

Doping and synthesis method effect on zirconium silicate conductivity

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The colour mechanisms of blue V- ZrSiO₄ and yellow Pr- ZrSiO₄ ceramic pigments which strongly depend on both fluorine addition and synthesis method, are still controversial. Complex impedance has been used as a useful tool to differentiate the materials as a function of the synthesis method, microstructure and observed colour, going deeply into the resolution of controversies about the nature of colours. Representative samples of these doping pigments prepared by both classical ceramic process and sol-gel method have been studied by complex impedance analysis. Vanadium doped zircon enhances resistivity and activation energy compared to undoped zircon powder and turquoise blue vanadium-zircon obtained by addition of NaF shows the highest bulk resistivity. Activation energy and conductivity decrease for Praseodymium doped zircon compared to undoped zircon. This feature is in agreement with the presence of cationic vacancies on green vanadium-zircon samples due to V⁴⁺ and V⁵⁺ coexistence and praseodymium oxide inclusions on Pr- ZrSiO₄ yellow pigment.

Keywords: zircon, ceramic pigment, solid solution, conductivity.

Efecto del dopado y el método de síntesis en la conductividad del silicato de circonio.

El mecanismo del color en el azul de los pigmentos cerámicos V- ZrSiO₄ y amarillo de Pr- ZrSiO₄ cuyos tintos dependen mucho de la presencia de fluoruros así como del método de preparación esta controvertido en la literatura. La impedancia compleja se ha utilizado como una herramienta útil para diferenciar los materiales en función del método de síntesis, la microestructura y el color con el fin de profundizar en la resolución de las controversias. Se han preparado muestras representativas de ambos sistemas dopados mediante diferentes métodos de síntesis cerámico y sol-gel que se han estudiado por análisis de impedancia compleja. El circonio dopado con vanadio aumenta su resistividad y sus energía de activación con referencia a la muestra no dopada y la muestra turquesa obtenida por adición de NaF presenta la mayor resistividad. Las muestras dopadas con praseodimio disminuyen la energía de activación y la conductividad respecto de la muestra no dopada. Este comportamiento está de acuerdo con la presencia de vacantes catiónicas en las muestras verdes de vanadio-circonio asociadas a la coexistencia de V⁴⁺ y V⁵⁺ en las muestras y de inclusiones de óxido de praseodimio en el pigmento amarillo de Pr- ZrSiO₄.

Palabras clave: Circonio, pigmento cerámico, disolución sólida, conductividad

1. INTRODUCTION

V-ZrSiO₄ and Pr-ZrSiO₄ are well-known turquoise and yellow ceramic pigments largely used in the ceramic industry since their discovery in 1948 (1). V-ZrSiO₄ shows three solid solution mechanisms of vanadium in zircon lattice (2): (a) V⁴⁺ in solid solution in zircon gives an unstable blue colour, (b) simultaneous solid solution of both V⁴⁺ and V⁵⁺ in zircon produces a stable green pigment and finally, (c) simultaneous fluorine and V⁴⁺ doped zircon gives a stable turquoise blue commercial pigment. Turquoise blue vanadium zircon turns green when is obtained without NaF addition but the difference between blue and green materials is still controversial (3). On the other hand, Pr-ZrSiO₄ shows Pr⁴⁺ ion stabilisation but the colour mechanism is controversial also, and probably is based on the inclusion of Pr₂O₃ particles into zircon crystals (4,5). Praseodymium yellow zircon colour decays in intensity when fired above 1.200°C, the resulting colour is similar to the yellow colour obtained on the praseodymium-zirconia systems associated to Zr⁴⁺ substitution by Pr⁴⁺ ion (4,6). The reactivity and the colour can be significantly enhanced using non conventional methods of synthesis in both systems (3-6).

The purpose of this paper is to study representative samples of these pigments by complex impedance as an useful tool to

analyse the materials obtained in function of the synthesis method, microstructure and observed colour, going deeply into the resolution of controversies about the mechanism of colour in both vanadium-zircon and praseodymium-zircon systems (7-9).

