

Combustion synthesis and characterization of Ba₂NdSbO₆ nanocrystals

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Abstract. Nanocrystalline Ba₂NdSbO₆, a complex cubic perovskite metal oxide, powders were synthesized by a self-sustained combustion method employing citric acid. The product was characterized by X-ray diffraction, differential thermal analysis, thermogravimetric analysis, Fourier transform infrared spectroscopy, transmission electron microscopy and scanning electron microscopy. The as-prepared powders were single phase Ba₂NdSbO₆ and a mixture of polycrystalline spheroidal particles and single crystalline nanorods. The Ba₂NdSbO₆ sample sintered at 1500°C for 4 h has high density (~95% of theoretical density). Sintered nanocrystalline Ba₂NdSbO₆ had a dielectric constant of ~21; and dielectric loss = 8×10^{-3} at 5 MHz.

Keywords. Ceramics; infrared spectroscopy; surface morphology; transmission electron microscopy.

1. Introduction

Perovskite-type oxides have attracted considerable attention in many applied and fundamental areas of solid-state science and advanced materials research because of their technological use and academic interest (Kimura and Tokura 2000; Lichtenburg *et al* 2001). Traditionally, the perovskite-type oxides are prepared through solid state reaction at elevated temperatures, but such reactions often lead to compositional and structural inhomogeneities in the production. The inhomogeneities impose certain limitations on the researches of applications and properties of these oxides. Wariar *et al* (1997) reported a complex perovskite material, Ba₂NdSbO₆, for its possible application as a substrate for superconducting YBa₂Cu₃O_{7- δ} (YBCO) films. A single phase Ba₂NdSbO₆ could be obtained through solid state reaction route only after prolonged calcinations of the reaction mixture at 1170°C in air for 36 h with several intermediate grindings. The Ba₂NdSbO₆ was synthesized through the conventional solid state reaction method where the particles were of many micron sizes. Zheng *et al* (1998) have reported the synthesis of Ba₂NdSbO₆ powders of grain size 0.5–2 μ m using hydrothermal synthesis which involves prolonged heating of the precursor material in an autoclave at temperature 240–260°C for 5–7 days to obtain a phase pure Ba₂NdSbO₆ powders.

Recently, synthesis of advanced ceramics and specialty materials as nanometer sized grains gained tremendous

attention. Properties of nanocrystals deviate from those of single crystals and coarse-grained polycrystals. This deviation results from reduced size of the nanocrystals and from numerous interfaces between adjacent grains (Gleiter 2000). In the case of ceramics, whose sinterability is a major issue, high surface to volume ratio of nanocrystals leads to enhanced sinterability and results in a microstructure retaining the initial nanocrystals. This microstructure is the source of the unique mechanical, electrical, dielectric, magnetic and optical properties of nanocrystals (Suryanarayana 1994; Karagedov and Lyakhov 1999; Ravichandran *et al* 1999; Wang *et al* 1999). We have now synthesized Ba₂NdSbO₆ as nanoparticles through a combustion process developed a few years ago (Jose *et al* 1999, 2000; John *et al* 2002). The attempts to synthesize Ba₂NdSbO₆ through a solid-state reaction between the constituent oxides yielded a powder that was non-sinterable up to a very high (~1600°C) temperature. To obtain the sample with more than 95% density, it was necessary to add a small amount of CuO to the reaction mixture to sinter this material at a temperature of 1550°C for more than 12 h. This difficulty was solved by synthesizing Ba₂NdSbO₆ as nanocrystals using a combustion process. Various researchers have successfully synthesized ceramic compounds through combustion techniques with different complexing agents, fuels, etc. at different conditions (Saber *et al* 2008; Vivekanandhan *et al* 2008; Yu *et al* 2008). But in the present work, we have synthesized phase pure Ba₂NdSbO₆ as nanoparticles through a combustion process using nitric acid as the oxidizer, citric acid as the complexing agent and ammonium hydroxide as fuel.

