RAPID COMMUNICATION

Preparation and characterization of photoluminescent praseodymium-doped ZrO$_2$ nanostructured powders

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Abstract
Praseodymium-doped ZrO$_2$ photoluminescent (PL) powders have been
prepared by a co-precipitation process. Different doping concentrations in
the start mixture and annealing temperatures for the precipitated were
studied. It is observed that the crystalline structure and the crystallinity of
the powders depend on the annealing temperature. For temperatures higher
than 750°C, the material presents the monoclinic phase with an average
crystalline grain size of 100 nm. Measurements on photoluminescence show
excitation and emission spectra. For an excitation wavelength of 294 nm, all
the PL emission spectra show the peaks located at 490, 505, 536, 567, 589,
616, 645, 725 and 745 nm associated with $^3P_0 \rightarrow {}^3H_4$, $^3P_0 \rightarrow {}^3H_4$,
$^3P_1 \rightarrow {}^3H_5$, $^3P_0 \rightarrow {}^3H_5$, $^3P_0 \rightarrow {}^3H_5$, $^3P_0 \rightarrow {}^3H_6$, $^3P_0 \rightarrow {}^3F_2$, $^3P_0 \rightarrow {}^3F_3$ and
$^3P_0 \rightarrow {}^3F_4$ transitions in the Pr^{3+} ion, respectively.

1. Introduction

The atomic structure, microstructure, defects, phase
transformations and processing [1–6], on the one hand, and
the thermal, mechanical, electrical and optical properties [7],
on the other, are intimately connected in the case of zirconia.
Zirconium oxide has a high thermal expansion coefficient
$(10.2 \times 10^{-6} °C^{-1})$, making it easy to adhere to metallic
substrates [8], and a low thermal conductivity $(2.0 \, W \, mK^{-1})$,
temperature-independent, suggesting that it can act like a
thermal barrier coating. In addition, due to its high refractive
index [9], wide energy bandgap, low optical loss, chemical and
photochemical stability and excellent mechanical, electrical,
thermal and optical properties, zirconium oxide has been used
widely as an interferometry filter and for coating high power
laser mirrors [10]. This has made it an ideal medium for
photonic applications. Also, the low phonon energy of ZrO$_2$,

when it is doped with rare-earths [11], increases the number
and the probability of radiative transitions.

Compared with the amount of work on the mechanical and
structural characteristics of zirconia [12–15], there have been
few papers published on its luminescent properties (e.g. [16]).
The growing interest in the luminescent area arises partially
from the potential usefulness of luminescent techniques in the
characterization of zirconia-toughened ceramics [17, 18] and
from the possibility of using zirconia crystal as a laser host [19].

The rare-earths have been recognized as the most
important optical activators for luminescent devices [20]. The
ability of the rare-earths to provide the three basic colours
needed in a full colour device has led to the intensive studies
of the doping of II–VI compounds with these activators [21].
There is also an interest in using rare-earth ions to produce an
emission in the near infrared range for medical applications
and communication purposes. Among the various rare-earth
luminescent centres, trivalent praseodymium is a unique
optical activator, providing the possibility of simultaneous

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blue, green and red emissions, satisfying the complementary colour relationship [22, 23].

On one hand, studies in praseodymium-doped materials have been done with a major focus on the laser area. May be this is due to the possible applications in chemical, biological and medical fields and new data storage and display techniques. On the other hand, praseodymium-doped samples have an emission spectrum with multiple peaks in the visible range, which facilitates a number of applications such as active optical windows, new generation television screens and phosphor materials.

This paper reports the crystalline structure and photoluminescent (PL) characteristics of praseodymium-doped ZrO_2 powders prepared by the co-precipitation technique. The role that some preparation parameters play in determining these characteristics has also been reported.

2. Experimental details

The co-precipitation technique was used to prepare praseodymium-doped zirconium oxide powders. This process consists of four steps: (1) precursor material dissolution in a compatible solvent to form the precursor mixture, (2) solvent evaporation and solute precipitation, (3) grinding and (4) powder annealing [24].

