OPACIFICATION INHIBITORS IN CERAMIC FLOOR AND WALL TILE GLAZES

J.B. Vicent, J.L. Ros(*), M.A. Tena, P. Escribano, G. Monrós,

Dept. of Organic and Inorganic Chemistry, Universitat Jaume I, Castellón.
(*)Ceramicas Cabrera S.A. (CERACASA), Alcora (Castellón).

ABSTRACT

Ceramic tile manufacturers can perform reasonable reformulations of their base glazes by small mill additions that allow them to personalise their production and adjust it to specific market segments with given aesthetic or mechanical preferences. The present study addresses the possibility of modifying glaze opacity by small additions of opacification inhibiting agents. Without changing the firing cycle, the addition was studied to ceramic bases typically used in single-fire floor tile production of: volatile fluorides (NaF, LiF), fixed fluorides (Na_3AlF_6 and BaF_2) and thermally stable carbonates (Li_2CO_3, $SrCO_3$), alone or accompanied by a devitrifying agent (WO_3 precipitating scheelite, Al_2O_3 precipitating gahnite, and MgO precipitating diopside), as well as a nucleant by immiscibility (ZrO_2). The results show that glaze transparency can be controlled, while improving gloss and hardness of the starting base. In this sense to be noted are cryolite and strontium carbonate.

1. INTRODUCTION

The development and implementation of ceramic technology in the ceramic tile branch have led to a drastic reduction in reformulations by in-plant mill additions, and the emergence of ceramic glaze and colour producers as technical service companies, which take care of reformulating and adjusting the materials to the models designed by the glaze producers themselves or by the ceramic tile manufacturer.

However, starting from some base formulations, the ceramic tile manufacturer can perform certain reasonable reformulations of these glazes by minor mill additions that allow personalising production or achieving significant modifications in the technological performance of the glassy bases, with a view to making a certain production model better suited to an given market segment for which such product enhancement is commercially attractive.

Additive solubility in the glassy matrix will to a great extent depend on matrix composition. However, generally, even minor additions of cassiterite, zircon and zirconia as well as titanium or cerium oxide, which are relatively insoluble in the glaze, crystallise in cooling by oversaturation, devitrification or crystalline segregation mechanisms. Moreover, when phosphate additions of As_2O_3 of Sb_2O_5 dissolve in the glass, they produce structural discontinuities (P^{5+}, As^{5+} or Sb^{5+} ions on replacing Si^{4+} in the glassy lattice form a double bond with oxygen in its tetrahedral coordination environment, which thus cannot bridge). These discontinuities are compositional segregation centres that evolve towards the separation of segregate droplets with the greatest surface tension, opacifying by a phase-separation mechanism[1], [2], [3].

In the devitrification mechanism, in accordance with the Tamman[1] nucleation-crystalline growth theory, homogeneous nucleation requires a critical nucleus size beyond which nucleation becomes effective. Effectivity depends on crystallisation energy and surface tension in the nucleus-melt interface. When nucleation is heterogeneous (as may be the case when there are unmelted particles of the opacifying additive), free energy maximum variation will also depend on a proportionality factor that will be a function of the affinity existing between the heterogeneous phase and the melt.

The lower the nucleation temperature (greater degree of undercooling), the higher the crystallisation energy (devitrification) and the lower the free energy of the system, encouraging nucleation up to a peak value corresponding to a value equal to free energy and diffusion activation energy. Beyond this point this last factor dominates the process: the nucleation rate drops as a strong increase in viscosity arises in the melt, therefore reducing possible diffusion. Crystal growth similarly exhibits a crystallisation rate peak. At high temperatures, crystallisation is held back by the difficulty of dissipating the crystallisation heat freed in the system, while at low temperatures it is hindered by the fast, continuous rise in viscosity, which also hampers diffusion processes[2], [3].

Generally, to obtain effective nucleation, optimum nucleation temperatures should lie within the thermal range corresponding to a viscosity value, which is equal to 10^{11} DP, that is, temperatures slightly higher than the glass transformation temperature (Tg), which represents the boundary between the plastic and elastic state of the glass (viscosity around $10^{13.3}$ DP). Furthermore, the highest crystallisation temperature in a glass-ceramic process will correspond to the heat-treatment range in which crystallisation peaks without the material deforming. This will generally depend on the liquidus temperature of the major crystalline phase.

2. OBJECTIVES

The present work studies addition systems that allow controlling surface smoothness, transparency and gloss, while keeping the usual industrial firing schedule and maintaining the mechanical strength of the bases. To do so it is necessary to avoid nucleation-growth of crystal phases or avoid opacification of the material, so that we can proceed in two directions[2], [3]:

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[1]. G. Tamman G, W. *Hesse, Die Abhängigkeit der vikosität von der Temperatur bei unterkühlten Flüssigkeiten*. Z. anorg. allog. Chem., 156(1926)245-256.

[2]. P.W. McMillan, *Glass-Ceramics, Academic* Press, 2a. ed., New York 1979.

[3]. Kenong Xia, Terence G. Langdon, *The toughening and strengthening of ceramic materials though discontinuous reinforcement, J. of Mat*. Sci. 29(1994)5219-5231.

