾, P. Agut⁽¹⁾, A. Barba⁽¹⁾, E. Añó⁽²⁾

⁽¹⁾ Instituto de Tecnología Cerámica (ITC).
Asociación de Investigación de las Industrias Cerámicas (AICE)
Universitat Jaume I. Castellón. Spain.

⁽²⁾ Instituto Tecnológico del Juguete (AIJU).
Ibi, Alicante. Spain.

ABSTRACT

The feasibility of using a zinc oxide obtained from zamak waste recovery as a raw material for frit synthesis has been studied. For this purpose, three widely used types of frit in the ceramic sector, which are characterised by their high ZnO content (a crystalline, a zirconium white, and a zinc matt frit), have been synthesised using ZnO made from zamak waste, and an industrial grade ZnO. The characteristics of these frits and of the glazes they yield have been compared. The results show that the recovered ZnO alters to a certain extent some frit properties, particularly those relating to the appearance of the resulting glazes, but that in certain cases the recovered ZnO can serve as an alternative raw material.

1. INTRODUCTION

Zinc oxide is an essential constituent in the ceramic frits used to prepare single-fire glazes, since it is related to a series of important characteristics, such as maturing range and sealing temperature. At temperatures above 950°C, zinc oxide acts as a flux which, in combination with other oxides, facilitates the obtainment of a smooth surface; however, when incorporated in excess it generates matt glazes^[1].

In recent years this raw material has become much more expensive, since its price is linked to that of metallic zinc, whose price has soared on the international market (the price of a ton of Special High Grade zinc on the London Metal Exchange has increased almost fourfold in the period from January 2000 to January 2007). Since many frit compositions contain this oxide (some even in proportions of almost 20% by weight), production costs have risen with adverse effects on the ceramic sector.

Price rises of raw materials tend to drive research into alternative raw materials, or the search for sources different from the usual ones. Indeed, studies have been published on zinc recovery from various industrial wastes, such as aqueous solutions^[2], catalysts^[3], or steel mill dust^[4]. The extraction of zinc oxide from industrial wastes may thus constitute an alternative supply route, at least for a certain range of frits in which the possible pollutants included in recovered ZnO will not adversely affect the ceramic application.

The alloys generally known as zamak (consisting mainly of zinc, with 4% by weight of aluminium and smaller quantities of magnesium and copper, which vary according to the particular alloy involved)^[5,6], are widely used in many industrial sectors, such as the toy and automotive sectors. Considerable waste is generated during the manufacture of these products, which cannot be readily reused in the process and tends to end up at landfills, though different avenues are being explored for reuse.

Zamak waste can be transformed into zinc oxide using a procedure developed by AIJU^[7]. The method is based on the use of an electric arc that allows the volatilisation and oxidation of the zinc contained in the zamak, and the resulting ZnO is collected in a filter system. This process has been tested on a pilot scale, which has provided representative samples for analysis of ZnO properties and of the effects of recovered ZnO incorporation into ceramic products (AIJU references).

The present study has been conducted using this recovered ZnO and a high-quality industrial zinc oxide to evaluate the differences in their characteristics, as well as in the properties of the frits obtained from both. First, both zinc oxides were thoroughly characterised. Three different frits were then synthesised, a zinc matt, a zirconium white, and a crystalline frit, the rest of the process variables being kept constant (raw materials and obtainment procedure). Finally, the six frits, as well as the glazes obtained from them, were characterised.

2. EXPERIMENTAL PROCEDURE

The zinc oxide used as a reference was an industrial product (specifically, a sample of Union Minière Gold Seal, which was referenced ZnO/E); the product supplied by AIJU from the recovery pilot plant was referenced ZnO/R. The other raw materials used in frit synthesis were of the quality customarily used in the ceramic frit sector.

The oxide characterisation included the determination of the chemical composition by X-ray fluorescence (XRF) (PW2400, Philips, Netherlands); fluorine was determined by a selective electrode (9655, Crison, Spain); the crystalline phases present were identified by X-ray diffraction (XRD) (Theta-Theta D8 Advance, Bruker AG, Germany); specific surface area was measured by nitrogen adsorption (TriStar 3000, Micromeritics, USA); particle size distribution was determined by laser diffraction (Mastersizer 2000, Malvern, UK); and particle morphology was characterised by scanning electron microscopy (SEM) (XL30, Philips, Netherlands).

The raw materials of each frit were proportioned by weighing, and were homogenised by wet milling in a ball mill, using acetone as fluid. The suspension obtained was dried under infrared lamps and the resulting powder was put through a 600 micron mesh sieve to avoid the presence of large agglomerates. Portions of 500 grams of each starting mixtures were placed in mullite crucibles, which were set inside an electric glass fusion furnace (BLF1800, Carbolite Furnaces, UK). The same thermal treatment schedule was used for all frits: heating at 10°C/min to the desired peak temperature, followed by a 30 min. dwell at that temperature. When the residence time had ended, the crucible was withdrawn from the furnace and its content poured into water (quenched) to vitrify the mass. The frit obtained in each fusion was dried under infrared lamps and stored for the different characterisation tests. Three fusions were performed of each frit, the product of these fusions being mixed before proceeding with the characterisation.

The frits obtained were characterised by XRD, hot stage microscopy (Misura 2, Expert Systems, Italy) and differential thermal analysis (SDTA851^e, Mettler, Switzerland). At the same time, glaze slips were prepared in a laboratory planetary mill, with a mixture of frit and kaolin in a ratio of 100:8 by weight, with the addition of carboxymethylcellulose and sodium tripolyphosphate in order to obtain stable suspensions. The slips were applied on to white tile biscuits; after the glazed pieces had been dried in an oven they were fired in an electric laboratory kiln (Pirometrol S.A., Spain) with a thermal treatment that simulated a rapid floor tile manufacturing cycle, with a 6 minute residence time at peak firing temperature (hereafter T_c), while a range of T_c values appropriate for each type of glaze were tested.

