# Yellow Pr-zircon pigments
# The role of praseodymium and of the mineralizer

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## Abstract

A sol–gel reaction starting from Si and Zr alkoxides, in water–ethanol mixtures, was employed to obtain praseodymium doped zirconium silicate powders (zircon).

The reactions were performed by modulating both: (a) the amount of praseodymium salt in the starting mixture and (b) the speciation of the mineralizers; chloride and fluoride salts of monovalent ($Na^+$, $Li^+$) and divalent ($Mg^{2+}$) were tested.

The products of the sol–gel reaction were calcined either at 1000 °C or at 1200 °C. The samples were characterised by X-ray diffraction, SEM micrographs, EDX analyses and diffuse reflectance spectroscopy; the colour of the pigments was characterized on the grounds of the Commission Internationale de l'Eclairage (CIE) standard procedure (CIE $L^*a^*b^*$ measurements). Results from the structural, morphological and optical characterisations are examined and cross-compared to produce a consistent picture of the key factors leading to the formation, growth and optical properties of the reaction products.

## 1. Introduction

Colour is usually introduced into enamels and ceramic bodies by dispersing a coloured crystalline phase into the matrix. This crystalline phase, commonly called pigment, must show structural and chemical stability toward dissolution during firing.

Pigments based on zircon ($ZrSiO_4$) are widely used in ceramic industries because they can withstand high temperatures and corrosive environments. Their colour, obtained by doping the zircon lattice with guest metal species, is yellow, blue or pink when, respectively, praseodymium, vanadium or iron ions are introduced.[1–5] $ZrSiO_4$ pigments are important from an industrial point of view not only for their structural and chemical properties but also for the interesting tonalities of colour they may develop.

The principal structural unit of zircon is a chain of alternating edge-sharing $SiO_4$ tetrahedra and $ZrO_8$ triangular dodecahedra, characterized by the presence of empty octahedric cavities. The metal dopant can be accommodated into the zircon network in interstitial positions, it can substitute either $Zr^{4+}$ or $Si^{4+}$ in their lattice positions or it can form an encapsulated phase. In several cases controversial conclusions are reached in the literature about the actual location of the metal ion and its valence in the zircon lattice.[2–16]

In the case of praseodymium doping, the cations are generally assumed to form a solid solution with the zircon lattice but the actual valence of the dopant (either 3+ or 4+) has not been definitely established yet. The position occupied by Pr ions has not been clarified, either. In general Pr ions are considered to be located at the triangular dodecahedral positions[3,6,14,15] of $Zr^{4+}$, however, Shoyama et al.[14] suggest that Pr(IV) may substitute for both $Zr^{4+}$ and $Si^{4+}$ of the zircon lattice.

The mixed oxide method is the traditional synthetic path through which Pr-$ZrSiO_4$ is industrially produced; this procedure implies the fusion of $ZrO_2$, $SiO_2$ and $Pr_6O_{11}$ and the subsequent calcination with NaF as the mineralizer. The presence of a mineralizer is necessary in order to achieve a complete or nearly complete reaction of all components but

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the specific function of NaF has never been fully clarified. Eppler studied in 1977 the role played by the mineralizer in the structure formation of $ZrSiO_4$ by means of the marker technique. He concluded that the acceleration of the zircon crystallization produced by NaF takes place through the formation of $SiF_4$ which volatilizes thus favouring the transport of Si species into the zirconia phase.[1,12,13]

Ocaña et al.[3] report differences in colour properties between samples of Pr-$ZrSiO_4$ prepared in the absence or in the presence of NaF.

Pigments generally cannot be produced directly mixing the dopant oxides and the already formed zircon powder. The colouring ion must be present at the time the $ZrSiO_4$ is formed by the reaction $ZrO_2 + SiO_2 \rightarrow ZrSiO_4$.[17] Various formulations in the literature indicate that to obtain an intense yellow, the praseodymium oxide content should be in the range of 3–8 wt.%. Lesser contents are too weak to produce a homogeneous bright colour. In high percentages, praseodymium oxide may impart a greenish yellow colour because the colouring component is not fully incorporated into the zircon lattice.

No literature references could be found concerning the relation between the level of Pr added and the amount that is actually incorporated in the lattice.

It can be assumed that homogeneous doping is facilitated if the un-calcined product is as homogeneous as possible.[17] Recently the sol–gel method has been developed as one of the low temperature processing of ceramic, in which the gels, made typically from metal alkoxides through hydrolysis and polycondensation reactions at low temperature, are converted to ceramics by heat-treating at much lower (1200 °C) temperature than that required in the conventional solid-state reaction method cited above (1400 °C). Moreover the sol–gel method reduces the energy-consuming crushing and grinding processes allowing a better possibility of controlling the morphology of the powders.[16]

In line with the above reported observations we have recently started a research on Pr-$ZrSiO_4$ pigments following a sol–gel route which we have previously optimized in the case of Fe-$ZrSiO_4$ pigments.[16]

The aim of the present work was to study the nature and localization of Pr species in the zircon matrix and the ensuing structural, morphological and colour properties of the powders. Sol–gel reactions were performed by modulating both: (a) the amount of praseodymium salt in the starting mixture and (b) the speciation of the mineralizers, testing both the $Cl^-$ and $F^-$ anions and monovalent ($Na^+$, $Li^+$) and divalent ($Mg^{2+}$) cations.

