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Optical Properties of $Ce_{1-x}Pr_xO_2$ Powders and Their Applications to the Coloring of Ceramics

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The development of red pigments with high temperature stability is of great importance for the ceramic industry. Stabilization of praseodymium (IV) in the refractory oxide CeO_2 leads to cerium-rich solid solutions $Ce_{1-x}Pr_xO_2$ in the red coloration range. Crystallographic and optical properties have been investigated. The detected color is consistent with Jørgensen's model. Thermal stability at high temperature has been studied for various glazes.

The classical red pigments used up to now in the ceramic industry were of two types. Iron oxide (Fe_2O_3 in zircon matrices at 1200°C) and lead oxide (Pb_3O_4 in tin oxide matrices at 1150°C) give pale red or pink colors, while cadmium sulfoselenide Cd (S, Se) or sodium uranates are poisonous and unstable above 900°C. Recent investigations indicate that these materials can be replaced by rare earth refractory oxides providing new stable red colors (*1–3*).

A previous description of the CeO_2–PrO_2 system under various oxygen pressures has shown the possibility to stabilize praseodymium (IV) within cerium dioxide CeO_2. A red material stable at high temperature (1350°C) can be obtained for low praseodymium contents (*4, 5*). Jørgensen and Rittershaus explained the color by ascribing the absorption band appearing at $\lambda < 600$ nm to an electron transfer from the ligands to the chromophore ion (*6*).

In the scope of a general investigation for obtaining new red pigments stable at high temperature, the preparation conditions and optical properties of the cerium rich part of the $Ce_{1-x}Pr_xO_2$ solid solution have been investigated. The coloration mechanism is also discussed.

Experimental

Various methods have been tested in order to establish the best preparation conditions for materials of $Ce_{1-x}Pr_xO_2$ compo-

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sitions (7). They can be prepared from stoichiometric mixtures of oxides (CeO_2, Pr_6O_{11}), nitrates ($Ce(NO_3)$, $6H_2O$; $Pr(NO_3)_3$, $6H_2O$), or coprecipitated oxalates. In all preparation processes the addition of a mineralizing agent (NaF 5% wt) allows lowering of the temperature of the final thermal treatment and results in more homogeneous grain sizes ($\overline{\Phi} = 10\ \mu m$). The $Ce_{1-x}Pr_xO_2$ ($0 \le x \le 0.50$) solid solution has a CaF_2-type structure. Decrease of the a parameter from 5.411 to 5.402 Å ($Ce_{0.50}Pr_{0.50}O_2$) is consistent with substitution of Pr^{4+} for Ce^{4+} and confirms the previous results reported by McCullough on a study of the CeO_2–PrO_2 system under oxygen pressure (4). Structural parameters for the cerium-rich solid solutions are summarized in Table I. For $x \le 0.05$ the powders are intensively red. Beyond $x = 0.05$ an evolution from brick to dark red can be observed. From the ESR and diffuse reflectance spectroscopy no trace of Pr^{3+} could be detected within the $x < x \le 0.10$ range.

Analysis by X-ray fluorescence spectrometry with a Sigma CGR apparatus (Rh tube) was performed on several powders of various compositions. The materials were ground in the presence of resin and then pressed in pellets. The measured Ce and Pr contents were determined on the basis of the results for pure CeO_2 and Pr_6O_{11} taken as standards. As an example, for the sample with nominal composition $Ce_{0.95}Pr_{0.05}O_2$, the average composition obtained from several measurements $Ce_{0.95\pm0.01}Pr_{0.05\pm0.01}O_2$.

TABLE I

STRUCTURAL PARAMETERS FOR THE CERIUM-RICH SOLID SOLUTIONS

Formula	Parameter (± 0.001 Å)	$\overline{\langle Pr–O \rangle}$ (Å) distances
$Ce_{0.99}Pr_{0.01}O_2$	5.411	2.343
$Ce_{0.95}Pr_{0.05}O_2$	5.409	2.342
$Ce_{0.90}Pr_{0.10}O_2$	5.408	2.341

TABLE II

TRICHROMATIC VALUES OF SOME SIGNIFICANT COMPOSITIONS OF THE SOLID SOLUTION $Ce_{1-x}Pr_xO_2$ ($0 < x \le 0.10$)

Pigment	x	y	z	L	a	b
$Ce_{0.97}Pr_{0.03}O_2$	0.41	0.36	0.23	54.0	+14.6	+22.8
$Ce_{0.95}Pr_{0.05}O_2$	0.42	0.35	0.23	40.1	+14.8	+17.8
$Ce_{0.92}Pr_{0.08}O_2$	0.41	0.34	0.24	34.8	+14.5	+13.8
$Ce_{0.90}Pr_{0.10}O_2$	0.40	0.33	0.27	34.6	+13.7	+11.3
HgI_2	0.55	0.36	0.09	53	+77	+44

Optical Properties

Trichromatic Parameters

Color measurements were carried out with an Leucometre LF 90 analyzer using the tristimulus method. The data were given with both CIE (x, y, z) and L, a, b systems (8). In the first system the components x, y, z represent the values associated to the primary colors: red, green, blue. In the L system, L is the lightness ($L = 100$, white; $L = 0$, black), the a and b parameters give the color coordinates ($a > 0$: red; $a < 0$: green; $b < 0$: blue; $b > 0$: yellow). The trichromatic values of some significant compositions of the solid solution $Ce_{1-x}Pr_xO_2$ for $0 < x \le 0.10$ are collected in Table II. For sake of comparison HgI_2 has been taken as red color standard. In both systems, when the praseodymium content increases, the red component (x or a) is slightly modified and the blue component (z or b) increases strongly giving rise to progressive darkness of the samples. As a compromise between two trends, the most attractive red color is obtained for $x \simeq 0.05$.