2. EXPERIMENTAL PROCEDURES

2.1 Preparation of powders

The following samples have been prepared by the ceramic method and several sol-gel methods: (a) pure ZrSiO₄ samples, (b) vanadium and praseodymium chromophore doped samples (Zr_{0.9}M_{0.1})SiO₄ M=V,Pr, (c) both chromophore and fluorine doped samples 0.2NaF.(Zr_{0.9}M_{0.1})SiO₄ M=V,Pr

Ceramic method, colloidal route and polymeric gels obtained by hydrolysis-condensation of alkoxides, were used for synthesis of samples and compared for both compositions. Zirconia ZrO₂ (baddeleyite) and quartz SiO₂ of a commercial technical grade supplied by SEPR, NH₄VO₃ and NaF analytical grade (from Aldrich) and Pr₆O₁₁ (from Rhone Poulenc) were

used as Zr, V and Pr precursors on ceramic method. Commercial colloidal silica (75% SiO₂) supplied by Quimidroga S.A., ZrOCl₂·8H₂O, VOSO₄·5H₂O and Pr(CH₃COO)₃·3H₂O, supplied by Merck, Aldrich and Johnson Matthey respectively, were employed instead of commercial technical grades on sol-gel procedures. In the case of polymeric gels, zirconium(IV) n-propoxide (Zr(OCH₂CH₂CH₃)₄ from Fluka) and tetraethyl orthosilicate TEOS (Si(OCH₂CH₃)₄ from Fluka) were used as Zr and Si precursors with vanadylsulphate pentahydrate (VOSO₄·5H₂O from Aldrich) and praseodymium (III) acetate trihydrate (Pr(CH₃COO)₃·3H₂O from Aldrich).

2.1.1. Ceramic method (CE)

The appropriate amounts of commercial oxides, were mixed and ball-milled in acetone for 20 minutes. Residual acetone was then removed by evaporation, and the resulting dried powder was finally homogenised in an agate mortar.

2.1.2. Colloidal gel method (CG)

A colloidal dispersion was obtained by dissolving zirconium oxychloride in water (50 mL) and colloidal silica at 70°C with continuous stirring followed by addition of vanadium and praseodymium sol-gel precursors thirty minutes later. The resulting mixture was left for 1 hour under the same stirring and heating conditions to provide the basic CG solution. The chromophore-doped solutions were prepared by the appropriate addition of vanadylsulphate pentahydrate or praseodymium (III) acetate (trihydrate). Half hour later NaF powder was added to dispersion in the case of chromophore-fluorine doped samples. When a homogeneous dispersion was reached, a concentrated ammonia solution was added dropwise until gelation occurred at pH= 5-6. The resulting homogenous bluish (vanadium) or light yellow (praseodymium) gel was aged and dried at room temperature in the open air. The dried gels were then crushed and ground in an agate mortar.

2.1.3. Polymeric method (PG)

Ethanol (ethanol: zirconium(IV) n-propoxide=1:26 molar ratio) supplied by Panreac was used as solvent. Acid catalyst (3M HNO₃ keeping the molar ratio acid: zirconium(IV) n-propoxide=1:0.18), acetylacetone and water (molar ratios: acetylacetone: zirconium(IV) n-propoxide= 1:1 and water: zirconium(IV) n-propoxide= 4:1) were added and refluxed at 70°C in the ethanol with continuous stirring. Then vanadylsulphate pentahydrate or praseodymium (III) acetate trihydrate were added and refluxed. Half-hour later TEOS were added and refluxed for prehydrolysis during 24 hours. Then zirconium (IV) n-propoxide was added continuously stirring to the solution and hydrolysed at 70°C for 6 hours. The dried gels obtained were dark red and yellow coloured for vanadium and praseodymium samples respectively.

To compare directly the behaviour of the prepared powders no washing and disaggregation treatments were carried out in any of the methods.

2.2. Firing and sample characterisation.

The powders were calcined in air at 1200°C for 6 hours and then sieved to 60 μm, uniaxially pressed in tablets (20 MPa) and fired at 1.480°C for 12h. The calcined powders were

characterised by XRD (X-ray diffraction), SEM (scanning electron microscopy) and CIE-L*a*b* colourimetric parameters. Colourimetric measurements were done on 5% glazed samples and were carried out using a C reference illuminant in a spectrophotometer Lambda 2000 and following the CIE-L*a*b* convention (10): in this system, L* measures the brightness, a* the amount of green(-) →red(+) colour, and b* the amount of blue(-)→yellow(+).

XRD powder diffractograms were obtained using a Philips X-ray diffractometer using CuK_α radiation. Microstructural SEM analysis was carried out on a LEICA LEO440I. Density was measured by the Archimedes method in water.

