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Enhanced Phase Stability and Photoluminescence of Eu$^{3+}$ Modified t-ZrO$_2$ Nanoparticles

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Abstract

Tetragonal (t) ZrO$_2$ of nanoparticles, have been achieved by a partial Eu$^{3+}$ → Zr$^{4+}$ substitution, synthesized using a simple oxalate method at a moderate temperature of 650°C in air. The Eu$^{3+}$ additive, 2 mol% used according to the optimal photoluminescence (PL), renders small crystallites of the sample. On raising the temperature further, average crystallite size $D$ grows slowly from 16 nm to a value as big as 49 nm at 1200°C. The Eu$^{3+}$:t-ZrO$_2$ nanoparticles have a wide PL spectrum at room temperature in the visible to near IR regions (550 - 730 nm) in the $^{5}D_0$ → $^{7}F_J$ (Eu$^{3+}$), $J = 1$ to 4, electronic transitions. The intensity of $^{5}D_0$ → $^{7}F_4$ group is as large as the characteristic $^{5}D_0$ → $^{7}F_2$ group of the spectrum in the forced electric-dipole allowed transitions. The enhanced t-ZrO$_2$ phase stability and wide PL can be attributed to the combined effects of an amorphous Eu$^{3+}$-rich surface and part of the Eu$^{3+}$ doping of ZrO$_2$ of small crystallites.

Key words: Chemical Synthesis; Oxalate processing; Eu$^{3+}$:t-ZrO$_2$ nanopowder; Phase stability in small particles; Tetragonal ZrO$_2$; X-ray diffraction; Photoluminescence.

I. Introduction

Nanocrystalline t-ZrO$_2$ has extensive use as catalysts or catalyst supports, and as oxygen sensor. It is known to have excellent mechanical properties and one of the so called ‘superplastic’ structural materials. Doped t-ZrO$_2$ with rare-earth ions can be employed as building blocks to develop a wide range of nanotechnological optical materials due to its chemical and physical stability, high refractive index, and low phonon energy. At atmospheric pressure, bulk ZrO$_2$ exists in three well-known polymorphs of P2$_1$/c monoclinic (m), P4$_2$/nm tetragonal (t), and Fm3m cubic fluorite (c) crystal structures, with m-ZrO$_2$ the equilibrium structure at low temperatures. The t- or c-ZrO$_2$ appears upon heating m-ZrO$_2$ to 1170°C or 2370°C.
A chemical doping of divalent and trivalent cations such as Mg$^{2+}$, Ca$^{2+}$, Cr$^{3+}$/Cr$^{4+}$, or rare-earth ions was used to obtain the c- and t-ZrO$_2$ phases at low temperature.$^{5,8-10}$ Small particle size, dopands, and possible O$^{2-}$ vacancies lead the system to the increase in the Gibbs free energy to cope with the values for such polymorphs. Part of the dopand segregates, forming a high-energy surface-strained core-shell structure of particles.$^{10}$ According to phase stability, at a certain critical temperature, m-ZrO$_2$ reverts back after relieving the excess energy.

The t-ZrO$_2$ in form of nanoparticles has been prepared at low temperature by several methods including polymer template,$^2$ sol-gel,$^{9,11}$ microwave irradiation,$^7$ or precipitation.$^{4,10,12}$ 3 mol% Y$^{3+}$ stabilized t-ZrO$_2$ of nanophase, prepared via an oxalate method, retains well up to 650°C.$^{13}$ In doped or coated t-ZrO$_2$ particles with 1 mol % Eu$^{3+}$, a mixed phase develops with m-ZrO$_2$ as early as 1000°C.$^{8,12}$ A single t-ZrO$_2$ phase was retained with as large as 9.4 mol % Eu$_2$O$_3$.$^{14}$ There is a growing demand for producing stable t-ZrO$_2$ with minimal doping. Few studies have been carried out concerning photoluminescence (PL) properties of nanoscale rare earth doped ZrO$_2$ crystallites.$^{6,7,8}$ PL has renewed the interest in Eu$^{3+}$:t-ZrO$_2$ nanoparticles to discover its potential applications. Here, we apply a simple oxalate method for synthesizing such nanoparticles, with a wide PL from 550 to 730 nm. Eu$^{3+}$ doping as small as 2 mol% renders a single t-phase to be stable up to a temperature as high as 1200°C in air.

