

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/228108773>

Nonconventional Synthesis of Praseodymium-Doped Ceria by Flux Method

ARTICLE *in* CHEMISTRY OF MATERIALS · JANUARY 2000

Impact Factor: 8.35 · DOI: 10.1021/cm990128j

CITATIONS

45

READS

62

5 AUTHORS, INCLUDING:



Federica Bondioli

Università degli studi di Parma

159 PUBLICATIONS **1,727** CITATIONS

SEE PROFILE



Cristina Leonelli

Università degli Studi di Modena e Reggio E...

316 PUBLICATIONS **2,745** CITATIONS

SEE PROFILE

Nonconventional Synthesis of Praseodymium-Doped Ceria by Flux Method

Federica Bondioli,* Anna Bonamartini Corradi, and Tiziano Manfredini

Department of Chemistry, Faculty of Engineering, Via Campi 183, 41100 Modena, Italy

Cristina Leonelli

Department of Materials Engineering and Production, University of Naples "Federico II", Piazzale Tecchio 80, 80125 Naples, Italy

Renzo Bertoncello

Department of Inorganic, Metallorganic and Analytical Chemistry, Via Loredan 4, 35131 Padova, Italy

Received March 2, 1999. Revised Manuscript Received October 19, 1999

The synthesis of $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$ solid solutions by three different methods (flux method, coprecipitation, and solid-state reactivity) has been investigated to establish optimal preparation conditions. The system studied was chosen because of its thermal and chemical properties and because of its utility as red and orange ceramic pigments. The results obtained showed that the $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$ solid solution can be achieved using all three preparation techniques. The three synthesis methods—flux, coprecipitation, and solid-state reaction—vary with regard to both the time and temperature used in the heat treatments, and the characteristics of the powders obtained (purity, morphology, granularity). In the preparation of powders by the flux method, the use of molten salts ensures a notable acceleration of the reaction kinetics. We found that the eutectic NaOH–KOH is particularly effective. The samples obtained exhibited a clearly spherical shape together with a considerable fineness. This nonconventional technique thus enables the synthesis of extremely homogeneous compounds that are especially suitable in industrial application such as pigments used in decorative ceramic materials. The solid solutions obtained are, indeed, able to develop an intense red coloring, especially these with a Pr content of 5 mol %.

Introduction

In the ceramic industry, highly refractory solid solutions, such as those formed by ZrO_2 , CeO_2 , and R_2O_3 ($\text{R} = \text{Al}$, Cr , etc.) with chromophore cations, are difficult to synthesize by calcination of raw materials in air below 1300–1500 °C without synthesis additives (mineralizer, generally fluorides) to lower the synthesis temperatures. Therefore, the possibility of obtaining them at lower temperatures and without mineralizers is of great interest as it could result in large reductions of toxic gas emissions and minimize investment in high-temperature technology.

The system studied here ($\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$, 0–10 mol % praseodymium) was chosen not only for its thermal and chemical properties but also (from an industrial point of view) because of its utility as red and orange ceramic pigments. Studies concerning this system as inorganic pigment are few, and those available^{1,2} involve only solid-state reactivity or coprecipitation synthesis.

In this work, molten salts, coprecipitation, and solid-state reaction methods we tested to establish the optimal preparation conditions for compounds of $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$ compositions. The flux method is a well-known method used for single-crystal growth³ but has seldom been applied to the synthesis of nanocrystalline particles. The method consists of adding precursors in the required ratio to a molten salt mixture which accelerates the kinetics of formation of the desired compounds by enhancing diffusion coefficients.^{4,5} This method is very simple and can lead to powders with desirable characteristics, including very fine size, narrow size distribution, single-crystal particles, high purity, and good chemical homogeneity. The influence of the type of molten salts used on the morphology and particle size distribution of the powders is discussed. In particular, the powders obtained were characterized with the objective of explaining the formation mechanism of the structure, its synthesis temperature, stability, and color efficiency.

(1) Olazcuaga, R.; Le Polles, G.; El Kira, A.; Le Flem, G.; Maestro, P. *J. Solid State Chem.* **1987**, *71*, 570.

(2) Olazcuaga, R.; Le Flem, G.; Alarcon, J. *Bol. Soc. Esp. Ceram. Vidrio* **1993**, *32*(4), 251.

(3) Stool, S. L.; Stacy, A. M.; Torardi, C. C. *Inorg. Chem.* **1994**, *33*(13), 2761.

(4) Durand, B.; Roubin, B. *Mater. Sci. Forum* **1991**, *73–75*, 663.

(5) Geantet, J. E.; Kerridge, D. H.; Decamp, T.; Durand, B.; Breysse, M. *Mater. Sci. Forum* **1991**, *73–75*, 693.