(i) Incorporating mill additions that lower the glass transformation temperature (while holding the industrial firing cycle), which permit an appreciable crystalline nucleation rate, developing numerous small crystals oriented in their growth, so that devitrified crystal formation cannot produce opacification[4].

(ii) Incorporating fluxing materials that allow reducing diffusion rates in devitrified crystal growth (around 700-850°C), in the glassy formulations for floor and wall tiles[5].

These additions also need to meet certain operating requirements:

(i) Low level of gas decomposition so that outgassing bubbles or pinholing will not arise.

(ii) Acceptable variation in the glassy matrix coefficient of thermal expansion to keep cracking from arising.

(iii) Compatible densification of the glaze containing the addition with the devitrification that is to occur subsequent to ending densification, in order to avoid it collapsing and producing matt, grainy materials with low mechanical consistency.

With these premises, this paper presents a study on the devitrification inhibition of three ceramic wall and floor tile bases with rising maturing temperatures, which exhibited the characteristics detailed in Table I.

BASE A: Glossy base rich in zinc and calcium, Mohs 6, PEI IV, K_{IC} 1.5 MPa.m$^{1/2}$, GLOSS 91 at 60°, devitrifies zircon (250 CPUs), softening point 1050°C, semisphering at 1080°C

BASE B: Semigloss base relatively rich in alumina, zirconium and sodium devitrifies zircon (648 cps),), softening point 1110°C, semisphering at 1140°C, Mohs 6-7.

BASE C: Aluminosilicate matt base with intermediate levels of zinc and calcium, devitrifies zircon (465 cps) together with quartz (65 cps) and anorthite (46 cps), softening point 1080°C, semisphering at 1110°C, Mohs 7.

Table I. *Characterisation of the bases used*

3. EXPERIMENTAL

Two types of additions were carried out:

(3.1). Simple inhibitor additions in incremental concentrations.

(3.2). Joint addition of nucleating and devitrifying agents.

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[4]. G.H. Beall, *Nucleation and Crystallization in Glasses*, The American Ceramic Society, eds. L.L. Hench y S.W. Friedman, 1972.

[5]. D.R. Stewart, *Concepts of Glass Ceramics, in Introduction to* Glass Science, ed. L.D. Pye, Plenum Press, New York, 1972.

Samples were prepared by mixing the base glaze slip adjusted to a bulk density of 1.6 g/mL with the relevant addition in a planetary type ball mill for 10 min at 800 rpm. The slip containing the addition was applied to an engobed single-fire stoneware body by the Doctor Blade method, always keeping the same glaze quantity/unit body surface (in grams), controlling basic rheological aspects for this purpose in terms of Ford Cup and bulk density. The glazed specimen was then fired at the industrial facilities of ceramic wall and floor tile manufacturer CERACASA, with the typical single-fire heating-treatment cycle used for the studied bases.

The samples were characterised by measuring gloss, X-ray diffraction (XRD), Mohs hardness and microstructural analysis by scanning electron microscopy (SEM). Gloss was measured with a Minolta, Multi-Gloss 268, reflectometer that meets standards DIN 67 530, ISO 2813, ASTM D523, BS 3900 (D5). Reflection at 60° was used, but when the value obtained exceeded 70 units, reflection at 20° was taken as the gloss value. XRD was run on the glazed specimens with a SIEMENS D500 using CuKα radiation filtered by Ni to characterise the devitrifying crystalline phases in the glaze. This involved measuring the number of counts/s assessed by the detector for maximum peak intensity of the relative phase, running at a goniometer rate of 0.05 °2Θ/s and 0.02 s time constant. Mohs scratch hardness was performed according to standard EN 101. SEM was conducted in a LEICA LEO440i instrument fitted with an OXFORD, LINK, energy-dispersive X-ray microanalysis system /EDX.

4. INCREMENTAL CONCENTRATIONS OF SIMPLE INHIBITOR ADDITIONS

The addition of two inorganic salt families was studied: block s carbonates and fluorides. Their physical constants are detailed in[7].

	f.p. (°C)	decomp. (°C)	e.p.(°C)
FLUORIDES			
LiF	845	-	1.676
NaF	993	-	1.695
Na_3AlF_6	1.000	-	-
BaF_2	1.355	-	2.137
CARBONATES			
Li_2CO_3	723	1310	-
$SrCO_3$	<1.700	1.340	

Table II. *Physical constants of the added inorganic salts.*

4.1. FLUORIDE ADDITION TO BASE A

The effect of fluorides in ceramic glazes is well known in ceramic practice: at low additions they act as fluidisers and at higher additions (4%) as opacifiers. The action of fluorides on the glassy lattice can be explained in terms of the substitution mechanism of oxide ions by fluoride according to Eq. (1).

$$\equiv Si - O - Si \equiv \; \rightarrow \; \equiv Si - F + {}^{-}O - Si \equiv \quad \text{(Eq. 1).}$$

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[6]. A. Escardino, *Vidriados Cerámicos de Naturaleza Vitrocristalina*, Ceram Inf., Junio 1997, 17-34, Anales de Qualicer 96.