## 2. Experimental

All the chemicals were of reagent grade purity and were used without further purification; doubly distilled water passed through a Milli-Q apparatus was used to prepare solutions and suspensions.

### 2.1. Sample preparation

The zircon samples were prepared by a previously reported sol–gel procedure consisting of two different hydrolysis steps.[16] At the beginning $Si(OC_2H_5)_4$ (0.20 mol) was added drop by drop to an aqueous solution containing variable amounts of the praseodymium(III) salt ($Pr(NO_3)_3 \cdot 5H_2O$ or $PrCl_3 \cdot 6H_2O$) previously stirred at 60 °C for about 20 min in order to achieve the complete dissolution of the dopant ion. Then 0.35 mol of ethanol and 0.10 mol of reaction catalyst ($HNO_3$ or HCl) were added to the mixture which was left under rapid stirring for 30 min (i.e. the time of the first hydrolysis step). Subsequently, a solution of $Zr(OC_3H_7)_4$ (0.20 mol) and water was added to the mixture. The final suspension was kept under stirring at 60 °C for 2 h (i.e. the time of the second hydrolysis step). The product, cooled at room temperature, was dried in oven at 60 °C and then the obtained xerogel was thermally treated at either 1000 or 1200 °C for 20 h.

Table 1 shows the relative molar ratios of the different reactants, which have been kept constant in both the two series of prepared samples.

The first series of samples was prepared by using a variable Pr/Zr molar ratio (0.00–0.01–0.02–0.03–0.05–0.08 and 0.10).

The second series of samples was obtained by using a constant Pr/Zr molar ratio of 0.05 but adding NaF, NaCl, $MgCl_2$ and LiCl as mineralizers (m) before the second hydrolysis step. The m/Zr molar ratio was 0.26 for the monovalent salts and 0.13 for $MgCl_2$.

The samples were denoted as following.

The un-doped sample (0% Pr) prepared in nitrate environment is denoted as Ref.

The other samples are denoted by:

- a letter that is relative to the anionic environment and the anionic partner of praseodymium (N: nitrate, C: chloride);
- a number that is relative to the Pr/Zr molar ratio;
- NaF, NaCl, $MgCl_2$ and LiCl that indicate the mineralizer used.

### 2.2. Sample characterisation

Structural characterisation of the powders was performed by X-ray diffraction, using a Siemens D500 diffractometer, using Cu Kα radiation in the 10–80° $2\theta$ angle range. The fitting program of the peaks was a particular Rietveld program,[19,20] named QUANTO,[21] devoted to the automatic

Table 1
Composition of the reacting preparative mixture (X = $NO_3^-$, $Cl^-$)

|  | Molar ratio |
| --- | --- |
| $CH_3CH_2OH/Zr(OC_3H_7)_4$ | 1.75 |
| $H_2O/Zr(OC_3H_7)_4$ | 150 |
| $HX/Zr(OC_3H_7)_4$ | 0.5 |

estimation of the weight fraction of each crystalline phase in a mixture.

The peak shape was fitted using a modified Pearson VII function. The background of each profile was modelled using a six-parameters polynomial in $2\theta^m$, where m is a value from 0 to 5 with six refined coefficients.

The mean dimension, $d$, of crystallites was obtained by elaborating the most intense X-ray peak of each phase by the Scherrer's equation

$$d = \frac{K\lambda}{\beta \cos\theta}$$

where $K$ is a constant related to the crystallite shape (0.9); $\beta$, pure breath of the powder reflection, free of the broadening due to the instrumental contributions. This calibration was performed by means of the spectrum of a standard Si powder. The accuracy with which the Scherrer's equation can be applied is limited by the uncertainties in $K$ and by the success with which $\beta$ can be deduced from the experimentally observed breadth. This equation is quite satisfactory for studies comparing the crystallite sizes of a number of samples belonging to a related series.

The particle morphology was examined by scanning electron microscopy using a Cambridge 150 Stereoscan. SEM–EDX analyses were performed using a Hitachi 2400 scanning electronic microscope equipped with a quantum Kevex energy-dispersive X-ray micro-analyser (EDX). Powder samples were coated with a thin gold layer deposited by means of a sputter coater.

Diffuse reflectance spectra were acquired in the VIS–NIR range from 350 to 1200 nm using a JASCO/UV/VIS/NIR spectrophotometer model V-570 equipped with a barium sulphate integrating sphere. A block of mylar was used as reference sample following a previously reported procedure.[22] The colour of the fired samples was assessed on the grounds of $L^*$, $a^*$ and $b^*$ parameters, calculated from the diffuse reflectance spectra, through the method recommended by the Commission Internationale de l'Eclairage (CIE).[23] By this method the parameter $L^*$ represents the brightness of a sample; a positive $L^*$ value stays for a light colour while a negative one corresponds to a dark colour; $a^*$ represents the green $(-) \rightarrow$ red $(+)$ axis and $b^*$ the blue $(-) \rightarrow$ yellow $(+)$ axis.