Experimental Section

Sample Preparation. The molten salt reactions were carried out in alumina crucibles at temperatures between 400 and 600 °C. As solvents, KOH/NaOH, NaNO₃/KNO₃, and LiCl/KCl eutectic mixtures were chosen because of their low melting temperatures (170, 225, and 355 °C respectively) and their basic properties necessary to form oxides.⁶ Powders containing praseodymium in the 0–10 mol % range were obtained from cerium(IV) ammonium nitrate ((NH₄)₂Ce(NO₃)₂, RPE, Carlo Erba, Milan, Italy) and praseodymium(III) nitrate (Pr(NO₃)₃·6H₂O, RPE, Carlo Erba, Milan, Italy). The precursors, in the required stoichiometry, were added in a 1:1 weight ratio to the molten salts at the reaction temperature and the melt was maintained at the maximum temperature for different times (15, 30, 60, and 120 min). After the melt was quenched to room temperature, the reaction products (hereafter indicated from the melt eutectis, hydroxides FH, nitrates FN, and chlorides FC) were separated from the soluble alkali salts by washing with distilled water and then oven-dried at 120 °C.

Powders with the same stoichiometry were prepared using the coprecipitation method and by solid-state reaction starting from oxides.

During the coprecipitation process, hydroxides were precipitated by changing the pH of the nitrates solution to 9 by using ammonia (NH₄OH, RPE, Carlo Erba, Milan, Italy). The hydroxides, carefully washed with distilled water, were air-dried at 120 °C and then ground in an agate mortar. The powders obtained (A) were calcined in an electric furnace for different times (30, 60, and 120 min) and at different temperatures (600, 700, 800, and 1000 °C).

Solid-state reaction of the oxide mixtures, commonly adopted for ceramic pigment preparation produced samples (B) by mechanical homogenization of cerium oxide (CeO₂, Ferguson Wild, The Netherlands) and praseodymium oxide (Pr₆O₁₁, RPE, Carlo Erba, Milan, Italy) followed by calcining in an electric oven for different times (30, 60, and 120 min) and at different temperatures (ranging from 1000 to 1450 °C).

Sample Characterization. To investigate the structure and crystallinity of the samples obtained by the three different methods, the powders were analyzed with a computer-assisted X-ray (Cu K α) powder diffractometer, XRD (Philips PW 3710, The Netherlands). The XRD patterns were collected in the 20–120° 2 θ range at room temperature. The scanning rate was 0.005°/s and the step size was 0.02°. The lattice parameters were determined by a least-squares refinement. Crystallite size was estimated from X-ray line broadening measurements;⁷ it was calculated using the CeO₂ (2,2,0) diffraction line according to the Sherrer formula:

$$D = \frac{0.9\lambda}{(\beta \cos \theta)}$$

where D is the crystallite size, λ is the wavelength of the X-ray (Cu K α , 1.542 Å), θ is the diffraction angle, and β is the corrected half width given by

$$\beta^2 = \beta_m^2 - \beta_s^2$$

where β_m is the measured half-width, and β_s is the half-width of a standard CeO₂ sample with a known crystal size greater than 100 nm.

Sample morphology and microstructure were examined by scanning electron microscopy, SEM, (Philips XL40, The Netherlands) with EDS (EDAX, CDU LEAP, Carrboro, NC) equipment and by transmission electron microscopy, TEM, (Philips EM400, The Netherlands). For TEM analysis, specimens were prepared by dispersing the as-obtained powder in

distilled water and then placing a drop of the suspension on a copper grid coated with a transparent polymer, followed by drying.

Surface area analyses were performed on the as-prepared powders by the BET⁸ method (Micromeritics Instrument, Gemini 2360, Norcross, GA), using nitrogen as an adsorbate. Particle size was also calculated from the data of specific surface area, using the equation:⁹

$$\phi = \frac{6}{S\rho}$$

where ϕ is the average diameter of the spherical particle, S is the surface area of the powder, and ρ is the theoretical density of ceria (7.184 g/cm³).¹⁰

To confirm that solid solution formation had taken place, leaching tests in boiling solutions of concentrated (36 wt %) hydrochloric acid were performed. The Pr content of the solutions was determined by ICP spectroscopy (Varian, mod. Liberty 200, Australia).

To determine the oxidation state of the praseodymium ion in the powders obtained by the three different methods, X-ray photoelectron spectra (XPS) were recorded in a spectrometer (VG Escalab MK II, UK) using non-monochromatized Al K α radiation (1486.6 eV) at 13 kV with a current of 20 mA on samples containing 10 mol % dopant. The working pressure was lower than 1×10^{-7} Pa. The spectrometer was calibrated by assuming the binding energy (BE) of the Au 4f_{7/2} line at 83.9 eV with respect to the Fermi level. Samples exhibited an average shift of about 4 eV due to surface charging. The 1s photoelectron peak from carbon, due to hydrocarbon contamination ($E = 284.80$ eV¹¹), was used as an internal reference for the charging effects. XPS spectra were carried out on pellets obtained by pressing powdered samples. The reproducibility of results was assured by repeating experiments on the same pellets. During the analysis, detailed scans were obtained for the C 1s, O 1s, Pr 3d_{5/2}, Pr 3d_{3/2}, Pr 4s, Ce 3d_{5/2}, and Ce 3d_{3/2} regions. The spectra were analyzed with a Shirley-type background subtraction¹² and were fitted using a program based on Gaussian–Lorentzian peak shape. To determine the oxidation states of cerium and praseodymium in the powders obtained by the three different methods, the peak positions were compared to reference standards of Pr₆O₁₁ and CeO₂, and to literature data.^{13,14} As far as Pr is concerned, the 3d_{5/2} line allows us to distinguish between PrO₂ (BE = 935.3 eV) and Pr₂O₃–Pr₆O₁₁ (BE = 932.9–933.0 eV); while the Pr 4s line allows us to distinguish among Pr₂O₃ (BE = 304.5 eV), Pr₆O₁₁ (BE = 302.7 eV), and PrO₂ (BE = 305.9 eV).

