ZIRCONIA STABILISATION FOR HIGH K_{IC} CERAMIC FLOOR AND WALL TILE GLAZES

G. Monrós, J.B. Vicent, J. Badenes, M.A. Tena, D. Casellas†, J. M. Campos(*)

Dept. of Organic and Inorganic Chemistry, Universitat Jaume I, Castellón.
†Dept. of Materials Science and Metallurgy Engineering,
Universitat Politècnica de Catalunya.
(*)Cerámicas Diago, Onda (Castellón).

ABSTRACT

Martensite stabilisation in tempering steel yields hardening by a solid solution mechanism. Similarly, tetragonal and cubic zirconia stabilisation with alkaline-earth (Ca, Mg) or transition and inner transition metal (Y, Ce, Nd) alloying entails hardening that is to be interpreted by a phase-transformation mechanism. The objective of the present work was to study possible zirconia stabilisation in ceramic floor and wall tile glazes and assess the effect on the mechanical properties of the resulting product. The findings indicate the possibility of stabilising cubic zirconia in low volume fractions in calcic glazes. It was also stabilised in films obtained with gels applied onto porcelain tile. The stability of the phase even allows developing yellow stains (colours) by doping the calcium-stabilised cubic phase with praseodymium.

1. INTRODUCTION

At normal pressure zirconium oxide ZrO_2, exhibits three sequentially stable polymorphic varieties on modifying temperature: at 2680°C the cubic variety Fm3m solidifies with a fluorite structure, at around 2370°C the cubic form becomes tetragonal with a distorted fluorite structure (instead of 8 oxygen atoms at 2.20 Å of the Zr in the cubic variety there are two oxygen groups: 4 at 2065 and another 4 at 2455 Å, integrating elongated and shortened ZrO_4 groups in a way resembling what happens with zircon), while at about 1170°C the tetragonal variety becomes monoclinic P21/c with Zr 7-coordination[1], [2].

The tetragonal→ monoclinic transition is of the martensitic type, that is, with characteristics similar to the transition of austenite (Fe_γ FCC) in austenitic steel (above eutectoid temperature 723°C up to about 1400°C, with carbon concentrations below 2%) on tempering. Martensite transformation is adiffusional and athermal, which implies high transformation rates and quite a wide thermal transformation range (from transformation start to end)[1], [2].

Martensite stabilisation in steel tempering yields hardening by a solid solution mechanism: martensite exhibits a tetragonal structure of iron atoms in which the carbon atoms dissolve interstitially in the octahedral gaps in the structure. The greater the carbon entry into the lattice, the higher the hardness (martensitic steel tempered with 0.6% C exhibits 800 HV compared to just 150 of the perlitic type)[3].

Similarly, tetragonal and cubic zirconia stabilisation by alkaline-earth (Ca, Mg) or transition and inner transition metal (Y, Ce, Nd) alloying yields hardening that is to be interpreted in terms of a phase transformation mechanism. Metastable tetragonal zirconia stabilisation is thermodynamically possible owing to the confinement of ellipsoidal particles of tetragonal zirconia in a matrix (usually residual cubic zirconia but also others): the surface tension energy that the transformation would involve in these facetted tetragonal zirconia particles plus the confinement energy of an only slightly elastic matrix with low thermal expansion are capable of compensating the energy released in the chemical tetragonal→ monoclinic transformation, so that tetragonal zirconia can remain metastable. The tetragonal→ monoclinic transition involves in its development a volume rise of 3 to 5% and a hike in shear stress of about 8%[2], [4].

This state of affairs in the metastable tetragonal zirconia system, when a stress field is brought to the material capable of relaxing the tetragonal particle confinement energy (e.g. a blow, an indenting stress, friction, etc.), makes the deconstrained tetragonal polymorph pass into the stable monoclinic form in the micro-surroundings of the crack stress front, with a resulting volume increase that compresses the crack front, blocking crack progress. This mechanism is what we have termed transformation hardening. The mechanism therefore provides the material with hardness, abrasion resistance, as well as resistance to crack progress (fracture toughness)[5].

2. OBJECTIVES

The present work aimed to synthesise and characterise stabilised zirconia with the alloying elements Ca, Y and Mg, in order to incorporate or use these as additives in glassy matrices developed by fusion as well as by sol-gel processing, analysing the results of

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[1]. F.F. Lange, J. of Mat. Sci., 17, 225-234, 240-246, 255-262 (1982).
[2]. I. Abraham, G. Gritzner, J. of Mat. Sci. letters, 12, 995-997 (1993).
[3]. E.C. Bain, H.W. Paxton, *Alloying Elements in Steel*, 2nd ed., American Society for Metals, 1966.
[4]. D. Michel, F. Faudot, E. Gaffet, and *L. Mazerolles*, J. Am. Ceram. Soc. 76, 2884-88 (1993).
[5]. Kenong Xia, Terence G. Langdon, J. of Mat. Sci., 29,5219-5231 (1994).

tetragonal zirconia stabilisation in glassy matrices used in ceramic floor and wall tile manufacture at four levels:

(I) Analysis of tetragonal zirconia stabilisation systems with Ca, Y and Mg alloyings and their mechanical characterisation.

(II) Development of tough tetragonal zirconia films on ceramic bodies by gel deposition.

(III) Development of ceramic colours by doping stabilised zirconia with chromophores.

(IV) Crystallisation of stabilised zirconia in glazes usually employed in ceramic floor and wall tile manufacture to enhance mechanical properties without affecting aesthetic qualities.

3. ANALYSIS OF TETRAGONAL ZIRCONIA STABILISATION WITH CaO, Y_2O_3 AND MgO ALLOYINGS AND THEIR MECHANICAL CHARACTERISATION

The three stabilising systems exhibit eutectoid behaviour:

(a) Zirconia stabilised with yttrium, Y-ZrO_2 presents a cubic crystallography that is practically impossible to decompose, on having a very low eutectoid temperature around 400°C[6].

(b) The cubic polymorph stabilised with CaO decomposes below a temperature estimated at 1140°C in 1977 by V.S. Stubican[7]. However, subsequent studies by the same authors[8] on analysing thermal destabilisation of cubic materials observed the extension of a cubic phase metastability region in the tetragonal ZrO_2-$CaZr_4O_9$ region of the Y_2O_3-ZrO_2. phase diagram More recent studies indicate that the eutectoid temperature lies below 1100°C[9].

