



Electrical and dielectric studies of substituted holmium based pyrochlore zirconates nanomaterials



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ABSTRACT

The effects of Ge⁴⁺ cation substitution on the structure, morphology, electrical and dielectric properties of rare earth pyrochlore oxides (Ho₂Zr_{2-x}Ge_xO₇, 0.00 ≤ x ≤ 1.0) were investigated. The pyrochlore oxides were prepared by the microemulsion method. The XRD data Ge⁴⁺ substituted Ho₂Zr_{2-x}Ge_xO₇ reveal a cubic structure. Room temperature DC electrical resistivity increases on increasing the Ge⁴⁺ contents. The value of exponent 'n' calculated from the plot of log(σ) versus log(ω) ranges 0.78–0.95 suggested that the conduction phenomena in the studied samples pursue hopping conduction. Nyquist plot (Cole–Cole plot) was used to study relaxation phenomenon in the material. The visualization of semicircles in plot represent that grain boundary occupies small volume. The dielectric loss with frequency shows resonance peaks. The dielectric losses were stable below 1.3 GHz. Such frequency independent characteristic of the high dielectric constants Ho₂Zr_{2-x}Ge_xO₇ ceramics and their low dielectric losses make them more attractive in the applications of multilayer ceramic capacitors and resonators. The increase in resistivity with substitution makes these materials suitable for microwave devices.

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1. Introduction

Rare Earth Zirconate oxides with a pyrochlore structure of a composition Ln₂Zr₂O₇ display a remarkable variety of applications namely semiconducting behaviour, radioactive waste immobilization, ion conductors for fuel cells, oxidation catalysts [1] and high-permittivity dielectrics [2]. They have also been considered as the most promising candidate for the next generation of thermal barrier coatings, because they exhibit excellent high-temperature phase stability, low sintering rate and low thermal conductivity [3].

The pyrochlore-type structure (*Fd3m*) of Ln₂Zr₂O₆O' is an O-deficient superstructure of the fluorite structure-type (*Fm3m*) with the a-axis doubled. Three sites (48f, 8a, 8b) are available for oxygen in this structure: six oxygen atoms occupy the 48f sites, surrounded by two Ln³⁺ cations and two Zr⁴⁺ cations, while the seventh oxygen atom (O') occupies the 8a site and is surrounded by four Ln³⁺

cations and the third (8b) surrounded by Zr⁴⁺ cations remains unoccupied in a perfectly ordered pyrochlore [4]. Three types of chemical bonds, Ln–O, Ln–O' and Zr–O' can be distinguished inside the complex crystal structure of the Ln₂Zr₂O₇ pyrochlore. These chemical bonds penetrate each other along three-dimensions, and this may bring out novel properties for pyrochlores comparative to fluorite counterpart [2].

The Ln³⁺ and Zr⁴⁺ cations form a face-centered cubic array and are ordered on two separate cation sites into rows in the ⟨1 1 0⟩ directions. The corner-shared ZrO₆ octahedra forms the back bone of the network and Ln³⁺ ions fill the holes created by six ZrO₆ octahedra in the crystal structure of Ln₂Zr₂O₇ pyrochlore. It can endure vacancies at the Ln³⁺, Zr⁴⁺ and O²⁻-sites without phase transformation [3]. Moreover, both the Ln³⁺ and Zr⁴⁺-sites can be substituted by many other elements with similar ionic radii in a way that the overall electrical neutrality of the structure is maintained and improving the chances of moulding its properties. Larger cations (i.e., Ln³⁺) are incorporated in the 8-coordinated site, with smaller cations, (i.e., Zr⁴⁺) occupying the 6-coordinated site. The stability of pyrochlore oxide, Ln₂³⁺Zr₂⁴⁺O₇²⁻, is described in term of radius ratio of the ions is $r_{Ln}/r_{Zr} = 1.26 - 2.3$, where r_{Ln} is radii of

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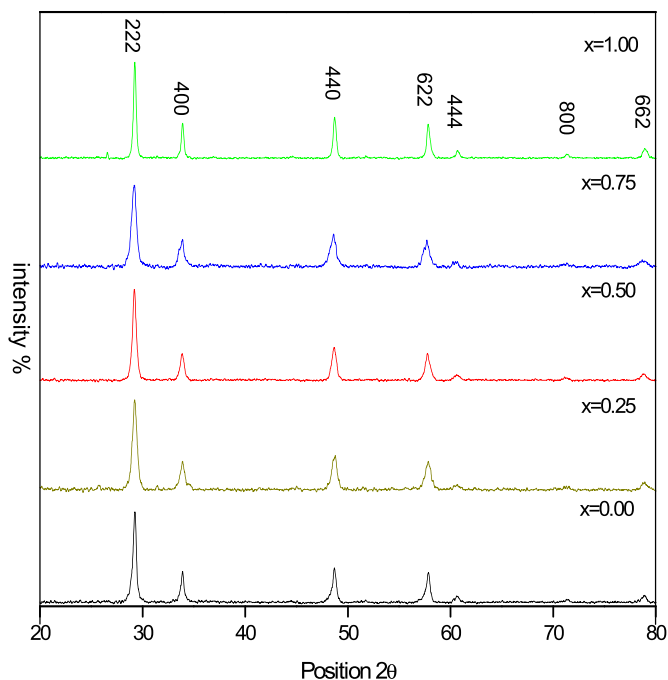


Fig. 1. Xrd pattern of $\text{Ho}_2\text{Zr}_{2-x}\text{Ge}_x\text{O}_7$.

8 coordinated rare earth ion and r_{Zr} is radii of 6 coordinated zirconium metal ion [5].