The thermal behavior of the samples obtained was studied by thermogravimetry and differential thermal analysis in air at a heating rate of 20°/min, using simultaneous TGA/DTA equipment (Netzsch STA 409, Selb, Germany).

To investigate the color and optical properties of the powders, the samples were analyzed with a UV–vis spectrophotometer with analytical software for color measurements (Perkin-Elmer, mod. Lambda 19, Norwalk, CT).

Results and Discussion

Powder Characterization. (1) *Flux Method.* To evaluate the effective precipitation of praseodymium in

(8) Svarovsky, L. *Powder Testing Guide: methods of measuring the physical properties of bulk powders*; Published on behalf of the British Materials Handling Board by Elsevier Applied Science: London, 1987.

(9) Kadera, K. In *Powders (Theory and Applications)*; Kubo, K., Suito, E., Nakagawa, Y., Hayakawa, S., Eds.; Maruzen: Tokyo, Japan, 1962.

(10) Zhou, Y. C.; Rahaman, M. N. *J. Mater. Res.* **1993**, 8 (7), 1698.

(11) Seah, M. P.; Smith, G. C. *Practical Surface Analysis*; Briggs, D., Seah, M. P., Eds.; Wiley: Chichester, 1990.

(12) Shirley, D. A. *Phys. Rev.* **1972**, 55, 4709.

(13) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. *Handbook of X-ray Photoelectron Spectroscopy*; Chastain, J., Ed.; Perkin-Elmer Corp.: Eden Prairie, MN, 1992.

(14) Sarma, D. D.; Rao, C. N. R. *J. Electron Spectrosc.* **1980**, 20, 25.

(6) Gopalan, K.; Virkar, A. J. *Electrochem. Soc.* **1993**, 140 (4), 1060.

(7) Klug, P.; Alexander, L. E. *X-ray Diffraction Procedure*; Wiley: New York, 1954; Chapter 9.

Table 1. Praseodymium (Pr) Content of the Washing Water of the Powders $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_2$ Obtained by the Flux Method

sample	T (°C)	t (min)	Pr (mol %)
FN	400	120	73.04
FN	600	15	0.008
FN	600	120	0.003
FC	400	120	99.89
FC	600	15	0.014
FC	600	120	0.004
FH	400	15	0.28
FH	400	120	0.08
FH	600	15	0.004
FH	600	120	0.001

Table 2. Release of Praseodymium from Powders Obtained by Flux Method after Leaching Test

sample	T (°C)	t (min)	Pr (mol %)
FN-5 mol % Pr	600	120	5.53
FN-10 mol % Pr	600	120	7.52
FC-5 mol % Pr	600	120	5.48
FC-10 mol % Pr	600	120	7.32
FH-5 mol % Pr	400	120	5.10
FH-10 mol % Pr	400	120	6.95
FH-5 mol % Pr	600	120	0.16
FH-10 mol % Pr	600	120	0.20

Table 3. Optimal Process Conditions for the Three Different Synthesis Methods to Obtain the $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$ Powders

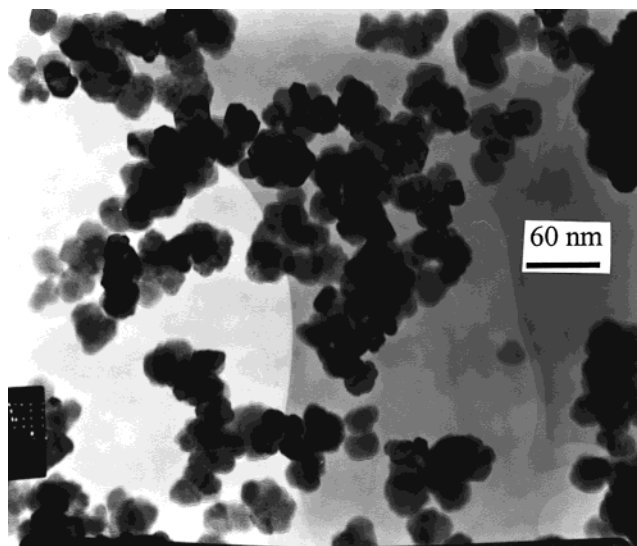
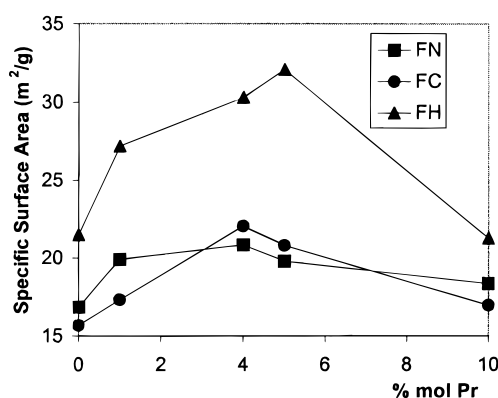
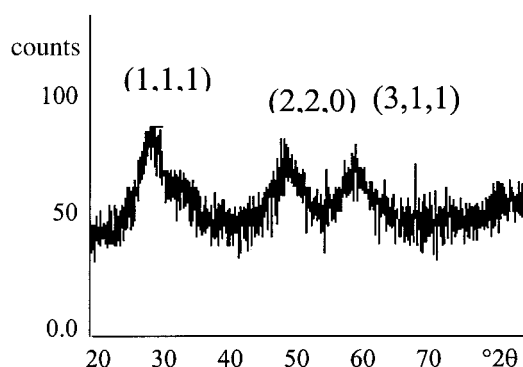
synthesis method	T (°C)	t (min)
hydroxides flux	600	30
nitrate flux	600	120
chlorides flux	600	120
coprecipitation	600	120
solid state	1300	120