[7]. *Handbook of Chemistry and Physics*, David R. Lide, 72 ed., 1991-1992, CRC Press, Boca Raton.

This situation entails the appearance of anionic structural discontinuities that rapidly anchor mobile lattice cations such as the alkaline cations, producing compositional segregation (some regions rich in silica and others rich in alkalis), with the phase exhibiting the greatest surface tension separating out as milky droplets. These droplets produced in phase separation evolve into crystalline forms when the fluoride amount is sufficient and/or crystallisation conditions arise in cooling, opacifying the glass[8], [9].

Fluoride opacification is known in glazes for sanitary ware and in enamelling metal sheeting. It is necessary to add excess fluorides with a view to achieving a 4% F- solid solution in the lattice. The excess compensates volatilisation losses in the form of NaF (liquid with high vapour tension) or SiF_4 (e.g. -65°C)[10]. Such volatilisation entails serious environmental problems in terms of fluorine emissions, as well as corrosion of kiln refractory materials[11], [12].

SAMPLE	APPEARANCE	GLOSS	XRD	MOHS
BASE A	opaque	80(20°)	Z(250)	5
LiF addition				
1%	transparent pinholing	64.2(60°)	Z(1789)	4
3%	transparency rises pinholing	37.8(20°)	Z(4502)	4
5%	transparency rises pinholing	38(20°)	Z(1787)	4/5
NaF addition F				
1%	similar to base	83,3(20°)	Z(500)	4
3%	transparency rises pinholing	79.3(20°)	Z(913)	4
5%	transparency rises pinholing rises	41.0(20°)	Z(953)	5
Na_3AlF_6 addition				
1%	transparent	90.2(20°)	Z(503)	5
3%	transparency rises	80.6(20°)	Z(857) G(81)	5
5%	transparency rises pinholing rises	76.3(20°)	Z(2140)	5
10%	transparency rises pinholing rises	60.4(60°)	Z(2503)	5
BaF_2 addition				
1%	transparency rises	90.5(20°)	Z(733)	6
3%	transparency rises	92(20°)	Z(952)	6
5%	transparency rises	89(20°)	Z(1032)	6

CRYSTALLINE PHASES: Z(Zircon $ZrSiO_4$), G(Gahnite $ZnAl_2O_4$). The number of counts/s is given in brackets for the greatest intensity peak of the glazed specimen obtained by XRD.

***Table III.** Incremental fluoride addition to BASE A.*

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[8]. J.M. Fernández Navarro, *El Vidrio*, CSIC, 2a. ed., Madrid, 1991.

[9]. W.D. Kingery, H.K. Bower, D.R. Uhlmann, *Introduction to Ceramics*,2ª. ed., New York, John Wiley and Sons, 1976.

[10]. E.M. Rabonich, D.M. Krol, N.A. Kopylov, P.K. Gallagher, *Retention of Fluorine in Silica Gels and Glass*, J. of Am. Ceram. Soc., 72, 1229-32 (1989).

[11]. *El fluor en los materiales cerámicos y el ambiente*, Cerámica Información, Marzo 1979.

Fluorine retention improves in glazes rich in CaO and/or Al_2O_3, as was the case of the glazes used in this study. This effect made cryolite Na_3AlF_6 an excellent fluorinating agent[9], [13].

Table III details the results obtained with rising fluoride additions to Base A.

The data presented in Table III allow certain general trends in development to be observed, which are discussed below.

4.1.1. VOLATILE FLUORIDE ADDITIONS TO BASE A (NaF, LiF)

The findings for these fluorides indicate:

(a.1) Rising additions raised the devitrified crystal mass fraction (zircon) as shown in Fig.1.

(a.2) Additions yielded opacification inhibition (rising transparency) and lower gloss.

(a.3) Pinholing appeared with relatively low additions (3%).

(a.4) Glaze hardness decreased with the additions.