Cubic type calcium-stabilised zirconia decomposition develops through slow kinetics[10], so that it is very difficult to destabilise the calcium-zirconia cubic polymorph.

(c) The Mg-ZrO_2 presents eutectoid decomposition at 1400°C and the decomposition kinetics is less favourable than in cubic zirconia calcium-zirconia, so that it destabilises by recalcination below this temperature[11]. Destabilisation takes place by a partition mechanism producing a selection of different polymorphs (C, C+T, T+M, T+M+MgO and MgO+M successively), which could be generalised to other metastabilisation systems[12].

In accordance with these considerations, compositions were prepared in the eutectoid region of each system as detailed in Table I.

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[6]. H.G. SCOTT, J. Mater. Sci, 10, 1527-1535 (1975).
[7]. S.P. RAY AND V. S. STUBICAN, Mater. Res. Bull, 12, 549 (1977).
[8]. V.S. STUBICAN AND J.R. HELLMANN, Adv. Ceram, 3, 25-36 (1981).
[9]. P. DURÁN, P. RECIO, C. MOURE, J. of Mat. Sci. Lett, 11, 727-730 (1992).
[10]. J.M. MARDER, T.E. MITCHELL, AND A.H. HEUER, *Acta. Metall.*, 31, 387-95 (1982).
[11]. C.F. GRAIN, J. *Am. Ceram. Soc.*, 50, 288-90 (1967).
[12]. M.L. BALMER, F.F. LANGE AND C.G. LEVEI, J. *Am. Ceram. Soc.*, 75, 946-52 (1992).

COMPOSITION	XRD (powder) 500°C/2 h	XRD (pressed specimen) 1500°C/2h	a=b=c (Å)	HV(GPa)	% theor. Density
$(ZrO_2)_{0.88}(MgO)_{0,12}$	M(mf)MgO(f)	C(m)M(f)	5.08	8	92
$(ZrO_2)_{0.8}(CaO)_{0.2}$	M(mf)$CaCO_3$(d)	C(mf)	5.14	4,4	85
$(ZrO_2)_{0.92}(Y_2O_3)_{0.04}$	M(mf) Y_2O_3(d)	T(mf)M(d)	a=b= 5.12 c= 5.16	1,3	90

CRYSTALLINE PHASES: M(monoclinic ZrO_2), T(tetragonal ZrO_2), C(cubic ZrO_2) PEAK INTENSITY: mf(very strong), f(strong), m(medium), d(weak). ASTM CELL UNIT VALUES: cubic ZrO_2 (a=b=c=5,09Å, File ASTM 7-337), tetragonal ZrO_2 (a=b=5,12Å, c=5.25Å, File ASTM 77-923).

Table I. Characteristics of zirconia stabilised with MgO, CaO, and Y_2O_3 alloyings.

Samples were prepared by mixing the raw materials used in acetone medium in a planetary mill. The following raw materials were employed: industrial quality ZrO_2 of mean size 8.8 mm and MgO supplied by J.J. NAVARRO, reagent grade $CaCO_3$ by PANREAC and reagent grade Y_2O_3 by ALDRICH.

The blends were heat treated at 500°C/2h (the calcium blend also underwent heat treatment at 900°C), subsequently screening at 40 μm to form specimens by uniaxial pressing (200 bars). The resulting specimens were fired at 1500°C/2h in a NANNETI electric kiln ramping at 10°C/min. Table I details the XRD data on the powder and pressed specimen. The sample containing calcium was also heat-treated at 900°C/2h with a view to breaking down carbonates so that they would not interfere with specimen forming. XRD of the sampled fired at this temperature indicated the presence of monoclinic zirconia with very intense peaks and $CaZrO_3$ with weak peaks. Fig. 1 shows the diffractograms of the samples heat treated at 1500°C/2h. It can be observed, as Table I also indicated that the sample containing calcium exhibited the cubic polymorph as sole phase in the pressed specimen. In the case of the sample with magnesium, monoclinic zirconia also appeared, and in the case of yttrium the tetragonal polymorph stabilised.

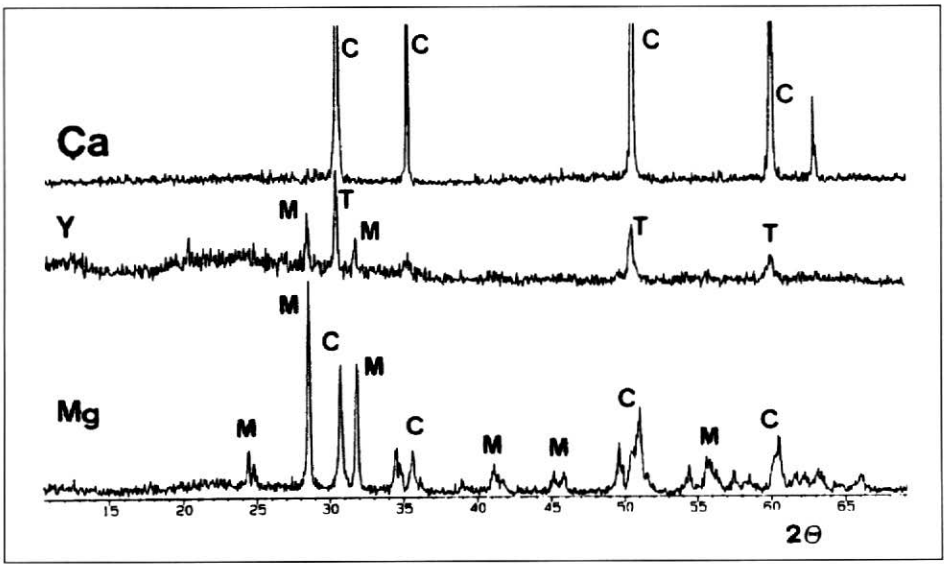

Figure 1. Diffractograms of the samples heat-treated at 1500°C/2h. C(cubic ZrO_2), T(tetragonal ZrO_2), M(monoclinic ZrO_2).