Table 4. Particle Size of $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_2$ Powders Calculated by Different Methods

methods	flux used		
	hydroxides	nitrate	chlorides
TEM (nm)	22	30	15
XRD (nm)	18	25	16
BET (nm)	23	28	20

the different flux mixtures, the waters used for washing the reacted powders were analyzed by ICP spectroscopy. The results (Table 1) showed that the praseodymium found in the washing waters as a soluble salt, in general, decreases as the temperature of the thermal treatment is increased. In particular, the praseodymium ion is not completely precipitated using nitrate and chloride fluxes at 400 °C, also for prolonged heat treatment, as occurs at 600 °C even for shorter times (15 min). On the contrary, the hydroxide flux mixture ensures a much higher reactivity of praseodymium at 400 °C independent of composition. Such behavior is due to the very low melting temperature, 170 °C, of the eutectic KOH/NaOH together with the lower solubility of hydroxides with respect to the chlorides and nitrates.

To investigate the nature of the samples obtained in the flux mixtures, all samples were subjected to X-ray powder diffraction. However the XRD patterns were not able to clearly define the conditions of the solid solution formation, since the peaks of the two starting oxides are found close to the diffraction angles themselves. Leaching tests in boiling solutions of concentrated (36 wt %) hydrochloric acid may be considered suitable to evaluate the solid solution formation,¹⁵ the effective diffusion of

**Figure 1.** Micrograph TEM of the $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_2$ powder obtained by hydroxides flux.**Figure 2.** Specific surface area of the powders obtained by flux method.**Figure 3.** XRD pattern of the coprecipitate dried powders.

praseodymium in the ceria lattice and the stability of the powders obtained. This selective chemical attack helps to determine the amount of unreacted praseodymium oxide. Free praseodymium oxide (Pr_6O_{11} , Pr_2O_3 , and PrO_2) is easily solubilized in hydrochloric acid to form soluble praseodymium chloride. In contrast, ceria is a very poorly soluble compound, being stable in most inorganic acids even in concentrated solutions. Tests for the FN and FC powders were carried out only on the samples obtained at the maximum temperature (600

(15) Bondioli, F.; Ferrari, A. M.; Leonelli, C.; Manfredini, T. *Mater. Res. Bull.* **1998**, *33* (5), 723.

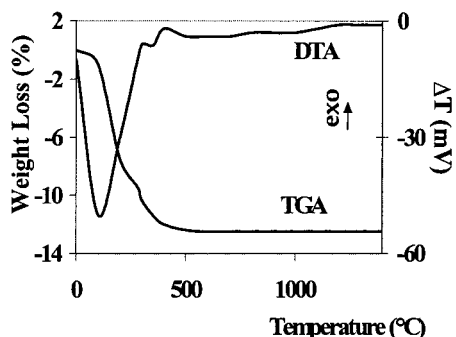


Figure 4. TGA and DTA curves of the coprecipitate dried powders.

°C), whereas for the FH powders the samples obtained at 400 °C were also characterized. As shown in Table 2, a lower praseodymium solubility is demonstrated in samples obtained at 600 °C, as compared to 400 °C, for a heating time greater than 120 min for all the fluxes used, although the best results were achieved with the hydroxide flux. The XPS measurements, performed on the powders obtained by all three preparation techniques utilized, showed that there is no evidence of the presence of a different oxidation state of Pr(IV).¹⁴ EDS analysis showed chemically homogeneous powders, and the absence of alkali ions indicates the efficiency of the washing treatment.

The TEM analysis showed that the optimized powders (Table 3) had nanosized faceted polyhedral morphologies, independent of the flux used (Figure 1). The particles also appear to be fairly uniform in size and particle aggregation is not exhibited. To evaluate the influence of the type of fluxes used on the particle size distribution, maximum diameters of more than 100 particles in TEM micrographs were measured. The particle size distribution is very narrow ranging from 10 to 20 nm. The as-calculated average particle size was reported in Table 4.