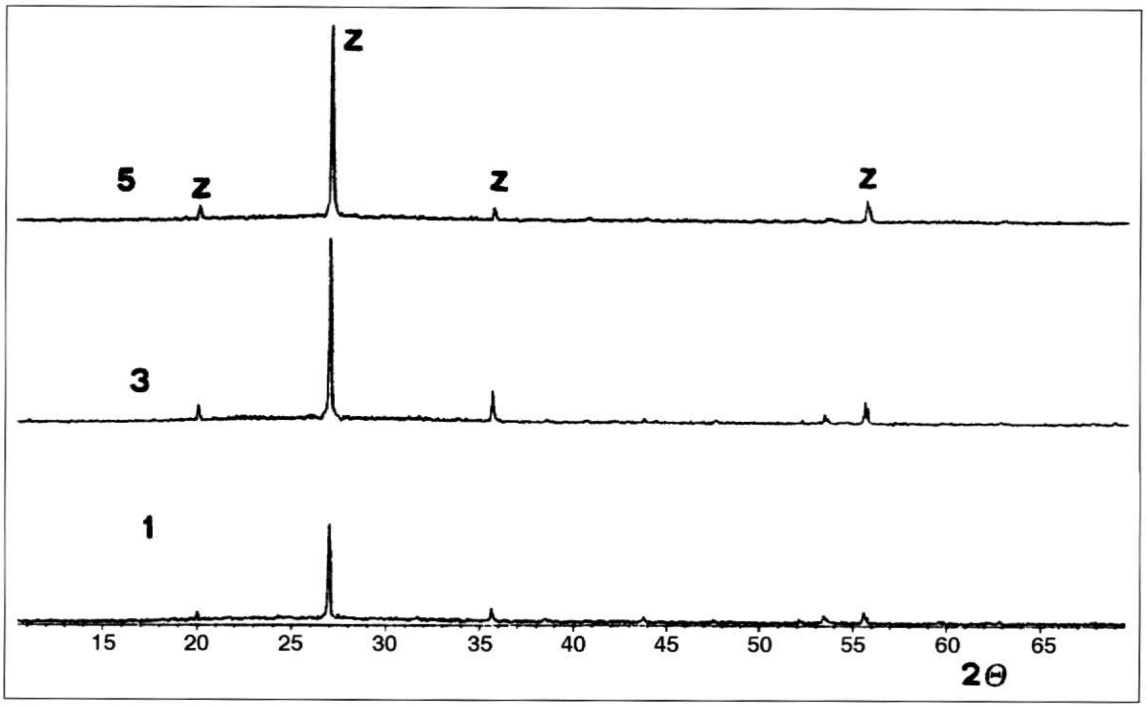

Figure 1. *XRD of the NaF additions to base A: (a)1%,(b)3%,(c)5%.*

The tested volatiles lowered glass transition temperature, by inducing the devitrification of small crystals (below 500 nm) that were unable to produce opacification. Glaze fluidisation impeded their growth. Volatilisation gases rapidly gave rise to pinholing and lower hardness.

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[9]. W.D. Kingery, H.K. Bower, D.R. Uhlmann, *Introduction to Ceramics*,2ª. ed., New York, John Wiley and Sons, 1976.

[13]. G. Rothwell, *The Crystalline Phase in Fluoride Opal Glasses*, J. of Am. Ceram. Soc., 39,407-414(1956).

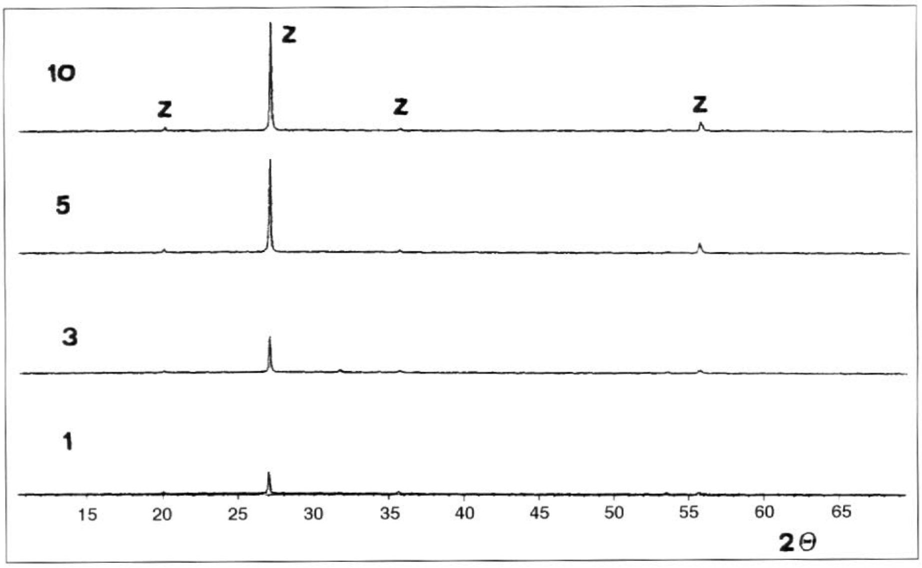

Figure 2. XRD of the cryolite Na_3AlF_6 additions to base A: (a)1%,(b)3%,(c)5%,(d)10%.

4.1.2. FIXED FLUORIDE ADDITIONS TO BASE A (BaF_2,Na_3AlF_6)

The findings for these fluorides indicate:

(b.1) Rising additions raised the devitrified crystal mass fraction (zircon) as shown in Fig.1. Cryolite also caused the gahnite spinel $ZnAl_2O_4$ to devitrify.

(b.2). Additions yielded opacification inhibition (rising transparency) and higher gloss

(b.3) Pinholing appeared with relatively high additions (>5%).

(b.4). Glaze hardness remained steady or increased with the addition

These fluorides were retained better in the glazes than the foregoing ones, so that environmental problems decreased as did pinholing-weakening. As in the previous case, the drop in glass transition temperature as a result of these fluoride additions produced a network of needle-like microcrystals (Fig. 3) incapable of producing opacification.

