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Evidence of luminescence modification with structure of zirconia phases

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ABSTRACT

Three crystallographic phases of nanocrystalline zirconium oxide (ZrO_2) are prepared by solution combustion technique. Tetragonal and cubic phases are stabilized at low temperature by adding yttrium content. Phase stabilization is confirmed by X-ray diffraction and Raman spectroscopy. The XRD results are analyzed using rietveld refinement and average crystallite size is found to be 50 − 60 nm. Characteristic PL emission of Dy^{3+} ions are observed at 490, 578, 672 and 764 nm corresponding to $^{44}F_{9/2}\rightarrow{}^6H_{15/}$, $^4F_{9/2}\rightarrow{}^6H_{13/2}$, $^4F_{9/2}\rightarrow{}^6H_{11/2}$ and $^4F_{9/2}\rightarrow{}^6H_{9/2}$ transitions respectively. The spectral peak shape changes and variation of blue to yellow intensity ratio in different symmetry of ZrO_2 has been discussed. CIE chromaticity color coordinates (x, y) are calculated for Dy^{3+} doped zirconia phosphors and fall near white light region. A high intense TL glow peak at 441 K and a less intense peak at 550 K are observed in monoclinic ZrO_2. The intensity of 441 K TL glow peak is drastically reduced and a new TL peak at 703 K is found in tetragonal ZrO_2. Whereas, cubic ZrO_2 exhibit a single TL glow with peak at 703 K. Dy^{3+} doped ZrO_2 (monoclinic) exhibit two prominent TL peaks at 457 and 695 K whereas tetragonal and cubic samples shows only high temperature peak. It is concluded that TL curve is modified in three zirconia system and TL kinetic parameters are discussed.

1. Introduction

Lanthanide (Ln) ion doped ceramic material exhibit efficient luminescence properties. Zirconium oxide (ZrO_2) is a potential ceramic material due to its superior properties such as high chemical, thermal stability and low thermal conductivity [1,2]. ZrO_2 exhibits three main crystalline phases such as monoclinic (m), tetragonal (t) and cubic (c) systems. The monoclinic phase of ZrO_2 is stable at room temperature and it transforms to tetragonal phase when heated to 1170 °C with lattice contraction. Further heating to 2270 °C, the tetragonal phase transforms to cubic phase with lattice expansion [2]. The tetragonal and cubic structure of ZrO_2 is stabilized partially (two mixed phase) or fully at room temperature with incorporation of rare earth (RE) oxides such as yttria (Y_2O_3) [3], ceria (CeO_2) [4] and alkaline earth oxides viz MgO and CaO [2]. In the present work, the yttrium ions are used to stabilize the structure of zirconia (t − and c − phase), which improves chemical stability and physical properties. Luminescence properties of RE doped zirconia viz ZrO_2: Eu^{3+} [5,6], ZrO_2: Dy^{3+} [7], YSZ: Tb^{3+} [8], YSZ: Tm^{3+} and Yb^{3+} [9], YSZ: Dy^{3+} [10], ZrO_2: Sm^{3+} [11] etc. are widely studied.

Among the trivalent lanthanum (Ln) ions, dysprosium is one of the interesting ion for studying luminescence properties. In general, Dy^{3+} ions exhibit four emission bands at 480 ($^4F_{9/2}\rightarrow{}^6H_{15/2}$), 578 ($^4F_{9/2}\rightarrow{}^6H_{13/2}$), 665 ($^4F_{9/2}\rightarrow{}^6H_{11/2}$) and 760 nm ($^4F_{9/2}\rightarrow{}^6H_{9/2}$) [12]. The blue (B – 480 nm) to yellow (Y – 578 nm) emission intensity ratio (B/Y) varies with Dy^{3+} concentration, excitation wavelength and also with crystalline phase [13,14]. Based on the B/Y ratio, one can identify the site symmetry around the Dy^{3+} ions. If Dy^{3+} ion occupies a lower symmetry, the yellow transition shows higher intensity than the blue transition. Conversely, the blue transition shows dominant over the yellow transition, when the Dy^{3+} ion occupies higher symmetry with inversion centers [13].

