Phase analysis and optical evaluation of ceria-zirconia-terbia prepared by coprecipitation method

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Abstract. A series of ceria-zirconia containing terbia samples were prepared by coprecipitation, and were characterized by XRD, Raman spectroscopy and UV-vis diffuse reflectance measurements. A single-phase solid solution with a cubic fluorite-type structure or tetragonal distorted fluorite structure was obtained for the samples heated at 900°C. Diffuse reflection spectra of the powders showed a broad band at 320-340 nm, which is assigned to interband transitions of CeO₂ in the UV region. The effect of ZrO₂ on the interband and absorption band of CeO₂ was investigated in a series of solid solutions.

1. Introduction
Mixed metal oxides in the system of ZrO₂-CeO₂ are useful for various applications such as ceramics, catalysts, and pigments [1,2]. The electronic band structures, which govern the transport and optical properties, depend on the mixed state of cations in the same fluorite-type structure. In the system of ZrO₂-CeO₂, one cubic, one monoclinic and three tetragonal forms exist, depending on the Zr concentration. These are assessed by UV-vis absorption and fluorescence spectroscopy. Also, based on these optical properties, new pigments containing CeO₂ (yellow) or Pr³⁺ or Tb³⁺ doped CeO₂ (brown or red) have recently been proposed by several researchers.[3-5] Since commercial yellow or red pigments contain toxic elements such as cadmium and lead that are hazardous to health and the environment, it is necessary to develop environmentally-friendly pigments. In the present work, we synthesized solid solution compounds of Zr₅Ce₀.₉₅₋ₓTbₓO₂₋ₓ by the coprecipitation method, and examined their UV-Vis diffuse reflectance characteristics.

2. Experimental
2.1. Synthesis of raw materials
The ZrₓCe₀.₉₅₋ₓTbₓO₂₋ₓ powder samples, where x=0, 0.20, 0.40, 0.60, 0.80 and 0.95, were synthesized by coprecipitation using ZrO(NO₃)₂·2H₂O, Ce(NH₄)₂(NO₃)₆, Tb(NO₃)₃·6H₂O and aqueous ammonia as starting materials. Aqueous solutions containing metal salts, corresponding to the composition ZrₓCe₀.₉₅₋ₓTbₓO₂₋ₓ (x=0-0.95), were prepared. Aqueous ammonia was added to the solution, and the mixed solution was agitated sufficiently. The obtained coprecipitates from mixed solution of salts and ammonia were filtered, and dried at 110°C. Powders were calcined at 600°C for 3 h, and then heated at 900°C for 3 h in air.
2.2. Evaluation of synthesized powder

2.2.1. Powder X-ray diffraction and Raman spectroscopy
Powder X-ray diffraction (XRD) patterns were recorded in order to determine the crystal phases in the products. The patterns were recorded using a Rigaku Rint X-ray Diffractometer (Japan) with Ni filtered CuKα radiation (λ=1.5418 Å) over the range of 20 from 20 to 80° at 40 kV and 20 mA to study the products. The JCPDS cards were used to identify the resultant phases. Raman spectroscopy of the samples was carried out using a laser with a wavelength of 532 nm.

2.2.2. Colour characterization
The CIE L*a*b* system was used for evaluation of the chromatic properties. The parameters were measured using a spectrophotometer (Konica Minolta CM-2600d, Japan). In this system, L* is the colour lightness (L* is 0 for black and L* is 100 for white), a* is the green (-)/red (+) axis, b* is the blue (-)/yellow(+) axis.

2.2.3. UV-vis diffuse reflectance spectroscopy
UV-vis diffuse reflection spectra were measured from 240 to 800 nm using a Hitachi U-3000 Spectrophotometer (Japan) with a BaSO₄ coated integrating sphere. The inner diameter of the integrating sphere is 60 mm, and the aperture ratio is 7.8%.

Kubelka-Munk functions for the samples were calculated using the formula

\[ F(R) = \frac{(1 - R)^2}{2R} = \frac{K}{S} \]

where \( R \) is the reflectance, \( K \) is the absorption coefficient, and \( S \) is the scattering coefficient. If it is assumed that the ratio of the scattered to incident light is constant, the spectra of the K-M function can be regarded as relative absorption spectra.