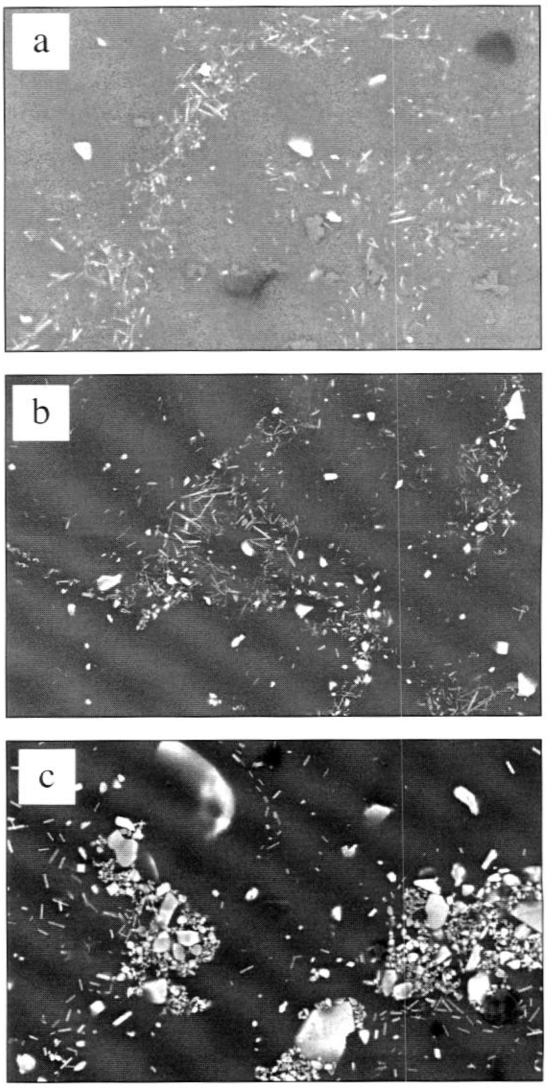

Figure 3. SEM micrographs with back-scattering detector of the cryolite Na_3AlF_6 additions to base A: (a)1%,(b)3%,(c)10%.

Fig. 3 presents the SEM micrographs of

the sample to which cryolite was added: on raising the addition, the needle-zircon crystals (confirmed by EDX analysis) grew in length and irregular particulates appeared, shown by EDX to be zircon. The needle-like crystals virtually disappeared in the sample at 10% in favour of the particulates, which prevailed in a relatively high mass fraction, though with a volume fraction incapable of producing opacification, so that the material was transparent.

4.2. BLOCKS CARBONATE ADDITIONS TO BASE A

Two "fixed" carbonates were used with a high thermal breakdown point: Li_2CO_3 and $SrCO_3$. Table IV reports the data obtained with these additions.

SAMPLE	APPEARANCE	GLOSS	XRD	MOHS	L*
BASE A	opaque	80(20º)	Z(250)	5	
Li_2CO_3 addition					
1%	pinholing	70.2(20º)	Z(1027)	5	83.33
3%	transparency rises, darkening, pinholing	21.5(60º)	Z(991)	5	67.23
5%	transparency rises, darkening, less pinholing, cracking	25.1(60º)	Z(215)	5	59.86
10%	transparency rises, darkening, cracking	44.8(20º)	Z(88)	5	51.81
$SrCO_3$ addition					
0.2%	similar to base	87.2(20º)	Z(320)	6	
0.5%	appearance similar to base	86.8(20º)	Z(392)	6	
1%	transparency rises pinholing	88.7(20º)	Z(708)	6	
2%	transparency rises pinholing rises	81.5(20º)	Z(470)	6	

CRYSTALLINE PHASES: Z(Zircon $ZrSiO_4$). The number of counts/s is given in brackets for the greatest intensity peak of the glazed specimen obtained by XRD.

Table IV. *Carbonate additions to BASE A:*

The results in Table IV indicate:

(c.1) Rising additions inhibited devitrification (zircon) as Fig. 4 shows for $LiCO_3$.

(c.2) Gloss was maintained or improved, while transparency rose. In the case of the Li_2CO_3 addition the material darkened, revealed by the L* brightness measurements of the CIE-L*a*b* system, which approximately assess surface whiteness (L=0 black, L=100 white).

(c.3) Pinholing appeared with Li but not with Sr additions.

(b.4) Glaze hardness was maintained or increased.

These compounds acted as true devitrification inhibitors. Fig. 5 shows how the micrographs of the glazed specimens evolved, in which the progressive decrease in crystalline fraction with the additions can be observed.

