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UV Raman spectroscopic study on the surface phase of ZrO_2 modified with Nd_2O_3

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ABSTRACT

The Nd_2O_3 modified ZrO_2 was synthesized using two methods of co-precipitation (Nd-ZrO_2) and wet impregnation (Nd/ZrO_2). The surface and bulk crystalline phases of Nd_2O_3 modified ZrO_2 were investigated by using UV Raman spectroscopy, visible Raman spectroscopy, and X-ray diffraction (XRD). It is observed that the tetragonal phase in the surface region of Nd-ZrO_2 was not effectively stabilized by Nd_2O_3, as Nd_2O_3 is mainly present in the bulk of Nd-ZrO_2. However, in Nd/ZrO_2, it is found that with the impregnation of 0.5 mol% Nd_2O_3 on ZrO_2, the surface tetragonal phase of Nd/ZrO_2 can be stabilized even after calcination at 700 °C. The UV Raman results indicate that a disordered structure, or intermediate structure, which is involved in the transition from the tetragonal to the cubic phase, is formed at the surface region of Nd/ZrO_2. The formation of the aforementioned intermediate structure inhibits the phase transition from tetragonal to monoclinic in the surface region of Nd/ZrO_2. Furthermore, it is observed that the mixed tetragonal and monoclinic phases in the surface region of ZrO_2 which has been impregnated with Nd_2O_3 can also be stabilized after calcination at 700 °C. This work provides a simple method for controlling the surface phase of ZrO_2 at high temperatures.

1. Introduction

Zirconia (ZrO_2), which is well known for its excellent thermal, optical, electrical, and mechanical properties, has been widely used in ceramics, solid oxide fuel cells, gas sensors, catalysts and catalyst supports [1,2]. ZrO_2 exhibits three different phases: monoclinic, tetragonal, and cubic [3,4]. The metastable tetragonal phase changes into the monoclinic phase with increasing temperature, and this transformation prevents applications of tetragonal ZrO_2 over a broad temperature range [5]. Many researchers have studied the mechanism of the phase transition of ZrO_2 [4,6] and the method for stabilization of the tetragonal phase, usually by alloying ZrO_2 with some oxides, such as CaO, MgO, and SiO_2 [7–9].

Our previous results [10] indicated that UV Raman spectroscopy is more surface sensitive than visible Raman spectroscopy and X-ray diffraction (XRD) for oxides, such as ZrO_2, which have strong electronic absorptions in the UV region. It was found that the phase transition of ZrO_2 starts in the surface region and then propagates into the bulk. Moreover, it is difficult to stabilize the tetragonal phase in the surface region of ZrO_2 although the tetragonal phase in the bulk of ZrO_2 is effectively stabilized by doping ZrO_2 with yttrium oxide or lanthanum oxide [11]. These findings prompted us to search for methods to stabilize the surface tetragonal phase of ZrO_2. The surface tetragonal phase can be stabilized if the phase transformation from tetragonal to monoclinic in the surface region of ZrO_2 is inhibited. This may be realized via a reaction between a stabilizer and the ZrO_2 surface.

In this study, we prepared neodymium oxide (Nd_2O_3) doped ZrO_2 and Nd_2O_3 loaded ZrO_2 by co-precipitation and wet impregnation methods, respectively. The influence of Nd_2O_3 on the surface and bulk crystalline phase of ZrO_2 was studied by UV Raman spectroscopy, visible Raman spectroscopy, and XRD. Furthermore, we discuss how these results can be used to control the surface phase of ZrO_2.

2. Experimental

Nd_2O_3 doped ZrO_2 (Nd-ZrO_2) was prepared by a co-precipitation method. A solution containing a mixture of zirconium oxychloride, at a fixed concentration of 0.4 mol/L, and variable concentrations of neodymium nitrate was stirred while an ammonia solution was slowly added to until the pH of the solution reached 10. The resulting white precipitate was stirred for 24 h, it was then washed three times with deionized water and subsequently dried at 100 °C for 12 h to obtain amorphous Nd-ZrO_2. To provide a comparison with the Nd-ZrO_2 sample, amorphous ZrO_2 was prepared via the same procedure without an added dopant. Amorphous Nd-ZrO_2 and ZrO_2 were then further calcined in air at 700 °C for 2 h. The ZrO_2 samples with 0.5, 2, and 5 mol% Nd_2O_3 are denoted as 0.5Nd-ZrO_2, 2Nd-ZrO_2, and 5Nd-ZrO_2, respectively.