The XRD analysis of the powders showed the same crystallinity for all the fluxes used. The crystal sizes of the synthesized solid solution powders, calculated by the Sherrer's formula, are reported in Table 4. Specific surface areas of the powders are plotted in Figure 2. The values generally increase as the praseodymium content of the powders rise to 5 mol %. The specific surface area values of the powders with a Pr content of 10 mol % are always smaller, independent of the flux used. With regard to the effect of the type of flux, in confirmation of the results from the XRD calculations, the powders obtained using the hydroxide flux have a greater specific surface area. Assuming the particles are closed spheres, reasonable hypothesis as highlighted by the TEM observation of the particle shape, with smooth surfaces and using a CeO₂ density of 7.184 g/cm³, the average diameter of the spheres calculated from BET values are reported in Table 4.

The small differences between the average particle size of the synthesized powders as determined by X-ray line broadening and as measured by TEM observation is a strong evidence of an absence of grain agglomeration. These results, confirmed by specific surface area values elaboration, agree with those reported in the literature regarding the synthesis of pure ceria powders obtained using the flux method,¹⁶ indicating that the

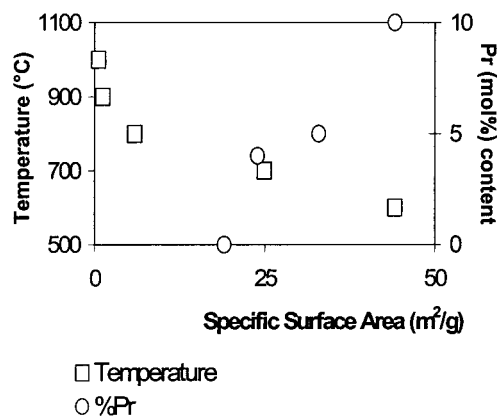


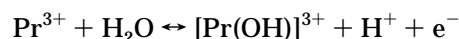
Figure 5. Specific surface area of powders obtained by coprecipitation as a function of the Pr (% mol) content and of the temperature (°C).

Table 5. Unit Cell Parameter *a* Values

composition	<i>a</i> (nm)	Δ <i>a</i> (nm)
CeO ₂	0.5416	±0.0003
Ce _{0.95} Pr _{0.05} O ₂	0.5407	±0.0004
Ce _{0.9} Pr _{0.1} O ₂	0.5388	±0.0008

praseodymium ion, in the concentrations used, does not affect the ceria powders morphology.

(2) *Coprecipitation Method.* Figure 3 shows the XRD pattern of the dried hydroxides obtained by coprecipitation. Note that immediately after drying the powders already displayed all of the major reflections of CeO₂ with a fluorite structure, as previously observed by Chen et al.¹⁷ Since the starting salt is Pr(NO₃)₃, the praseodymium ion, that is Pr(IV) in the powders obtained as evaluated by XPS measurements, it requires the oxidation of Pr³⁺ to Pr⁴⁺ in the solution. This may be due to the addition of large quantities of NH₄OH which increase the pH values, therefore enhancing the oxidation of the ion according to the following mechanism:



$$E^\circ = -2.86 \text{ V}$$

The very high pH value also favors the hydrolysis of the relatively large Pr³⁺ ion. Apparently these combined factors are sufficient to induce a Pr oxidation. The subsequent precipitation reaction of the Pr⁴⁺ ion seems entirely similar to that put forward for the Ce⁴⁺ ion.¹⁷

The TGA and DTA analyses (Figure 4) indicated two endothermic weight losses corresponding, respectively, to the elimination of the humidity (100 °C) and the adsorbed (400 °C) water. The sharp exothermic peak at about 450 °C, is not related to a weight loss and is probably due to the formation of the (Ce,Pr)O₂ solid solution. The analysis, performed up to 1400 °C, showed the effective thermal stability of the solid solution obtained. A different amount of praseodymium does not lead to any qualitative differences in the DTA/TGA curves.

As X-ray diffraction could not be used, the effective solid solution formation was determined by SEM and EDS analysis and correlated to the leaching test results.

(16) Bondioli, F.; Leonelli, C.; Manfredini, T. *Mater. Res. Bull.* **1999**, 34 (15), in press.

(17) Chen, P.-L.; Chen, I.-W. *J. Am. Ceram. Soc.* **1993**, 76 (6), 1577.

