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Preparation and characterization of SiO_2-CeO_2 particles applicable for environment-friendly yellow pigments

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Optical properties of oxide materials based on silica and ceria have attracted attention. For example, cerium oxide-doped silica materials are intensively investigated from the viewpoint of their potential applications as stable luminescent materials for phosphors, scintillators and detectors [1]. Optical absorption properties of the silica-coated CeO_2 materials have also been reported in recent works [2, 3]. In the case of the core-shell-type particles, however, the optical absorbance is dominated by the cerium oxide core and the position of the absorption edge is fundamentally untunable.

In addition, development of new inorganic pigments has been explored recently, because it was enforced by the national laws and regulations in the ecological and toxicological area to replace well-known inorganic pigments containing toxic elements such as Cd, Co, Cr, Hg, Pb, Sb, and Se with more environmentally friendly pigments or less toxic substances [4]. The use of high-performance organics is one way to get several colors, but thermal and ultraviolet (UV)-ray radiation stabilities are not satisfactory for these pigments.

Recently, new pigments without toxic metals from yellow to deep red have been developed, which are based on solid solutions of the perovskites $CaTaO_2N$ and $LaTaON_2$ [5]. Although the pigments themselves are not toxic and show excellent color hue, it is necessary to heat the starting materials in a flow of toxic and inflammable ammonia gas for a long time (20–60 hr) to synthesize them.

In this letter, therefore, we have chosen silica and ceria as fundamental substances to prepare a new nontoxic pigment from a viewpoint of the environmental conservation, and have improved the color by forming their multicomponent system. Not only silica is nontoxic and stable as exists in some minerals with the second Clarke number (28%), but also ceria is a harmless material as applied in glass polishing agents and sunscreen cosmetics. These materials' high stability has been guaranteed for a long time as well as high durability against humidity, and therefore, they have potential to be new pigments. In addition, these pigments could be obtained in a particle form by a simple and safety sol–gel method in an ethanol solvent and there is no need to use toxic and inflammable gases which were essential for the synthesis of the conventional pigments.

Although there are a few reports on the optical properties of silica–ceria thin films [6–8], their potentiality as color materials has not been examined yet. In the present study, we examined the absorption spectra of $(1-x)SiO_2$–$xCeO_2$ samples in a particle form. As a result, we have found that the absorption spectra of the particles strongly depend on the composition and that the absorption profile shifts to the highest wavelength (red-shift) in the $0.45SiO_2$–$0.55CeO_2$ (in mol%) sample. Here, the reason for such a behavior is discussed, as well as characterization and potentiality of the ceria–silica particles as a new pigment.

The $(1-x)SiO_2$–$xCeO_2$ particles were synthesized by a sol–gel method. Tetraethyl orthosilicate (TEOS) and an aqueous solution of cerium nitrate ($1\ mol\cdot dm^{-3}$) were dissolved in 80 dm^3 of ethanol. The molar ratio of ceria to silica was adjusted from 10 to 90 mol%, and total cation amount in the solution was fixed to 20 mmol. The mixed solution was added to 60 dm^3 of $3.0\ mol\cdot dm^{-3}$ ammonia water. The precipitates were aged with stirring for three days and then the solvent was vaporized at 363 K. The powder obtained was calcined at 823 K for 1 hr.

The particles prepared were characterized by means of X-ray powder diffraction (XRD, 40 kV and 50 mA, Cu K_α, Rigaku Multiflex). The compositions of the samples were determined using an X-ray fluorescence spectrometer (Rigaku, ZEX-100e). Optical reflectance and FT-IR spectra of the powder were measured with a UV–Vis spectrometer (Shimadzu UV-2450) using barium sulfate as a reference and an FT-IR spectrometer (Bruker TENSOR27), respectively.

From the XRD patterns of the SiO_2, CeO_2, and $(1-x)SiO_2$–$xCeO_2$ particles shown in Fig. 1, typical diffractions corresponding to pure ceria by increasing the amount of CeO_2 were found, and there is no evidence for the presence of crystalline SiO_2. However, the presence of Si and Ce in the samples was identified by the X-ray fluorescence analysis. Although there was no peak shift in XRD patterns with the composition change in the $(1-x)SiO_2$–$xCeO_2$ samples, it is considered that a part of the cerium is incorporated into amorphous silica network and the remainder being in the crystalline phase, because the color of the $(1-x)SiO_2$–$xCeO_2$ evidently depended on their compositions as summarized in Table I.