II. Experimental Procedure

ZrOCl$_2$·8H$_2$O, Eu$_2$O$_3$, and oxalic acid of 99.99 % purity were used as raw materials. Aqueous solutions (1.0 M) of ZrOCl$_2$·8H$_2$O and oxalic acid were prepared. A requisite amount of Eu$_2$O$_3$ (0.02 M/dl in HCl) was admixed to the ZrOCl$_2$·8H$_2$O solution and then the oxalic acid was added drop-wise to perform the reaction by stirring with a magnetic stirrer at room temperature. The molar ratio of the (Eu + Zr)/oxalic acid solution was 1/1. The obtained gelly product of Eu-Zr oxalates was filtered and washed with distilled water to remove chlorides and other byproducts. Nanophase Eu$^{3+}$:t-ZrO$_2$ was formed after heating a dried (at 200°C in air) and pulverized powder at 650°C for 2 h in air.

The Eu$^{3+}$:t-ZrO$_2$ structure was analyzed with X-ray diffraction (XRD). The XRD was recorded on a Philips P.W. 1710 X-ray diffractometer with 0.15418 nm CuK$\alpha$ radiation. Average D-value was calculated from the peak broadening with the Debye-Scherrer relation. A Jobin-Yvon Ramnor-HG-2S spectrophotometer was used to study Raman spectra by exciting the samples at 488.0 nm of an Ar$^+$ laser. The microstructure was studied using a JEOL JEM-200C transmission electron microscope (TEM). The PL was obtained by irradiating the sample at 465.8 nm of an Ar$^+$-ion laser, with 90 mW power and 3.0
A mm beam diameter. A monochromator (SPEX model 500M) of a 600 lines/mm grating and an InGaAs detector collected the data.

III. Results and Discussion

Figure 1 shows XRD pattern of a typical sample 2 mol% Eu\(^{3+}\):ZrO\(_2\) after heating the oxalate at (a) 650°C, (b) 1000°C, and (c) 1200°C in air for 2 h. As marked therein all the peaks belong to a single phase t-ZrO\(_2\). Broad and asymmetric peaks in small crystallites, D = 16 nm, of powder (a) are distinguished to those of c-ZrO\(_2\) with a close observation of the splitting in some of the peaks and the appearance of the (103) and (211) peaks. Such peaks are well resolved in symmetric and narrowed profiles in other two samples with 29 and 49 nm D-values, respectively. As portrayed in Fig. 2, the lattice parameters \(a\) and \(c\) changed as much as 0.3 and 0.6 %, respectively, on raising the temperature from 650 to 1200°C, with \(a = 0.3587\) nm and \(c = 0.5150\) nm after 650°C while \(a = 0.3599\) nm and \(c = 0.5180\) nm after 1200°C. Tetragonality \(\tau = c/a\) improved from 1.436 to 1.439 (Fig. 2a). At early temperatures below 800°C, primarily the \(a\)-value continues to be increasing followed by the \(c\)-value so that \(\tau\)-value decreases until it approaches 800°C and then rises rapidly, with no much change after 1000°C. Preferably, Eu\(^{3+}\) occupies the sites primarily along the \(a\)-axis at temperatures below 800°C while along the \(c\)-axis at higher values.

As plotted in the inset (b) to Fig. 2, the lattice volume \(V_0\) is increasing nonlinearly against the temperature, which is typical of a high-energy microstructure. A value of 0.06708 nm\(^3\), which is larger than the 0.06678 nm\(^3\) value in undoped t-ZrO\(_2\)\(^{15}\), is achieved after 2 h of heating at 1200°C. It is 1.2% larger than the value obtained in the sample heated at 650°C for 2 h in air.