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2. Experimental

Starting materials were barium nitrate, $\text{Ba}(\text{NO}_3)_2$ (99.9%, CDH), neodymium oxide, Nd_2O_3 (99.9%, CDH), antimony oxide, Sb_2O_3 (purified, Merck), citric acid (99%, CDH), ammonium hydroxide and nitric acid. Stoichiometric amount of $\text{Ba}(\text{NO}_3)_2$, Nd_2O_3 and Sb_2O_3 for the formation of $\text{Ba}_2\text{NdSbO}_6$ were separately dissolved in distilled water, nitric acid and tartaric acid respectively. Citric acid was added to the solution containing the metal ions to get a precursor complex, maintaining the citric acid cation ratio at unity. Oxidant/fuel ratio of the system was adjusted using nitric acid and ammonium hydroxide. The solution containing the precursor complex at neutral pH was then heated on a hot plate at $\sim 250^\circ\text{C}$. The solution boiled on heating and underwent dehydration followed by decomposition leading to smooth deflation and to foam. The foam ignited on further heating giving voluminous and fluffy product of combustion. While comparing with conventional solid-state reaction for the synthesis of ceramic oxides, combustion process has energy and cost saving advantages.

The phase purity and homogeneity of the obtained material was determined by powder x-ray diffractometry. X-ray diffraction (XRD) measurements were performed at 2θ values ranging between 10 and 70° using an X-ray diffractometer (Model Bruker D-8) with nickel filtered $\text{CuK}\alpha$ radiation. To determine whether there is any phase transition or solid-state reaction, differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the combustion product was conducted using Perkin-Elmer TG/DTA thermal analyzer in the temperature range 40 – 1200°C at a heating rate of $20^\circ\text{C}/\text{min}$ in nitrogen atmosphere. The infrared (IR) spectra of the samples were recorded between 4000 and 400 cm^{-1} with a Thermo-Nicolet Avatar 370 Fourier transform infrared (FT-IR) spectrometer using KBr pellet method. Particulate properties of the combustion product were examined using transmission electron microscope (TEM, JEOL 2010Fas) operating at 200 kV . The samples for transmission electron microscope (TEM) were prepared by ultrasonically dispersing the combustion product in methanol and allowing a drop of this suspension to dry on a carbon-coated copper grid.

To study the sintering behavior of the nanocrystalline $\text{Ba}_2\text{NdSbO}_6$, the powder obtained by the combustion was mixed with a binding agent, polyvinyl alcohol (PVA, 5% aqueous solution) and uniaxially pressed at 350 MPa in the form of circular discs of 13 mm in diameter and $\sim 2\text{ mm}$ in thickness. Density of the pressed green discs was $\sim 55\%$. The binder was removed by heating the pellet at 700°C for 30 min . Then the binder burn-out components were sintered at 1500°C for 4 h in a programmable furnace in air at a heating/cooling rate of $10^\circ\text{C}/\text{min}$ to get sintered density of 6.437 g cm^{-3} (which is $\sim 95\%$ of the theoretical density). The surface morphology and energy

dispersive X-ray analysis (EDAX) of the sintered $\text{Ba}_2\text{NdSbO}_6$ samples were analyzed using scanning electron microscope (SEM, JEOL Model-JSM-6390LA). The dielectric constant and loss factor ($\tan \delta$) were determined from the capacitance measurements on samples in which $\text{Ba}_2\text{NdSbO}_6$ form a dielectric (thickness $\sim 1\text{ mm}$). Silver electrodes were fabricated on either side of the sintered pellet and dried in an oven at $\sim 80^\circ\text{C}$ for 15 min . Capacitance measurements were taken in the frequency range 50 Hz to 5 MHz at room temperature using an LCR meter (HIOKI 3532-50).

3. Results and discussion

The XRD pattern of the products prepared by combustion synthesis is shown in figure 1. It was found that the perovskite-type product formed had a higher degree of crystallinity. All the major peaks for perovskite-type oxide are present in figure 1. Based on the analysis of XRD data, $\text{Ba}_2\text{NdSbO}_6$ oxide could be indexed for the cubic structure having space group $Fm\bar{3}m$ with a cell parameter of $a = 8.537\text{ \AA}$ that agrees with the reported XRD data in JCPDS file (JCPDS 38-817) for $\text{Ba}_2\text{NdSbO}_6$. No secondary phase was observed in the XRD patterns in the as-prepared powder, thereby indicating that $\text{Ba}_2\text{NdSbO}_6$ phase formation was complete during the combustion process itself.