## 3. Results and discussion

### 3.1. Structural characterisation

Fig. 1 reports the comparison between the X-ray pattern of three samples, calcined at 1200 °C, obtained in the same experimental conditions with a Pr/Zr molar ratio of 0.00, 0.03 and 0.10, respectively. In the absence of the guest ion (Fig. 1a) the only crystalline phase is pure monoclinic zirconia. No crystalline phases related to silica can be appreciated. Upon addition of 3% praseodymium (Fig. 1b), instead,
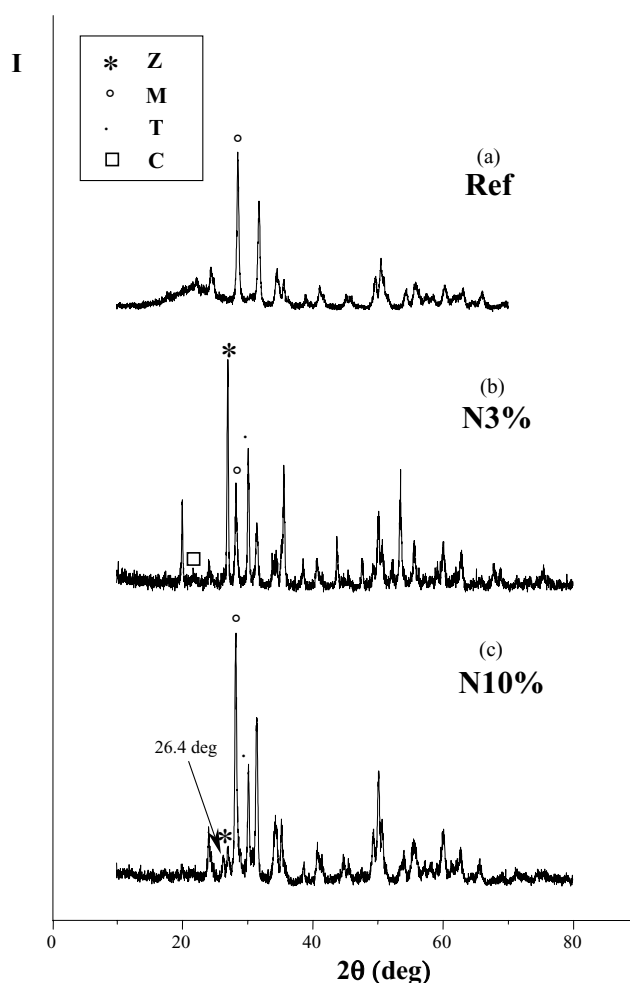


Fig. 1. Powder X-ray diffraction spectra of samples calcined at 1200 °C: (a) un-doped sample (Ref, Pr/Zr = 0%); (b) doped sample (3% Pr/Zr) in the nitrate environment; (c) doped sample (10% Pr/Zr) in the nitrate environment.

different phases are appreciable: the desired phase zircon ($ZrSiO_4$) and $ZrO_2$ both in the monoclinic and in the tetragonal form.

The role played by the metal on the promotion of the zircon lattice is apparent. This effect has been observed previously in the literature[5] also in the case of other metal dopants (Fe, V) of the zircon lattice. Several authors interpret this occurrence as due to the initiator role, played by the metal, in the nucleation of the zircon structure within the zirconia lattice.[6,11,12]

The fraction of crystallised zircon decreases (Fig. 1c) at increasing of praseodymium content (10%): the dominant phase is m-$ZrO_2$ accompanied by the presence of zirconia in the tetragonal form. At this concentration other crystalline phases are appreciable: two weak peaks at 29.0 and 32.3° could be associated to some of the most intense reflections of $Pr_2Zr_2O_7$, another peak at 26.4° could not be assigned to any known Pr compound. This latter peak was observed also by Ocaña et al.[3] who could not, in their turn, attribute it to any specific Pr containing phase.
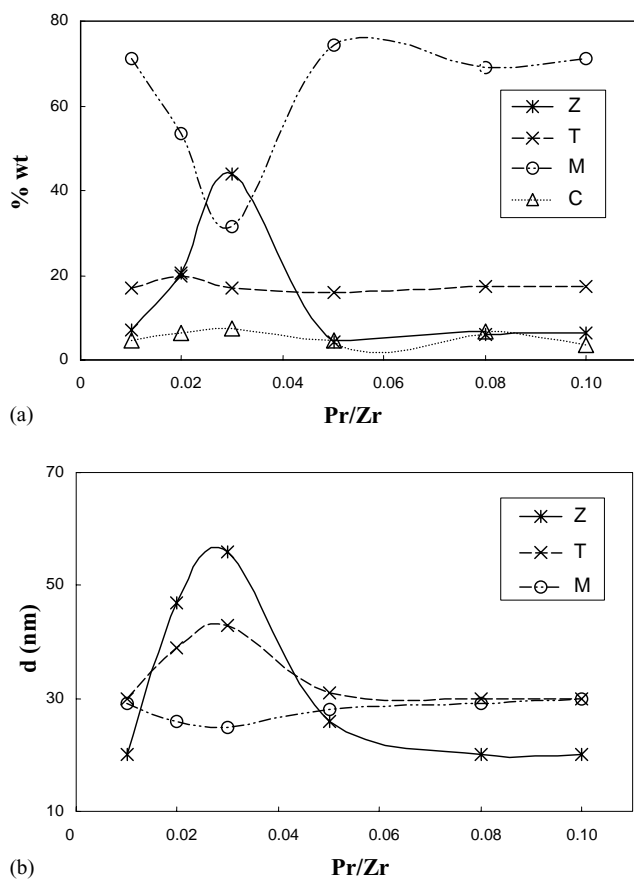
Fig. 2. Structural features of 1200 °C calcined samples at variable Pr/Zr molar ratios. No mineralizers. (a) Quantitative phase composition by the QUANTO elaboration of X-ray diffractograms; (b) Crystallite sizes by Scherrer's equation.