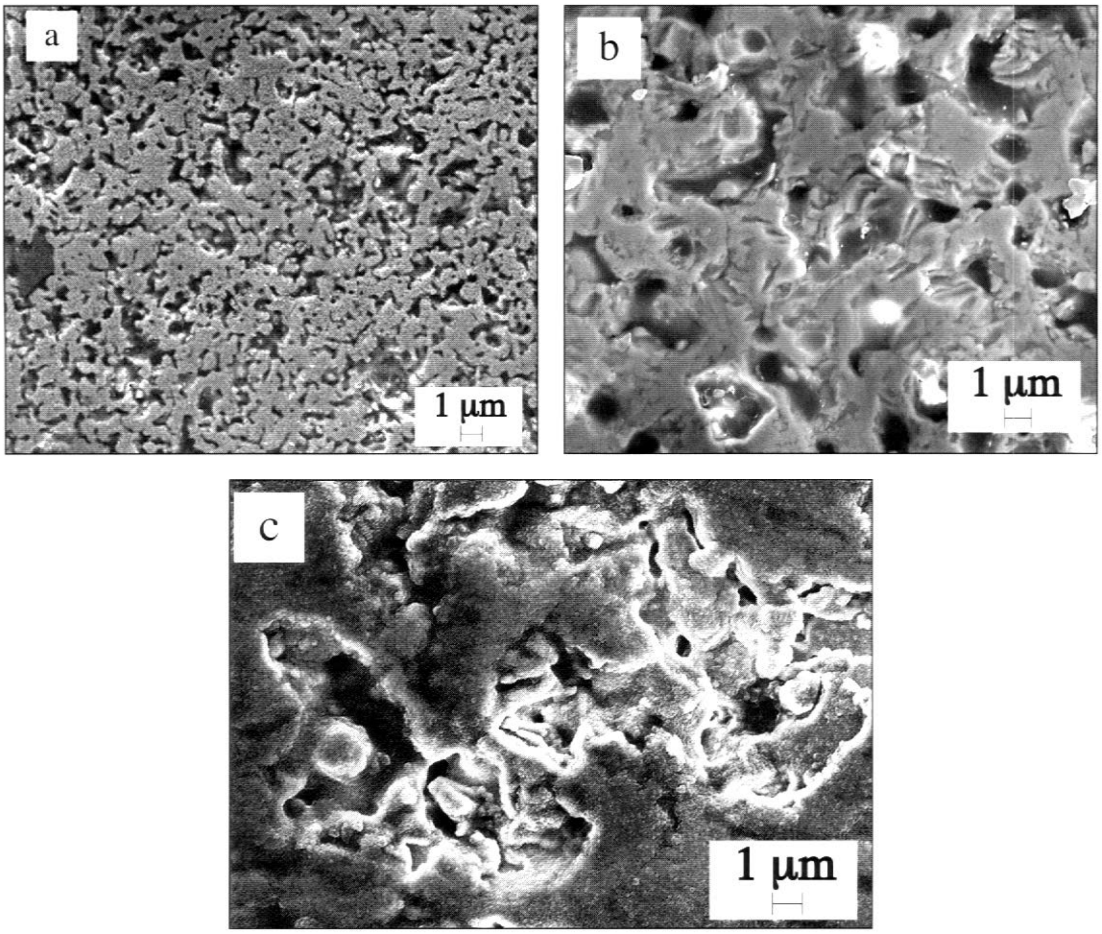

Figure 2. SEM micrographs of the pressed specimens densified at 1500°C/2h. (a) Mg-ZrO_2, (b) Ca-ZrO_2, (c) Y-ZrO_2.

Bulk density of the sintered samples was measured by the Archimedes water immersion method. Table I presents the % densification versus theoretical density of the samples obtained by the additive method, which considers total dopant entry in the corresponding lattice (C or T). The data reveal the worst densification in the case of the sample with calcium. Fig. 2 presents SEM micrographs obtained with a LEICA LEO440i instrument of the pressed specimens, which were carefully polished with silicon carbide paper and diamond paste. The micrographs revealed apparent porosity in all samples. The sample with calcium exhibited a greater profusion of pores than those with magnesium and yttrium, on the other hand interparticle sintering was greater in the sample with magnesium. In the sample with calcium a certain intergranular porosity was found, while in the sample with yttrium, grains sized below 0,1 μm could clearly be observed, which had aggregated keeping clear grain boundaries. Density measurements therefore matched the microstructural observations relating to porosity.

Table I also reports the Vickers microhardness values found with a MATSUZAWA micro-indenter, loading at 400 g for 25 s. The findings indicate good behaviour of the sample with magnesium, worse behaviour in the case of calcium and low microhardness with yttrium. These data in turn matched the SEM microstructural outcomes: the densified microstructure of magnesium was strong; the lesser densification with intergranular microcracks and greater porosity lowered strength in the sample with calcium; and finally, low sintering of the clearly visible grains in the case of the sample with yttrium yielded very low strength.

Lastly, Table I details the lattice parameter measurements of the respective zirconia elementary cell, measured by the POWCAL software for fitting interplanar spacings with an internal standard (α-Al_2O_3) and LSQC least square fit of the foregoing data with the ASTM cell[13]. The data agreed with demonstrated fact of dopant solid solution in the zirconia lattice: the entry of Ca^{2+} (Pauling radius 0.99 Å) replacing Zr^{4+}(0.80 Å) enlarged the crystalline cell, whereas Mg^{2+} (0.65 Å) made it slightly smaller; the lattice also decreased (c axis) in the case of Y^{3+} (0.93 Å). This drop was due to the presence of oxygen vacancies in the lattice, required to keep electroneutrality and basis for the ion conducting properties of stabilised zirconia.

Given the processing characteristics, in order to incorporate cubic zirconia in the ceramic glazes discussed below, the zirconia-calcium system was chosen. In this system stabilised zirconia was obtained by two alternative methods:

(a) By the ceramic method described above. On firing powders that were previously heat treated at 500°C, at 900°C, $CaZrO_3$ was obtained without yet detecting tetragonal zirconia by XRD. At 1200°C/12 h the specimen remained without reacting and at 1400°C/6h the phase was fully stabilised (Fig. 3).

(b) By coprecipitation of a gel having composition $(ZrO_2)_{0.8}(CaO)_{0.2}$ from reagent grade $ZrOCl_2.8H_2O$ supplied by ALDRICH and reagent grade $CaCO_3$ supplied by PANREAC. Zirconium oxychloride was dissolved in water (5 g/100 ml), calcium carbonate was added, partly neutralising the acidity of the zirconium salt solution. The gel was obtained by slowly adding ammonia dropwise to the solution under constant stirring at 70°C. A compact, homogeneous white gel was produced at pH=4-5. The gel, which was oven dried at 110°C, was amorphous in X-ray diffraction, and was heat treated at 600°C precipitating Garvie tetragonal zirconia (particle size below 30 nm)[1,2]. Firing at 1200°C/2h produced ultrafine cubic zirconia (Fig. 3).