In this work, the precursor powder material and the solvent were zirconium oxichloride ($ZrOCl_2 \cdot 8H_2O$, Aldrich Chemical Co.) and ethyl alcohol, respectively. Doping with Pr^{3+} was achieved by adding $PrCl_3 \cdot 6H_2O$ to the precursor mixture in the range from 1 to 10 at% (a/o) in relation to the Zr content in this mixture. An agate mortar was used to crush the obtained mixture and produce a fine powder. The powders were annealed in air at different temperatures (T_a) in the range from 350˚C to 950˚C for 120 min. Particle size and shape qualitative measurements were performed by scanning electron microscopy (SEM) and chemical composition characterization using energy dispersive spectroscopy (EDS), both with a Leica Cambridge Electron Microscope Mo. Stereoscan 440 equipped with a beryllium window x-ray detector. The crystalline structure of the powders was analysed by x-ray diffraction (XRD), using a Siemens D-5000 equipment with Cu Kα radiation at 1.5426 Å. The excitation and emission PL spectra were obtained using a Perking-Elmer LS50B fluorescence spectrophotometer with a resolution of <2 nm; the lamp intensity correction is performed automatically by this instrument, which measures the excitation light intensity with an additional photomultiplier and performs the correction accordingly before displaying the data. All the PL spectra were obtained at room temperature.

3. Results and discussion

The particle shape of the powders obtained was irregular; this may be appreciated from the SEM micrograph shown in figure 1. There is a wide variety of particle sizes, between 10 and 100 μm approximately, due to the grinding process.

The results for EDS measurements performed on powders annealed at 950˚C for 120 min are shown in table 1. The relative content of oxygen, zirconium and praseodymium present in the powders as a function of the content of $PrCl_3$
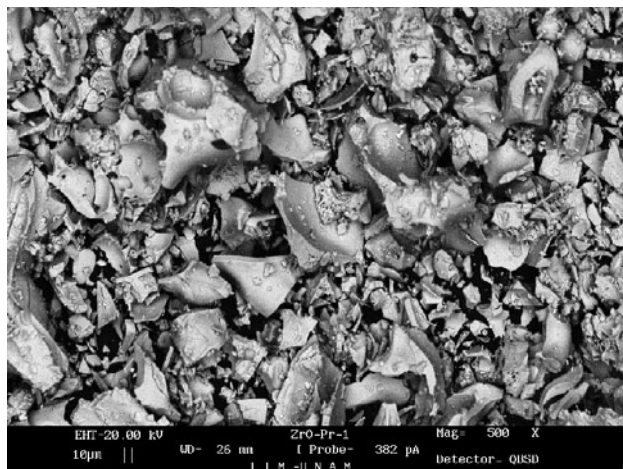

Figure 1. A SEM micrograph of praseodymium-doped zirconia powder, $T_a = 950$˚C.

Table 1. Atomic per cent content of oxygen, zirconium and praseodymium in the powders as measured by EDS for different $PrCl_3$ concentrations in the precursor mixture. In this case, the annealing temperature was 950˚C.

$PrCl_3$ concentration in the precursor mixture (a/o)	Oxygen	Zirconium	Praseodymium
0	67.85	32.15	0.00
1	76.55	23.30	0.15
3	74.32	25.03	0.65
5	70.08	29.21	0.71
10	75.00	23.36	1.64

incorporated into the precursor mixture is summarized in this table. The relative content of praseodymium in the resulting powders increases as the doping concentration in the precursor mixture is raised.

XRD patterns for undoped zirconia powders annealed at 350˚C, 550˚C, 750˚C and 950˚C are shown in figure 2. The crystallinity of the powders evolves into a well-defined structure as T_a is increased. Also, there is a transition from a cubic/tetragonal phase at 350˚C to a monoclinic phase at 950˚C. A mixture of both phases is observed at intermediate temperatures (according to the JCPDS-37-1484). The lattice parameters obtained from these patterns (the inter-plane distances were $d_{-111} = 3.1848$ Å and $d_{111} = 2.8407$ Å, respectively) are $a = 5.3129$ Å, $b = 5.2125$ Å and $c = 5.1471$ Å. An average crystalline grain size of 100 nm for powders annealed at 950˚C was calculated by the Scherrer formula on the peaks (111), (110), (-111) and (001).