The chromatic coordinates were determined on the fired test pieces, depending on the type of glaze, with a spectrophotometer (CE7000, Gretag Macbeth, Switzerland), and gloss was determined with a reflectometer (Statistical Novo-Gloss, Rhopoint, UK) at an angle of 60°.

3. RESULTS

3.1. CHARACTERISATION OF THE OXIDES

The results of the oxide chemical analysis (see Table 1) indicated that sample ZnO/R was less rich in zinc oxide than ZnO/E, which would not be too problematic in principle, provided the quantity remained steady. From the viewpoint of the ceramic application, the presence of SiO₂ and Al₂O₃ is not a problem in frit processing since all frits contain these elements. However, the CuO and Fe₂O₃ impurities are a problem because of their chromophore properties.

From a mineralogical viewpoint, ZnO/E consisted of a single zincite phase (see Figure 1), whereas ZnO/R (in addition to the zincite) included a small quantity of

unoxidised zinc. Note, further, that given the lower intensity and greater width of the sample ZnO/R reflections in the diffractogram, there are likely to be differences in the size of the primary crystallites between both oxides, which may entail differences in their reactivity.

constituent	ZnO/E	ZnO/R
ZnO	99.8	96.1
SiO ₂	<0.1	0.19
Al ₂ O ₃	<0.05	2.30
Fe ₂ O ₃	<0.01	0.14
CaO	<0.01	0.04
MgO	<0.01	0.07
K ₂ O	<0.01	<0.01
TiO ₂	<0.01	<0.01
MnO	<0.01	<0.01
P ₂ O ₅	<0.01	<0.01
CuO	<0.01	0.31
S	<0.01	<0.01
Cl	<0.01	0.06
F	<0.01	<0.01
LOI at 900°C	0.13	0.85

Table 1. Chemical composition (% by weight).

ZnO/E particle size distribution indicated that it was made up of much finer particles than ZnO/R (see Figure 2 and Table 2). In addition, the ZnO/R particle size distribution was practically monomodal, with a maximum at 11 microns, while that of the ZnO/E was clearly bimodal with two maximums, at about 0.15 and 0.63 microns. However, this fact was not reflected in the specific surface area, which was about five times larger in ZnO/R. It was possible to interpret this apparent anomaly thanks to the electron microscopy images, which showed that ZnO/R consisted of highly sponge-like, large particles, with a very small primary particle size (Figure 3), whereas ZnO/E was made up of smaller agglomerates, whose primary particles were appreciably larger (Figure 4).

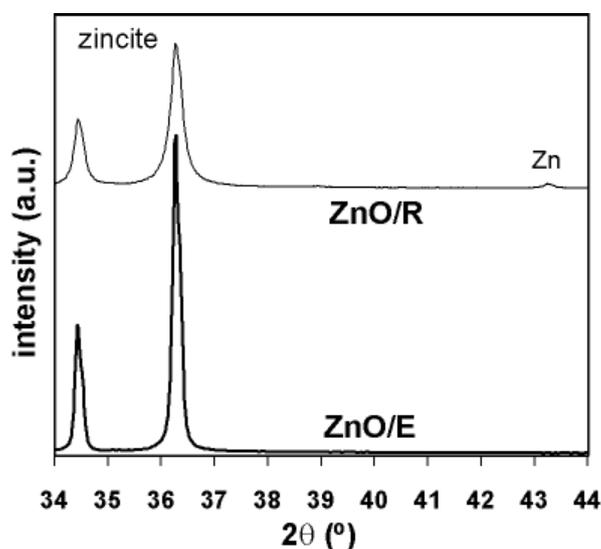


Figure 1. Detail of the zinc oxide diffractograms.

Parameter	ZnO/E	ZnO/R
d_{90} (μm)	1.19	20.4
d_{50} (μm)	0.45	10.03
d_{10} (μm)	0.12	4.16
d_v (μm)	0.56	11.31
d_s (μm)	0.29	6.96
Specific surface (m^2/g)	4.2	23.0

Table 2. Particle size distribution and specific surface area parameters.

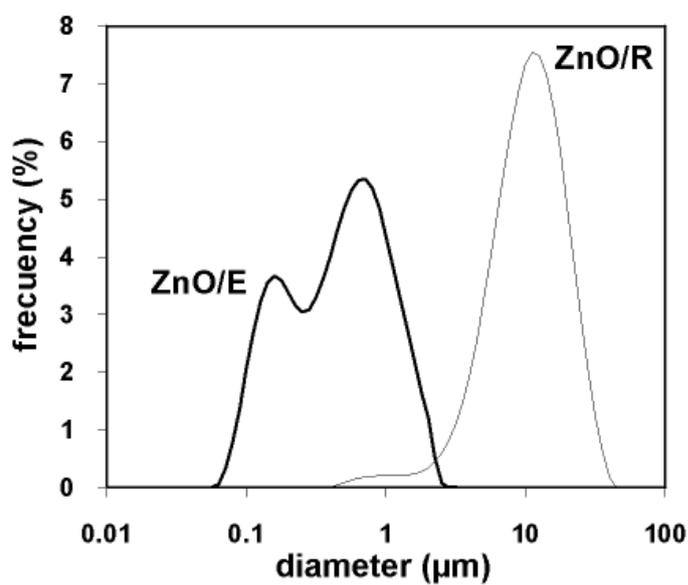


Figure 2. Zinc oxide particle size distributions.