In order to obtain an accurate quantitative estimation of the phases present in the powder, the spectra of all samples have been fitted with the Rietveld program QUANTO; the results are reported in Fig. 2a. The picture emerging from the elaboration is very interesting and several considerations can be made (Fig. 2a). (a) The amount of zircon phase is not a simple function of the Pr concentration in the starting mixture but it goes through a maximum (up to 40%) for Pr molar ratios around the 3% and then it levels off to very low contents. (b) The parallel formation of the monoclinic zirconia polymorph seems to closely balance the zircon crystallization, the quantity present in the phase mixture being at a minimum at the peak of the zircon phase formation. (c) The amounts of tetragonal zirconia and of crystobalite seem, instead, to be almost independent of the Pr content and range around 20 and 3% for t-ZrO$_2$ and crystobalite, respectively. It must be noted that the quantity of crystalline silica, present in the samples, is very low indicating that the major part of the starting silica is still amorphous at this temperature. The amount of crystobalite, further, is not affected by the fraction of Si species crystallized into the zircon structure.

Fig. 2b reports the relation between the crystallite sizes and the amount of Pr present in the samples. The size of

the crystallites was obtained by the Scherrer's equation. The method yields exhaustive values of the relative sizes even though the inflexible premises upon which the formula rests may result in considerable uncertainty as to the absolute sizes.[22] Data in Fig. 2b show that the conditions of best zircon promotion correspond also to the largest size of the crystallites for both the zircon and the tetragonal phase. The size of the m-ZrO$_2$ crystallites seem, instead, to be un-affected by the Pr content.

The parallel between the growth of the size of the crystallites and the promotion of the zircon phase suggests that up to 3% Pr might be present in a solid solution within the t-ZrO$_2$ lattice favouring nucleation and growth of the zircon structure. The 3% might represent a solubility limit for the solid solution; larger Pr quantities might support the formation of different crystalline Pr containing phases (see, e.g. the phase Pr$_2$Zr$_2$O$_7$ appreciable into the 5, 8, 10% sample diffractograms) encapsulated in the lattice.

The absence of a monotonic increasing promotion by Pr of the zircon structure has never been reported previously in the literature, in the authors best knowledge. The major part of literature works are performed at constant Pr content.[3,4,14,15,18] Some data[1,17] concerning the colour performance of the pigments as a function of the Pr content are reported but in the absence of any structural characterisation of the powders.

Fig. 3 reports the comparison between X-ray spectra obtained by either varying the anionic partner of the chromophor or adding NaF as the mineralizer. The spectra in Fig. 3a (PrCl$_3$) and b (PrNO$_3$) show no appreciable differences. This result can be considered to be rather unexpected in the light of previous results. In fact in the case of iron doped zircon pigments[16] a definite promoting effect by Cl$^-$ ions (used as the anionic partner of Fe(III)) was evidenced. Consistently with this, on the basis of Eppler's nucleation mechanism, a promoting effect by Cl$^-$ ions through silica fluidification could have been predicted. Apparently in the case of yellow Pr pigments the key step for the zircon formation is not mainly controlled by the transport of silica within the zirconia matrix. To the authors knowledge no direct comparison between the role played by the anionic partner of Pr on the zircon crystallisation is present in the literature.

The presence of NaF as the mineralizer (Fig. 3c) provokes definite variations in the diffractogram. The peaks of zircon are much more intense and the peak at 22.0° relative to crystobalite totally disappears. The promoting role of NaF have been reported frequently in the case of Pr-zircon pigments. Ocaña et al.[3] observe that by adding NaF, the valence of most of the Pr cations is mainly four-fold and this is the reason of the stronger yellow colour observed in this case.

On the grounds of the key role played by the mineralizer, apparent in Fig. 3c, several other salts have been tested. Fig. 4 reports the data obtained by the Rietveld quantitative analysis on the spectra of samples prepared by adding, to the sol–gel mixture, salts with different speciation. As a general trend all the mineralizers definitely promote
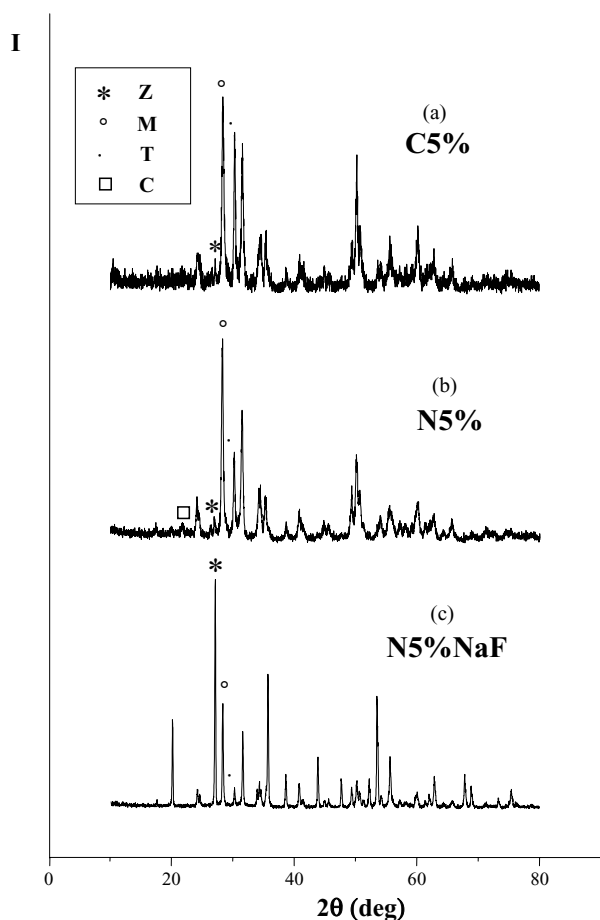
Fig. 3. Powder X-ray diffraction spectra of doped samples (5% Pr/Zr) calcined at 1200 °C: (a) chloride environment; (b) nitrate environment; (c) nitrate environment with addition of 0.26 NaF/Zr molar ratio.