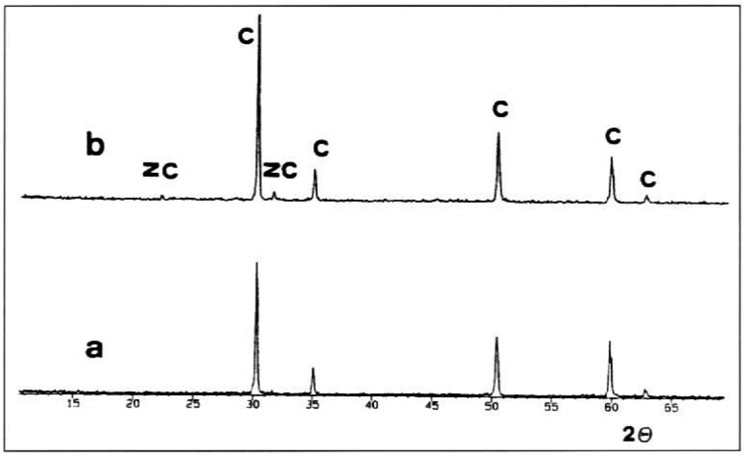

Figure 3. *Diffractograms: (a) of ceramic sample Ca-ZrO_2 heat-treated at 1400°C/6h, (b) of the colloidal gel heat-treated at 1200°C/2h. C(cubic ZrO_2), ZC($CaZrO_3$).*

4. DEVELOPMENT OF TOUGH TETRAGONAL ZIRCONIA FILMS ON CERAMIC BODIES BY GEL DEPOSITION

Considering the high zirconia stabilisation capacity exhibited by the coprecipitated gels,

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[1]. F.F. LANGE, J. of *Mat. Sci.*, 17, 225-234, 240-246, 255-262 (1982).

[2]. I. ABRAHAM, G. GRITZNER, J. of *Mat. Sci. letters*, 12, 995-997 (1993).

[13]. POWCAL y LSQC, *programas desarrollados por el Dpto. de Química de la Universidad de Aberdeen* (U.K:).

the possibility was studied of producing a glaze by coprecipitation of a gel having a composition that would stabilise cubic or tetragonal zirconia on being deposited on a ceramic body and fired (engobed single-fire porous body, engobed red stoneware body and porcelain tile body).

The Seger formulation of the selected composition is given in Table II.

(a) without yttrium	ZnO 0,52 CaO 0,48	Y_2O_3 0,00	B_2O_3 SiO_2	4,63 1,52
(b) without yttrium	ZnO 0,52 CaO 0,48	Y_2O_3 0,04	B_2O_3 SiO_2	4,63 1,52

Table II. *Seger formulation of the glazes developed by coprecipitation.*

The blend of raw materials used (reagent grade $ZnCl_2$, $CaCl_2.6H_2O$, H_3BO_3 from PANREAC, reagent grade colloidal silica from DEGUSSA and hydrated yttrium acetate from ALDRICH), was diluted in water (10 g $ZnCl_2$ were dissolved in 400 cm^3, then adding the remaining components, first the acid reaction and then the base reaction constituents). The slow addition of concentrated ammonia under constant stirring at 70°C first yielded (pH=3-4) a suspension with an acceptable viscosity for deposition by dipping on the ceramic bodies. Half of this suspension was kept and the other half was gelled by successive ammonia additions (pH=4-5). The resulting gel was oven dried at 110°C and heat-treated at 600°C/2h.

In designing the glaze composition, two stabilisers were added in sample (b) (Y and Ca), while in sample (a) just calcium was incorporated. The glaze film coatings were obtained on the different ceramic bodies by two procedures according to the Sakka methodology[14]:

(a) DIPPING (Dip-Coating) in the suspension with optimised viscosity.

(b) SPRAYING (Spray-drying) of a colloidal gel calcined at 600°C/2h dispersed in water.

Fig. 4 presents the micrographs obtained with an OLYMPUS optical microscope of the resulting films on dipping and spraying the sample without yttrium and the sample with yttrium on a porcelain tile body fired in a fast industrial cycle of 42 min, with a 1200°C peak temperature. The films on porcelain tile generally exhibited better adhesion and covering. Moreover, the sprayed-on coatings exhibited better properties than those applied by dipping.

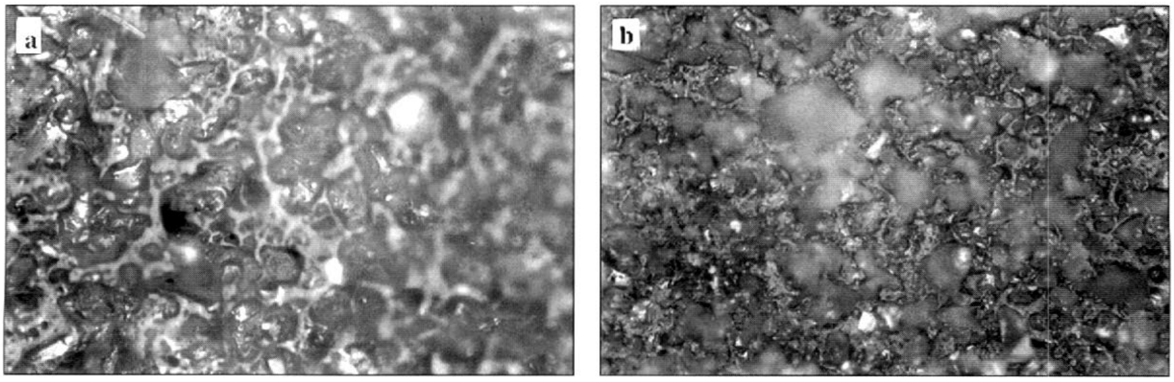

Figure 4. *Optical micrographs (200x) of the films: (a) Dipping without yttrium, (b) Spraying with yttrium.*

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[14]. S. Sakka, *J. of Sol-Gel and Technology*, 2,451-455(1994).

Table III reports the mechanical measurements run on the resulting films.