Diffuse Reflectance Spectra

Diffuse reflectance spectra were recorded on a Cary 17 spectrophotometer in the visible region. The spectra obtained for CeO_2 and $Ce_{0.99}Pr_{0.01}O_2$ are shown in Fig. 1. According to Jørgensen and Rittershaus (6) the occurrence of a red color of the praseodymium-doped sample is related to a charge transfer band due to electron transfer from the ligand orbitals to the praseodymium cation.

The evolution of the diffuse reflectance spectra for pigments of $0 < x \leq 0.10$ composition is given in Fig. 2. The position of the reflection edge depends critically on the praseodymium content. It is red shifted with increasing Pr^{4+} content. This evolution is consistent with the observed charge transfer spectra of tetravalent lanthanide ions in oxides (*9, 10*). The red color obtained for $x \simeq 0.05$ corresponds to a pigment with a strong absorption for $\lambda < 600$ nm; beyond this value a steep slope of the reflection band edge can be observed as for HgI_2, but the slope change decreases with increasing praseodymium content.

Discussion

To improve the understanding of the color mechanism, single crystals have been grown by a flux technique for the material with composition close to $Ce_{0.95}Pr_{0.05}O_2$. The detailed conditions will be described elsewhere (*11*). Whatever the flux (PbF_2 or a $Na_2B_4O_7-NaF$ mixture) red crystals with cubic or octahedral shape are obtained. In both cases X-ray diffraction analysis is consistent with a CeO_2-type structure.

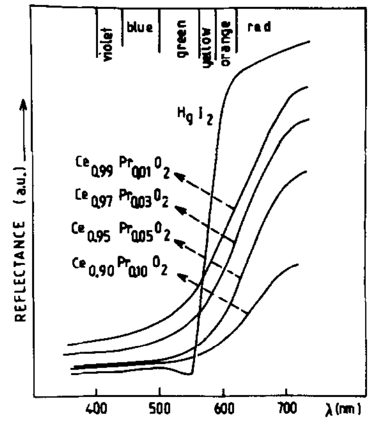

FIG. 2. Diffuse reflectance spectra obtained for HgI_2 and various compositions of the solid solution $Ce_{1-x}Pr_xO_2$.

One of the crystals grown in the borate flux was analyzed by electron microprobe (Camebax) and compared with the standards CeO_2 and Pr_6O_{11}. The results, which gave a composition $Ce_{0.96}Pr_{0.04}O_2$, confirmed that the observed red color is due to the presence of praseodymium in cerium oxide.

The absorption spectrum of the crystal shows a sharp edge at 640 nm corresponding to an optical energy gap of 1.94 eV (Fig. 3). This result can be ascribed to electron

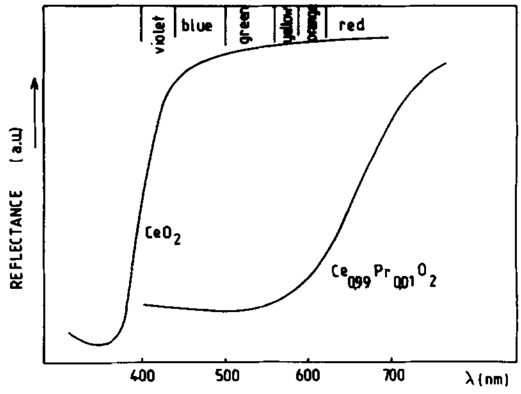

FIG. 1. Diffuse reflectance spectra of CeO_2 and $Ce_{0.99}Pr_{0.01}O_2$.

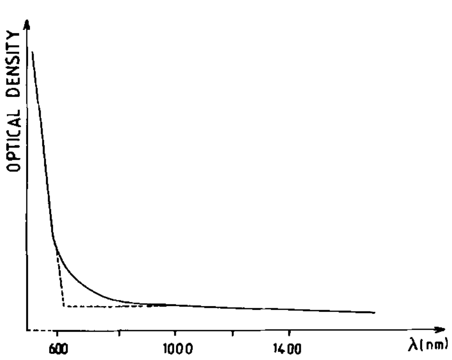

FIG. 3. Absorption spectrum for a $Ce_{0.96}Pr_{0.04}O_2$ single crystal.

transfer from the ligand orbitals to the localized $4f^1$ level of the Pr^{4+} cation according to the band structure model calculated by Koelling for CeO_2 and PrO_2 (*12*).

Applications

Several thermal tests werre carried out on porcelain tiles obtained with different frits. Up to 1000°C the pigments are perfectly stable (*13*). At higher temperature the color tends to be orange. An explanation for the behavior of the pigment under such drastic conditions is being sought.

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