Electrical behaviour of sintered materials has been studied by complex impedance spectroscopy in a LF Impedance Analyser 4192 supplied by Hewlett-Packard. Silver electrodes were deposited on sample surfaces previously to impedance analysis.

3. RESULTS AND DISCUSSION

XRD of powders and CIE-L*a*b* parameters of 5% glazed samples are shown in Table I and Fig. 1 shows the XRD diffractograms (undoped and V-ZrSiO₄ samples in Fig. 1.a and Pr-ZrSiO₄ samples in Fig. 1.b). For undoped samples, zircon appears well crystallised but very weak peaks can be detected associated to monoclinic zirconia that remains unreacted. For V-ZrSiO₄ samples zircon is obtained in all samples but only in low vanadium VCG sample appears as the only crystalline phase detected. On the other samples, weak peaks of monoclinic zirconia and/or cristobalite appear. For Pr-ZrSiO₄ samples it is necessary the presence of NaF flux agent in order to obtain zircon, in colloidal gel sample only weak peaks of ZrSiO₄ are detected and in the polymeric gel sample metastable tetragonal zirconia is stabilised as the only crystalline phase. From CIE-L*a*b* parameters white undoped samples show low values of a* and b*, in the case

TABLE I. XRD AND L*A*B* MEASUREMENTS.

SAMPLE	method	XRD	L*a*b*
Undoped			
CE	Ceramic	Z(vs)M(w)	98/1/2
CG	Colloidal Gel	Z(vs)M(vw)	99/0/1
V-ZrSiO ₄			
VCE	Ceramic	Z(s)M(w)	93/-4/-2
VCG*	Colloidal Gel	Z(vs)	87/-5/-8
VPG	Polymeric Gel	Z(s)C(w)	84/-9/-11
VFPG	Polymeric Gel with NaF addition	Z(vs)M(w)C(w)	70/-13/-19
Pr-ZrSiO ₄			
PFCE	Ceramic with NaF addition	Z(vs)M,PF(vw)	90/-6/42
PCG	Colloidal Gel	Z,T,M,C(vw)	97/2/23
PFPG	Colloidal Gel with NaF addition	Z(vs)T,M,PF(vw)	90/-7/43
PPG	Polymeric Gel	T(vs)	94/-6/25

(* low V composition (Zr_{0.96}V_{0.04})SiO₄. CRYSTALLINE PHASES: Z(ZrSiO₄),M(monoclinic ZrO₂), T(tetragonal ZrO₂), PF(Na₂Pr₆(SiO₃)₆F₂), C(cristobalite), PEAKS INTENSITY: vs (very strong), s(strong), w(weak), vw(very weak).