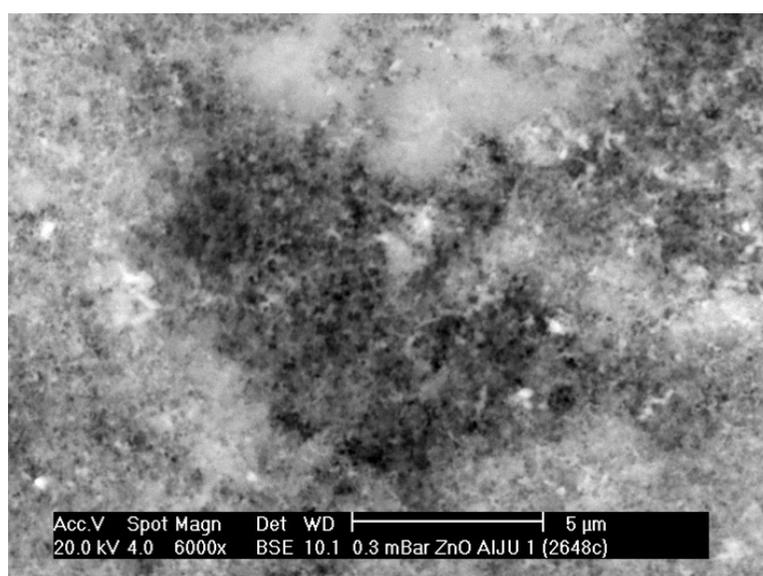


Figure 3. Micrograph of ZnO/R (6000x).

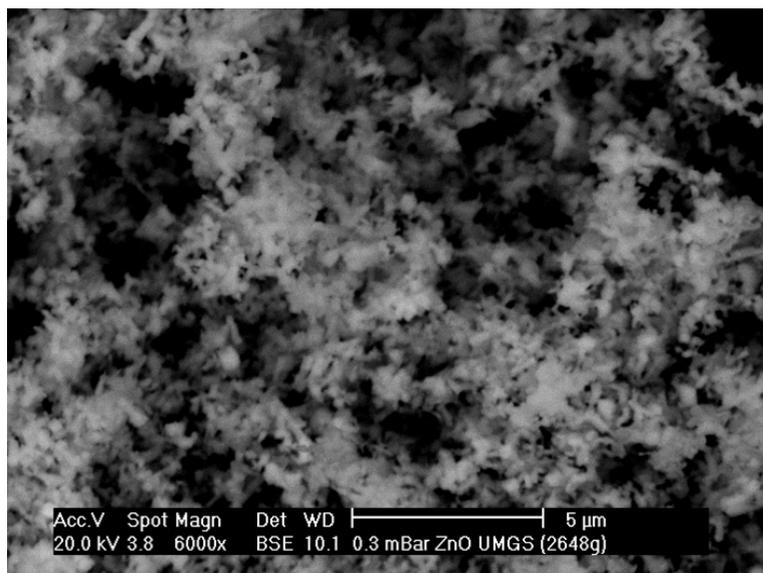


Figure 4. Micrograph of ZnO/E (6000x).

3.2. SYNTHESIS AND CHARACTERISATION OF THE FRITS AND GLAZES

The three synthesised types of frits were given the general references FM (zinc matt), FB (zirconium white), and FC (crystalline), to which the termination /E or /R was added, depending on the zinc oxide used in synthesis. The compositions of the mixtures designed to obtain the frits is detailed in Table 3. A melting temperature of 1550°C was used except for the matt frit, whose melting temperature was 1500°C.

Frit	SiO ₂	Al ₂ O ₃	B ₂ O ₃	MgO	CaO	BaO	ZnO	Li ₂ O	Na ₂ O	K ₂ O	ZrO ₂
FM	46.60	5.25	5.75	3.65	11.95	-	21.25	1.35	2.80	1.05	0.35
FB	61.25	2.80	3.50	4.10	12.00	-	9.75	-	-	2.80	3.80
FC	65.43	3.54	3.09	0.62	15.80	1.93	6.89	-	0.67	2.03	-

Table 3. Frit compositions (mole %).

The first effect of the zinc oxide substitution was detected in the frits themselves. The three frits synthesised from the ZnO/E oxide displayed a transparent appearance with a greenish-yellowish shade, whereas the three frits synthesised from ZnO/R exhibited very different appearances, without any loss of transparency. The FC/R frit had a bluish colour; the FB/R frit contained some reddish-coloured particles, while the FM/R frit clearly consisted mainly of reddish-coloured particles. Despite their great differences in appearance, the six frits can be considered practically amorphous, since no defined reflections were detected in any of them by XRD (see Figure 5 and Figure 6), which indicates that the zinc substitution causes no important devitrifications during frit synthesis.

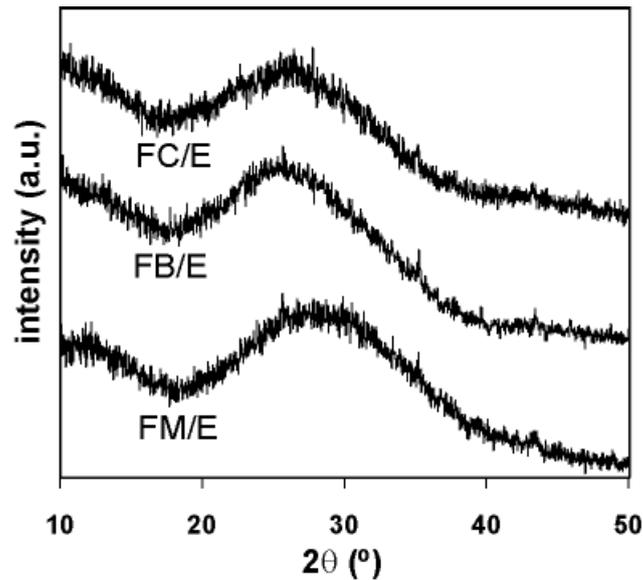


Figure 5. Detail of the diffractograms of the frits synthesised from ZnO/E.

