ABSTRACT

The research work in this investigation describes synthesis of a novel series of magnetodielectric (or spintronic) materials of spin doped ZrO_2, e.g., $Zr_{1-x}Cr_xO_2$ ($x \leq 0.2$). This includes a detail study of the crystal structure and microstructure with magnetic, optical, and transport properties useful for pertinent applications. In optimizing their functional values, $Zr_{1-x}Cr_xO_2$ ($x \leq 0.2$) was prepared of small crystallites by two independent chemical methods involving an autocombustion of (i) a solid precursor powder or a derived paste in glycerol and (ii) a liquid precursor of $ZrO(OH)_2 \cdot \alpha H_2O$ grafted with a chromium salt in a polymer structure. A specific objective is to vary the $3d^2$-Cr^{4+} electrons/spins density which can tune dielectrics, electrical conductivity as well as the photonics with useful magnetic properties.

The thermal analyses (DTA/TG thermograms) of $Zr_{1-x}Cr_xO_2$ ($x \leq 0.2$) precursor powders reveal possible transformation temperatures. The powders were annealed based on these results in order to produce a single c- or t-ZrO_2-type phase of small crystallites (D = 3−14 nm), analyzed by X-ray diffraction patterns in the samples with varied Cr^{4+}-content (x = 0.05, 0.10, and 0.20 over the limited solubility of Cr^{4+} in ZrO_2). The microstructure (FESEM and HRTEM images) reveals a thin surface Cr_2O_3 layer (1-2 nm thickness) on the crystallites useful to modulate the functional properties in a core-shell structure. An intense light emission bandgroup appears over 565–600 nm in a $^3T_1 \leftarrow {}^3A_2$ electronic transition in confirming the Cr^{4+} oxidation state. A sample $Zr_{1-x}Cr_xO_2$ (x = 0.2) of D = 5 nm (of an ideal single domain) exhibits a maximum saturation magnetization M_s = 5.4 emu/g at room temperature {M_s = 103.0 emu/g (1.5 μ_B per Cr^{4+} ion) at 5 K}, with the Curie point T_C = 870 K. A dielectric permittivity as large as 60–70 is tuned in D = 5 nm crystallites and it has a controlled loss of 0.02–0.09 (over 295–473 K at 100 kHz). At room temperature, an ac conductivity 3.5×10^{-7} Scm^{-1} at 100 kHz gets promoted by three orders with frequency raised to 10^4 kHz. The parameters measured over temperature exhibit a distinct T_C point.

Keywords: Nanostructure; Chemical synthesis; Optical properties; Magnetic and transport properties; Magnetodielectrics; Spintronics