Research Article

Structural and Raman Vibrational Studies of CeO₂-Bi₂O₃ Oxide System

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A series of ceramics samples belonging to the CeO₂-Bi₂O₃ phase system have been prepared via a coprecipitation route. The crystallized phases were obtained by heating the solid precursors at 600°C for 6 hours, then quenching the samples. X-ray diffraction analyses show that for x < 0.20 a solid solution Ce_{1-x}Bi_xO_{2-x/2} with fluorine structure is formed. For x ranging between 0.25 and 0.7, a tetragonal β' phase coexisting with the FCC solid solution is observed. For x ranging between 0.8 and 0.9, a new tetragonal β phase appears. The β' phase is postulated to be a superstructure of the β phase. Finally, close to x = 1, the classical monoclinic α Bi₂O₃ structure is observed. Raman spectroscopy confirms the existence of the phase changes as x varies between 0 and 1.

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1. Introduction

In the past, several systems based on cerium dioxide CeO₂ (ceria) were extensively investigated for their electrochemical, conduction, or catalytic properties [1–15]. Nanostructured powders of pure and doped ceria can be obtained in various ways [16, 17]. In the present work we deal with the bismuth cerium oxide system CeO₂-Bi₂O₃. This system might be of a high interest for catalytic applications and integration in gas sensors. At present, the cerium bismuth oxide phase diagram (CeO_2 -Bi₂O₃) is not well known. For low Bi fractions, it was clearly established that a solid solution was formed. The substituted phase $\operatorname{Ce}_{1-x}^{4+} \operatorname{Bi}^{3+} x \operatorname{O}_{2-x/2} (V)_{x/2}$ with x < 0.20 (where oxygen vacancies are noted V) is cubic and its cell parameter increases with x because of size of Bi³⁺ ionic radius: $r(Bi^{3+}) = 0.117 \text{ nm}$ and $r(Ce^{4+}) =$ 0.097 nm [18, 19]. However, above the composition x =0.20, the nature of phases is not well known. In the present work, we describe a new series of observed phases prepared via a coprecipitation route and after heating at 600°C.

2. Experimental

Fourteenth polycrystalline samples were prepared by mixing bismuth and cerium nitrates solutions (Bi(NO₃)₃, 5H₂O + Ce(NO₃)₃, 6H₂O) and adding NH₄OH [20, 21] to obtain precipitation of NH₄NO₃ and bismuth cerium hydroxides. Bismuth compositions ranged from 0% Bi to 100% Bi. The solid obtained by coprecipitation was then heated under air at 600°C for 6 hours. Experiments carried out at intermediate heating times showed that the observed crystallized phases appear as being stable above heating times of 2 hours.

3. Results

The polycrystalline samples were analyzed by X-ray diffraction, using a D5000 Siemens-Bruker diffractometer, equipped with a copper X-ray source (wavelength λ = 1.54 10⁻¹⁰ m; tension V = 45 kV, intensity I = 35 mA), and with a monochromator eliminating K_{β} radiation. The



FIGURE 1: XRD patterns ($\lambda_{CuK\alpha 1} = 1.54 \cdot 10^{-10}$ m) of pure samples (1 – *x*) CeO₂, *x*/2 Bi₂O₃heated at 600°C. (a) XRD patterns for 0 < *x* < 0.20; (b): XRD patterns for 0.25 < *x* < 0.70 biphasic system; (c) *x* = 0.8 and 0.9; (d) *x* = 1 α -Bi₂O₃.

analyses were carried out using the classical θ -2 θ configuration, with 2 θ angle steps of 0.02° and counting times of 19 s per step. Raman spectroscopy was used to characterize the observed various phases. A micro-Raman system Horiba. Jobin-Yvon Labram HR 800 equipped with argon laser source (Raman wavelength $\lambda = 514.5$ nm) was used to observe the various vibrational spectra. All spectra were acquired with a recording time of 30 seconds.

3.1. Structural Studies. X-ray diffraction shows that a strong evolution occurs in the phase system as bismuth atom fraction increases. Figures 1(a), 1(b), 1(c), and 1(d) show the X-ray diffraction patterns for samples noted $(1-x)CeO_2$,

 $x/2Bi_2O_3$ with x varying between 0 and 1. The cell parameters of substituted samples $Ce_{1-x}Bi_xO_{2-x/2}(V)_{x/2}$ noted as a(x)were refined. From x = 0 to x = 0.25, the cell parameters linearly vary with x: $a(x = 0) = 0.5409 \pm 0.0001$ nm; $a(x = 0.05) = 0.5413 \pm 0.0001$; $a(x = 0.10) = 0.5417 \pm 0.0004$; $a(x = 0.15) = 0.5419 \pm 0.0003$; $a(x = 0.20) = 0.5421 \pm 0.0002$.