The as-prepared powder was further characterized using DTA, TGA and FT-IR. Figure 2 shows DTA and TGA curve of the combustion product recorded in the range 40 – 1200°C . TGA shows a weight loss of $\sim 5\%$ at $\sim 100^\circ\text{C}$, which is due to the liberation of adsorbed moisture in the sample. The weight change corresponds to an endothermic peak in the DTA curve $\sim 100^\circ\text{C}$. Thereafter

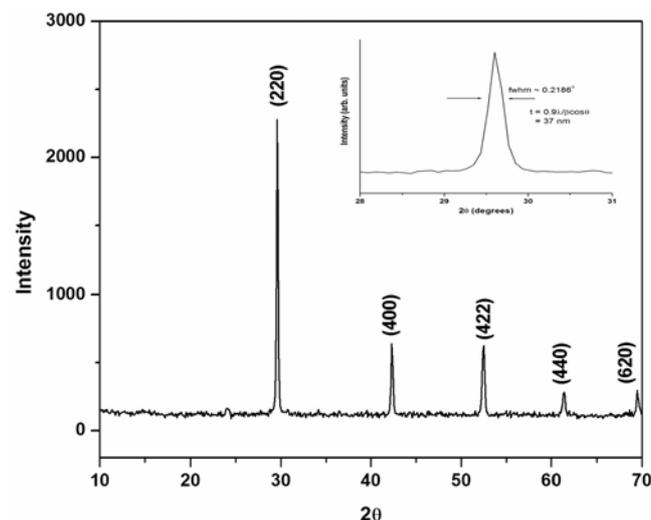


Figure 1. XRD pattern of as-prepared $\text{Ba}_2\text{NdSbO}_6$. Inset: Isolated peak at $2\theta \sim 30^\circ$.

neither weight nor enthalpy of the sample changed up to 1200°C . These observations revealed that the combustion was complete and there was no solid-state reaction or phase transition in Ba_2NdSbO_6 on further heating.

Figure 3 shows the IR spectra of Ba_2NdSbO_6 oxides. The IR spectra show two strong absorption bands around $\sim 620\text{ cm}^{-1}$ and $\sim 400\text{ cm}^{-1}$. In addition, there are weak bands around $1500\text{--}1700\text{ cm}^{-1}$, $1300\text{--}1500\text{ cm}^{-1}$ and $\sim 850\text{ cm}^{-1}$. In the spectrum of $A_2BB'O_6$, two strong absorption bands around 600 and 400 cm^{-1} were reported which are assigned to the ν_3 and ν_4 modes of BO_6 octahedra (Corsmit *et al* 1972). Accordingly the two strong absorption bands in the $600\text{--}400\text{ cm}^{-1}$ region may be assigned to the ν_3 and ν_4 modes of SbO_6 octahedra.

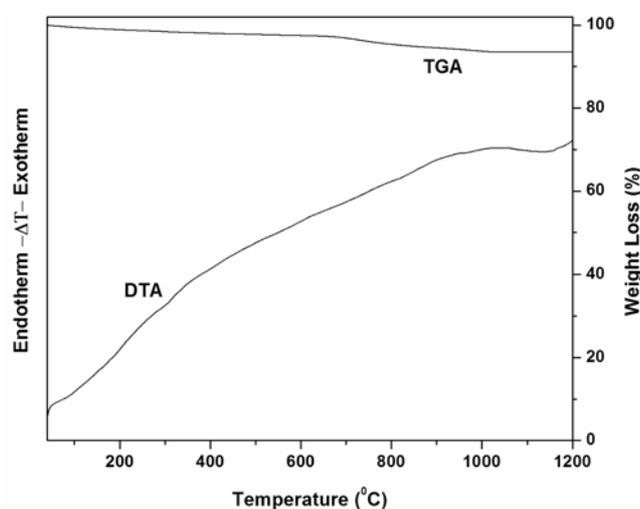


Figure 2. DTA and TGA traces of as-prepared Ba_2NdSbO_6 nanopowder in the temperature range $40\text{--}1200^\circ\text{C}$ in nitrogen atmosphere at a heating rate of $20^\circ\text{C}/\text{min}$.