As the substitution of other cations take place at the sites of the Ln^{3+} and Zr^{4+} cations, greater disorder between the cation sites can occur leading to the transformation of the pyrochlore phase which alter the radius ratio and properties. Further (intense) interest in this particular system has been generated by the detailed insight into the mechanism of order/disorder involved in the phase transformation as a function of substitution at Zr^{4+} site by Ti^{4+} , Hf^{4+} and Sn^{4+} [6–8]. The present paper concerns the systematic research on the effect of substitution of larger ionic radius cation (Zr^{4+}) by smaller (Ge^{4+}) which shift structure toward more ordered pyrochlore form. The structural, electrical and dielectric properties are discussed to ensure the importance of these materials for electrical and microwave devices.

2. Experimental

2.1. Chemical used

The chemical used in present work were holmium nitrate

pentahydrate [$\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 99.9%, Aldrich], Germanium dioxide [GeO_2 , 99.9%, Aldrich], Zirconyl chloride tetrahydrate [$\text{ZrOCl}_2 \cdot 4\text{H}_2\text{O}$, 98%, Hopkin & William] as precursors, cetyltrimethyl ammonium bromide (CTAB) [97%, Merck] as a surfactant, ethanol [$\text{C}_2\text{H}_5\text{OH}$, 99.8%, BDH] as a washing agent and Ammonium hydroxide [NH_4OH , 35%, Riedel-de Haen] as a precipitating agent. All the chemicals were of analytical grade and were used as received without further treatment.

2.2. Synthesis procedure

The zirconates with composition $\text{Ho}_2\text{Zr}_{2-x}\text{Ge}_x\text{O}_7$ ($x = 0.0, 0.25, 0.5, 0.75$ and 1) were prepared by a microemulsion method. Appropriate quantities of holmium nitrate pentahydrate [$\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$], germanium dioxide [GeO_2], zirconyl chloride tetrahydrate [$\text{ZrOCl}_2 \cdot 4\text{H}_2\text{O}$], were dissolved to form molar solutions in stoichiometric ratio. Microemulsion solution was prepared by mixing cetyltrimethyl ammonium bromide (CTAB) in deionized water (3 M). The metal salts in their respective stoichiometry i.e., $\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (100 ml of 0.2 M), $\text{ZrOCl}_2 \cdot 4\text{H}_2\text{O}$ (75 ml of 0.2 M) and GeO_2 (25 ml of 0.2 M) in case of $\text{Ho}_2\text{Zr}_{1.50}\text{Ge}_{0.50}\text{O}_7$ and similar for other value of x , were added in the one part of prepared microemulsion solution and magnetically stirred for half an hour. In the second part of microemulsion solution, 100 ml of 2 M NH_4OH solution was added. Then these two microemulsions were mixed under vigorous magnetic agitation for 4 h. The precipitated pale yellow product was filtered, washed several times with ethanol until the pH value reached neutral and final product was dried in an oven at 110°C . The samples were annealed at 1123K for 8 h to get the desired phase. The schematic diagram for the synthesis process is shown in the Fig. 2.

2.3. Characterization

The prepared $\text{Ho}_2\text{Zr}_{2-x}\text{Ge}_x\text{O}_7$ nanoparticles were characterized by X-ray Diffraction (XRD) using the X'Pert PRO 3040/60 diffractometer from Philips Company, using $\text{Cu K}\alpha$ (1.54 Å) as X-ray source. The operating voltage and current were kept at 40 kV and 30 mA, respectively. FTIR spectra of the samples in the range of $400\text{--}4000\text{ cm}^{-1}$ were recorded by using FTIR spectrophotometer (8400 Shimadzu). The surface morphology and particle size of the prepared samples were determined using a scanning electron microscope (SEM) model Hitachi S4800 FE-SEM. The elemental composition of the synthesized $\text{Ho}_2\text{Zr}_{2-x}\text{Ge}_x\text{O}_7$ nanoparticles was confirmed by energy dispersive X-ray fluorescence spectroscopy (ED-XRF, Horiba, MESA-500). The dc electrical resistivity was measured in the temperature range of 298–673K by a two-point probe method using a laboratory built apparatus described by

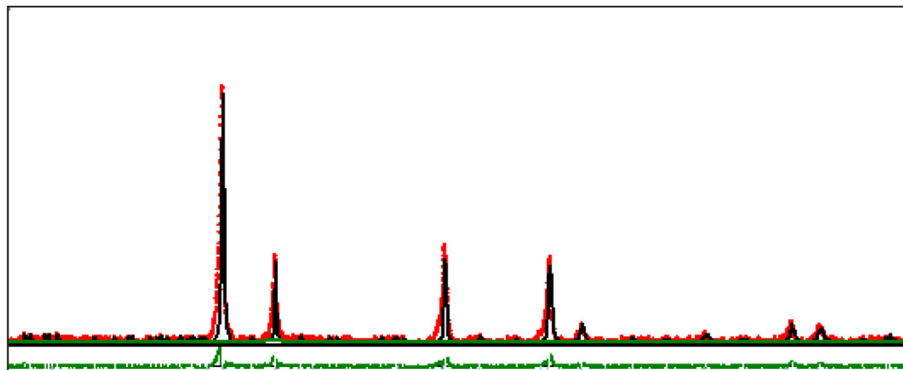


Fig. 2. Observed (solid red circles) and calculated (solid black line) X-ray powder diffraction patterns Observed for $\text{Ho}_2\text{ZrGeO}_7$. Residual errors (green) are drawn at the bottom of the figure. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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