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TABLE I Optical energy gap (E_{opt}) and CIE color coordination of the $(1-x)SiO_2$–$xCeO_2$ samples

x in $(1-x)SiO_2$–$xCeO_2$	(x, y)	E_{opt} (eV)
0	(0.310, 0.317)	–
0.20	(0.339, 0.357)	2.96
0.55	(0.365, 0.383)	2.90
0.70	(0.344, 0.363)	3.04
0.80	(0.339, 0.357)	3.18
1.0	(0.331, 0.348)	3.20

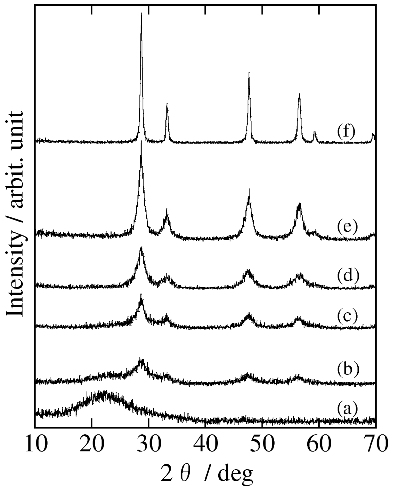

Figure 1 X-ray powder diffraction of the $(1-x)SiO_2$–$xCeO_2$ samples: (a) $x = 0$, (b) $x = 0.20$, (c) $x = 0.55$, (d) $x = 0.70$, (e) $x = 0.80$, and (f) $x = 1.0$.

Fig. 2 depicts the absorbance of the $(1-x)SiO_2$–$xCeO_2$ samples represented by the Kubelka–Munk fuction, $f(R) = (1-R)^2/2R$, where R is reflectance [9, 10]. The absorption of the $(1-x)SiO_2$–$xCeO_2$ samples showed the red-shift by CeO_2 doping and the maximum absorption in longer wavelengths was attained at the composition of $45SiO_2$–$55CeO_2$ (in mol%) in comparison with the other samples. The apparent bandgap energies of the $(1-x)SiO_2$–$xCeO_2$ samples determined from the absorbance spectra are also summarized in Table I. The bandgap energy strongly depends on the composition and varies with x from 2.90 to 3.18 eV. The minimum value was obtained in the $0.45SiO_2$–$0.55CeO_2$, corresponding to the result of the reflectance spectrum.

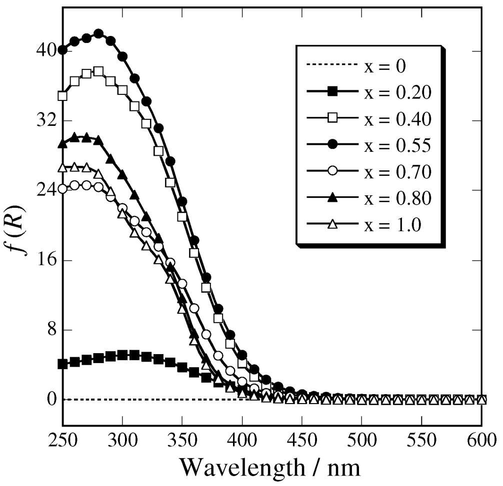

Figure 2 Absorbance spectra of the $(1-x)SiO_2$–$xCeO_2$ pigments.