An undoped sample heated at 500°C consists of both t- and m-ZrO\(_2\) phases. Mostly the m-ZrO\(_2\) develops as early as 650°C. The doping of 2 mol % Eu\(^{3+}\) by the oxalate route shifts the t \(\rightarrow\) m-ZrO\(_2\) transformation dramatically at temperature as high as 1450°C. As reported by Gutzov et al.\(^{12}\), only a mixture of the two phases persists for 1 mol% Eu\(^{3+}\) doped ZrO\(_2\) samples, obtained by the coprecipitation from the ZrOCl\(_2\)-8H\(_2\)O and Eu(NO\(_3\))\(_3\) with NH\(_4\)OH in water and followed by calcining at over 350-1000°C. A coprecipitate containing even a larger Eu\(_2\)O\(_3\) content of 6.4 mol% evolves a similar t-/m-ZrO\(_2\) mixture up to a temperature of 1300°C.\(^{14}\) In the equilibrium ZrO\(_2\)-Eu\(_2\)O\(_3\) phase diagram, t-ZrO\(_2\) occurs in a single phase compound over a limited Eu\(^{3+}\) content 3.0 mol% or lower after heating at and above 850°C.\(^{16}\) Andrievskaya and Lopato proposed a non-equilibrium phase-diagram (metastable phase
diagram) based on XRD data at room temperature. According to it, the metastable t-phase of ZrO$_2$ is stabilized by a narrow range of 3-6 mol\% Eu$_2$O$_3$ after heating a precipitate at 1170°C in air.

The Eu$^{3+}$:t-ZrO$_2$ phase is characterized further with its distinctive Raman spectrum, which shows six normal modes of vibration A$_{1g}$, 2B$_{1g}$, and 3E$_g$.

It differs from the c-ZrO$_2$, which has only one Raman active band F$_{2g}$. Figure 3 shows a typical spectrum for the sample Eu$^{3+}$:t-ZrO$_2$ heated at 650°C for 2 h. The six bands at 150, 265, 318, 468, 609 and 640 cm$^{-1}$ are very similar to the values for undoped t-ZrO$_2$. In general, the present values stand 5-15 cm$^{-1}$ larger in the modified force fields in the presence of Eu$^{3+}$ ions and/or possible O$^{2-}$ vacancies. The TEM images in Fig. 4a reveal the particles of 13 to 65 nm diameters self-assembled in a specific structure with enclosed pores in between the particles. Some of the particles (dark) accompany distinct thin surface layers with rather less darkness. Average lattice spacing in the high resolution lattice images in Fig. 4b is 0.2925 nm, which is in proximity to the value of 0.2931 nm of the (101) reflection in XRD in Fig. 1. In the top corner in Fig. 4b, a cation column with a markedly low level of intensity is denoted by an arrow. In the vicinity, one observes a strong deviation from the image contrast of the perfect structure, possibly due to deficiency of Zr$^{4+}$, i.e., presumably the Eu$^{3+}$ $\rightarrow$ Zr$^{4+}$ substitution. A distinct amorphous surface layer (denoted as a-layer) is very much visible in Fig. 4b.

There are reasons to believe that part of the Eu$^{3+}$ used forms the Eu$^{3+}$:t-ZrO$_2$ surface layer with controlled D-value of the surface modified crystallites. This let the structure survive in extended D-values up to 49 nm, which is well above the critical value of D$_c$ = 30 nm for pure t-ZrO$_2$ stabilization. Shukla et al.$^{19}$ observed similarly large spherical particles (45 nm) of pure ZrO$_2$, which exhibits t-phase at room temperature. The tendency of nanocrystallites to form hard-aggregates is observed to be responsible for stabilizing within the large sized ZrO$_2$ particles in the range of 500-600 nm. In the thermodynamics$^{5,10}$, the D$_c$ value depends on the particle surfaces, interfacial energy, strain energy, and the volume Gibbs free energy (affected by the vacancies and the local site symmetries).