Nd_2O_3 loaded ZrO_2 (Nd/ZrO_2) was prepared by a wet impregnation method [12]. The as-prepared amorphous ZrO_2 was calcined at 400 °C

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and 500 °C prior to the usage as a support for Nd/ZrO_2 (400 °C) and Nd/ZrO_2 (500 °C), respectively. These Nd/ZrO_2 (400 °C) and Nd/ZrO_2 (500 °C) samples, containing varying amounts of Nd_2O_3 (0.5–5 mol%), were also calcined at 700 °C. The surface crystalline phase of Nd-ZrO_2 and Nd/ZrO_2 was characterized by UV Raman spectroscopy (Jobin-Yvon T64000 with 244 nm excitation line), while visible Raman spectroscopy (Jobin-Yvon U1000 with 532 nm excitation line) and XRD (Rigaku MiniFlex diffractometer, Cu Kα) were used to characterize their bulk crystalline phases [10].

3. Results and discussion

Fig. 1a shows the UV Raman spectrum of ZrO_2 and Nd-ZrO_2 calcined at 700 °C. We conclude that the surface region of ZrO_2 which has been calcined at 700 °C is in the monoclinic phase because only typical UV Raman bands due to the monoclinic phase (181, 220, 308, 338, 380, 476, and 638 cm^{-1}) [13] are observed. The monoclinic phase is the only crystalline phase observed in the surface region of the 0.5Nd-ZrO_2 and 2Nd-ZrO_2 samples calcined at 700 °C. For 5Nd-ZrO_2 there are low intensity bands due to tetragonal ZrO_2 at 149 and 269 cm^{-1}. These results show that the phase transition in the surface region of ZrO_2 is not effectively retarded after doping Nd_2O_3 into ZrO_2.

The bulk region in ZrO_2 samples calcined at 700 °C is dominated by the monoclinic phase with some tetragonal phase (Fig. 1b). For Nd-ZrO_2 calcined at 700 °C, the amount of the tetragonal bulk phase increases with increasing Nd_2O_3 and the tetragonal phase is the main phase in the bulk of 5Nd-ZrO_2. The oxygen vacancies induced by neodymium ions may be responsible for the improvement of the stability of the tetragonal phase [14]. The bulk crystalline phases of Nd-ZrO_2 samples were also probed by visible Raman spectroscopy (Fig. 1c), and the result is similar as that of XRD (Fig. 1b).

It should be noted that the visible Raman bands of both tetragonal and monoclinic phases decrease in intensity, increase in band width, and some peaks (264, 476, and 635 cm^{-1}) shift to lower energy with increasing amounts of Nd_2O_3. These changes in the Raman bands can be ascribed to structural disorder resulting from the introduction of oxygen vacancies and dopant ions [15]. Keramidas [15] attributed these disordered structures to the breakdown of the wave vector selection rule by translational disorder, through random substitution of anion vacancies and cations. Analysis of transmission electron microscopy (TEM) data indicates that the Nd-ZrO_2 particle size decreases from 90 to 78 nm when the Nd_2O_3 content is increased from 0.5 to 5 mol%. This decrease in particle size can also contribute to the broadening of visible Raman bands observed in Fig. 1c.

Though it is not observed in the XRD data, the Raman data, which provides information on the bulk phase(s) of ZrO_2 [10], suggests that some structural disorder forms mainly in the bulk region of Nd-ZrO_2. In other words, Nd_2O_3 may be more enriched in the bulk of the Nd-ZrO_2 sample. As a consequence the Nd^{3+} concentration on the surface of ZrO_2 is far below than that in the bulk region of ZrO_2. This explains why the phase transition in the surface region of ZrO_2 cannot be effectively inhibited by Nd_2O_3. However, the propagation of the monoclinic phase from the surface into the bulk region of ZrO_2 is remarkably slowed by Nd_2O_3. Once the phase transformation starts, the monoclinic phase formed on the surface of ZrO_2 must diffuse into the bulk region of pure ZrO_2 [9]. For Nd-ZrO_2, diffusion of monoclinic ZrO_2 through the bulk Nd_2O_3 doped tetragonal phase may become difficult, inhibiting the phase transition in the bulk of the Nd_2O_3 doped ZrO_2 matrix [16].