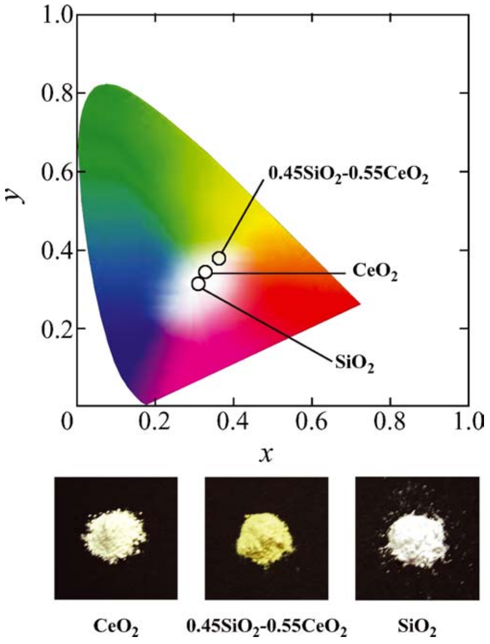

Figure 3 Graphic presentation of the color coordinates and a representative photograph of the $(1-x)SiO_2$–$xCeO_2$ samples.

Accompanying with the change of the bandgap energies, all the mixed oxide samples except for pure SiO_2 and CeO_2 have brilliant colors varying from white to bright yellow, which depends on the Si/Ce ratio. The CIE (x, y) color coordinates of $(1-x)SiO_2$–$xCeO_2$ are also given in Table I, while Fig. 3 offers a graphic presentation of the color coordinates and a representative photograph of the samples. The bright yellow powder of $0.45SiO_2$–$0.55CeO_2$ has enough thermal stability against the temperatures at least 823 K for the manufacturing of color plastics and paints. Therefore, it seems that this material has a potential to be a substitute, taking into consideration the economics and ecologies in comparison with the toxic cadmium yellow pigments.

FT-IR spectra were measured in order to clarify the reason for the change of the hue in the present samples. The results are shown in Fig. 4. The broad spectra observed are the features often seen in amorphous

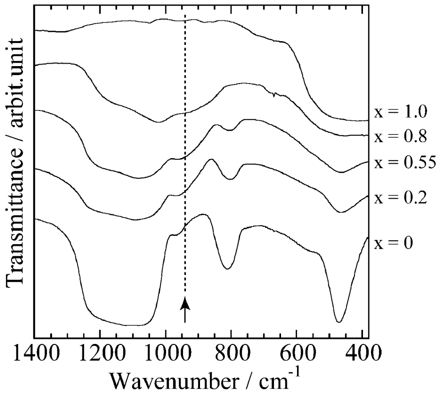

Figure 4 FT-IR spectra of the $(1-x)SiO_2$–$xCeO_2$ samples.

and low-crystalline materials. The principal transverse-optical modes of the Si—O—Si group were identified as a rocking mode at 460 cm^{-1}, a bending mode at 800 cm^{-1}, and the asymmetric stretching mode at 1070 cm^{-1} [11]. The overlapping peak around 1200 cm^{-1} corresponded to a transverse optical mode and an associated lateral mode which are the features of the structural disorder of the materials [12]. In addition, a typical broad band of —OH groups is also detected at approximately 3400 cm^{-1} (not shown in the spectra).

It is notable that the intensity of the band around 940 cm^{-1} (shown as an arrow and a dotted line) increased and those of bridging oxygen (around 460, 800, and 1070 cm^{-1}) decreased with increasing CeO_2 content. The absorption intensity of the 940 cm^{-1} band reached maximum at the composition of $0.45SiO_2$–$0.55CeO_2$, and this band is assigned to the stretching vibrations of the nonbridging oxygen [11, 13]. These results suggest that the fraction of cerium ions linking through bridging oxygen becomes the minimum at the $0.45SiO_2$–$0.55CeO_2$ composition in the $(1-x)SiO_2$–$xCeO_2$ samples. Since it has been reported that the breaking of the bridging oxygen decreases the E_{opt} value in several amorphous materials [14, 15], it is considered that the red-shift accompanying the appearance of the brilliant yellow color of the $(1-x)SiO_2$–$xCeO_2$ with the increase of cerium content is attributed to the introduction of cerium ions which are linked to silicon and oxide ions without bridging oxygen. This is supported by the fact that the maximum red-shift in optical reflectance spectra was observed at $0.45SiO_2$–$0.55CeO_2$ which corresponded to the composition that the highest absorption intensity of the 940 cm^{-1} band was observed in the FT-IR spectra, and that the bandgap energy increases again in the range of $x > 0.55$ because of the gradual increase of Ce—O—Ce bond in the samples.

Acknowledgments

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