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Optical and dielectric characterization of gadolinium aluminate ceramic nanoparticles synthesized by combustion technique

S.K. Saji [a], R. Vinodkumar [a], Shibu M. Eappen [b], P.R. Sobhana Wariar [a, *]

[a] Department of Physics, University College, Thiruvananthapuram, 695034, India
[b] STIC, Cochin University of Science and Technology, Cochin, 682 022, India

HIGHLIGHTS

- All the corrections recommended by the reviewers were done.
- Significance of the research work has been included in the introduction part.
- New studies such variation of dielectric properties with frequency and temperature has been carried out as suggested by the reviewers.

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ABSTRACT

Single phase nanocrystalline Gadolinium aluminate ($GdAlO_3$) has been synthesized from Gadolinium oxide and Aluminium nitrate by auto-ignition citrate complex combustion process. The thermal decomposition of precursor and successive phase formation has been investigated using X-ray diffraction analysis (XRD), Thermo-Gravimetric Analysis and Differential Thermal Analysis (TGA/DTA) and Fourier Transform Infrared (FT-IR) spectroscopy analysis. X-ray diffraction analysis (XRD) revealed the formation of $GdAlO_3$ with orthorhombic perovskite structure in the Pbnm space group. Transmission Electron Microscopy (TEM) has been employed for the particle-size analysis. The nanoparticle size is in the range of 30–50 nm. Surface morphology of the sintered pellet was obtained from High Resolution Scanning Electron Microscopy (HR-SEM). The absorption spectrum of the $GdAlO_3$ nanoparticles shows characteristic cut edge which was attributed to direct allowed transitions through optical band gap of 3.15 eV. The dielectric measurements as a function of temperature have been carried out on the sample in the frequency range 1 Hz-1 MHz. Values of dielectric constant ε' and loss tangent tan δ were found to be temperature and frequency dependent. The dielectric constant and loss tangent at 100 KHz were ~ 8.62 and ~0.02 respectively.

1. Introduction

Rare-earth aluminates having perovskite structure are of great interest in advanced materials research due to their excellent potential for optical, magnetic, electronic and structural applications. Because of their high chemical stability, rare-earth compounds, especially the oxides, form a promising class of materials [1–5]. These materials are widely used in number of applications like host for solid state lasers, solid electrolytes, chemical sensors, magnetic refrigeration materials, catalyst support and thermal barrier coatings [6–8]. Gadolinum aluminate ($GdAlO_3$) belongs to the family of ABO_3 type perovskite oxides and is considered as useful material owing to their several applications in diverse field such as phosphor [9–11], scintillator [12] and host systems for materials with oxygen ion conductivity [13], dielectric resonators [14] and regenerator material for sub- 4 K cryo-coolers [15].

The perovskite oxides have the general stochiometry ABO_3 (A cation is larger than B cation). Typical perovskite structures consist of large-sized 12-coordinated cations at the A site and small-sized 6-coordinated cations at the B site. The ideal perovskite structure possess cubic lattice, where the atoms touch one another following the relation, $r_A + r_O = \sqrt{2}(r_B + r_O)$, where r_A, r_B and r_O are the ionic radii of A and B cations, and oxygen, respectively. The measure of deviation from the cubic structure is defined by tolerance factor t, given by the relation, $t = (r_A + r_O)/[\sqrt{2}(r_B + r_O)]$. Although, for a cubic perovskite structure t is unity, different distortions of the

* Corresponding author.
E-mail address: prswariar53@gmail.com (P.R.S. Wariar).

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cubic structures, such as orthorhombic, rhombohedral and tetragonal were also appear in this structure for lower t values ($0.75 < t < 1.0$). The tolerance factor of $GdAlO_3$ is t = 0.95 and has the orthorhombically distorted perovskite structure in the binary system gadolinium sesquioxide-aluminium oxide with melting point about 2237K [2].

The synthesis of rare earth ceramic oxide nanocrystals is one of the major challenges in materials processing technology [16]. Nanocrystalline ceramic materials have superior powder properties such as phase homogeneity, better sinterability and often show modified mechanical, electrical, dielectric, magnetic, optical and catalytic properties over their microcrystalline counterparts [17–19]. Conventionally, $GdAlO_3$ is produced by solid-state reaction of Gd_2O_3 and Al_2O_3 that requires an extensive mixing combined with lengthy heat treatment and intermediate grinding. These parameters prevent fine control over the powder particles size and microstructure of the sintered body [12]. In order to improve the characteristics of the powder, especially its sinterability and phase purity, several wet-chemical techniques, such as polymerized complex route, combustion synthesis and sol-gel process have been utilized to synthesize Gadolinium aluminate.