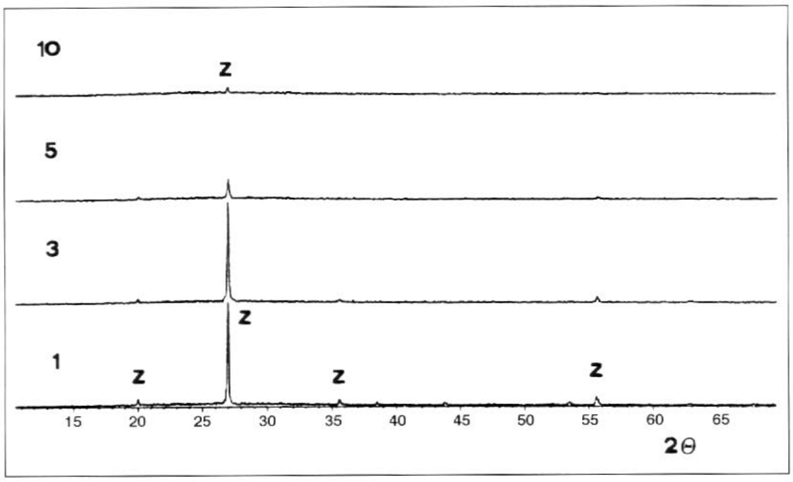

Figure 4. XRD of the Li_2CO_3 additions to base A: (a)1%,(b)3%,(c)5%,(d)10%.

4.3. FLUORIDE AND CARBONATE ADDITIONS TO BASES B AND C

Table V details the results obtained with these additions.

The data reveal that adding BaF_2 to these bases followed the trends highlighted in point 4.1.2.: the devitrified zircon mass fraction rose, as did that of quartz in base C. The low addition of Li_2CO_3 behaved as it did in the base A addition, slightly raising the zircon content.

Hardness fell in all cases, becoming more marked as the frit maturing degree rose.

5. JOINT NUCLEATING AND DEVITRIFYING AGENT ADDITIONS

Monoclinic zirconia was chosen as the nucleating agent. This finds widespread use together with other oxides such as TiO_2, P_2O_5 and V_2O_5 in 1-10% proportions as an effective nucleating agent in glass-ceramic nucleation[2], [4], [5], [14]. The nucleating mechanism involved in the nucleated crystalline phase is of the immiscibility type: the nucleant partially

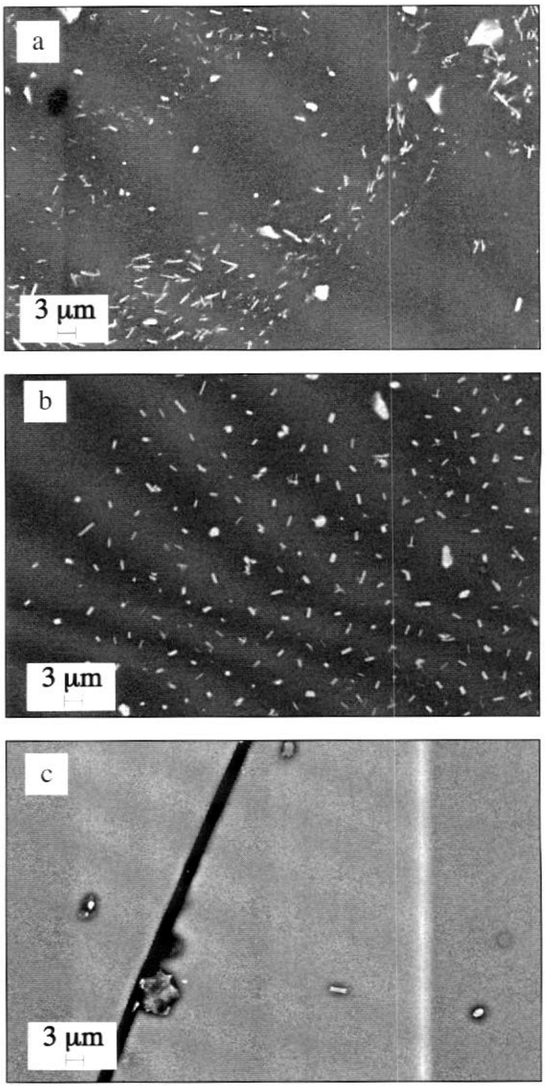

Figure 5. SEM micrographs with back-scattering detector of the Li_2CO_3 additions to base A: (a)1%,(b)3%,(c)10%(visionado de una grieta).

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[2]. P.W. McMillan, *Glass-Ceramics*, Academic Press, 2a. ed., New York 1979.

[4]. G.H. Beall, *Nucleation and Crystallization in Glasses*, The American Ceramic Society, eds. L.L. Hench y S.W. Friedman, 1972.

[5]. D.R. Stewart, *Concepts of Glass Ceramics, in Introduction to Glass Science*, ed. L.D. Pye, Plenum Press, New York, 1972.

[14]. S.D. Stookey, *Catalyzed Crystallization of Glass in Theory and Practice*, V. Internat. Glaskongress, Munich 1959, Glastech. Ber. 32 k,1-8(1959).

dissolves in the molten glaze, nucleating homogeneously on cooling. These nuclei act as a heterogeneous nucleating phase relative to the nucleated phase, which grows epitaxially, producing microcrystallisations with a high volume fraction, which are characteristics that define a glass-ceramic. The nucleant has a markedly falling solubility with temperature, exhibits high rates of homogeneous nucleation, low interface surface tension with the nucleated phase, and similar lattice parameters to the nucleated phase, which allow its eptaxial growth on the nucleant. In the present study, the nucleated phase was zircon in almost every case (anorthite, quartz and gahnite were minor phases), and consequently zirconia met all nucleant requirements regarding this crystalline phase.