SAMPLE	HV (Kg/mm^2)	K_{IC}(MPa.m$^{1/2}$)
(a) Without Y-Dipping	554	1,6
(a) Without Y-Spraying	583	1,8*
(b) Y-Dipping	622	2,1
(b) Y-Spraying	602	>2,2

Table III. *Mechanical properties of the films coating porcelain tile.*

The measurement of the stress intensity factor K_{IC} critical value, which represents a material's fracture toughness, was obtained by the technique that measures local, well-developed indentation cracks. Using the application of the Lawn and Fuller law[15] to radial crack development by Roesler[16] for elastic linear solids, a correlation can be found between indentation fracture and the energy involved. The Roesler treatment for a Vickers indentation yields the equation:

$$K_{IC} = 0{,}0824\ P\ c^{-3/2}\ (\mathrm{GPa.m}^{1/2}).$$

where c is crack length in μm (satisfying the requirement that $c/a>2$, in which a is the diagonal mean measured for Vickers indentation), and P is test load in N.

The data in Table III show greater fracture toughness in the film coatings containing yttrium. The sprayed-on coatings exhibited better toughness and Vickers microhardness properties than the dip-coatings. The properties were directly related to the XRD data found for the samples (Fig. 5): the samples with yttrium stabilised cubic zirconia in a greater proportion in the case of the sprayed coatings, which was probably related to the heat treatment undergone by these samples.

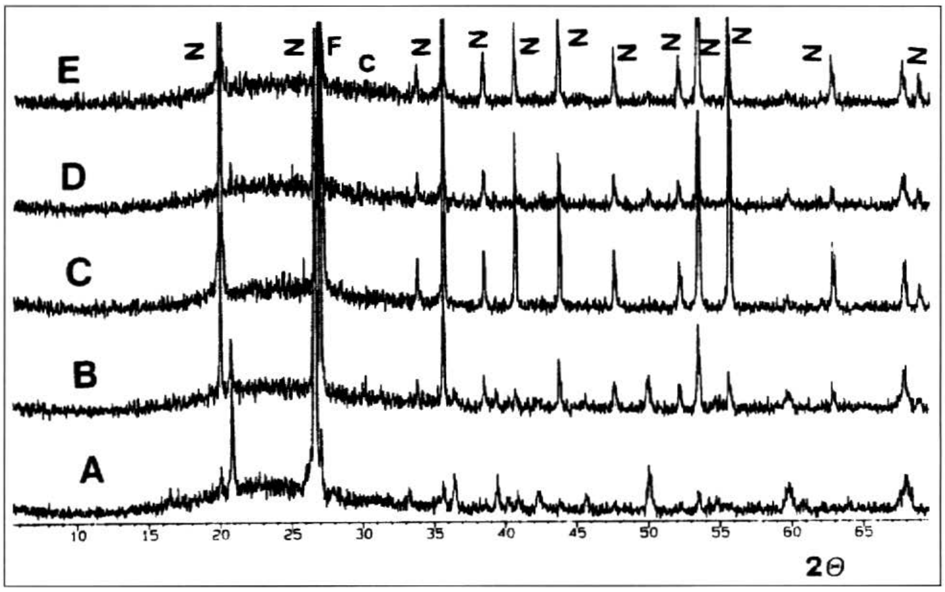

Figure 5. *Diffractograms of the film coatings on porcelain tile: C(cubic ZrO_2), Z($ZrSiO_4$), F(Feldspar): A(BASE A), B(without Y-Dipping), C(without Y-Spraying), D(Y-Dipping), E(Y-Spraying).*

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[15]. B.R. Lawn, E.R. Fuller, J. of *Mat. Sci.*, 10,2016 (1975).

[16]. F.C. Roesler, *Proc. Phys. Soc.*, B69,55 (1956).

5. DEVELOPMENT OF CERAMIC COLOURS BY DOPING STABILISED ZIRCONIA WITH CHROMOPHORES

In order to assess the interest of calcium-stabilised zirconia in developing ceramic pigments, compositions doped with praseodymium ($Ca_{,0.2}Pr_{0.1}Zr_{0.7}O_2$) were prepared. The samples were prepared by the ceramic method, ammonia coprecipitated colloid gel, and the gelatin method[17]. Table IV details the results of the crystalline phases detected with temperature in the samples.

SAMPLE	Unfired	500°C/6h	900°C/6h	1100°C/6h	1200°C/6h	1450°C/24h
Ceramic	M(f) grey	M(f)PR(d) grey	M(f)PR(d) ZC(d) grey	M(f)PR(d) ZC(m)ZP(d) grey	M(m)C(d) ZP(d)ZC(m) Grey	C(f) yellow
Colloidal gel	NH_4Cl(d) white	C(d) Greyish	C(m) yellow	C(f) yellow	-	C(f) yellow
Gelatin	Amorph. black	C(d) Greyish	C(m) yellow	C(f)ZC(d) yellow	-	C(f) yellow

CRYSTALLINE PHASES: M (monoclinic ZrO_2), C (cubic ZrO_2), ZC($CaZrO_3$), ZP(Pr2Zr2O7), PR(Pr6O11), PEAK INTENSITY: f(strong), m(medium), d(weak).

Table IV. Colour and XRD evolution of samples $Ca_{0.2}Pr_{0.1}Zr_{0.7}O_2$.

The ceramic samples were prepared by the method set out in Sections 3 and 4. The gelatin sample was prepared by the same procedure and precursors as the coprecipitated colloidal gel in Section 4, however, on homogenising the suspension at 70°C, gelatin was added (6 g/100 ml reagent grade gelatin supplied by PANREAC). This was then homogenised and kept in a cooling chamber at 4°C for 6 hours. The resulting gel was a homogenous creamy colour.

XRD indicated better reactivity in the gels than in the ceramic route, in which the praseodymium and calcium zirconates were stabilised. At 1450°C cubic zirconia stabilisation had become general in all the samples.

Fig. 6 presents the XRD evolution of the gelatin sample up to 1100°C.