The solution combustion synthesis is a better method to get the fine powder, with better sinterability at relatively lower temperature. This method offers an easy and cost effective technique for the synthesis of nanostructured materials. The solution combustion synthesis method has the advantages of homogeneous mixing of reactants at molecular level, accurate stoichiometry control and short process period. This process involves an exothermic redox reaction between the fuel and the oxidizer (ie. nitrates). The combustion once ignited is then self-sustaining. The rapid evolution of large volume of different gases during combustion dissipate the heat of combustion and limit the rise of temperature. This inhibits particle size growth by reducing the possibility of premature local partial sintering among the primary particles and favors nano-sized powders with high specific surface area that makes combustion synthesis an attractive technique for the nanomaterial synthesis [20]. ABO_3 perovskites prepared by auto-igniting combustion technique exhibits a reduction of sintering temperature of about $150^0C - 200^0C$, with a reduced sintering time of 2–3 h [21,22].

Dielectric properties of $GdAlO_3$ have been studied thoroughly in the past [2,8], however investigations on the dielectric response of this material in radio frequency range is scarce. As most of the electrical devices are operating in electrical mode, the investigation of ac electrical properties is important. In the present work, we report the details of preparation of nanosized gadolinium aluminate by auto-igniting combustion synthesis employing citric acid as complexing agent and ammonia as fuel. Also, we report the optical properties of $GdAlO_3$ nanoparticles obtained by combustion synthesis and the dielectric properties of the sintered pellets of the same material in the frequency range 1 Hz to 1 MHz and in the temperature range from 303 to 743 K.

2. Experimental

2.1. Synthesis

$GdAlO_3$ nanoparticles were synthesized by auto-combustion process, via citrate-nitrate method, using stoichiometric amounts of analytical grade gadolinium oxide Gd_2O_3 (99.99% purity, Sigma Aldrich), and $Al(NO)_3.9H_2O$ (99.99% purity, Sigma Aldrich). As starting materials, metal oxides Gd_2O_3 was dissolved in nitric acid and $Al(NO)_3.9H_2O$ in de-ionized water and the two solutions are mixed to form an aqueous solution. Proper amount of citric acid was added into the solution containing Gd^{3+} and Al^{3+} ions in maintaining citric acid to cation ratio at unity. The solution acidity was finally adjusted by adding suitable amount of ammonium hydroxide, considering too acidic solution prevent the complexations by the undissociated forms of citric acid, while too basic solutions promote the formation of metal hydroxides. The solution containing the complex precursor at neutral pH was heated on a hot plate to about 250^0C in a ventilated fume hood. The solution boiled on heating, which underwent dehydration and decomposition leading to a smooth deflation, producing foam. The foam, then self-ignited on persistent heating resulting in a fluffy and voluminous powder.

2.2. Characterization

The sample in the powder form was characterized using TGA/DTA, FT-IR spectroscopy, XRD, TEM, UV–Vis–NIR spectroscopy, SEM observation and dielectric measurements. The thermogravimetric analysis (TGA) and the differential thermal analysis (DTA) were carried out using TG/DTA thermal analyzer Perkin Elmer, Diamond TG/DTA in the temperature range 30 – 1000 °C at the heating rate of 10 °C/min in N_2 atmosphere. X-ray powder diffraction (XRD) patterns were recorded with a X'pert Pro Bruker D-8 diffractometer with CuK_α radiation (λ= 0.15418 nm). Data were collected with steps of 0.017^0 (2θ). FT-IR transmission spectra have been recorded with a Thermo-Nicolet Avatar 370, double beam spectrometer using KBr pellet method. FT-IR technique was used in the transmission mode in the 400–4000 cm^{-1} range. High Resolution Transmission Electron Microscope, Jeol-JEM 2100, was used for electron diffraction (ED) studies. The optical measurements of the $GdAlO_3$ powder were carried out at room temperature using a UV–Vis (Varian, Cary 5000 model) spectrophotometer in the wavelength range of 200–2000 nm. The powders calcinated at 1000^0C for 2 h have been mixed with PVA, pressed in cylindrical compacts at the pressure about 350 MPa using a hydraulic press and, then, sintered at 1400^0C for 4 h. The bulk density of the sintered pellet was measured using the Archimedes method. Micrographs of the polished and thermally etched samples were taken with the help of high resolution scanning electron microscope (FEI Quanta FEG 200) while Energy Dispersive X-ray (EDX) technique was employed for elemental analysis. The dielectric measurements were then performed on these samples as a function of frequency at various temperatures using NOVO-CONTROL (Alpha-A) high-performance frequency analyzer. For this purpose the sample was mounted in a sample holder between two parallel electrodes, forming a capacitor. Proper shielding of the sample holder was done in order to minimize the noise disturbance.

3. Results and discussion

3.1. TGA/DTA analysis

The TGA/DTA results are shown in Fig. 1. The TGA curve shows continuous weight loss up to temperature around 780^0C that is due to the removal of water and residual organics. There is no formation of stable products during precursor decomposition up to this temperature. The small exothermic peak observed in DTA curve at 880^0C and corresponding weight loss (3%) observed in the temperature region 780 – 900^0 C are due to the $GdAlO_3$ crystallization. The TGA/DTA analysis reveals that calcination of the combustion product is needed to get the desired phase formation.

3.2. XRD analysis

The XRD patterns of the combustion product calcinated in air at 700^0C, 800 C, 900^0C, 1000^0C and 1100 °C for 2 h are shown in Fig. 2. The XRD pattern obtained for the combustion product indicates partial-crystallization with certain reflections from major