We also prepared Nd/ZrO_2 samples by an impregnation method so that Nd^{3+} resided mainly in the surface region of ZrO_2. As revealed by the UV Raman spectrum (Fig. 2a) the surface region of the ZrO_2 (400 °C) support is almost a pure tetragonal phase. It is observed that the surface tetragonal phase of the ZrO_2 (400 °C) support can be effectively stabilized after calcination at 700 °C when impregnated with only 0.5 mol% Nd_2O_3. However, there are differences between the UV Raman spectrum of ZrO_2 (400 °C) and that of Nd/ZrO_2 (400 °C) calcined at 700 °C. For 2Nd/ZrO_2 (400 °C), the bands due to the tetragonal phase become wider and the band at 269 cm^{-1} shifts to 261 cm^{-1}. Meanwhile, a broad band is observed at 697 cm^{-1}. The appearance of a band at 697 cm^{-1} is attributed to structural disorder [15] or the presence of a cubic phase [17] on the surface of Nd/ZrO_2 (400 °C).

It is possible that the changes observed in the UV Raman spectra of Nd/ZrO_2 (400 °C) are associated with the disordered structure or with the transition structure from the tetragonal to the cubic phase which is formed in the surface region of Nd/ZrO_2 (400 °C).These results suggest that the Nd^{3+} ions might be enriched in the surface region of tetragonal ZrO_2, and thus prevent the monoclinic phase from forming in the surface region of tetragonal ZrO_2 [11]. Based on XRD data (Fig. 2b) and visible Raman spectra (not shown), it is clear that the bulk phase of Nd/ZrO_2 (400 °C), calcined at 700 °C, maintains the tetragonal phase of the ZrO_2 (400 °C) support. No structural distortion induced by Nd_2O_3 is observed in Nd/ZrO_2 (400 °C) by either XRD or visible Raman spectroscopy.

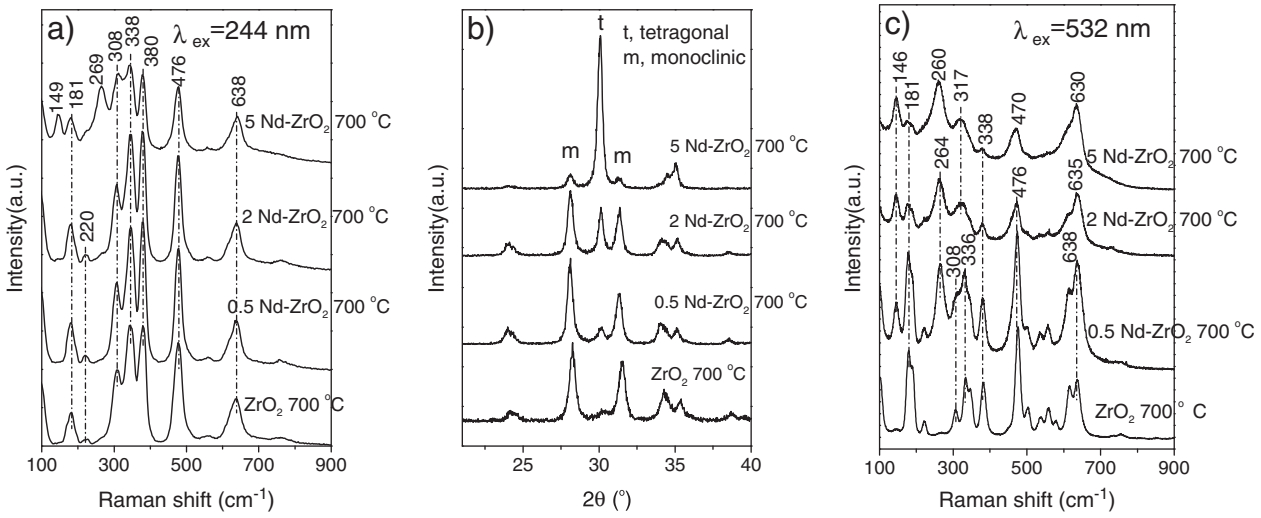

Fig. 1. UV Raman spectra (a), XRD patterns (b), and visible Raman spectra (c) of ZrO_2 and Nd-ZrO_2 calcined at 700 °C.