the crystallization of zircon with the parallel decrease of monoclic zirconia; the undesired phase $Pr_2Zr_2O_7$ is never appreciable and crystobalite is present in traces only in the case of the Mg salt. Between the different mineralizers NaF and NaCl provoke indistinguishable effects while $MgCl_2$ and LiCl further promote the zircon formation. The trend apparent in Fig. 4 suggests that the successful formation
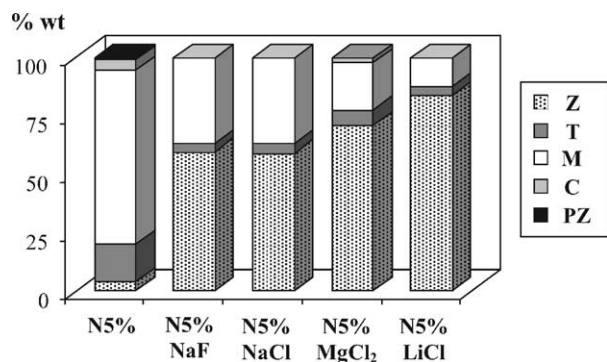


Fig. 4. Quantitative phase composition of samples calcined at 1200 °C, for various mineralizers. N5% represents the samples obtained in the same conditions but in the absence of mineralizers.

of Pr-zircon compounds is to be mainly related to the role played by the cation of the mineralizer. This observation is also consistent with the lack of effects (between nitrates and chlorides) observed in Fig. 3.

In the case of the addition of NaF and NaCl the promotion of the zircon structure was accompanied by the improvement of the colour which from white/yellow in the absence of salt turned to intense ochre/yellow. The colour of the Li-doped pigment was bright yellow but with shades of green. The addition of Mg salts, instead, although promoting the zircon structure was not effective for the pigment colour which was whitish. Following the consideration by Ocaña et al.[3] the presence of $Pr^{4+}$ in a solid solution within the zircon lattice can be considered as the origin of the colour in NaF and NaCl samples.

Li ions, although monovalent do not match closely the action of $Na^+$; the zircon structure is better promoted and the colour is different.

The role played by $Mg^{2+}$ is definitely atypical, as on one side the zircon structure is promoted but the colour is totally unsatisfactorily.

In the following, in the optical properties part, this discussion will be resumed.

### 3.2. Morphological characterisation

SEM micrographs of selected samples are reported in Fig. 5. In the case of the absence of mineralizer, (Fig. 5a, Pr/Zr = 5%) the presence of large shapeless aggregates, composed by rounded particles can be appreciated. The most apparent feature in this micrograph is the presence of a "blanket" covering the sample. It must be recalled that in the case of this sample $SiO_2$ is still amorphous for about the 90% of the initial amount. Preliminary EDX and XPS determinations show that the amorphous silica is located at the surface of the particles. The external layers of amorphous silica might be responsible of the peculiar aspect of the sample.

The aspect of the powder changes dramatically by the addition of the mineralizer, NaF, to the starting mixture (Fig. 5b). No more "covering" effects are appreciable, possibly because in this sample the fraction of amorphous silica is much lower. The particles appear as platelets, with variable sizes in the range (0.5–2 μm). The morphology changes again when the mineralizer is $MgCl_2$ (Fig. 5c). The particles, possibly aggregates of smaller ones, are spheroidal and much smaller than in the case of the monovalent mineralizer (Fig. 5b).