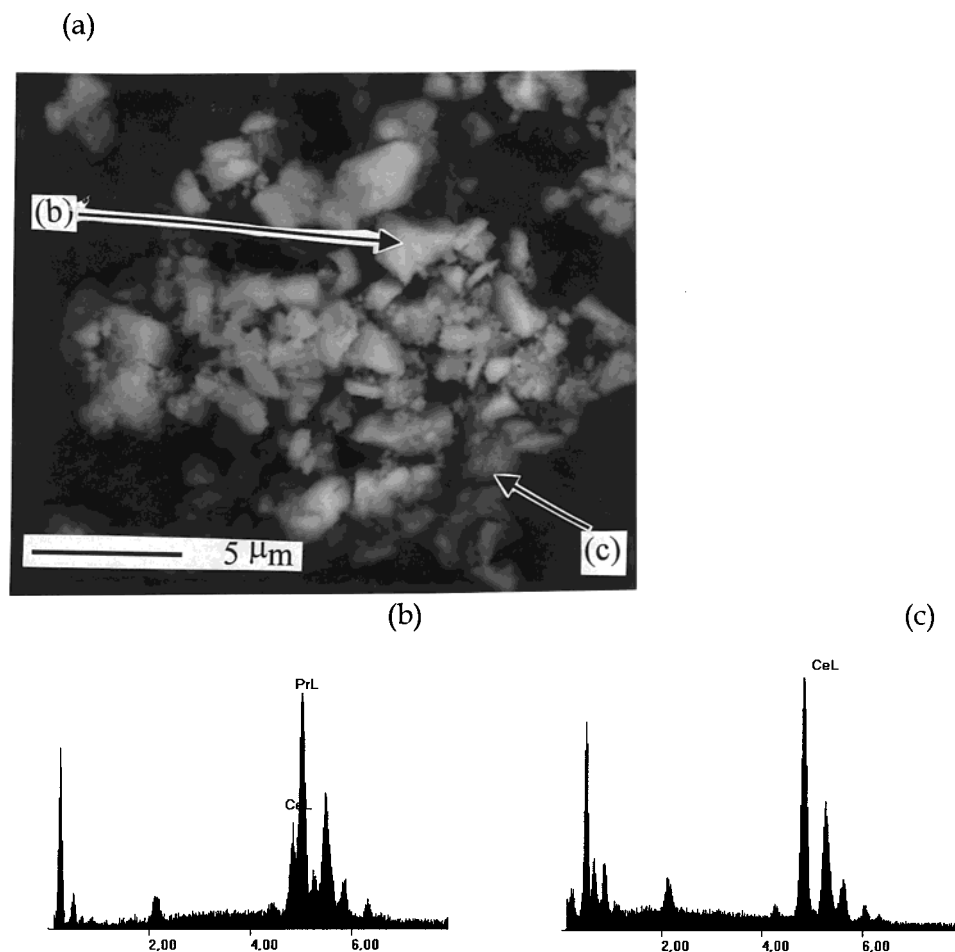


Figure 6. Micrograph (a, 5000 \times) and EDS analysis (b and c) of powders obtained by ceramic method (1000 $^{\circ}$ C, 2 h).

From the analyses performed, the temperature at which the solid solution is formed is obtained by heating the samples for 2 h at 600 $^{\circ}$ C (release of Pr < 3%), confirming the DTA peak interpretation. The specific surface areas of the powders as a function of temperature and praseodymium content are shown in Figure 5. The values increase at 600 $^{\circ}$ C as the praseodymium content increases, whereas the $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_2$ compositions decrease with an increase in temperature as the particles of the solid solution begin to coalesce and compact. The powders as-obtained are characterized by a high degree of purity, as shown by EDS and XPS analyses, even if the coprecipitation method has little control over the shape and size of the precipitate, owing to the rapid change in solution concentration and the localized, discontinuous nature of ligand introduction and reaction.

The XRD analysis showed the shift of the peaks of cerium(IV) oxide. In particular, increasing the powder's Pr content caused the distances between ceria planes to decrease, indicating a contraction of the elementary cell following the introduction of the Pr^{4+} ion substituting for Ce^{4+} , due to the reduction of characteristic size of the ions of the lanthanide series that have the same charge. Table 5 shows the a lattice parameter obtained after data refinement: according to Vegard's law, the change in the unit cell parameter is linear in composition ($r = 0.9794$) and decreases with praseodymium content.

(3) Solid-State Reaction. As mentioned above, an effective solid solution formation was determined by SEM and EDS analysis and correlated with the leaching test results. From the analyses performed, a solid solution formation by this synthesis method occurs at 1300 $^{\circ}$ C. The powders obtained at lower temperatures show (Figure 6) the typical spongy crystals of praseodymium oxide as well as cerium oxide. Only at temperatures higher than 1300 $^{\circ}$ C (Figure 7) can homogeneous powders be achieved. These powders are characterized by the presence of the solid solution alone. In particular, the powders obtained are composed of aggregates of size around 10 μm . However leaching test results show that, even prolonged heat treatments (2 h) at 1300 $^{\circ}$ C are not sufficient to achieve a complete transformation of the reagents in the solid solution (release of Pr > 5%).

The XRD patterns showed the shift of the peaks of cerium (IV) oxide due to the diffusion of Pr^{4+} in the ceria crystal structure. The values of the lattice parameter a obtained after data refinement agree with the data reported in Table 5. The XPS measurements confirm the presence of only Pr(IV).

Color of the Obtained Powders. Diffuse reflectance spectra obtained on the powders (Pr content 0–10 mol %) are shown in Figure 8. The presence of the tetravalent Pr ion in the host lattice results in the occurrence of broad absorption bands in the spectra.