As shown in Fig. 5, a typical sample Eu$^{3+}$:t-ZrO$_2$ consists of four PL bandgroups (i) 560 - 600, (ii) 600 - 645, (iii) 645 - 680, and (iv) 680 - 730 nm in the $^5$D$_0$ $\rightarrow$ 7F$_1$, $^5$D$_0$ $\rightarrow$ 7F$_2$, $^5$D$_0$ $\rightarrow$ 7F$_3$, and $^5$D$_0$ $\rightarrow$ 7F$_4$ (Eu$^{3+}$) transitions, respectively. The peak intensities of the representative members are in the ratio of 63: 100: 34: 87. Characteristically weak $^5$D$_0$ $\rightarrow$ 7F$_0$ band has no visible value. The $^5$D$_0$ $\rightarrow$ 7F$_1$ (592 nm) band, which is a magnetic-dipole allowed transition,$^{20,21}$ has a relatively enhanced value. The $^5$D$_0$ $\rightarrow$ 7F$_3$ (658 nm) band, a forbidden transition by the electric-dipole as well as the magnetic-dipole$^{20}$, appears to
be the weakest band of the spectrum. As a hypersensitive forced electric-dipole transition, the $^5D_0 \rightarrow ^7F_2$ (608 nm) band stands to be the predominant group in the $^5D_0 \rightarrow ^7F_J$, $J = 0 \rightarrow 4$, series. The implication is that Eu$^{3+}$ occupies the sites of presumably distorted symmetries in the Eu$^{3+}$:t-ZrO$_2$ nanocomposite particles.

Unusually, the $^5D_0 \rightarrow ^7F_4$ (714 nm) transition (forced electric-dipole$^{20}$) represents the second most intense bandgroup in this example of Eu$^{3+}$:t-ZrO$_2$ nanoparticles. Eu$_2$O$_3$ doped or coated sample of mostly m-ZrO$_2$, prepared by Ghosh and Patra$^8$, has no significant intensity in this transition. Two prominent bands at 596 and 617 nm were observed in such samples annealed at 1000 and 1100°C.$^8$ The Eu$^{3+}$-Eu$^{3+}$ ionic and electron–phonon interactions are a function of the microstructure in tuning the spectrum sensitively according to the local and the long range structures of hybrid composite nanoparticles. Presence of small pores is another important issue to control such interactions.$^{10,21}$ Small particles and intergranular Eu$^{3+}$ doping of Eu$^{3+}$:ZrO$_2$, with a huge strain, thus seems to be a major source of inducing the optical properties.

**IV. Conclusions**

Metastable t-ZrO$_2$ has been successfully synthesized using oxalate method with as small doping as 2 mol% Eu$^{3+}$. This synthesis route provides a simple and economic method in comparison with the sol-emulsion-gel or other processes for producing t-ZrO$_2$ nanoparticles. The Eu$^{3+}$:t-ZrO$_2$ formation, stability, and PL properties were studied with the X-ray diffraction, microstructure and PL techniques. This specific phase stands to be stable up to a temperature as high as 1200°C in air. The grain surface, the internal distribution of Eu$^{3+}$ within the Eu$^{3+}$:t-ZrO$_2$ lattice, and possible O$^{2-}$ vacancies play important role in stabilizing this phase, with a wide and intense PL in the visible-near IR regions. The results suggest that Eu$^{3+}$:t-ZrO$_2$ nanoparticles can be used as building blocks to develop a wide range of nanomaterials for photonics and other devices.

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References


**Figure captions**

**Fig. 1.** X-ray diffractograms of Eu$^{3+}$: t-ZrO$_2$ after heating an oxalate precursor at (a) 650°C, (b) 1000°C, and (c) 1200°C in air for 2 h.

**Fig. 2.** Variations in the $a$ and $c$-values in Eu$^{3+}$: t-ZrO$_2$ as a function of the processing temperature. The plots for $c/a$ and $V_0$ are given in the insets (a) and (b) respectively.

**Fig. 3.** Raman spectrum of Eu$^{3+}$: t-ZrO$_2$ heated at 650°C for 2 h in air.* Electronic Raman band.

**Fig. 4.** (a) TEM and (b) lattice images of Eu$^{3+}$: t-ZrO$_2$ heated at 650°C for 2 h in air.

**Fig. 5.** PL of Eu$^{3+}$: t-ZrO$_2$ heated at 650°C for 2 h in air.
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