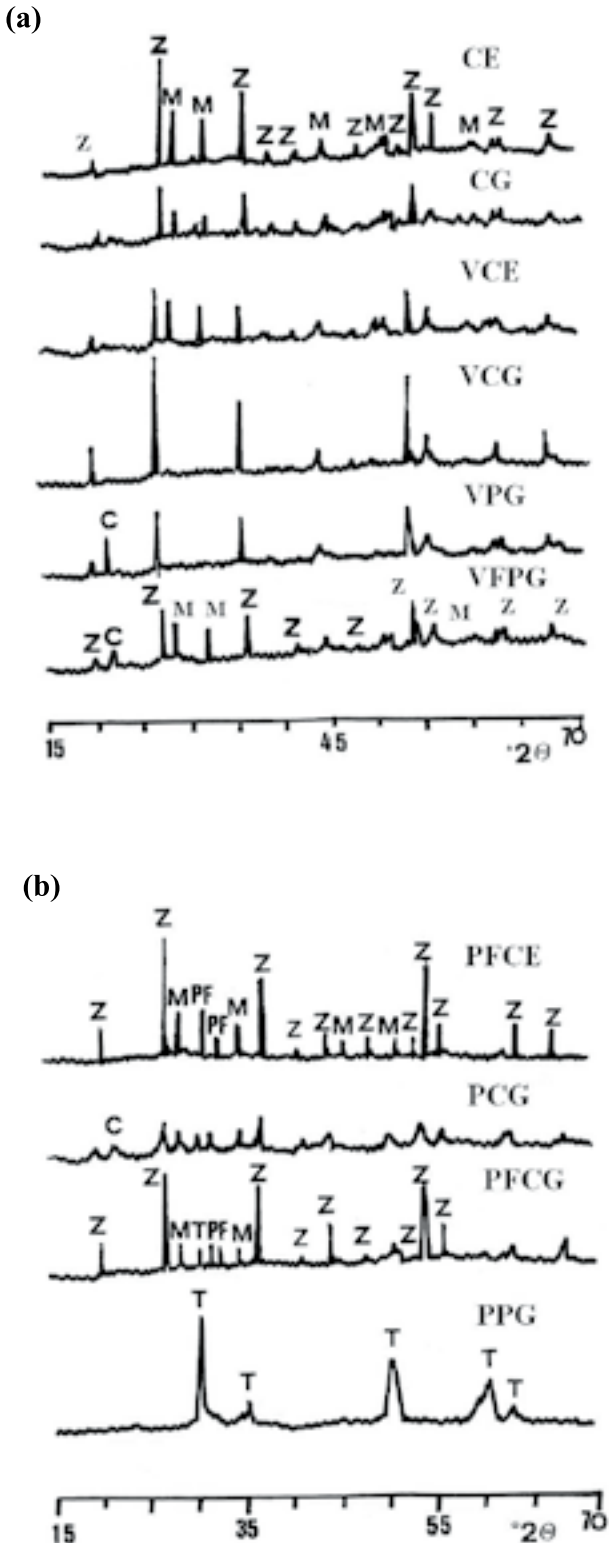


Fig. 1- XRD diffractogrammes of samples: (a) undoped and V-Zircon samples, (b) Pr-Zircon samples. CRYSTALLINE PHASES: Z($ZrSiO_4$), M(monoclinic ZrO_2), T(tetragonal ZrO_2), PF($Na_2Pr_8(SiO_4)_6F_2$), C(cristobalite).

of V- $ZrSiO_4$ samples turkish blue colours ($L^*a^*b^*=70/-13/-19$) are obtained when fluorine is present, but green colours without NaF addition (i.e. $L^*a^*b^*=84/-9/-11$ of VPG sample),

finally free fluorine ceramic sample appears colourless. For Pr- $ZrSiO_4$ samples intense yellow colour is obtained in NaF containing samples ($b^*=43-46$) but in free NaF samples a light yellow colour is observed ($b^*=23$); intense yellow is due to the praseodymium-zircon yellow pigment and the light colour to Pr- ZrO_2 yellow colour (4,6).

The morphology of powders is shown in Figure 2. The ceramic powders are built by heterogeneous particles between 1-5 μm of size in both vanadium and praseodymium systems. Particles are larger (7-10 μm), homogenous and sintered on colloidal samples. Finally, on polymeric samples, particles sintered in large aggregates (about 50-100 μm).