The luminescence characterization in this work was focused only on the best quality powders (those synthesized at 950˚C), that is, those with a well-defined crystalline structure and intense luminescence emission when doped with the Pr^{3+} ion. Figure 3 shows the PL emission spectrum for an undoped zirconia powder annealed at 950˚C obtained with 270 nm excitation light. A broad band of about 120 nm wide, centred at 450 nm, is observed, indicating a blue emission due to the ZrO_2 [25]. The inset shows the excitation spectrum for this emission presenting two peaks, one at 270 nm and another at 330 nm.
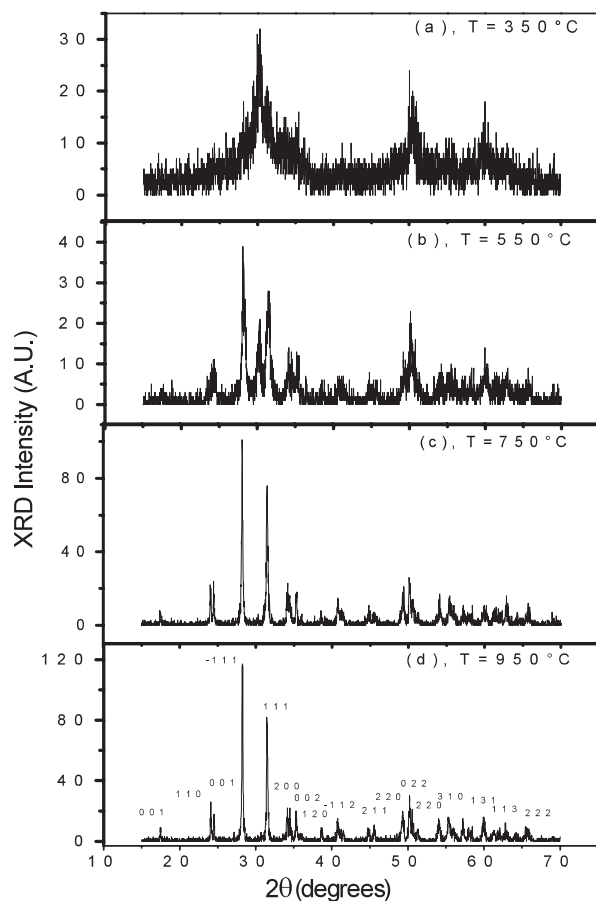
Figure 2. XRD patterns of undoped zirconia powders, as a function of annealing temperature: (*a*) 350°C, (*b*) 550°C, (*c*) 750°C and (*d*) 950°C.
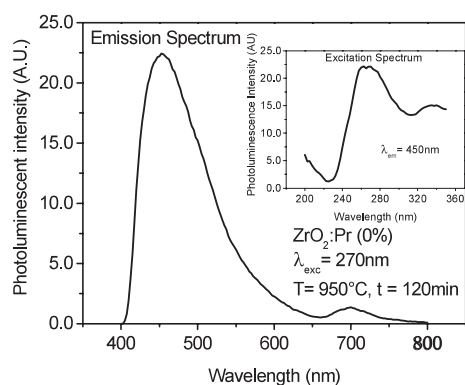

Figure 3. PL emission spectrum of undoped zirconia powder. Inset shows its excitation spectrum corresponding to the emission peak centred at 450 nm.