3. Results and discussion

3.1. Powder X-ray diffraction and Raman Spectroscopy
The XRD patterns for ZrₓCe₀.₉₅₋ₓTb₀.₀₅O₂₋ₓ (x=0, 0.2, 0.4, 0.6, 0.8, and 0.95) samples heated at 900°C are shown in Figure 1. The patterns revealed that a single phase solid solution with a cubic fluorite-type structure was obtained for ZrₓCe₀.₉₅₋ₓTb₀.₀₅O₂₋ₓ in the range of x=0 to 0.80. For x=0.20 to 0.80, the XRD results indicated lower crystallinity with broader peaks than that for x=0. The diffraction peaks shifted toward higher angle with increasing x (Zr content) in the region from x=0 to x=0.80. The Raman spectra for ZrₓCe₀.₉₅₋ₓTb₀.₀₅O₂₋ₓ (x=0, 0.2, 0.4, 0.6, 0.8 and 0.95) samples heated at 900°C are shown in Figure 2. For x=0, a sharp band around 455 cm⁻¹ and a broad band at 582 cm⁻¹ were observed. For x=0.2 to 0.6, weak bands around 300 and 600 cm⁻¹ became prominent with increasing Zr. Based on a published study on the CeO₂-ZrO₂ system [6], these were attributed to displacement of oxygen atoms from their ideal fluorite lattice positions and to oxygen vacancies, respectively. For x=0.8 and 0.95 several bands associated with the tetragonal phase, which has six Raman-active modes, were detected. In the CeO₂-ZrO₂ system one cubic, one monoclinic and three tetragonal (two metastable phases and a stable phase) forms exist, depending on the Zr content [7]. The XRD results suggest that a metastable tetragonal phase with a distorted fluorite-type structure exists in the range from x=0.2 to 0.6, a stable tetragonal phase exists for x=0.8, and a stable tetragonal phase and a minor monoclinic phase exist for 0.95. For x=0, a band at 583 cm⁻¹ appeared due to the presence of Tb. This is probably associated with a cubic phase with a fluorite-type structure including oxygen vacancies produced by the presence of Tb³⁺.
3.2 Colour characterization

The L*a*b* parameters measured for a series of the samples of Zr_xCe_0.95-xTb_0.05O_2-δ heated at 900°C are listed in Table 1. The lowest L* value of 35, the lowest a* value of 7.1, and the lowest b* value of 8.1 were observed for x=0. The L* value increased with increasing x in the range x=0 to 0.6 and decreased with increasing x in the range x=0.6 to 0.95. The highest L* value was 73.2 for x=0.6. The highest a* value was 18.4 for x=0.95. The a* value was higher than 10 for x=0.2 to 0.95, compared to a value of around 0 for the CeO_2-ZrO_2 system, and the Zr_xCe_0.95-xTb_0.05O_2-δ sample powders appeared slightly more reddish. The b* value increased with increasing x, and the highest b* value was 45.7 for x=0.95. The colour of the sample powder was dark brown for x=0, yellow-brown from x=0.2 to 0.8 and vivid orange for x=0.95.

3.3 UV-Vis diffuse reflectance spectroscopy

Figure 3 shows the UV-Vis diffuse reflectance spectra of Zr_xCe_0.95-xTb_0.05O_2-δ (x=0, 0.20, 0.40, 0.60, 0.80, and 0.95) powders. A strong absorption maximum was found in the range 290-300 nm for all the samples. In addition, another peak appeared in the range 320-340 nm for x=0 to 0.60. Although the former absorption at around 300 nm is common, its intensity changed with the Ce content. This was identified as being due to Ce^{4+}→O²⁻ (at 297 nm) charge transfer transitions for Ce-O in each crystal phase with different Zr content. The latter absorption is strongly affected by the Zr content and is assigned to interband transitions in CeO_2 and its solid solution. In CeO_2 doped with ZrO_2, the absorption due to interband transitions occurs at longer wavelengths than 400 nm, so that the band gap falls in the blue wavelength region. The complementary light yellow colour is observed because of the blue absorption associated with the modified interband structure in the crystalline solid solution. We found that Tb-doped CeO_2 and Tb-doped ZrO_2 and their solid solutions absorbed light in a broad range of wavelengths and showed new colours. Other peaks appeared around 500 nm for Tb-doped CeO_2 (x=0) and around 390 nm for Tb-doped ZrO_2 (x=0.95). These peaks appeared for Tb doping with x=0.2 to 0.80. However, the absorption in the wavelength region below 600 nm was slightly higher than the case without Tb, and hence the sample appeared yellow-brown.
4. Summary

Zr$_x$Ce$_{0.95-x}$Tb$_{0.05}$O$_{2-\delta}$ powders were synthesized by the coprecipitation method, and their UV-Vis absorption properties were characterized. From the XRD measurements, a mixed oxide with a fluorite-type cubic structure or a tetragonal distorted fluorite-type structure was formed in the single phase for $x = 0$ to 0.8. By doping CeO$_2$ with ZrO$_2$, the band gap of the crystal fell in the blue region of the visible spectrum, so that the mixed oxide powders had a yellowish colour. Thus, the addition of Tb to CeO$_2$-ZrO$_2$ will allow the possibility of controlling the optical properties.

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