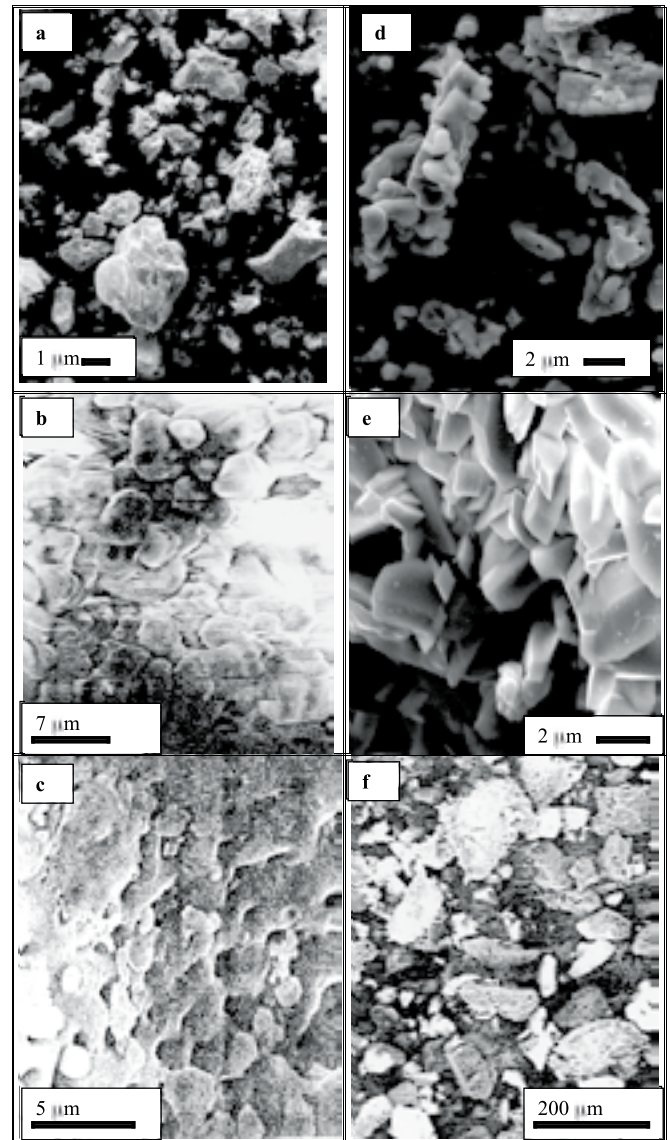


Fig. 2- SEM micrographs of samples: (a) VCE, (a) VCG, (c) VPG, (d) PFCE, (e) PCG, (f) PPG.

Sintered compacts densified poorly ($\approx 80\%$ theoretical in polymeric samples, $\approx 85\%$ in ceramic samples and $\approx 90\%$ in colloidal samples, Figure 3 and Table II) indicating that the samples had not reached the final step of densification. The method of synthesis has a great influence on densification. Gel samples densified better than ceramic ones, and the polymeric

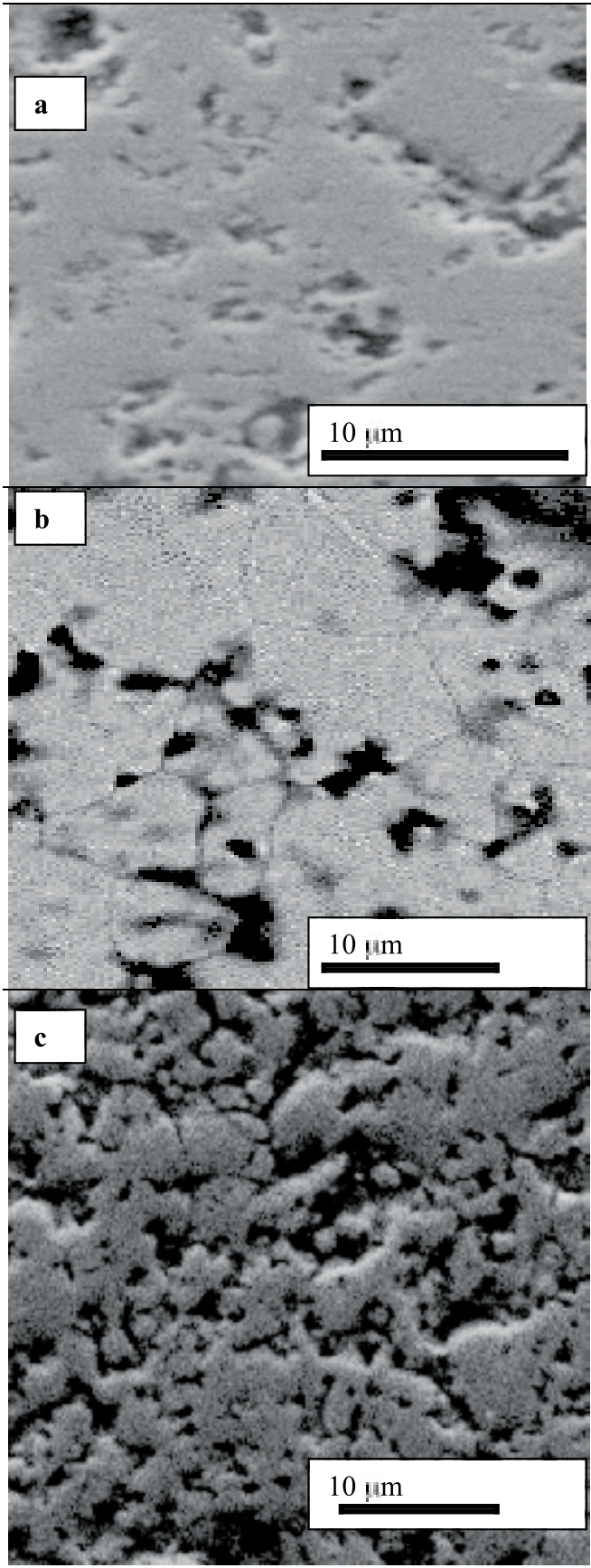


Fig. 3- SEM micrographs of sintered pellets surfaces. (a) VCE, (b) VCG, (c) VFPG.

