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Abstract

High-surface-area rare-earth (RE) modified zirconia powders prepared by solution methods can be used as catalytic support of noble metals and as electrolyte oxygen sensors in an automobile exhaust-emission-control system. A previous neutron-scattering study showed that substituting zirconium with trivalent RE ions not only stabilizes the cubic and tetragonal phases over a wide range of temperatures but also creates oxygen vacancies in the RE-Zr oxide solid solution. This work focuses on the fluorescence of Nd in $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ powders under laser excitation of the Nd^{3+} ground state to the ${}^4\text{G}_{7/2}$ states. Distinct features were observed at 8K in the ${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{7/2}$ excitation and ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$ emission spectra using two sets of incident and emission frequencies, respectively. The results are discussed in terms of site-sensitive local structures surrounding the Nd ions in the two-phased oxide structure.

Keywords: site-selective spectroscopy, fluorescence, rare-earth modified zirconia, zirconia catalytic support

Introduction

Rare-earth dopants in zirconias play an essential role in tailoring material properties to suit different demands for technological applications. For high-surface-area zirconia used as a catalytic support in automobile exhaust-emission-control, rare-earth modification enhances structural stability and prevents sintering of the material at high temperatures. This is achieved in part by stabilizing the cubic and tetragonal phases in the RE-ZrO₂ system. Furthermore, since the dopant cations (3+ RE ions) have a lower valency than the Zr (4+) ions, oxygen vacancies are formed to preserve the overall electronic neutrality of the lattice. These vacancies give rise to adsorption sites and strong metal-support interactions that are needed for effective catalytic functions. Ionic conductivity resulted from oxygen diffusion via vacancy sites in response to a dynamic oxygen environment has led to the development of zirconia electrolyte oxygen sensors. Recently, Ozawa and coworkers reported the preparation of high-surface-area RE-ZrO₂ powders from a coprecipitation method and studied the accelerating effect of CO oxidation from an Fe catalyst supported by Nd-doped ZrO₂. [1-2]

Knowledge of microscopic crystal phases and vacancy-induced defect structure in RE-ZrO₂ is essential to the eventual understanding of the surface chemistry and catalytic reactions in zirconia-supporting catalysts. Spectroscopic studies have provided valuable information in this regard. A recent neutron-scattering study has characterized the mixed cubic and tetragonal crystal phases, defects and dynamics of adsorbed hydroxyl groups and water in La- and Nd-ZrO₂. [3] While the neutron results have provided useful insights into the *global* structures, information regarding local structural fluctuations is not complete. Site-selective laser spectroscopy is a powerful method for identifying *local* structure of RE ions in solids. Laser-induced fluorescence transitions between the 4f electronic states of a RE ion provide fingerprint energy-level patterns characteristic of the local crystalline environment surrounding the ion. Ions on different lattice or defect sites can be easily identified. Particularly, the high sensitivity of this optical technique permits the detection of RE dopants of trace-level concentration (~0.1

atm%). In the paper we report a site-selective laser spectroscopic study of the local environment of RE ions in the Nd-ZrO₂ system.

The energy level splitting of a RE ion in a solid bears a signature of the local environment surrounding the ion. As a result of vacancy-induced defects and phase inhomogeneities in Nd_{0.1}Zr_{0.9}O_{1.95}, trivalent Nd³⁺ ions occupying the Zr⁴⁺ sites exhibit different sets of crystal-field energy splitting. A superposition of optical transitions between these sets of crystal-field states gives rise to large inhomogeneous broadening of the linewidths. A narrow band laser, on the other hand, can be tuned to excite the ions that have the same energies between the ground state and the excited state. Assuming that there is a correlation between the crystal-field energy splitting and the surrounding local crystalline structure for each Nd³⁺ ion, this spectrally selective excitation thus permits the detection of a subset of ions having similar local environments. The present study aims at probing the local structural properties of Nd³⁺ ions in Nd_{0.1}Zr_{0.9}O_{1.95} and examining the optical data in light of findings obtained from complementary spectroscopic techniques.

Results and Discussion

Nd 10-mol% doped into zirconia powders, Nd_{0.1}Zr_{0.9}O_{1.95}, were prepared by a coprecipitation technique described elsewhere. [1] The BET surface areas of these powders heat-treated at 600 and 800°C for 3h in air were determined to be 73 ± 0.8 and 51 ± 0.7 m²/g by nitrogen adsorption at 77 K. A dried powder sample was sealed inside a quartz tubing which in turn was mounted in an optical cryostat for low-temperature (8 K) measurements. A tunable dye laser pumped by a pulsed Nd:YAG laser was used in the fluorescence experiments. The laser linewidth was 0.4 cm⁻¹. Fluorescence emission from the lowest ⁴F_{3/2} multiplet of Nd³⁺ ions was dispersed by a monochromator and detected by a cooled photomultiplier. Signals from the photomultiplier were averaged using a DEC minicomputer. The optogalvanic effect in a uranium-argon hollow-cathode lamp was used for a wavelength calibration of the excitation spectra.