The definite role played by the presence of the mineralizer on the features of the samples is evidenced also by EDX analyses obtained for samples with Pr/Zr 5% (Fig. 6). In the absence of mineralizer, the amount of Pr is found to vary significantly in different positions of the same sample (see, e.g. Fig. $6a_1$ and $a_2$) showing a non-homogeneous distribution of the chromophor in the matrix. When a mineralizer is present (Fig. 6b and c) the amount of Pr is low and invariant throughout the samples.
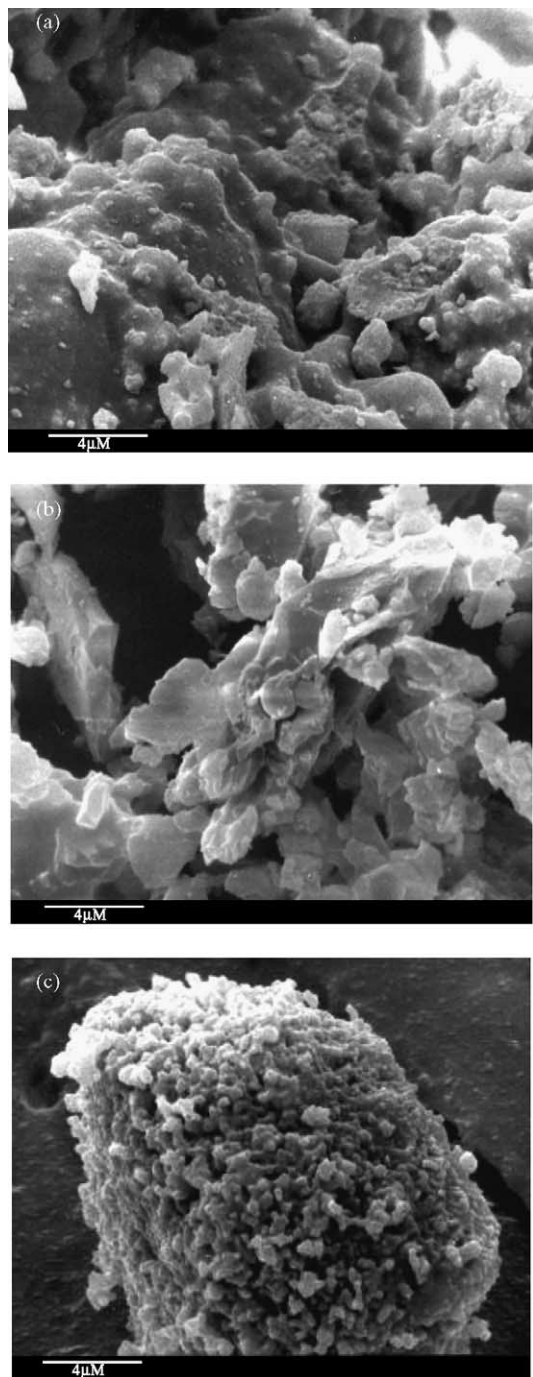
Fig. 5. SEM images of 1200 °C calcined samples: (a) N5%; (b) N5%NaF; (c) N5%MgCl$_2$.



Fig. 6. EDX analyses of 1200 °C calcined samples: (a$_1$) and (a$_2$) different regions of a N5% sample with no mineralizer; (b) N5% sample with MgCl$_2$ as the mineralizer; (c) N5% sample with LiCl as the mineralizer.

### 3.3. Optical characterisation

Samples fired at 1200 °C and characterized by different Pr concentration have been analysed by VIS–NIR diffuse reflectance spectroscopy.

The reported spectra (Fig. 7) show absorption bands at 590–600 nm and 1020 nm due to Pr(III) transitions.[6] Peaks at 495, 481 and 483 nm, evidenced in the figure by asterisk (*), which can be attributed to Pr(III) as well, are more
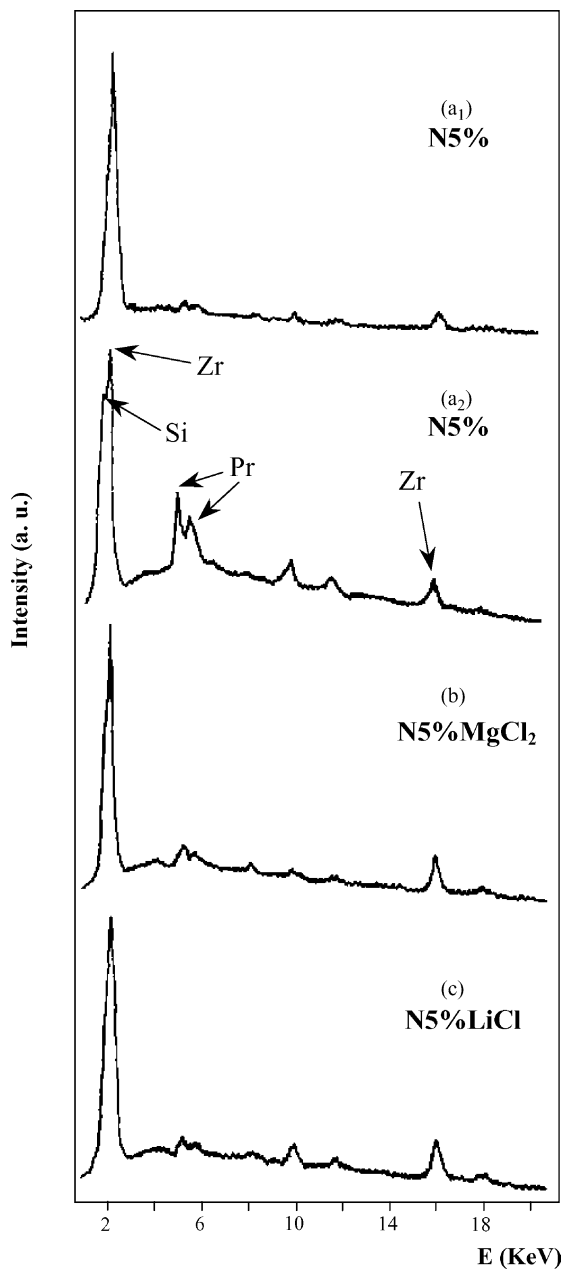
difficult to detect because of the absorption due to zirconium oxides. The presence of Pr(IV) cannot be detected as it does not present absorption in the visible and near infrared region of the spectrum.[24] In addition since 4f orbitals of praseodymium are shielded from the surroundings it is not possible to obtain information related to its geometry co-ordination sphere.[25]