The samples were glazed at 5% in a borosilicic transparent glaze composition to evaluate their

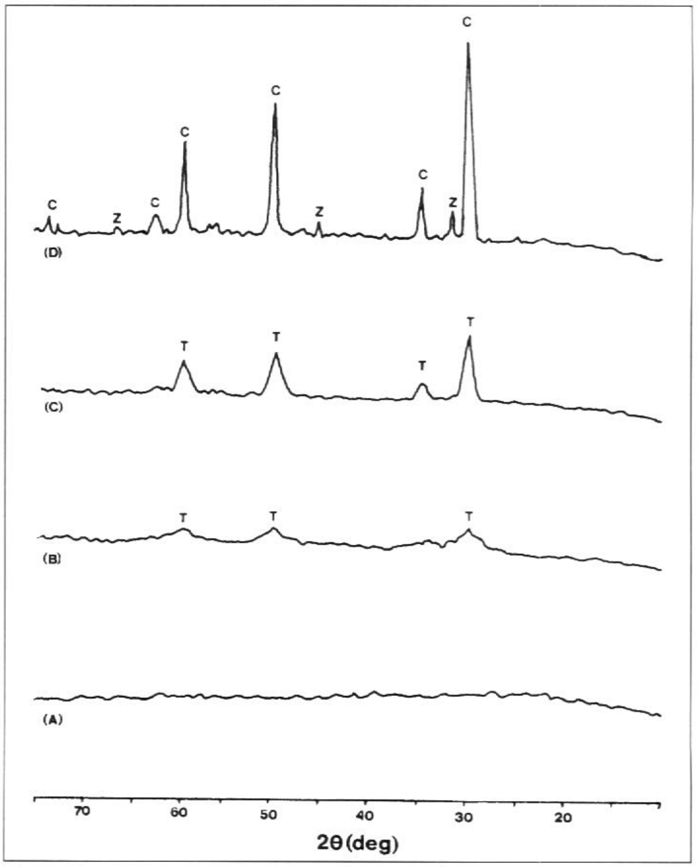

Figure 6. Evolution of crystalline phases in the sample with gelatins: T(low crystallinity Garvie zirconia), C(cubic ZrO_2), Z($CaZrO_3$).

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[17]. G. Monrós, J. Carda, P. Escribano, J. Badenes, E. Cordoncillo, *J. Mat. Chem*, 5(1), 85-90 (1995).

pigmenting properties. Table V details the CIE L*a*b* measurements[18] of the gel samples at 1100°C (at which they already produced a yellow colour and fully developed cubic zirconia), together with the values of a commercial praseodymium yellow for comparative purposes.

SAMPLE	L*	a*	b*
Commercial praseodymium Yellow	91	-6,7	41,4
$Ca_{0,2}Pr_{0,1}Zr_{0,7}O_2$ Colloidal gel	72	6,0	23,0
$Ca_{0,2}Pr_{0,1}Zr_{0,7}O_2$ Gelatin	76	4,0	24,0

Table V. *CIE L*a*b* coordinates.*

The data in Table V reveal that the resulting yellow colour was considerably inferior to the commercial praseodymium in zircon (b* value), darker (L value) and with a reddish hue (positive a* value), compared to the greenish hue of the commercial zircon (negative a* value).

With a view to establishing the stability of the cubic phase in the glaze, the gelatin sample was applied as a glaze at 20% in the above glaze composition. XRD of the glazed sample is shown in Fig, 7. It can be observed that the cubic zirconia peaks were kept though the monoclinic zirconia peaks were also quite marked.

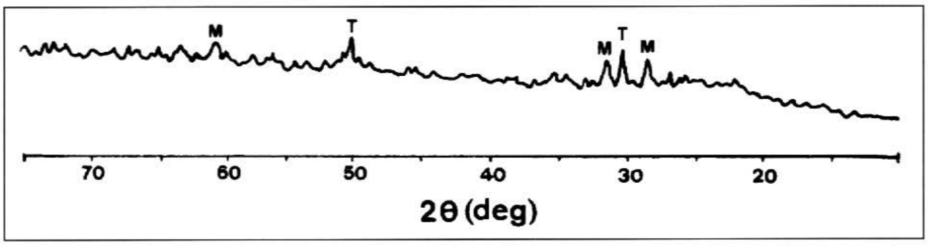

Figure 7. *XRD of the specimen glazed at 20% with praseodymium doped stabilised zirconia.*

6. CRYSTALLISATION OF STABILISED ZIRCONIA IN CERAMIC FLOOR AND WALL TILE GLAZES

The ultimate aim of this study, after investigating the characteristics of stabilised zirconia, stabilisation method involved and stability, was the crystallisation of stabilised zirconia in typical glazes used in ceramic floor and tile manufacture, in order to enhance glaze properties without impairing aesthetic qualities.

This was done by additions to commercial glazes, using the following different approaches.

IV.1. Addition of monoclinic zirconia and neodymium oxide with an alternative opacifier to zircon (wolfram or anatase) to calcium-rich matrices that yield stabilisation on firing the glaze.

As discussed above, calcic bases would be candidates for stabilising tetragonal or cubic zirconia. A ceramic base was used for ceramic floor tile, whose Seger formulation is given in Table VI.

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[18]. CIE, *Recommendations on uniform colour spaces, colour difference equations, psychometrics colour terms*, Supplement N° 2 of CIE Publications N° 15 (E1-1.31) 1971; 1978, Paris, Bureau Central de la CIE.

Table VII indicates low fraction stabilisation of cubic zirconia (40 counts under operating conditions), in the samples with an addition of wolfram and monoclinic zirconia together with calcium wolframate and zircon (which dropped dramatically on raising the zirconia addition). This decrease is to be understood as a result of occlusion in the matrix. The random oriented powder method employed did not allow assessing the volume fractions of the various crystalline phases.

In the samples containing anatase (TiO_2) and neodymium, a low cubic zirconia fraction also stabilised jointly with zircon and esphene ($CaTiSiO_5$) in the 8% anatase additions.

K_2O	0.05				
Na_2O	0.01			ZrO_2	0.07
MgO	0.05	Al_2O_3	0.15		
CaO	0.67			SiO_2	0.88
ZnO	0.22				

MECHANICAL CHARACTERISTICS

The glazed base in a fast floor tile cycle devitrified zircon (307 counts under usual diffraction conditions: 0.05°2Θ/s and time constant 0.02 s), Mohs 5, PEI IV, HV 520 kg/mm^2, K_{IC} 1,4 MPa.m$^{1/2}$)

Table VI. *Seger formula of the calcic floor tile base and mechanical characteristics.*