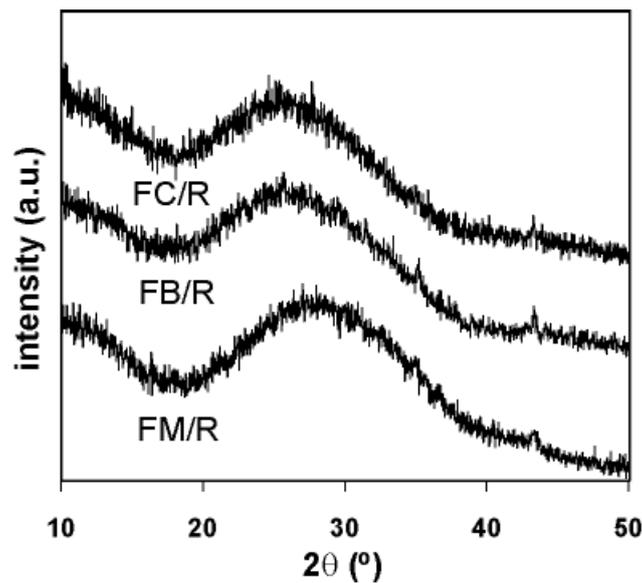


Figure 6. Detail of the diffractograms of the frits synthesised from ZnO/R.

The sintering curves (Figure 7 and Figure 8) and the characteristic temperatures (Table 4) obtained using hot stage microscopy, indicated that ZnO/R produced slightly more fluxing frits, with slightly lower characteristic temperatures compared with those obtained with ZnO/E. However, the variations were not high, these being most pronounced in the shrinkage end temperature (30°C at most), and they were much smaller in the half-sphere and melting temperatures (10°C at most).

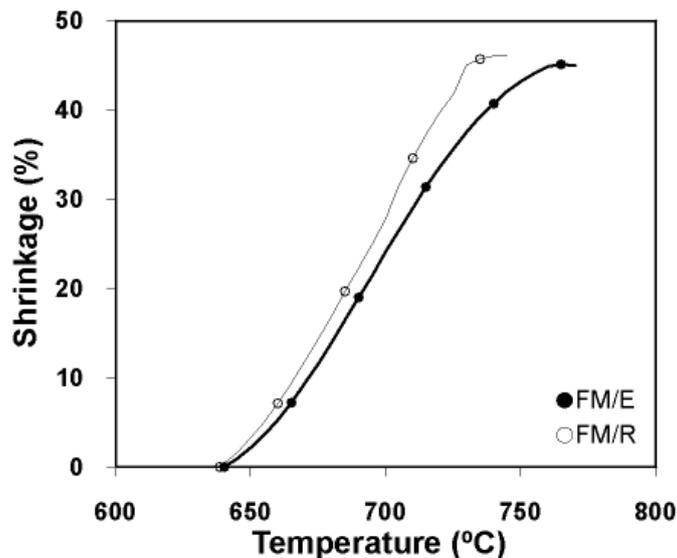


Figure 7. Shrinkage–temperature curves of the zinc matt type of frits.

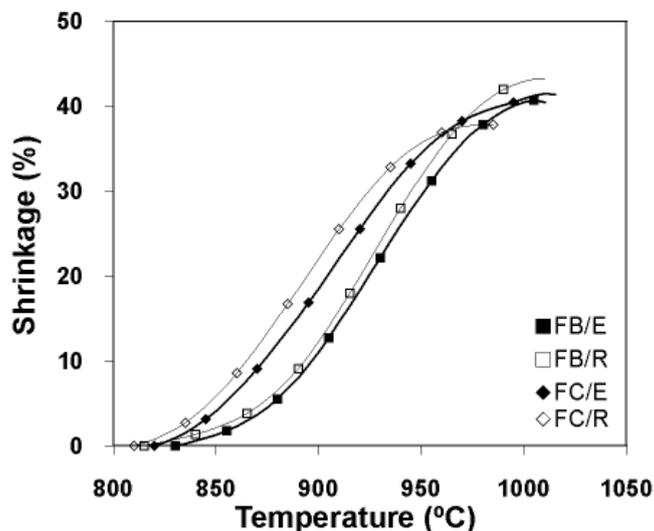


Figure 8. Shrinkage–temperature curves of the zirconium white and crystalline types of frits.

Temperature	FM/E	FM/R	FB/E	FB/R	FC/E	FC/R
Shrinkage start	650	645	845	830	830	820
Shrinkage end	770	745	1010	1010	1015	985
Softening	780	780	1075	1055	1030	1035
Sphere	875	915	1100	1105	1065	1065
Half-sphere	1020	1010	1160	1150	1130	1125
Melting	1035	1025	1190	1185	1170	1160

Table 4. Characteristic frit temperatures (°C).

It was verified by differential thermal analysis that the frits synthesised from ZnO/R displayed much less defined exothermic devitrification peaks than their counterparts made from ZnO/E (see Figure 9, Figure 10, and Figure 11), though they showed no displacement in the maximum temperature of the peaks.

The properties of the glazes obtained from the frits reflected an appreciable influence of the type of zinc oxide used. First, a displacement of the firing range towards lower temperatures was detected, evidenced by bubble formation in the FM/R frit at slightly lower firing temperatures with respect to FM/E (1080°C in comparison with 1090°C). No surface defects were detected in the white and crystalline frits within the explored ranges of firing temperatures, but the evolution of the properties of the resulting glazes in relation to this variable suggest a similar trend, as set out below.

Glaze gloss behaviour was analysed by dividing the frits into two groups:

- The gloss of the glazes obtained from the matt frits was slightly higher at the start of the firing range when ZnO/E was used instead of ZnO/R (Figure 12); the gloss increased slightly when T_C rose until it reached a maximum, followed by a drop in gloss just before bubbles developed, a drop that was much more pronounced in the FM/R glaze.
- The glazes obtained from the white and crystalline frits behaved similarly (Figure 13 and Figure 14). The frits synthesised using ZnO/E gave rise to glazes with a slightly higher gloss across the entire range of tested firing temperatures, which in addition reached maximum values at the same temperature (FB) or higher temperature (FC) and which, once the maximum had been reached, exhibited a much more gradual decrease in gloss.