PL measurements on Pr-doped powders show multiple peaks centred at 490, 505, 536, 567, 589, 616, 645, 725 and 745 nm, associated with the Pr^{3+} energy level transitions $^3P_0 \rightarrow {}^3H_4$, $^3P_0 \rightarrow {}^3H_4$, $^3P_1 \rightarrow {}^3H_5$, $^3P_0 \rightarrow {}^3H_5$, $^3P_0 \rightarrow {}^3H_5$, $^3P_0 \rightarrow {}^3H_6$, $^3P_0 \rightarrow {}^3F_2$, $^3P_0 \rightarrow {}^3F_3$ and $^3P_0 \rightarrow {}^3F_4$, respectively; the maximum emission intensity corresponded to the peak centred at 616 nm, as illustrated in figure 4 for a 3 *a/o* (the optimal doping concentration) doped powder annealed at 950°C. The intensity of this 616 nm peak seems
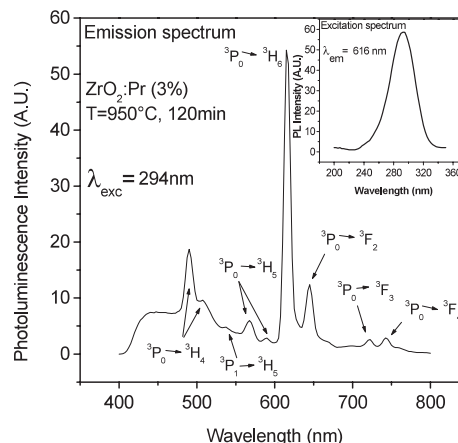

Figure 4. PL emission spectrum of praseodymium-doped zirconia powder. Inset presents its excitation spectrum corresponding to the emission peak centred at 616 nm.

rather strong with respect to the rest of the Pr^{3+} ion transitions, and at the present moment the exact nature of this behaviour is not understood. The inset of this figure shows the excitation spectrum for the maximum emission intensity (peak centred at 616 nm). Here, it is a remarkable band centred at 294 nm. Radiation with this wavelength was employed to excite the powders studied. The inter-configurational allowed transitions of rare-earth ions are of two different types: charge-transfer transitions (CTTs) and $4f^n \rightarrow 4f^{n-1}5d$ transitions. The CTTs are found for rare-earth ions such as Eu^{3+} and Sm^{3+}, which are likely to be reduced. For trivalent rare-earth ions having a tendency to become tetravalent, such as Pr^{3+} and Tb^{3+}, the 4f $\rightarrow$ 5d absorption band in the ultraviolet region is often observed [26]. From this argument, the absorption band centred at 294 nm can be associated with the 4f $\rightarrow$ 5d transition of Pr^{3+} in a ZrO_2 matrix. The electronic structure of praseodymium has been reported to be very sensitive to crystal field changes, in particular the 4f $\rightarrow$ 5d band. In fact, shifts of more than 30 nm (from 322 to 285 nm) have been reported for the excitation spectra of Pr^{3+} in the $Y_2O_3 : Pr^{3+}$ system under thermochemical reduction treatments. These shifts are associated with the formation of oxygen vacancies [12]. Therefore some structure could be expected in this peak, if the material homogeneity allows significant variations in the ion's crystal field in a given sample. The non-structured 294 nm band in this case could indicate that there is a dominant spectroscopic site associated with the praseodymium in these samples. In addition, no evident 4f $\rightarrow$ 4f absorption characteristics were observed in the excitation spectrum due to the parity selection rule forbidding these transitions. Finally, it was observed that the overall PL emission intensity increased as T_a was increased.

4. Conclusions

Nanostructured $ZrO_2 : Pr^{3+}$ powders synthesized using a low-cost process have been studied. The evolution of the crystalline structure and the PL properties of these powders are strongly dependent on the annealing temperature. The form and the size (higher than 10 μm) of the powder particles were irregular and determined by the grinding process of the powders. The

crystalline structure evolved from a cubic/tetragonal phase to a monoclinic phase as the annealing temperature was increased. The optimal emission intensity was obtained with $3\,a/o$ Pr^{3+} concentration doping ($0.65\,a/o$ inside the powder as measured by EDS). A concentration quenching was observed at higher doping values. The photoluminescence spectrum exhibited emission peaks associated with the electronic energy inter-level transitions of the Pr^{3+} ion. It is possible to observe emissions in the wavelength range associated with the three basic colours: blue colour due to the contributions of the zirconia host and Pr^{3+} ion and the green and red colours due to the Pr^{3+} ion. To our knowledge, no previous work has been reported on the luminescence characteristics of praseodymium-doped zirconia powders.

Acknowledgments

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