SAMPLE	APPEARANCE	GLOSS	XRD	MOHS
BASE B	semigloss	65.3(20º)	Z(648)	6/7
BaF_2 addition				
1%	similar to base	68 (20º)	Z(820)	6
4%	similar to base	53.2(20º)	Z(772)	6
Li_2CO_3 addition				
1%	slight pinholing	75(20º)	Z(984)	6
BASE C	matt	75.8(20º)	Z(465) Q(65)A(46)	7
BaF_2 addition				
1%	semigloss	63.2(20º)	Z(701)	6
BASE + 4% BaF_2	semigloss more transparent	69.2(20º)	Z(978) Q(101)	6
Li_2CO_3 addition				
1%	semigloss more transparent	78(20º)	Z(928) Q(106)	6

CRYSTALLINE PHASES: Z(Zircon $ZrSiO_4$), Q(Quartz SiO_2), A(Anorthite $CaAl_2Si_2O_8$). The number of counts/s is given in brackets for the greatest intensity peak of the glazed specimen obtained by XRD.

Table V. *Fluoride and carbonate additions to BASES B and C.*

The following devitrification promoters were chosen, which acted by neoformation of insoluble phases on reacting with the melt: tungsten oxide WO_3 that devitrifies scheelite ($CaWO_4$), alumina that precipitates gahnite $ZnAl_2O_4$ and MgO that devitrifies diopside $CaMg(SiO_3)_2$[15], [16], [17], [18].

Table VI details the results of the additions to base A containing 3% LiF.

The WO_3 addition devitrified scheelite, partially inhibiting zircon devitrification, however devitrification decreased on raising the addition. The material exhibited the pinholing already to be observed with the simple LiF addition. Gloss dropped and hardness rose.

The alumina addition did not devitrify gahnite although it had a certain nucleating

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[15]. J.L. Rodrigo, F. Sanmiguel, A. Gozalbo, M.J. Orts, J.L. Amorós, A. Belda, *Estudio de algunas variables que influyen sobre el brillo de vidriados obtenidos a partir de mezclas de frita y óxido de wolframio*, Anales de Qualicer 94, pp. 47-59.

[16]. M. Hashiba, M. Shigemitsu, Y. Nurishi, *Microstructural Observation of $ZnAl_2O_4$ formation affected by the Physical nature of Al_2O_3 in the presence of LiF*, J. of Mat. Sci., 23, 4267-4272 (1988).

[17]. V.G. Chistoserdov, N.A. Shmeleva, A.M. Smerdyuk, *Study of Crystallization Products in the Magnesium Aluminosilicate System with Additions of TiO_2, Catalyzed Crystallization and Glass*, pp. 172-174, ed. Consultants Bureau, New York, 1964.

[18]. C.S. Hurlbut, C. Klein, *Manual de Mineralogía de Dana*, Reverté, 1989.

effect on the zircon. The material exhibited the pinholing already to be observed with the simple LiF addition. Gloss dropped and hardness rose.

SAMPLE	APPEARANCE	GLOSS	XRD	MOHS
BASE A	opaque	80(20°)	Z(250)	5
WO_3 addition				
4%	pinholing, transparent	32.2(60°)	S(1453)Z(155)	5
9%	pinholing, transparent	38.6(60°)	S(929) Z(110)	5/6
Al_2O_3 addition				
3%	pinholing, transparent	14.2(60°)	Z(896)	5
6%	pinholing, transparent	29.3(60°)	Z(2609)	5/6
Addition of 10% ZrO_2 + 2% Al_2O_3	matt	42.1(60°)	Z(2949) M(49)	7

CRYSTALLINE PHASES: Z(Zircon $ZrSiO_4$), M(monoclinic ZrO_2), S(Scheelite $CaWO_4$). The number of counts/s is given in brackets for the greatest intensity peak of the glazed specimen obtained by XRD.

Table VI. Additions to base A –LiF (3%).

The joint action of the nucleating and devitrifying agents greatly increased devitrification. The effect of the nucleant was particularly striking, and was also detected in XRD (monoclinic ZrO_2).

Table VII details the results of the additions to BASE A- 5% BaF_2

The WO_3 addition devitrified scheelite, raised gloss and hardness as well as transparency.

The Al_2O_3 addition devitrified more zircon, decreased or held gloss and hardness, while raising transparency.

SAMPLE	APPEARANCE	GLOSS	XRD	MOHS
BASE A	opaque	80(20°)	Z(250)	5
WO_3 addition				
4%	transparent	81.5(20°)	S(12145)Z(246)	6
9%	less transparent	90(20°)	S(12223)Z(217)	6
Al_2O_3 addition				
3%	transparent	81.3(20°)	Z(797)	5
6%	transparent	55.3(20°)	Z(686)	5
MgO addition				
10%	matt	9.3(60°)	D(147) Z(122)	8
Addition of 10% ZrO_2 + 2% Al_2O_3	semigloss	59(20°)	Z(922) M(47)	6

CRYSTALLINE PHASES: Z(Zircon $ZrSiO_4$), M(monoclinic ZrO_2), S(Scheelite $CaWO_4$), D(Diopside $CaMg(SiO_3)_2$). The number of counts/s is given in brackets for the greatest intensity peak of the glazed specimen obtained by XRD.