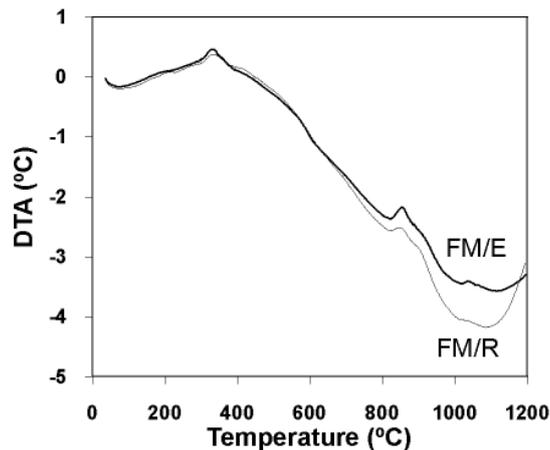


Figure 9. Differential thermal analysis of the zinc matt type of frits.

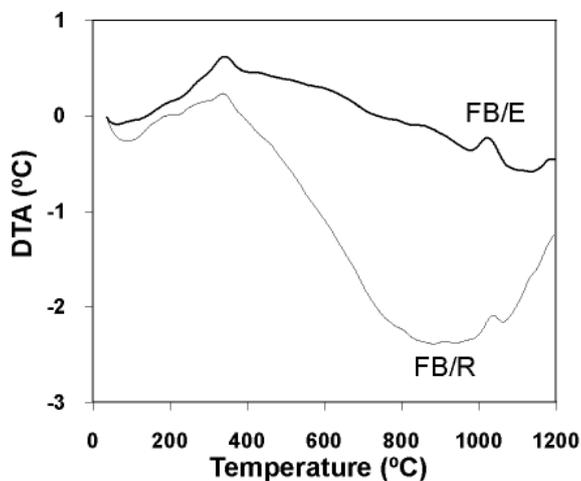


Figure 10. Differential thermal analysis of the zirconium white type of frits.

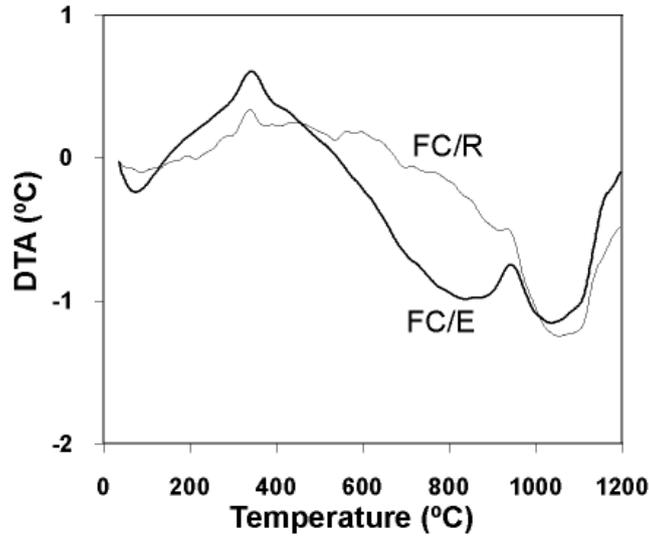


Figure 11. Differential thermal analysis of the crystalline type of frits.

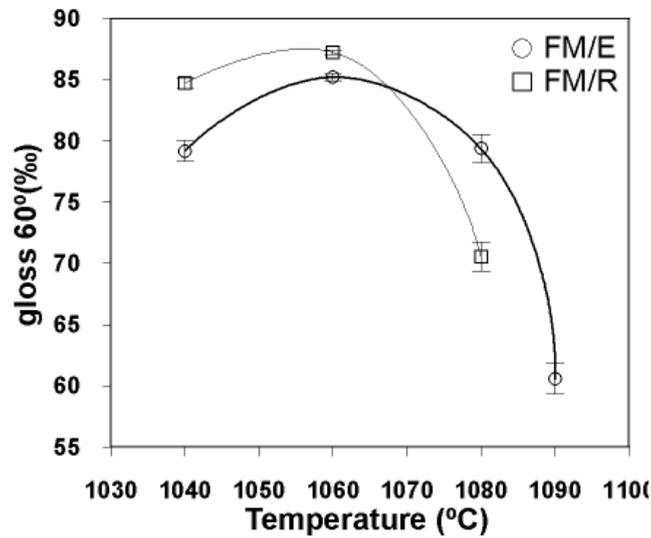


Figure 12. Evolution of the gloss of the zinc matt type of glazes with firing temperature.

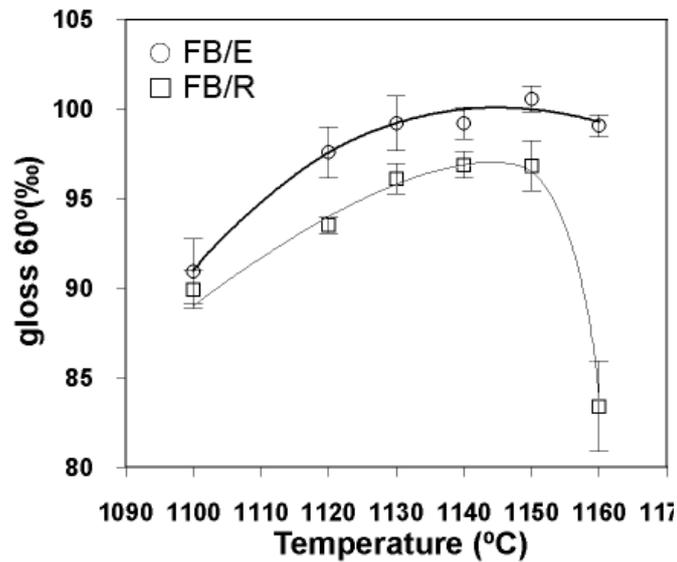


Figure 13. Evolution of the gloss of the zirconium white type of glazes with firing temperature.