Thermoluminescence (TL) glow peak position depends on the crystalline phase of ZrO_2. Undoped ZrO_2 exposed to UV rays exhibit TL glow peaks at 343, 403, 498 K corresponding to monoclinic phase and 673 K corresponding to tetragonal phase [15]. TL response of undoped and RE doped ZrO_2 under the irradiation of beta rays are reported [16–18]. In the present investigation, the high temperature phase of zirconia is stabilized at room temperature by adding yttrium content and effect of structural modification on Raman, PL and TL spectra of the Dy^{3+} doped zirconia phases are discussed as an evidence for luminescence modification.

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2. Experimental

2.1. Material synthesis

Nanocrystalline zirconia (undoped) and yttria stabilized zirconia (YSZ) powders are synthesized by solution combustion technique. Undoped ZrO_2 sample is labeled as Y0, while the series of five YSZ (2, 4, 6, 8, 10 mol%) samples are labeled as Yn, where 'n' is a number corresponding to the percent molar fraction of substitutional Y^{3+} ions. Zirconium (IV) oxynitrate hydrate, carbohydrazide and yttrium (III) nitrate hexahydrate are used as precursors. All the chemicals used in the present work are procured from Sigma – Aldrich (India) company. In a typical experiment, the stoichiometric amount of ingredients are dissolved in 50 ml of double distilled water in a cylindrical beaker of ≈ 300 ml capacity. The redox mixture of aqueous solution containing beaker is introduced into a muffle furnace preheated at 350 ± 10 °C. Initially, the solution boils and undergoes dehydration followed by decomposition with liberation of large amount of gases. Finally voluminous power is obtained [2,19]. Dy^{3+} doped samples are also synthesized using the same procedure. The obtained nanocrystalline powders are ground into a fine powder using agate mortar and pestle. All the samples are annealed at 850 °C for three hour for further characterization.

2.2. Characterization

The samples are characterized by X-ray diffraction (XRD) using advanced X – ray diffractometer (Bruker D8 AXS) with 1.5406 Å of Cu-K_α radiation. The operating current and voltage are 40 mA and 40 kV respectively. Raman spectra of the samples are recorded using LabRAM HR spectrometer (Horiba Scientific, Jobin Yvon Technology) with He-Ne Laser (632.8 nm). Photoluminescence (PL) spectra of the samples are carried out by using FLS980 fluorescence spectrophotometer (Edinburgh Instruments). PL excitation and emission spectra are recorded using 450 W continuous xenon arc lamp (Xe1) and data acquisition technique used as single photon counting PMT. Lifetime measurements carried out in a time range from microseconds to seconds under the excitation of 60 W xenon microsecond flashlamp (μF2) and data acquisition technique used in multichannel scale (MCS). TL measurements are carried out at a linear heating rate of 5 K/s using automated Riso TL/OSL reader (model DA-20) having an inbuilt $^{90}Sr/^{90}Y$ beta source (dose rate: 0.082 Gy/s). The glow curves are recorded under a nitrogen atmosphere to avoid spurious signals that may interfere with TL signals from the samples.

3. Results and discussion

3.1. X – ray diffraction

Fig. 1(a) shows XRD patterns of combustion synthesized YSZ. Diffraction peaks of Y0 sample are assigned to monoclinic phase of ZrO_2 (JCPDS file No. 86–1451). The XRD patterns contain main diffraction peaks at 28.14° and 31.42° corresponding to (−111) and (111) planes which are characteristics of monoclinic phase. Tetragonal and cubic phase of ZrO_2 is stabilized by adding to yttrium content. Tetragonal phase (Y6) is fully stabilized by adding 6 mol% yttrium ions. A strong diffraction peak at 30.10° corresponding to (101) plane confirms tetragonal phase (JCPDS file no. 86-1007). Fully stabilized cubic phase (Y10) is obtained by the addition of 10 mol% yttrium ions. Main diffraction peak appears at 30.04° with plane (111) for cubic phase (JCPDS file no. 81-1550). The small difference between main peak appearance in both t − phase and c − phase, but can be examining at ~35° and 60° of 2θ regions as shown in Fig. 1(b). The planes (200) and (311) of c − phase are splits into two planes (002), (110) and (103), (211) in tetragonal phase of ZrO_2 respectively. The added Y^{3+} ions substitutes into the Zr^{4+} sites of the zirconia lattice, oxygen vacancies