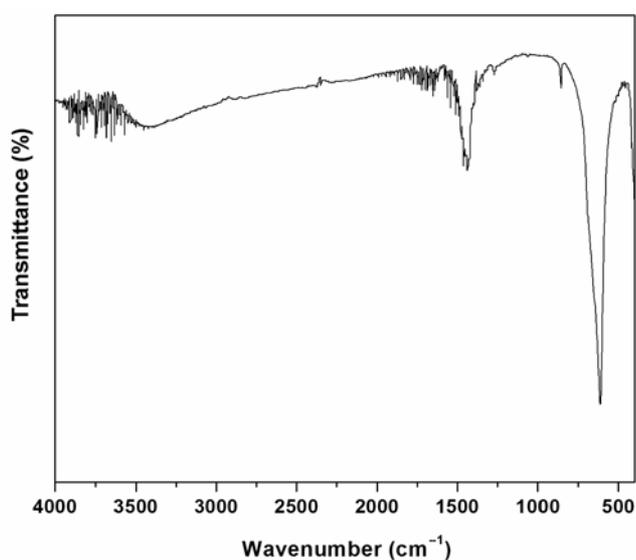


Figure 3. FT-IR spectrum of Ba_2NdSbO_6 oxides.

The weak band at $\sim 850\text{ cm}^{-1}$ that may be ascribed to ν_1 mode of SbO_6 octahedra is usually an IR inactive vibration. Its occurrence in the IR with weak intensity indicates that it becomes partially allowed because of

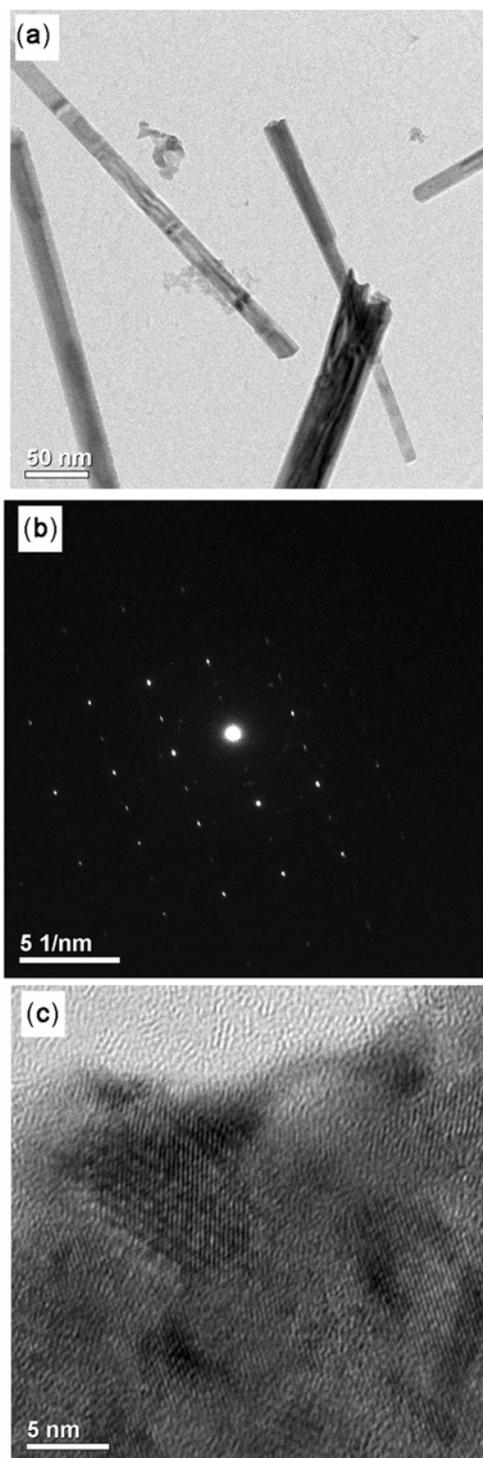


Figure 4. (a) TEM bright field image of the as prepared Ba_2NdSbO_6 powder showing predominantly the rod morphology (b) corresponding selected area electron diffraction pattern and (c) HRTEM lattice image of the rod structure.

was sintered to high density at 1500°C without any sintering aid. The dielectric constant of Ba₂NdSbO₆ at 5 MHz is 21 and tan δ is 8×10^{-3} at room temperature.

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