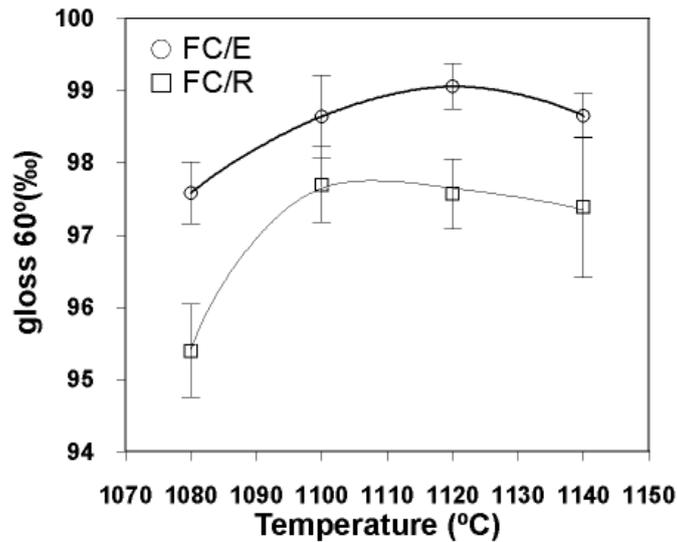


Figure 14. Evolution of the gloss of the crystalline type of glazes with firing temperature.

The lightness of the glazes was always lower in those obtained from the frits synthesised with ZnO/R, independently of the type of frit considered (Figure 15, Figure 16, and Figure 17), though the differences were more pronounced in the matt glaze than in the white and transparent glazes (in this last case, the glaze should be colourless, so that the colour of the body would essentially be measured, but the variations in the chromatic coordinate measurements indicated a modification in the glaze characteristics, since the body had been subjected to the same thermal cycle and should therefore display the same background colour). In regard to the evolution of lightness with T_C , no changes were observed in the matt and transparent glazes, since the replacement of ZnO/E with ZnO/R may be considered only to move the curve towards lower values of L^* . In contrast, in the white glaze the replacement of ZnO/E with ZnO/R converted a slightly decreasing evolution into a different evolution, which was practically independent of the firing temperature.

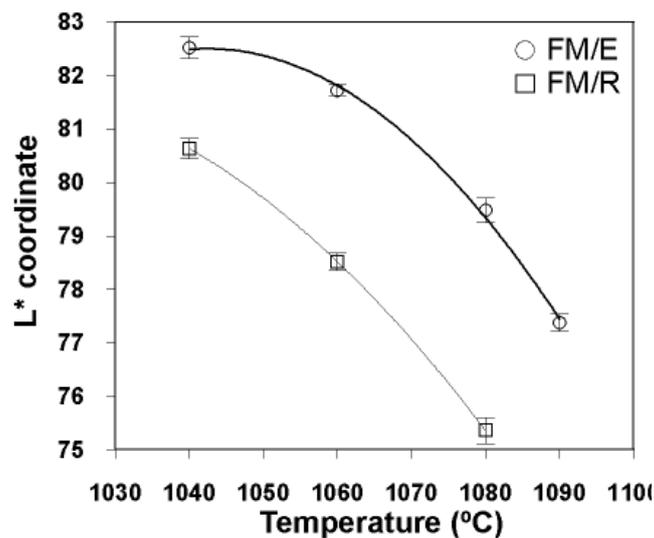


Figure 15. Evolution of the L^* coordinate of the zinc matt type of glazes with firing temperature.

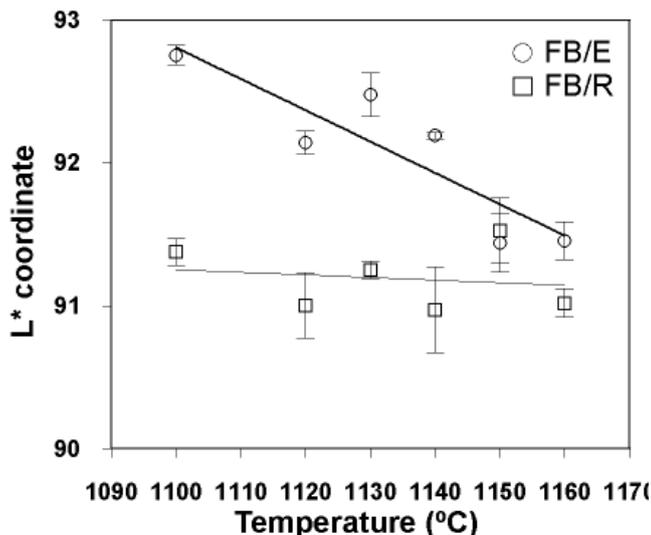


Figure 16. Evolution of the L* coordinate of the zirconium white type of glazes with firing temperature.

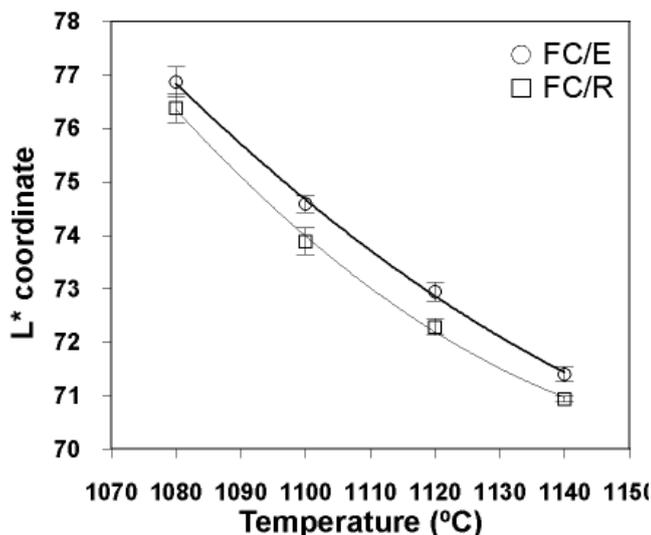


Figure 17. Evolution of the L* coordinate of the crystalline type of glazes with firing temperature.

The chromaticity coordinates (a^* and b^*) of the glazes presented a quite general trend when ZrO/E was replaced with ZrO/R, since a displacement towards lower values of a^* (less reddish or more greenish colours) and higher values of b^* (less bluish or more yellowish colours) was observed in the three types of glazes, though the magnitude of the displacement depended in the first place on the type of frit, and secondly on T_c (Figures 18 to 23). The most pronounced changes occurred in the matt glaze, whereas in the white and transparent glazes the variations were of a smaller magnitude. Regarding their evolution in relation to T_c , the differences in a^* were quite steady in the range of T_c explored for each type of frit, while the differences in b^* displayed a greater variation, these being higher at the intermediate temperatures of the explored ranges, while they tended to differentiate to a lesser extent at the extreme temperatures.