The intensity of the signals at about 600 and 1020 nm increases with the increase of the Pr amount employed during the sol–gel preparation. It is worth noting that for samples characterized by 5 and 10% Pr content, the signals at 495,
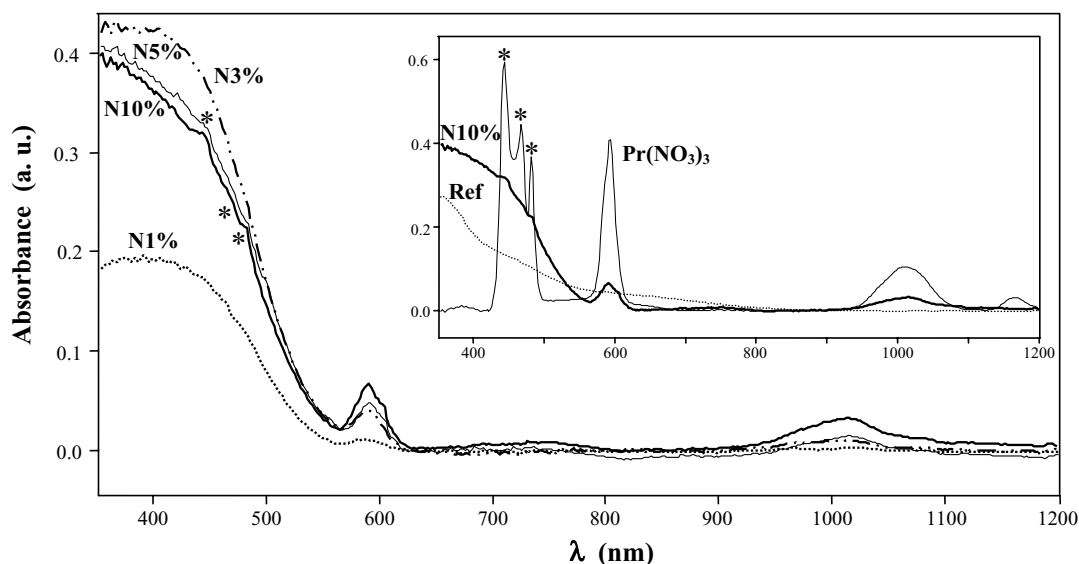
Fig. 7. Diffuse reflectance spectra of 1200 °C samples at variable Pr/Zr molar ratios. Inset: comparison between the spectra of Ref (undoped, Pr/Zr = 0%), N10% (Pr/Zr = 10%) and Pr(NO₃)₃ salt.

481 and 483 nm can be appreciated. It is known that these bands tend to split during the densification of the matrix as a consequence of the distribution of Pr(III) in an asymmetric environment.[25] The possibility to distinguish these signals in the most concentrated samples suggests that part of Pr(III) is not homogeneously distributed into the host lattice, but is crystallized in a given Pr(III) containing phase. As a comparison the inset in the figure reports the spectrum of a Pr(III) salt showing the above mentioned peaks at 495, 481 and 483 nm, the spectrum of the sample at Pr/Zr 10% with shoulders appreciable at the same wavelengths and the undoped (Pr/Zr = 0%) Ref sample spectrum.

It is worth noting that in the region 400–500 nm (Fig. 7) the intensities of the signals reflect the increase of Pr in the sample up to 3% and then decrease for larger concentrations. The presence of Pr(III) in a separate phase may provoke the observed decrease in intensity.

The trend reported in Fig. 7 closely matches the dependence of the quantitative phase distribution shown in Fig. 2a. The zircon formation is promoted as long as Pr is present in the matrix in a solid solution. The segregation of Pr in a separate phases, shown by VIS–NIR in Fig. 7 for concentrations larger than 3% and appreciable also by X-ray, lowers the nucleating action of the chromophor and reduces the general crystallinity.

As concerns the chromophor counter-anion, diffuse reflectance spectra have been recorded on samples prepared from PrCl₃ and from Pr(NO₃)₃, keeping the Pr content constant and no significance differences have been observed in agreement with results in Fig. 3a and b. Curves in Fig. 8 are relative to the various mineralizers adopted in the reaction.

The curve of N5% (no mineralizer) is reported for comparison. The spectra of the samples with NaF, NaCl are superimposable, showing identical effects of the two salts. This trend fully supports results in Fig. 4 relative to the phase

compositions. Further Fig. 8 gives a very relevant information. The spectra of NaF, NaCl do not show any shoulder or small peak at 495, 481 and 483 nm, indicating the Pr is not appreciably segregated in separate phases. The role of these two mineralizers might be that of extending the solubility limit of Pr species in the lattice.

The curve of LiCl sample shows the largest intensity and the total absence of shoulders at 495, 481 and 483 nm. Further the intensity at 590 nm is the highest indicating that this sample contains the largest Pr(III) amount. The origin of the light green shades in the yellow colour of this sample can be due to the high Pr(III) level.

The intensity of the curve relative to the MgCl₂ sample is the lowest among the different samples. The shoulders at 495, 481 and 483 nm are clearly appreciable indicating the formation of Pr containing phases. The almost total lack of colour of this sample might be the result of the competition between Mg and Pr species for the zircon-lattice positions. The crystal size of Mg²⁺ ions may support this possibility.