Table VII. Additions to BASE A- 5% BaF_2.

The MgO addition devitrified diopside to the detriment of zircon, losing gloss and raising hardness.

The joint action of the nucleating and devitrifying agents greatly increased devitrification. The effect of the nucleant was particularly striking, and was also detected in XRD (monoclinic ZrO_2).

Table VIII details the results of the additions to BASE A-3%Li_2CO_3.

The WO_3 addition devitrified scheelite, and raised gloss and hardness as well as transparency.

The Al_2O_3 addition devitrified more zircon, raised or held gloss and hardness, while raising transparency.

SAMPLE	APPEARANCE	GLOSS	XRD	MOHS
BASE A	Opaque	80(20°)	Z(250)	5
WO_3 addition				
4%	Transparent	62.7(20°)	S(13372)Z(246)	6
9%	Less transparent	82.3(20°)	S(39191)Z(238)	7
Al_2O_3 addition				
3%	Transparent	80.7(20°)	Z(489)	5
6%	Transparent	69.3(20°)	Z(3470)X (68)	6
MgO* addition				
10%	Matt	9.4(60°)	D(165) Z(149)	8
Addition of* 10% ZrO_2 + 10% Al_2O_3	Matt	5.3(60°)	Z(272)M(99) A(78)	8/9

CRYSTALLINE PHASES: Z(Zircon $ZrSiO_4$), M(monoclinic ZrO_2), S(Scheelite $CaWO_4$), D(Diopside $CaMg(SiO_3)_2$), A(Anorthite $CaAl_2Si_2O_8$). The number of counts/s is given in brackets for the greatest intensity peak of the glazed specimen obtained by XRD.
(*) In these samples the Li_2CO_3 addition was 1%.

Table VIII. *Additions to BASE A-3%Li_2CO_3.*

The MgO addition devitrified diopside to the detriment of zircon, losing gloss and raising hardness.

The joint action of the nucleating and devitrifying agents devitrified anorthite ($CaAl_2Si_2O_8$). The effect of the nucleant was also detected in XRD (monoclinic ZrO_2).

Table IX details the results of the additions to Bases B and C.

SAMPLE	APPEARANCE	GLOSS	XRD	MOHS
BASE B	semigloss	65.3(20°)	Z(648)	6/7
0.5% Li_2CO_3 2% $CaSiO_3$ 3% WO_3	semigloss	59.8(20°)	Z(962) S(679)	6/7
BASE C	matt	75.8(20°)	Z(465) Q(65)A(46)	7
0.5% Li_2CO_3 4% WO_3	semigloss	81.7(20°)	S(3821)Z(394) A(180)	6

CRYSTALLINE PHASES: Z(Zircon $ZrSiO_4$), M(monoclinic ZrO_2), S(Scheelite CaWO4), D(Diopside $CaMg(SiO_3)_2$), A(Anorthite $CaAl_2Si_2O_8$). The number of counts/s is given in brackets for the greatest intensity peak of the glazed specimen obtained by XRD.

Table IX. *Additions to BASES B and C.*

The addition was studied of WO_3 with Li_2CO_3, raising the calcium proportion in base C by adding 2% wollastonite, so as to favour scheelite devitrification in this base, which was not so rich in calcium.

The data reveal holding or improving gloss and transparency. Zircon, scheelite and anorthite devitrified with the addition to base C (quartz devitrification was inhibited).

6. CONCLUSIONS

The data and discussion presented allow drawing the following conclusions:

(1) The addition of volatile fluorides (NaF, LiF) to typical single-fire floor tile bases produced pinholing at relatively low concentrations (3%), inhibiting opacification by developing small, non-opacifying microcrystallisations.

(2) The addition of non-volatile or fixed fluorides (Na_3AlF_6 and BaF_2) to these bases inhibited opacification by producing microcrystal groupings in larger-sized clusters. The resulting materials exhibited higher scratch hardness, as well as greater gloss and transparency. To be highlighted are the results obtained with cryolite.

(3) Carbonates exhibiting high-temperature thermal decomposition (Li_2CO_3 and $SrCO_3$) acted as true inhibitors to zircon devitrification. In the case of the alkaline earth ion with less relative ionic potential, no pinholing arose at addition proportions below 3%.

(4) The joint addition of the studied devitrification inhibiting organic salts with devitrifying agents (WO_3, Al_2O_3 and MgO) and nucleants by immiscibility (ZrO_2), inhibited opacification without interfering in the devitrification processes of the devitrifying agents, instead the crystal mass fraction rose especially in the presence of the nucleant.

(5) The calcic-aluminous composition of most of the glazes used in producing single-fire glazes for floor tile manufacture would allow retaining fluorides, minimising corrosion and environmental problems relating to fluoride use in the concentrations considered in the present study (0,5-3%) on a slip with a bulk density of 1.6 g/ml.