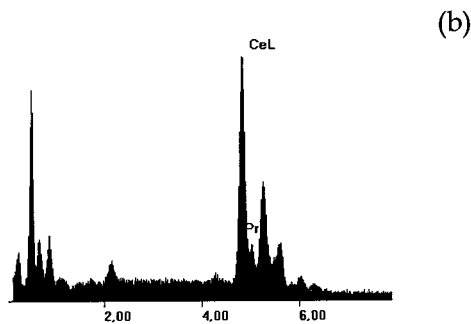
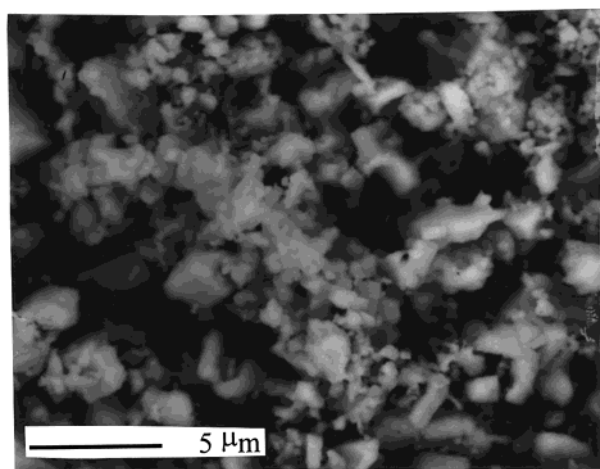


Figure 7. Micrograph SEM(a, 5000 \times) and EDS analysis (b) of traditional powders (1300 $^{\circ}$ C, 2 h).

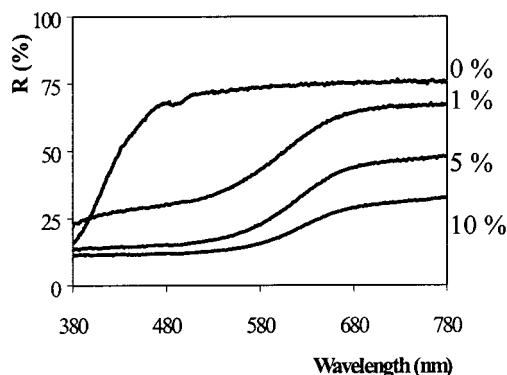


Figure 8. Diffuse reflectance spectra obtained for various compositions.

According to Jørgensen and Rittershaus,¹⁸ the red color of the praseodymium-doped samples is related to a charge-transfer band due to an electron transfer from the ligand orbitals to the praseodymium cation. The evolution of the diffuse reflectance spectra for samples of a $0 < x < 0.10$ composition shows how the position of the reflection edge critically depends on the praseodymium content.¹⁹ It is red-shifted with increasing Pr^{4+} content. The red color obtained corresponds to powders with a strong absorption for $\lambda < 600$ nm; beyond this value a steep slope of the reflection band can be observed that decreases as the praseodymium content increases. The trend observed is independent of the method of synthesis used.

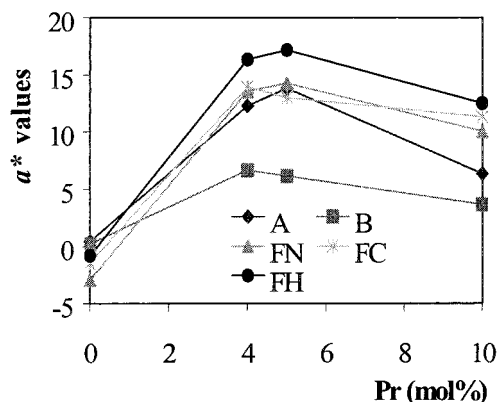


Figure 9. a^* values vs composition and synthesis methods used.

On the basis of the theory of the trichromacy of visual matching, the color can be measured in terms of the relative amounts of three primary colors (X for the red, Y for the green, and Z for the violet), which can be mixed additively to match each wavelength of the visible spectrum.²⁰ To specify the color of a powder, the CIE-Lab method is usually accepted. The method defines a color through three parameters, L^* , a^* , and b^* , measuring brightness, red/green and yellow/blue color intensities, respectively, a mathematical elaboration of the tristimulus values X , Y , Z .²¹ The color measurements, performed on all the powders obtained, showed systematic changes in the CIE-Lab parameters directly correlated with the structural alterations of the solid solutions as a function of the composition of the system, of the method for obtaining the powders, and of the calcination time and temperature.

The a^* parameter, in relation to the scale extending from green ($-a^*$) to red ($+a^*$), is undoubtedly the most significant parameter for defining the color change as a function of the variables considered. Figure 9 shows the variation of the a^* parameter for powders of types A, B, FN, FC, and FH. The a^* parameter for type A samples calcinated at 800 $^{\circ}$ C for 2 h reaches maximum value at a praseodymium content of 5 mol %. With higher praseodymium content, the value of a^* tends to diminish appreciably. With regard to type B samples calcinated at 1300 $^{\circ}$ C for 2 h, the a^* parameter reaches a maximum value at a praseodymium content of 4 mol %, tending to fall slightly at 5%, thereafter decreasing markedly when the praseodymium content attains 10%. For the powders obtained using the flux method heat treated for 2 h at 600 $^{\circ}$ C, a^* reaches a maximum value at a praseodymium content of 5 mol % for FN and FH type samples, while for FC type samples the value of a^* is slightly greater at 4 mol %.

The results obtained also show how the powders of the FH series, prepared using the flux method, develop more red coloring for all praseodymium contents.

The L^* and b^* parameters vary slightly (Table 6) as the praseodymium content increases, justifying the gradual darkening of the samples. Table 6 shows that L^* and b^* parameters generally decrease as the Pr content of the powders increases, regardless of the

(18) Jørgensen; Rittershaus. *Mat. Fys. Medd. K. Dan. Vidensk. Selsk.* **1967**, 35, 15.