Table 2 reports the CIE $L^*a^*b^*$ parameters of the pigments fired at 1200 °C. The yield of yellow colour is

Table 2
CIE $L^*a^*b^*$ parameters of 1200 °C heated samples

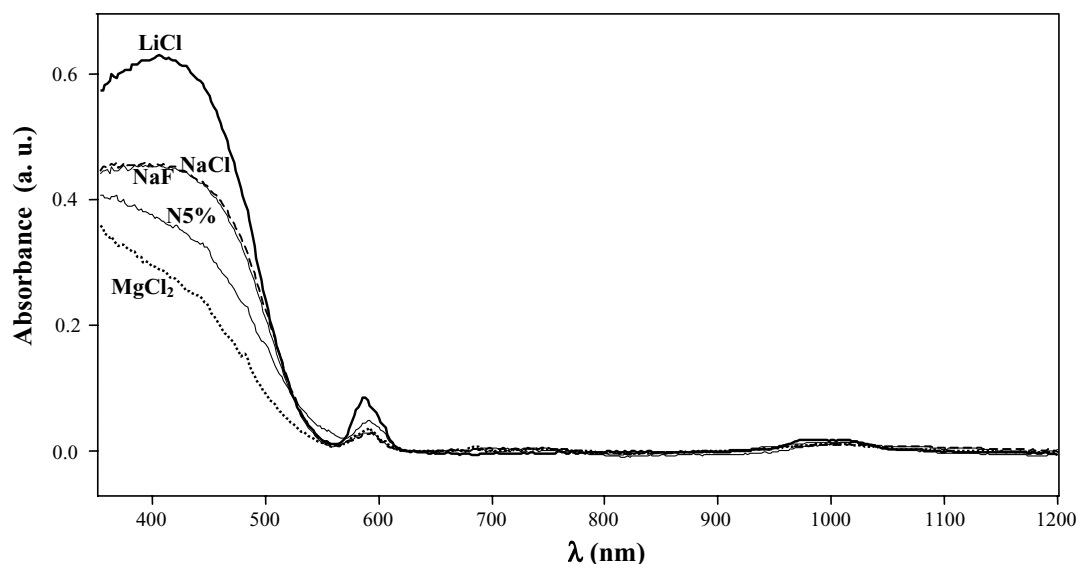| Sample | CIE | | |
| --- | --- | --- | --- |
| | $L^*$ | $a^*$ | $b^*$ |
| N3% | 94.8 | 5.2 | 31.6 |
| N5% | 94.3 | 5.0 | 27.8 |
| N10% | 95.9 | 3.7 | 26.2 |
| N5%NaF | 94.1 | 5.0 | 38.3 |
| N5%NaCl | 90.9 | 5.7 | 38.3 |
| N5%MgCl₂ | 97.2 | 2.7 | 21.6 |
| N5%LiCl | 92.3 | 4.7 | 46.7 |

Fig. 8. Diffuse reflectance spectra of 1200 °C samples prepared with different mineralizers.

described by the value of the $b^*$ parameter, more positive $b^*$ values corresponding to more intense colour hues. All samples are characterized by high brightness ($L^*$ value); the largest $L^*$ values occur for the samples with Pr/Zr 10% and the ones with $MgCl_2$ as the mineralizer. These latter samples are characterized also by lower values of $a^*$ and $b^*$, indicating a tendency to achromatism. Better results, in terms of hue of yellow colour, are obtained with the use of LiCl as the mineralizer; the use of NaCl and NaF lead to samples with similar values for CIE parameters.

As concerns the effect of modification of metal concentration on sample colour (samples P3, P4 and P5), it can be seen that P4 and P5 are described by similar $L^*$, $a^*$ and $b^*$ values, indicating that better colour appearance was obtained with lower metal contents (3 and 5%).

## 4. Conclusions

Pr doped zircon pigments were prepared by a sol–gel procedure for variable Pr concentrations and with the addition of several mineralizers.

The presence of Pr was observed to promote the crystallization of the zircon phase, in agreement with literature results and with the effects provoked by other doping metals (V, Fe). However, the promoting effect did not increase regularly with the Pr amount but showed a maximum for intermediate concentrations (3%). The Pr amount relative to the best zircon promotion corresponded also to the largest sizes of zircon and tetragonal zirconia crystallites. At the same time VIS–NIR reflectance spectra showed that in the region 400–500 nm the absorption intensity increased regularly up to 3% Pr content and then decreased for the samples containing larger Pr amounts. Further, in the case of these latter samples, the presence of shoulders in the spectra at

495, 481 and 483 nm showed that Pr ions, besides being distributed into the host matrix, were present also in separate crystalline phases. The presence of separate Pr containing phases (either encapsulated into the host lattice or not) was appreciable also in X-ray spectra in the case of the larger Pr amounts and EDX analyses showed, at the same time, a non-homogeneous distribution of the metal.

The addition of mineralizers to the reacting sol–gel mixture provokes in any case a definite increase in the amount of zircon formed. The addition of NaCl and NaF, besides promoting the growth of $ZrSiO_4$, produces an intense ochre-yellow colour. At 5% Pr the analysis by VIS–NIR shows that Pr is entirely distributed in the zircon lattice. The role of these two mineralizers can be that of extending the solubility range of Pr species in the zircon lattice. The samples obtained in the presence of LiCl contain the largest amount of zircon phase with respect to the other samples and present a brilliant canary-yellow colour. This samples show the largest Pr(III) content and the total absence of segregated phases. The addition of Mg salts supports the formation of the zircon phase but gives rise to a whitish colour. If as suggested by Ocaña et al.[3] the intense yellow colour of the NaF samples is the result of the stable formation of a Pr(IV)-zircon solid solution, then in the case of Mg salts a possible competition between Mg and Pr might cause the segregation of Pr(III) containing phases decreasing the colour intensity.

the elaboration of X-ray spectra by the program QUANTO is gratefully acknowledged.

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