TABLE II. ACTIVATION ENERGY, DENSITY AND ELECTRICAL CONDUCTIVITY AT 1000°C OF SINTERED SAMPLES.

SAMPLE	method	d (%theoretical)	E(eV)	σ ($\mu\text{S/cm}$) 1000°C
Undoped				
CE	Ceramic	86	0.75(3)	25.5(4)
CG	Colloidal Gel	91	1.39(6)	1.0(3)
V-ZrSiO ₄				
VCE	Ceramic	85	0.86(4)	3.8(3)
VCG	Colloidal Gel	89	1.33(2)	4.3(2)
VPG	Polymeric Gel	82	1.03(4)	0.83(5)
VFPG	Polymeric Gel with NaF addition	80	1.18(4)	0.4(2)
Pr-ZrSiO ₄				
PFCE	Ceramic with NaF addition	84	0.59(2)	3.9(4)
PCG	Colloidal Gel	90	0.47(3)	0.47(2)

method was the poorest for densification for both vanadium and praseodymium samples. Methods with a heterogeneous crystallisation mechanism, such as citrate or colloidal, gave the best results in agreement with previous studies in zirconia systems (8). Praseodymium or vanadium doping lowered slightly density (see % theoretical density attained on Table II).

Samples were characterised by complex impedance spectroscopy. The evolution of impedance spectra with temperature of VCG as representative sample is shown in Figure 4 and the Arrhenius plots of bulk contribution of samples is presented on Figure 5 (praseodymium) and Figure 6 (vanadium). The activation energy and conductivity measurements are shown in Table II. The bulk and grain boundary contributions are not well resolved as can be seen on Figure 4 for VCG sample, thermal evolution is similar for all samples, therefore it is necessary to apply a deconvolution procedure in order to obtain the bulk contribution plotted in Fig. 5 and Fig. 6 (11).

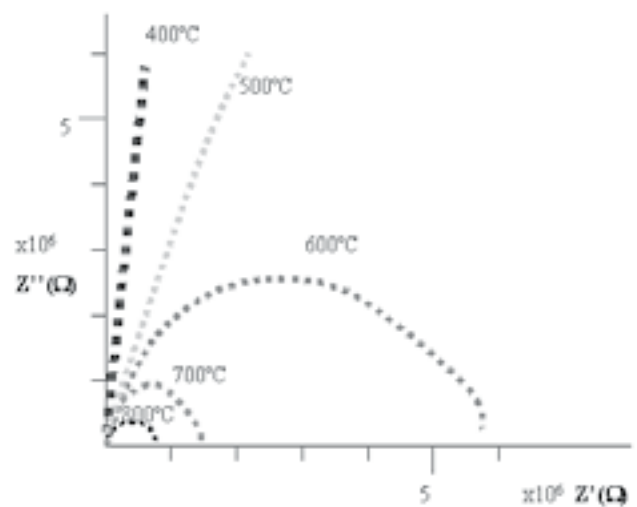


Fig. 4- Representative Impedance spectra evolution with temperature (VCG).

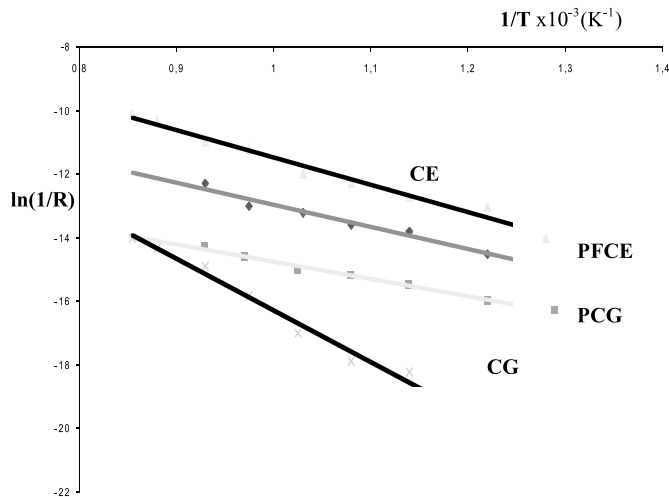


Fig. 5- Arrhenius plot of bulk contribution of Pr- ZrSiO₄ samples.