First, we sought site-selective excitation of Nd^{3+} from the $^4\text{I}_{9/2}$ ground state to the $^4\text{G}_{7/2}$ excited state at an energy level near 19000 cm^{-1} . The fluorescence intensities of the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ emission at a given wavelength was monitored as the laser incident energy was scanned over the $18500\text{-}19800\text{ cm}^{-1}$ region, and the process was repeated over a range of emission wavelengths. In a $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ sample heat treated at 600°C , we obtained two dominant sets of excitation spectra at 8 K at corresponding emission energies of 11205 cm^{-1} and 11396 cm^{-1} , as shown in Fig. 1. For a Nd^{3+} ion in $4f^3$ electronic configuration, the Kramers degeneracy cannot be lifted by crystal-field interaction. Therefore, the crystal-field levels are at least two-fold degenerate. For a single ionic site symmetry lower than cubic point-symmetry, we expect four lines in the lower energy region ($18400 - 18900\text{ cm}^{-1}$) of the excitation spectrum corresponding to transitions from the ground doublet of the $^4\text{I}_{9/2}$ multiplet to the four doublets of the $^4\text{G}_{7/2}$ excited states. The lines above 18900 cm^{-1} correspond to the transitions to the $^4\text{G}_{9/2}$ and $^2\text{K}_{13/2}$ multiplets. The two distinct excitation spectra (see Fig. 1) indicate that the observed excitations originate from Nd^{3+} ions on two distinct sites rather than from a unique environment. We denote the two site-configurations and the corresponding spectra as A and B in Fig. 1. The line with lowest energy in each of the two excitation spectra corresponds the energy of the lowest crystal-field level within the $^4\text{G}_{7/2}$ multiplet. For site A, this level is at 18450 cm^{-1} , and for site B the level is at 18600 cm^{-1} . Thus the energy-level difference between the two Nd^{3+} sites is 250 cm^{-1} . Such differences in the crystal-field energy levels and in the splitting patterns imply rather different local environments for the two Nd^{3+} sites.

The two Nd^{3+} environments were also detected in the emission spectra. At a fixed incident laser wavelength, fluorescence was measured over a range of emission frequencies. Again two different emission spectra were obtained. The fluorescence emission from the metastable state $^4\text{F}_{3/2}$ to the $^4\text{I}_{9/2}$ ground state is shown in Fig. 2. The laser excitation was set at 18552 cm^{-1} for site A spectrum and at 18941 cm^{-1} for site B spectrum. In both emission spectra two lines were observed with a separation of less than 60 cm^{-1} which corresponds to the crystal-

field splitting of the Nd^{3+} ground multiplet. The higher-energy line, which measures the energy level of the emitting states, is 11205 cm^{-1} for site A and 11420 for site B. Therefore, a difference of 215 cm^{-1} was obtained for the two Nd^{3+} sites in the ${}^4\text{F}_{3/2}$ emitting states as compared with 250 cm^{-1} for the ${}^4\text{G}_{7/2}$ excited states. We also observed similar excitation and emission spectra from another $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ powder that was heat treated at 800°C . This implies that the local structures were not altered significantly by heat treatment at such a higher temperature.

Two nominal crystal phases (cubic and tetragonal) in the Nd-doped zirconia powders were observed previously in a neutron-scattering study. [3] In the 600°C heat-treated $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ sample, molar fractions of 58.7 and 41.3% were found for the cubic and tetragonal phases, respectively. In the present experiment, we estimated that the average fluorescence intensities of site-B Nd^{3+} ions were about 8 times stronger than those of the site-A Nd^{3+} ions. Assuming a fluorescence intensity proportional to the number of ions in the sample, this result suggests that site-B Nd^{3+} ions may be associated with the cubic phase. However, crystal-field selection rules for a cubic site-symmetry allows fewer lines than those observed in the site-B spectra. Therefore, the geometry of the Nd ions in the cubic phases is locally distorted to a lower symmetry than the crystallographic symmetry. In fact, local distortions around atomic sites in rare-earth modified zirconias are well-known due to charge-compensation effect in the lattice. An analysis of the diffuse-scattering background of the previous neutron-diffraction measurements using a Fourier-filtering technique provided evidence of static, oxygen vacancy-induced atomic displacements along the pseudocubic $\langle 111 \rangle$ and other symmetry directions. [3]

In all cases the observed linewidths vary from ~ 50 to 200 cm^{-1} , which are much larger than the homogeneous linewidths expected from a crystalline compounds. This underscores the extensive distribution of local environments over the Nd sites, in agreement with evidence revealed by neutron and x-ray diffraction experiments. [3-4] The average crystalline grain sizes for the tetragonal and cubic phases was 60 and 184 \AA respectively according to previous

neutron-diffraction data. These small grain sizes imply a considerable fluctuation of local environments at the grain boundaries. It is thus not surprising to find the broad and overlapping lines in the fluorescence spectra.

In addition to the presence of two crystal phases (tetragonal and cubic) in these Nd-doped zirconia powders, small-angle neutron scattering studies revealed distinct character in the local-density variation over two length scales. [5] Such finding is consistent with the two major pore-size distributions deduced from a BET adsorption-desorption measurements. [6] Furthermore, neutron and infrared spectroscopy [3,7] as well as *ab initio* Hartree-Fock calculations [8] showed that the surface of zirconia powders is covered by chemisorbed hydroxyl species formed in two configurations. Therefore, it is tempting to correlate the two site-selected spectra of the present study with the two regimes of local structures found in other experiments. More laser experiments on Nd-ZrO₂ powders with controlled OH and water coverage are under way to clarify the effects of surface chemistry on local structures.

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Figure Captions:

Figure 1 Laser-excitation spectra of the $^4I_{9/2}$ to $^4G_{7/2}$ transitions of Nd^{3+} in $Nd_{0.1}Zr_{0.9}O_{1.95}$ at 8 K monitored with fluorescence emission energies of 11205 cm^{-1} and 11396 cm^{-1} , respectively, for site A and site B.

Figure 2 The emission spectra of the $^4F_{3/2}$ to $^4I_{9/2}$ transitions of Nd^{3+} in $Nd_{0.1}Zr_{0.9}O_{1.95}$ at incident laser energies of 18552 cm^{-1} for site A and 18941 cm^{-1} for site B. The observed fluorescence intensity for site B was divided by a factor of ~ 8 in order to bring it on a scale comparable to the intensity for site A.

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