SAMPLE	**HV**	**MOHS**	**K_{IC}(MPa·m$^{1/2}$)**	**XRD(counts)**	**APPEARANCE**
(A1) Addition of 5% WO_3 and monoclinic ZrO_2 (8.7 μm)					
10	589	6	1.6 ± 0.2	Z(1320) S(5646)**C(49)**	Glossy
15	88.7 (polished area)	6	>2.2	Z(365) S(1649)**C(52)**	Matt
20	52.2 (polished area)	8	>2.2	Z(281) S(267)**C(43)**	Matt
(A2) Addition of 4% TiO_2 and Nd_2O_3					
0.5	605	5	1.7 ± 0.2	Z(292)	Glossy
1	594	5	1.6 ± 0.2	Z(380)M(164)	Glossy
2	576	7	1.6 ± 0.2	Z(238)**C(40)**	Matting
(A3) Addition of 8% TiO_2 and Nd_2O_3					
0,5	605	5	>2.2	Z(107) $CaTiSiO_5$(113)	Glossy
1	594	5	>2,2	Z(158) $CaTiSiO_5$(157)	Glossy
2	573	6	1.5 ± 0.2	Z(112) $CaTiSiO_5$(121)**C(41)**	Matting

CRYSTALLINE PHASES: Z(Zircon), M(monoclinic ZrO_2), C(cubic ZrO_2), S($CaWO_4$ Scheelite).

Table VII. *Stabilisation of cubic zirconia by reaction with the calcic base.*

The presence of stabilised zirconia raised the material's mechanical performance (HV, Mohs and K_{IC}). Higher reagent additions did not lead to stabilisation of a greater stabilised zirconia mass fraction, and raising mechanical performance led to gloss loss.

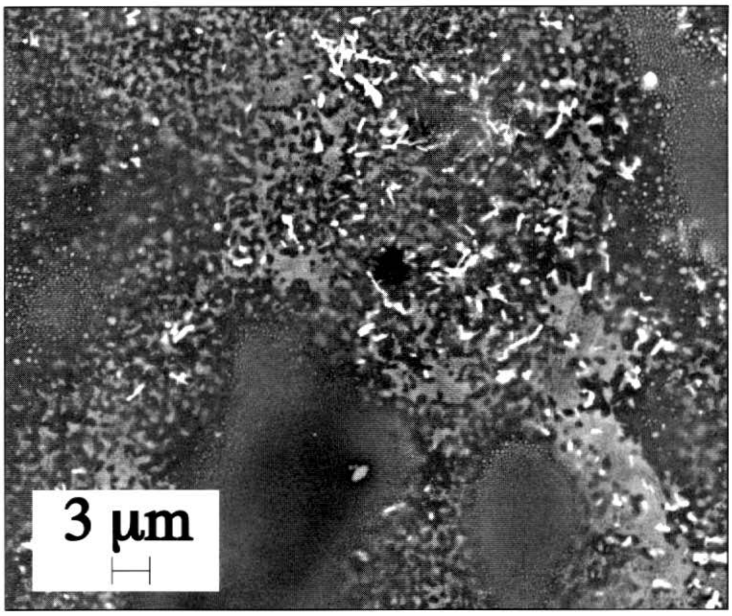

***Figure 8.** SEM micrograph of sample (A3)1% Nd_2O_3.*

Fig. 8 shows the SEM micrograph of sample (A3)1% obtained with a back-scattering detector at 20,000 KV: a network of dark devitrified crystals with some contrasting needle-like crystals and irregular particulates can be observed. On applying the mapping technique (Fig. 9) the low contrasting crystals were shown to be sphene, the needle-like ones zircon and the particles cubic zirconia. The devitrified fraction in the sample was very high, and did not correspond to the low count levels registered by XRD, which did not permit reliable assessment when the crystals were hidden in the glassy mass that acted as a screen to the X-rays. Thus, visualisation of the devitrified network in Fig. 7 needed to be run with a detector of back-scattered electrons coming from the sample's deepest layers. The image obtained with a secondary electron detector did not allow seeing further than the particulates and some surface aciculars, providing a totally distorted image of the sample.

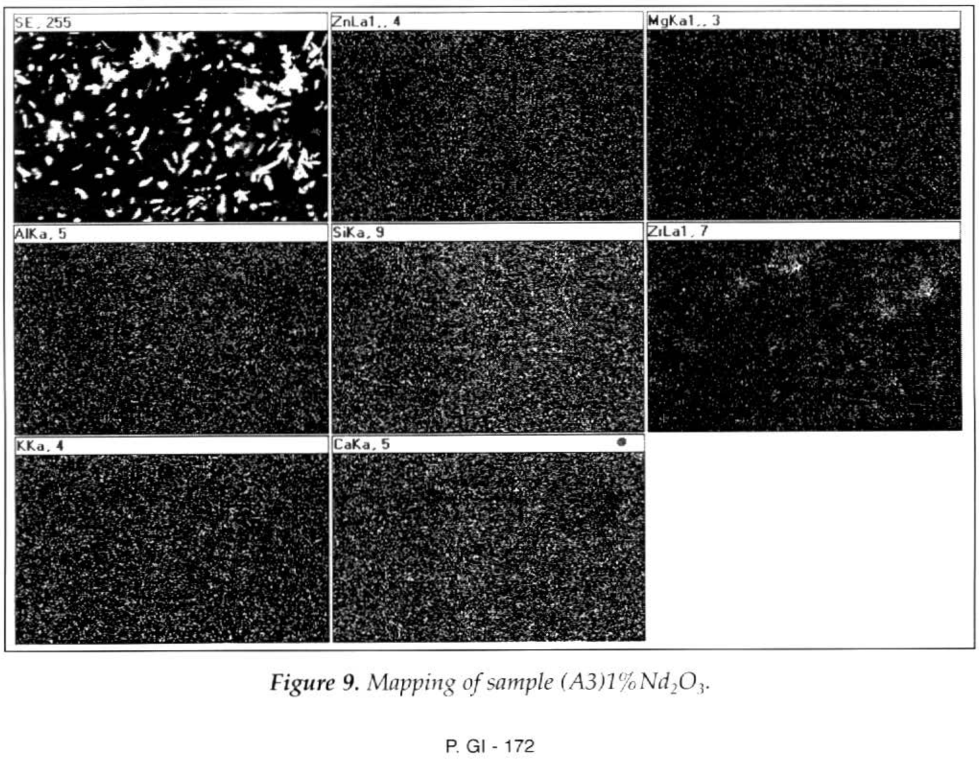

***Figure 9.** Mapping of sample (A3)1% Nd_2O_3.*

IV.2. Direct addition of stabilised zirconia to a glaze.

The stabilised zirconia in Section 3 was used as an additive to the calcic base. Table VIII reports the data.