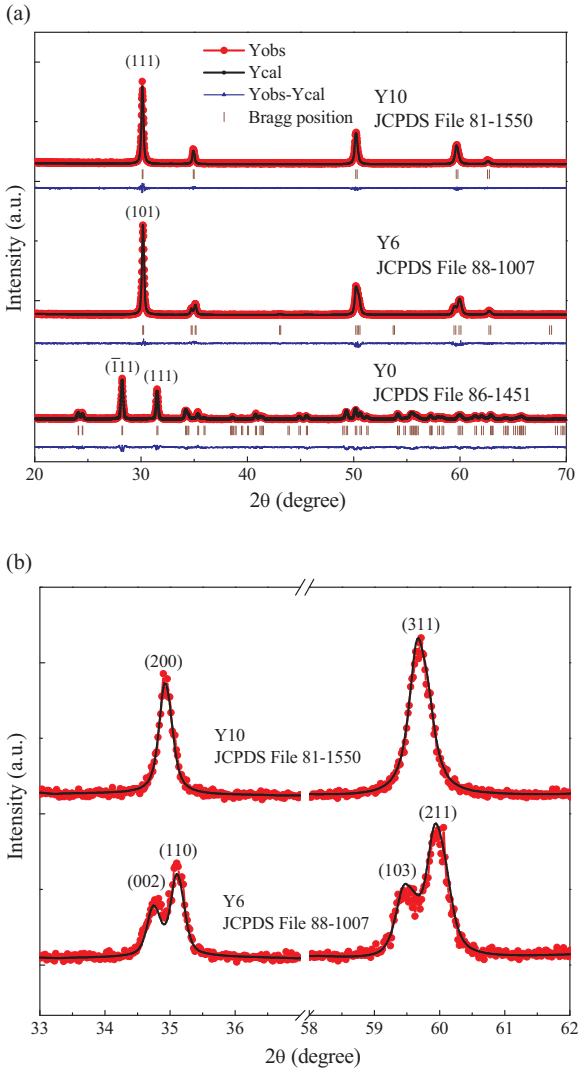

Fig. 1. (a) XRD patterns of YSZ, (b) enlarged view in small angle range.

are created due to charge compensation because of the difference in valency. Subsequently, a tetragonal unit cell is formed. Further increase in the amount of oxygen vacancies due to addition of Y^{3+} ions causes lattice distortions that result in the formation of cubic phase [20].

The crystallite size and effect of lattice strain (both are independent) are distinguished by Hall-Williamson plot [21] using Eq. (1).

$$\frac{\beta\cos\theta}{\lambda} = \frac{1}{D} + \frac{4\varepsilon\sin\theta}{\lambda}(\text{Hall} - \text{Williamson equation}) \quad (1)$$

Where D is crystallite size, β is full width at half maximum (FWHM), θ is Bragg angle, λ is the wavelength of X − ray (1.5406 Å) and ε is microstrain present in the samples. The W−H equation represents straight line for a plot of (β × cos θ)/λ (y−axis) versus 4sinθ/λ (x−axis). The crystallite size is obtained from the inverse of the intercept of straight line on y−axis and slope of the line gives microstrain (ε) present in the samples. The unit cell parameters of YSZ samples are calculated by Rietveld refinement method [22] using fullprof program [23]. The peak shape assumes as a pseudo−voigt function. The structural parameters are calculated and tabulated in Table 1. The quality of the structural refinement data is checked by measuring two parameters called Bragg's contribution (χ^2) and goodness of fit (GOF). The obtained χ^2 and GOF values indicating a good fit between the calculated and observed XRD pattern. Further, 1 mol% of dysprosium ions are doped to all the three crystallographic phases of ZrO_2 and the XRD patterns are shown in Fig. 2. A new trivial diffraction peak at 30.10° corresponding