From impedance spectroscopy results it can be pointed out the insulator characteristics of pure zircon and vanadium and praseodymium doped zircon. CG undoped sample shows the higher activation energy and lower conductivity, this sample is the purest between all analysed samples (the undoped ceramic is produced from technical grade oxides precursors and the other samples are all doped with vanadium or praseodymium). Thereby, undoped ceramic sample CE shows the higher conductivity and low activation energy.

Vanadium doped samples increase their activation energy compared to CE undoped sample and are similar or slightly lower than CG undoped sample. Green samples (due to V⁴⁺ and V⁵⁺ simultaneous doping ions into zircon lattice (3)) show conductivity values between CE and CG undoped samples (Fig. 6). Only stable turquoise blue sample VFPG shows higher insulator characteristics; in this sample, V⁴⁺ is the predominant ion in zircon solid solution substituting Zr⁴⁺ ion (2,3). The presence of V⁵⁺ in green samples can be associated to cationic vacancies in order to preserve lattice electroneutrality; these

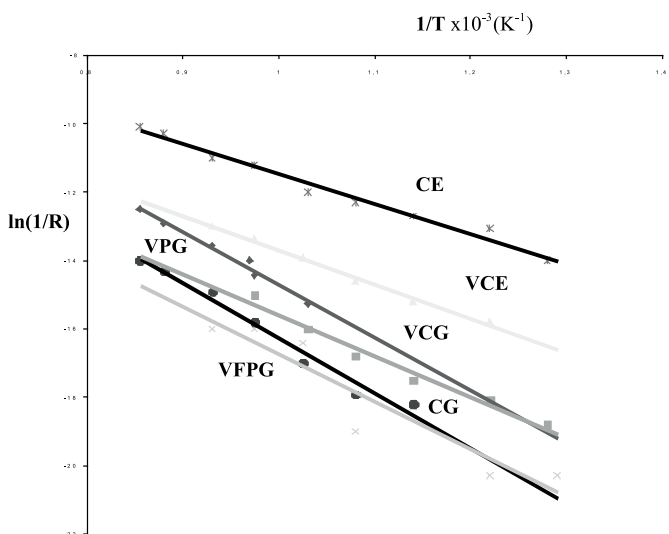


Fig. 6- Arrhenius plot of bulk contribution of V- ZrSiO₄ samples.

vacancies enhance conductivity in vanadium-zircon green samples.

Praseodymium doped samples show lower activation energy than undoped samples and their conductivity thermal evolution is between CE and CG undoped samples (Fig. 5). PCG sample have only weak intensity of zircon on powder (Table I), but after the sintering treatment, zircon is detected as the main crystalline phase together with weak peaks associated to monoclinic zirconia by XRD (not shown). Therefore the conductivity effect of praseodymium is not dependent on colour (stable yellow of praseodymium-zircon on PFCE sample or light yellow colour on PCG sample) and microstructure of samples in agreement with the hypothesis that associates the intense yellow colour to an inclusion mechanism of praseodymium oxide crystallites into zircon host crystals (4).

4. CONCLUSIONS

Zircon powders prepared from high purity precursors and homogeneous colloidal gel (CG) or alkoxides precursors (PG) show higher insulator characteristics than ceramic powders CE prepared from technical grade oxides. From density measurements, samples prepared by ammonia coprecipitation method (CG) sinter better than samples prepared by the ceramic method (CE) or from alkoxides hydrolysis method (PG).

Resistivity and activation energy increase for Vanadium doped zircon compared to undoped zircon CE powder, but only stable turquoise blue vanadium-zircon obtained by addition of NaF shows higher resistivity than undoped CG sample. This behaviour is in agreement with the hypothesis of the existence of cationic vacancies associated to V⁵⁺ ion in green samples obtained without NaF stabiliser agent.

Praseodymium doped zircon shows a decrease of the activation energy and conductivity compared to undoped zircon CE powder. This feature is independent of the colour stabilised (intense praseodymium-zircon yellow or light yellow associated to a Zr⁴⁺ substitution by Pr⁴⁺ ion) in agreement with the hypothesis that considers an encapsulated mechanism for the nature of intense yellow of praseodymium-zircon pigment.

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