% Ca-ZrO_2 addition	XRD	Mohs	HV(Kg/mm^2)
2	Zircon (180)	5	573
5	“ (360)	5	569
7	“ (420)	5	561
10	“ (400)	5	607

Table VIII. *Results of the calcium-stabilised zirconia addition by the ceramic method (1400°C).*

The data indicate rheological problems with the zirconia stabilised at low temperatures by coprecipitation. The results obtained for cubic zirconia by the ceramic method at 1400°C moderately raised the material's mechanical properties, although no tetragonal zirconia stabilisation was detected in the glassy matrix.

IV.3. Addition of stabilised zirconia together with opacifiers that modify the glassy matrix's confining properties.

Zirconia -stabilised with calcium at 1400°C by the ceramic method was used in every case. Table IX presents the addition of high concentrations of stabilised zirconia with the monoclinic zirconia, alumina or quartz contribution.

SAMPLE	HV	MOHS	K_{IC}(MPa·m$^{1/2}$)	XRD	Appearance
(B1) 15% Ca-ZrO_2	-	7	1.8 ± 0.1	Z(720) M(41)C(45)	Semigloss
(B1.1)15% Ca-ZrO_2. 10% m-ZrO_2 (5.8 μm)	569 (polished area)	9	>2,2	Z(1493) M(63)C(38)	Matt
(B1.2)15% Ca-ZrO_2. 10% Al_2O_3	622 (polished area)	9	>2,2	Z(310)A(97) M(81)C(60)	Matt
(B1.3)15% Ca-ZrO_2. 10%SiO_2	-	5	1.7 ± 0.2	Z(328)M(45) C(45)	Gloss
(B2) 20% Ca-ZrO_2	-	7	1.8 ± 0.1	Z(497) M(45)C(57)	Matt
(B2.1) 15% Ca-ZrO_2 10% m-ZrO_2 (5.8 μm)	690 (polished area)	8	>2,2	Z(494) M(71)C(44)	Matt
(B2.2) 15% Ca-ZrO_2 10%Al_2O_3	666 (polished area)	8	>2,2	Z(325)M(91) A(85)C(52)	Matt
(B2.3) 15% Ca-ZrO_2 10%SiO_2	-	7	1.7 ± 0.2	Z(367)M(44) C(51)	Semigloss

CRYSTALLINE PHASES: Z(Zircon), M(monoclinic ZrO_2), C(cubic ZrO_2), A($CaAl_2Si_2O_8$ Anorthite).

Table IX. *High stabilised zirconia additions.*

The addition of high concentrations of stabilised zirconia produced partition into monoclinic zirconia as already observed in Section 4. The stabilised zirconia fraction was small (3-5%), and did not rise with 10% additions of monoclinic zirconia and alumina (which raised mechanical performance but caused gloss loss), or quartz (which maintained mechanical performance and aesthetic properties): in this sense the B1 and B2.3 additions are to be highlighted with high toughness values (1.7 MPa·m$^{1/2}$), Mohs 7 and semigloss appearance. Alumina devitrified anorthite, which acted as an opacifier, raising mechanical properties.

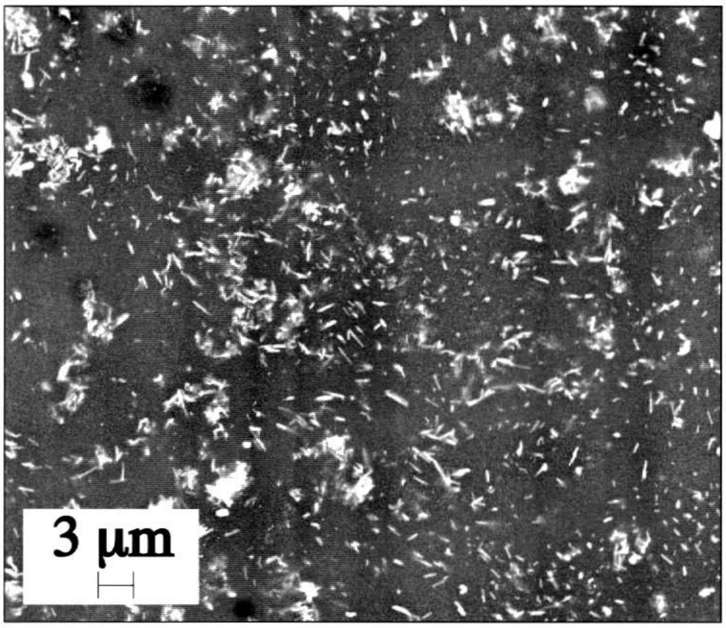

Figure 10. *SEM micrograph of sample B2.*

Figure 10 shows the micrograph of sample B2 obtained with a back-scattered electron detector. Together with the needle-like zircon particles, zirconia clusters of greater contrast can be observed.

6. CONCLUSIONS

The following inferences were drawn from the results obtained in the study:

(a) It was possible to obtain calcium-stabilised zirconia under standard operating conditions in a frit and ceramic glaze producing facility (1400ºC). Moreover, this material can be processed under the typical operating conditions employed in ceramic floor and wall tile manufacture when gels are used (1000-1200ºC).

(b) The application of glazes with a suitable formulation (introduction of calcium and yttrium) by coprecipitated gels allowed obtaining films with stabilised cubic zirconia in low volume proportions (3-6%), which were greater in the case of the samples with yttrium, and raised the fracture toughness of the resulting films.

(c) Calcium oxide-stabilised zirconia can be doped with praseodymium to produce a yellow ceramic colour that is stable in transparent ceramic glazes, with an acceptable colour yield. Stabilised zirconia kept good structural stability in the glaze although it was partly dissolved by the devitrifying glaze in the form of monoclinic zirconia.

(d) Cubic zirconia can be stabilised in the ceramic matrices rich in calcium oxide commonly used in ceramic tile manufacture in low volume fractions (5%) by adding agents such as neodymium oxide, anatase or wolfram oxide. The resulting materials exhibited noticeably improved mechanical properties. In the case of anatase esphene devitrified as did scheelite in wolfram oxide, which both acted as alternative opacifiers to zircon.

(e) The direct addition of stabilised zirconia calcic glazes only stabilised cubic zirconia at high additions (15%) and in low volume fractions. The addition of modifiers did not raise cubic zirconia devitrification, but allowed optimising mechanical properties in terms of aesthetic properties.