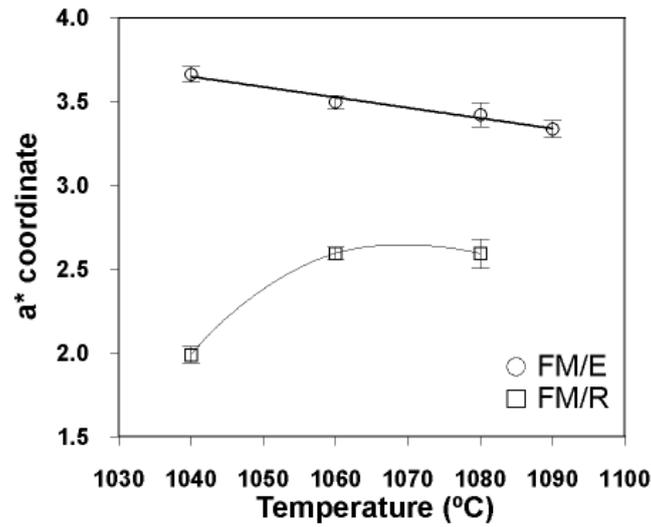


Figure 18. Evolution of the a^* coordinate of the zinc matt type of glazes with firing temperature.

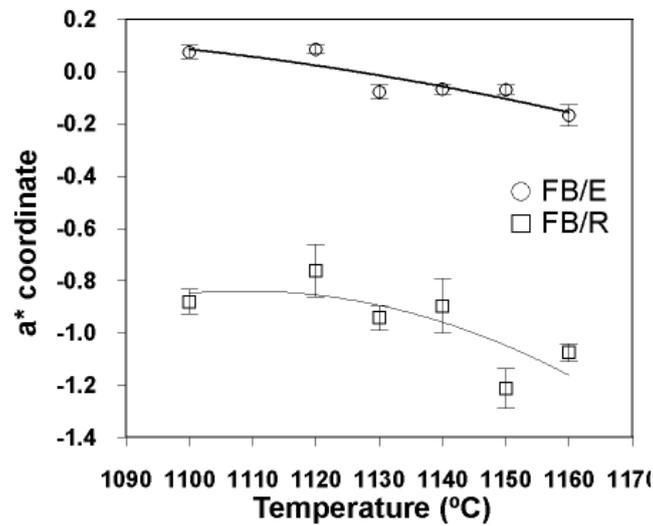


Figure 19. Evolution of the a^* coordinate of the zirconium white type of glazes with firing temperature.

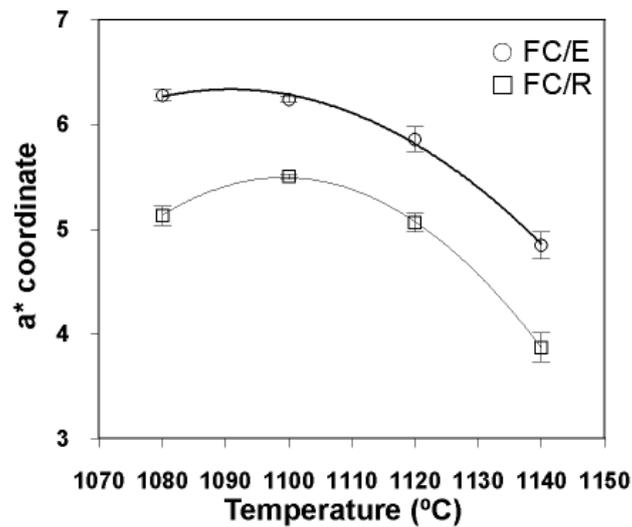


Figure 20. Evolution of the a^* coordinate of the crystalline type of glazes with firing temperature.

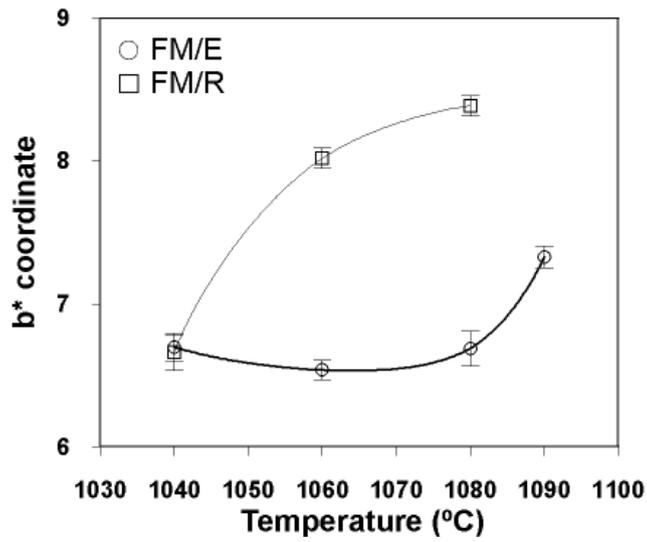


Figure 21. Evolution of the b^* coordinate of the zinc matt type of glazes with firing temperature.