(19) Olazcuaga, R.; El Kira, A.; Le Flem, G.; Maestro, P. *C. R. Acad. Sc. Paris* **1986**, 303 (5), série II, 361.

(20) Johnston, R. M. In *Pigment handbook*; Putton, T. C., Ed.; Wiley-Interscience Publication: New York, 1973; Vol. 3, pp 229–88.

(21) Hunter, R. S. *J. Opt. Soc. Am.* **1958**, 48, 985.

Table 6. L^* and b^* Hunter Values

samples	Pr (%mol) content					
	L^*			B^*		
	4%	5%	10%	4%	5%	10%
A (800 °C, 2 h)	57.39	56.62	53.91	5.22	4.83	3.41
B (1300 °C, 2 h)	59.65	53.41	51.41	10.42	11.19	4.62
FN (600 °C, 2 h)	52.75	52.62	45.31	12.42	12.8	7.82
FC (600 °C, 2 h)	58.39	56.15	50.16	14.17	15.71	10.68
FH (600 °C, 2 h)	54.59	54.74	57.16	14.04	14.25	14.61

processing method used. The L^* and b^* values of the powders obtained using the hydroxide flux have a different trend and remain almost constant with an increasing praseodymium content. This trend can be related to the higher reactivity of this flux. In fact, in these samples (as shown by the lowest praseodymium release after leaching test, Table 2), black unreacted Pr oxides were not detected.

However, for pink and reddish colors, a complex function of the L^* and a^* values, there are some real difficulties, and more understandable and usable information can be obtained by employing the Kubelka–Munk absorption function, obtained from the absorption spectra.²² This parameter is given mathematically as

$$A = \frac{(1 - r)^2}{2r}$$

where A is the Kubelka–Munk absorption of the powder and r is the corrected diffuse reflectance, taking into account specific and internal reflectance, given as

$$r = \frac{R - k_1}{1 - k_1 - k_2(1 - R)}$$

where k_1 is the Fresnel reflection coefficient²³ which is 0.04 for ceramic surfaces, k_2 is an empirical constant for which 0.4 has proved to be generally satisfactory,²⁴ and R is the measured diffuse reflectance.

The Kubelka–Munk data confirmed the relation between color and praseodymium content of the pigments (Figure 10); in particular, from analysis of the trends obtained, the powders synthesized using the flux method show a greater absorption and, among them, those of FH type display the highest values.

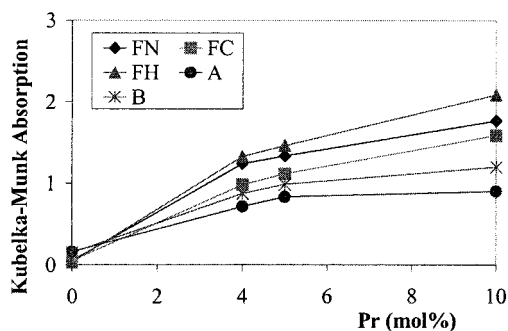


Figure 10. Kubelka Munk parameter vs composition and synthesis methods used.

Conclusions

Nanosized and well-crystallized $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$ ($x = 0-10$ mol %) powders were prepared using the flux method at a relatively low temperature, 600 °C, in different eutectic mixtures of molten salts (KOH/NaOH, $\text{NaNO}_3/\text{KNO}_3$, and LiCl/KCl). Such a technique allowed atomic-scale homogenization, new compound formation, and powder precipitation at a time (2 h). Impurities, such as K or Na, were eliminated by washing, and crystalline phases other than solid solution, were not observed. The dimensional range of the powders was very narrow, ranging from 10 to 20 nm, as observed by TEM and confirmed by XRD and BET results. When hydroxides were used as molten salts, the solid solution was synthesized more rapidly with respect to the nitrates or the chlorides eutectics. Moreover, an increase in the host cation content even at lower temperatures was observed. As a consequence, such powders do not contain unreacted Pr_6O_{11} which develops a more intense red-shaded color. With respect to the other synthesis method investigated, the flux method produces powders with enhanced chemical and physical properties.

It can be concluded that with respect to the other synthesis methods that can lead to powders with desirable characteristics, the main advantages of flux method are, like hydrothermal synthesis, not only its lower cost but also the elimination of high-temperature calcination process. Moreover this method does not involve high-pressure apparatus (i.e., for pure ceria 4 h at 10 MPa¹⁰) as for hydrothermal technique.

Acknowledgment. The authors thank Dr. Andrea Vecchi for performing the experimental procedure, and Dr. Paola Miselli, DemoCenter, Modena, for her assistance in obtaining ICP data.

CM990128J

(22) Eppler, D. R.; Eppler, R. A. *Ceram. Eng. Sci. Proc.* **1996**, 17 (1), 77.

(23) Campbell, E. D.; Billmeyer, F. W. *J. Colour App.* **1971**, 1 (2), 39.

(24) McLaren, K. *The Colour Science of Dyes and Pigments*; Hilger, A., Ed.; Bristol, UK, 1986.