Above the composition x = 0.20, a multiphase system is evidenced and the ceria-based phase presents a constant cell parameter a = 0.5421 nm: the two new additional phases are identified as being tetragonal and closely related to bismuth oxide structural varieties: their cell parameters were refined. In the composition range from 0.3 to 0.7, a tetragonal β' phase is observed with refined cell parameters:



FIGURE 2: Raman spectra ($\lambda = 514.5 \text{ nm}$) of bismuth cerium oxide phases, $(1 - x) \text{ CeO}_2$, x/2. Bi₂O₃; (a) solid solution for x = 0 to 0.25; (b) multiphase system for x = 0.30 to 1. Raman shift island are in cm⁻¹, x values from 0 to 1. The bands at 520 and 590 cm⁻¹ are linked to structural defects.

 $a = 1.5542 \pm 0.0003$ nm; $c = 0.5645 \pm 0.0001$ nm. It is a superstructure of the tetragonal β phase observed for compositions 0.7 < x < 0.9, with refined cell parameters: $a = 0.7742 \pm 0.0001$ nm; $c = 0.5633 \pm 0.0001$ nm. These substituted phases were never observed, and testing structural models are in progress to better describe these phases.

3.2. Vibrational Studies. raman spectroscopy data are reported on Figures 2(a) and 2(b): in Figure 2(a), the solid solution (0 < x < 0.25) is characterized by a main vibrational band at 460–465 cm⁻¹ with complementary

small bands at 520-590 cm⁻¹ associated with the presence of Bi³⁺ and oxygen vacancies in the cubic lattice. In Figure 2(b) the Raman spectra of other samples are represented for x compositions ranging between 0.3 and 1. The vibration bands are increasingly more complex as Bi composition increases. The cubic phase of CeO_2 is well characterized by the 465 cm⁻¹ Raman band. In the composition range from x = 0.05 to 0.20 the bands located at 462–516–595 cm⁻¹ might be associated with the solid solution $Ce_{1-x}Bi_xO_{2-x/2}$ (V)_{x/2}. The additional bands are underlined and should be linked to presence of Bi3+ ions and vacancies (clusters $Bi^{3+}-V-Bi^{3+}$). In the range x = 0.30to 0.70, the Raman bands 460, 520, 590, 94, 126, 316, 530 (in cm^{-1}) might be related to the biphasic system: cubic solid solution + tetragonal superstructure β '. In the range x = 0.80 to 0.90, a new biphasic system associated with the bands 95, 120, 315, 450, 538 (tetragonal phase) and 70, 85, 140, 152, 184, 212, 285, 418, 630 (monoclinic lattice) is observed: these vibration bands could characterize the system "Tetragonal β + Monoclinic α ." Finally for the Bi₂O₃ sample, the standard α monoclinic structure is observed.

4. Conclusions

New correlations between XRD data and Raman spectroscopy have been established for the system CeO₂-Bi₂O₃. From samples prepared at 600°C, a partial phase diagram is proposed with the probable existence of at least 4 domains. The X-ray diffraction and Raman spectroscopy analyses clearly show that phase changes occur at 600°C, with at least (i) a solid solution domain (cubic phase), (ii) a biphasic domain (tetragonal phase β' rich in bismuth coexisting with the cubic phase), (iii) a biphasic system with coexistence of two β and β' tetragonal phases, the β phase being highly rich in bismuth), and finally (iv) a biphasic domain in which monoclinic and tetragonal β phases coexist. The solid solution can be represented from the basic CeO₂ face-centered cubic lattice. The tetragonal phase $\beta(x > 0.8)$ can be represented by a cell built on the ceria fcc structure, with lattice vectors $(a_1/2, a_2/2, a)$: this structure was previously observed in the literature as a tetragonal variety of pure or non stoichiometric Bi2O3 phase [22, 23]. The Bi rich phase (0.25 < x < 0.70) having the superstructure noted β' can be represented by a cell built on lattice vectors $(2a_{1/2}, 2a_{1/2}, a)$. The observed pure Bi₂O₃ phase is monoclinic. The effective compositions of the β and β' new cerium bismuth phases are not clearly known and new studies using transmission electron microscopy analyses are in progress.

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