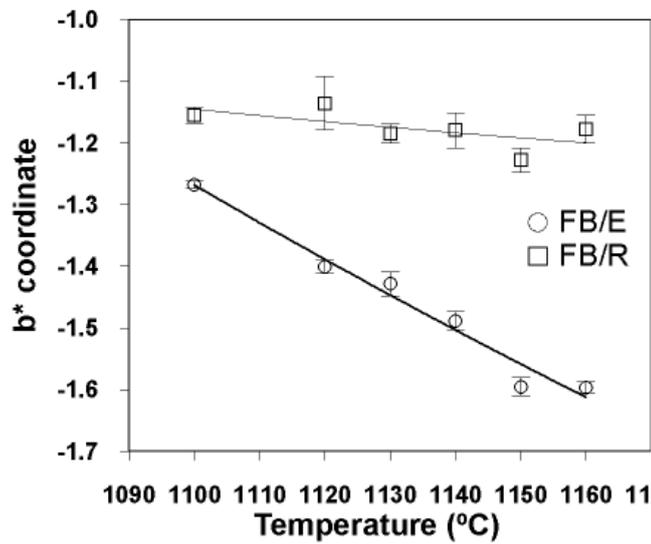


Figure 22. Evolution of the b^* coordinate of the zirconium white type of glazes with firing temperature.

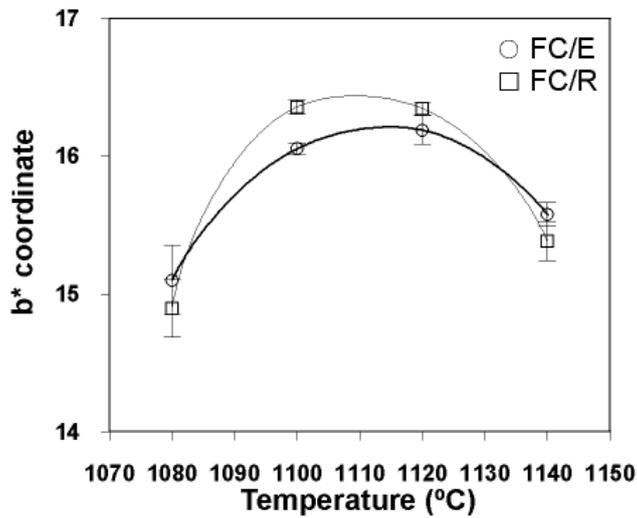


Figure 23. Evolution of the b^* coordinate of the crystalline type of glazes with firing temperature.

3.3. DISCUSSION

The variations found in the frit and glaze properties when ZnO/E was replaced with ZnO/R can be related to the differences in the characteristics of both oxides, especially in the impurities content, in which the presence of CuO plays an essential role, together with iron oxide, metallic zinc, and alumina.

The origin of the reddish colour mainly displayed by the frit FM/R particles, and more sporadically by those in FB/R, may be assigned to CuO in combination with the presence of metallic zinc as a reducer. This shade would be due to the reduction of copper during frit fusion, and the precipitation of colloidal particles of Cu₂O during quenching^[8], though the quantity is so small that it is below the XRD detection limit and, therefore, was not identified in FM/R. This phenomenon can obviously only appear in frits with a high ZnO/R content, which is why it does not appear in FC/R, since this contains a smaller quantity of ZnO/R, and the bluish colour corresponding to the presence of CuO in the glass is only detected in this frit^[9].

The changes in the thermal behaviour may be interpreted by considering that ZnO/R includes an additional contribution of alumina, an oxide that characteristically makes devitrification processes difficult¹⁰. Consistently with this interpretation, the three frits synthesised from ZnO/R display less pronounced and more diffuse devitrification processes at high temperature. In addition, the characteristic temperatures that undergo a greater variation are the ones immediately above the devitrification temperatures (the sphere temperature in FM, the softening temperature in FB, and the shrinkage end temperature in FC), which decrease. This is consistent with a smaller quantity of devitrified crystals, which involve a lower apparent viscosity of the glass and, therefore, greater facility for the sintering progress. Once the maximum densification has been reached, the lower apparent viscosity would also facilitate swelling of the bubbles and hence the earlier appearance of surface defects, as detected in the glaze obtained from the matt frit. However, the effect of the smaller quantity of crystals on viscosity would be partly compensated by the smaller quantity of zinc oxide contributed by ZnO/R; for that reason, a highly pronounced variation in thermal behaviour does not occur.

The enhanced sinterability of the glazes obtained from the frits synthesised with ZnO/R should mean greater ease in obtaining a smooth surface and, therefore, high gloss. This occurs in the case of the matt glaze, except when defects start appearing in the surface, but the same fails to happen in the transparent glaze and the white glaze, in which lower gloss values are obtained with the frits synthesised from ZnO/R. This phenomenon might be interpreted by considering that the lower apparent viscosity allows the devitrified crystals to alter the surface roughness of the glaze, even though the number of crystals is smaller, a phenomenon that would occur to a lesser extent with the glazes obtained from frits FB/E and FC/E.

The changes in the lightness of the matt and white glazes can be interpreted by considering the lesser devitrification to be noted in the glazes obtained with ZnO/R, which means a smaller number of glass–crystal interfaces and, therefore, decreased light scatter. In the case of the transparent glaze, the small reduction in lightness may be more closely related to selective absorption phenomena by the chromophore impurities, which are also responsible for the colour change.

Although the matt and white frits exhibit reddish areas, this colour disappears in the glazes, which indicates that the colloidal Cu₂O oxidises to CuO during firing.

This oxidation state generates greenish colorations in silica glasses, while the Fe(III) impurities tend to generate yellowish shades¹¹, so that the combined action of these cations would be responsible for the change in colour observed in the glazes, i.e. the decreased a^* would be assignable to Cu(II), while the decreased b^* would be caused by Fe(III).

4. CONCLUSIONS

The results described indicate that ZnO/R could be an acceptable raw material in the synthesis of frits that do not contain large quantities of zinc oxide, since in this case the occurring alterations in frit behaviour would be small. Complete substitution in zinc-rich frits like those used in this study would involve greater alterations in both thermal behaviour and final glaze appearance (reflected in gloss and colour), whose importance would need to be evaluated in each case. However, an intermediate solution may be proposed, in which ZnO/R could constitute part of the zinc oxide contributed to the frit composition, and in this case the alterations would be much smaller. A slight change in frit composition might also be considered in order to accommodate the variations that this zinc oxide could generate in thermal behaviour and, in this case, only the effects on end glaze appearance would need to be evaluated.

5. ACKNOWLEDGEMENTS

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