ABSTRACT

The present research work deals with synthesis of pure and modified ZrO_2 nanoceramics useful as structural and electronic materials, gas sensors, catalysis, and optical materials. Two independent methods (i) hydrolysis and (ii) oxalate method in water are developed in order to derive pure and Al^{3+} or Eu^{3+} modified polymer precursors of $ZrO(OH)_2 \cdot xH_2O$ or $ZrO(C_2O_4) \cdot xH_2O$ and in turn their ceramic derivatives of monolithic ZrO_2 and Al^{3+}: ZrO_2 and Eu^{3+}: ZrO_2 in different polymorphs by heating in air at elevated temperatures. The reaction in water extends viability of the methods for a mass scale production of them at an economic cost. The work involves a systematic study and analysis of the structures, microstructures, EPR and PL properties of samples prepared under different conditions. Thermal-thermogravimetric analyses of precursors show a manifested thermal stability in the additive modified compositions so that they stand with no significant mass loss to as high temperatures as 200°C in air. The additives support formation of a transparent Al^{3+}: $ZrO(OH)_2 \cdot xH_2O$ and Eu^{3+}: $ZrO(C_2O_4) \cdot xH_2O$ polymer or glass.

A structural model is proposed to describe formation of an inorganic polymer structure of $ZrO(OH)_2 \cdot xH_2O$ and its reaction through NH_4^+ in small groups or micelles to form a precursor complex in a lamellar or ring shape. Another model is developed to describe structural relaxation in reconstructive $ZrO(OH)_2 \cdot xH_2O$ thermal decomposition that occurs in a controlled manner in an extended polymer structure. On heating, a molecularly ordered precursor structure governs a reconstructive nucleation and growth in small t-ZrO_2 of nanoparticles in controlled morphologies of cubic, acicular, thin platelets, nanotubes, nanowires, nanorods or mesoporous depending on the final temperature, additives, and other experimental conditions.

A spontaneous decomposition of precursor occurs at an elevated temperature, i.e., as low as 200°C, and results in a substantially stabilized t-ZrO_2 of nanoparticles with a sharp size distribution. A small Al^{3+} or Eu^{3+} additive of 2.0 to 5.0 mol% is sufficient to stabilize the t-ZrO_2 structure over an extended temperature as high as 1450°C. Thus, the Al^{3+} and Eu^{3+} contents are varied from 0.5 to 20.0 mol% by optimizing the conditions to derive the stabilized t-ZrO_2 of nanoparticles. In general, it is observed that part of the Al^{3+} (undersize) or Eu^{3+} (oversize) additives occupies the ZrO_2 interstitial sites and the part modifies the grain surface or grain boundaries in a complex manner. As analyzed with X-ray diffraction, their distribution in two regions depends on (i) their total content in the precursor, (ii) the precursor structure, and (iii) the final processing temperature. Unless the temperature is raised above a critical value, below which the t-ZrO_2 phase retains, the intergranular Al^{3+} or Eu^{3+} retains in the integral part of Al^{3+}: t-ZrO_2 or Eu^{3+}: t-ZrO_2 particles and does not recrystallize in an independent phase. The additives inhibit grain growth in a desired controlled microstructure.

A new *Pmnb* o-ZrO_2 polymorph of orthorhombic structure is synthesized. It occurs in a mesoporous structure in heating a mesoporous $ZrO(OH)_2 \cdot xH_2O$ precursor at 350 to 500°C in air. No external surfactant is used to design and support the precursor structure. The results of the t-ZrO_2, o-ZrO_2, Al^{3+}: t-ZrO_2 and Eu^{3+}: t-ZrO_2 formations and their stabilities and phase transformations are studied with X-ray diffraction, microstructure, BET measurements, and XPS, and vibrational spectra. The Eu^{3+}: ZrO_2 shows PL of manifested intensity in the 550 to 780 nm region in $^5D_0 \rightarrow {}^7F_J$, J = 1 to 5, electronic transitions in the

Eu^{3+} ($4f^6$) cations. Band positions and intensity distribution in the various bandgroups vary as the functions of the (i) microstructure, (ii) Eu^{3+}-concentration, and (iii) Eu^{3+}: ZrO_2 polymorphism. The $^5D_0 \rightarrow {}^7F_2$ transition in particular occurs at significantly different positions in Eu^{3+}: t-ZrO_2 and Eu^{3+}: m-ZrO_2 polymorphs and thus provides a sensitive probe for an unambiguous analysis.

Keywords: Chemical synthesis; Controlled hydrolysis and polycondensation; Inorganic polymer precursors; ZrO_2 polymorphs; Metastable nanoceramics; Stabilized tetragonal ZrO_2 nanopowder; Amorphous materials; Intergranular additives; Powder-chemical preparation; Orthorhombic ZrO_2; Self-stabilized t-ZrO_2 nanoceramics; Al^{3+}: t-ZrO_2 nanoceramics; Eu^{3+}: t-ZrO_2 nanoceramics; Mesoporous ZrO_2 powder, Reconstructive phase transformations; Controlled grain growth, ZrO_2 nanocrystals, Modification in ZrO_2 polymorphs, t-ZrO_2 nanoclusters, ZrO_2 nanoceramics and applications.