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Synthesis of nanocrystalline magnesium titanate by an auto-igniting combustion technique and its structural, spectroscopic and dielectric properties

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ABSTRACT

Nanocrystalline magnesium titanate was synthesized through an auto-ignited combustion method. The phase purity of the powder was examined using X-ray diffraction, thermo gravimetric analysis, differential thermal analysis, Fourier transform infrared spectroscopy and Raman spectroscopy. The transmission electron microscopy study showed that the particle size of the as-prepared powder was in between 20 and 40 nm. The nanopowder could be sintered to 98% of the theoretical density at 1200 °C for 3 h. The microstructure of the sintered surface was examined using scanning electron microscopy. The dielectric constant (ε_r) of 16.7 and loss factor (tan δ) of the order of 10^{-4} were obtained at 5 MHz when measured using LCR meter. The quality factor ($Q_u \times f$) 73,700 and temperature coefficient of resonant frequency (τ_f) −44.3 ppm/°C, at 6.5 GHz are the best reported values for sintered pellets obtained from phase pure nanocrystalline $MgTiO_3$ powder.

1. Introduction

$MgTiO_3$ is one of the important electronic ceramic materials finding application as dielectric in resonators, filters and antennas for communication, radar and global positioning systems operating at microwave frequencies [1–4]. For many of its applications, $MgTiO_3$ powder is synthesized by conventional solid-state reaction method. The solid-state method of preparation requires repeated grinding and calcinations at high temperatures, which cause agglomerated crystallites of different micron sizes with impure phases due to incomplete reactions. Attempts were made to sinter $MgTiO_3$ powder synthesized through solid-state route by heating at temperatures above 1450 °C for several hours but the sintered samples still contained a metastable phase of $MgTi_2O_5$ [5]. Various methods of synthesis of $MgTiO_3$ such as thermal decomposition of peroxide precursors, hydrothermal mechano-chemical complexation routes, MOSD, and sol–gel routes have also been reported recently [6–10]. The synthesis of high quality $MgTiO_3$ nanopowder with good sinterability and better dielectric properties is of great importance because of its technological applications. Many researchers have attempted to decrease the sintering temperature, improve the microstructures and the microwave dielectric properties of $MgTiO_3$ ceramics by adding various additives [11–18].

In this paper, we report, for the first time, the synthesis, characterization, Raman and IR spectroscopic studies of phase pure nanocrystalline $MgTiO_3$ (20–40 nm) powder prepared using an auto-ignited combustion method [19,20]. The sintering behavior and the dielectric properties in the frequency range 50 Hz to 10 GHz of nanocrystalline $MgTiO_3$ are discussed in detail in this paper.

2. Experimental

The basic step for the preparation of $MgTiO_3$ by the combustion method is to prepare an aqueous solution containing Mg and Ti ions. Magnesium ions were prepared by dissolving high purity $Mg(NO_3)_2{\cdot}6H_2O$ (99%, Himedia, India) in double distilled water. Titanium ions were prepared by dissolving $C_{12}H_{28}O_4Ti$ (>98%, Acros Organics, USA) in ethyl alcohol. To obtain the precursor complex, the stoichiometric solution containing Mg and Ti ions was mixed with citric acid solution, keeping the citric acid to the cation ratio unity. Citric acid was used as complexing agent. Conc. HNO_3 was then added to the precursor. The product was stirred well for uniform

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mixing. Liquor ammonia was added to the solution to adjust the oxidant–fuel ratio to unity and it acts as the fuel for combustion. The solution was heated on a hot plate at ~250 °C, it boils and undergoes dehydration followed by decomposition, leading to a smooth deflation, producing dark foam. On persistent heating the foam gets auto-ignited giving a voluminous white fluffy powder of $MgTiO_3$ with traces of black organic impurities.

The structure of the as-prepared and heated $MgTiO_3$ nanopowders were examined using X-ray Diffractometer with Nickel filtered Cu Kα radiation (Model—Philips Expert Pro). The thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using PerkinElmer TG/DT thermal analyzer in the range 30–1100 °C at 20 °C/min in nitrogen atmosphere. The Fourier transform–Raman spectrum of the nanocrystalline $MgTiO_3$ heated at 800 °C was carried out at room temperature in the wave number range 50–1000 cm^{-1} using Bruker RFS/100S Spectrometer at a power level of 150 mW and at a resolution of 4 cm^{-1}. The samples were excited with an Nd:YAG laser lasing at 1064 nm and the scattered radiations were detected using Ge detector. The infrared (IR) spectra of the as-prepared sample and that of the heated samples at 400 and 800 °C were recorded in the range 400–4000 cm^{-1} on a Thermo-Nicolet Avatar 370 Fourier Transform Infrared (FT-IR) Spectrometer using KBr pellet method. The transmission electron micrograph of $MgTiO_3$ nanopowder and their corresponding selected area diffraction patterns were taken using FEI Tecnai G2 S-TWIN 300 kV HRTEM. The structure of the sintered samples was examined using X-ray diffractometer with nickel filtered Cu Kα radiation (Model—Philips Expert Pro). The sintered samples were polished and the experimental densities were estimated by the Archimedes method. The surface morphology of the sintered $MgTiO_3$ sample was studied by scanning electron microscope (SEM, JEOL Model 6390 LV). The low frequency dielectric properties were studied using an LCR meter (Hioki-3532-50) in the frequency range 50 Hz to 5 MHz. For microwave frequency range, the dielectric properties of the samples were tested using Scalar Analyzer (model Aeroflex 6823).

3. Results and discussion

The X-ray diffraction patterns of the as-prepared $MgTiO_3$ nanopowder and the powders heated at temperatures 600, 800 and 1000 °C for 1 h are shown in Fig. 1(a)–(d). The $MgTiO_3$ nanopowder heated upto 800 °C, shows a metastable phase of $MgTi_2O_5$ (ICDD file 35-792), marked as (*), in the XRD pattern. When the powder was heated to 1000 °C for 1 h, the metastable phase $MgTi_2O_5$ completely disappeared and a phase pure white $MgTiO_3$ nanopowder was obtained. All the peaks in the XRD patterns were indexed for a phase pure rhombohedral (hexagonal) $MgTiO_3$ structure (ICDD file 6-494). The lattice constants calculated from the XRD data using the least square method are a = 5.0603 Å and c = 13.9098 Å. The crystalline size calculated from full width half maximum (FWHM) using the Scherrer formula for the major ($h\ k\ l$) reflections of phase pure $MgTiO_3$ nanopowder (Fig. 1(d)) is found to be ~27 nm. The DTA and TGA curves up to 1150 °C of the $MgTiO_3$ nanopowder are shown in Fig. 2. The TGA curve shows a weight loss of ~9% for a temperature range of 30–1150 °C. The weight loss ~3% at ~300 °C is due to the liberation of adsorbed moisture and organic impurities in the sample and the weight loss of ~6% in the range 300–1000 °C may be due to the decomposition of $MgTi_2O_5$ metastable phase. The enthalpy changes observed in the DTA curve at different temperatures in Fig. 2 confirm the above results.

Fig. 3 shows the FT-IR spectra of (a) the as-prepared $MgTiO_3$, (b) the sample heated at 400 °C and (c) the sample heated at 800 °C, for 1 h. In Fig. 3(a) and (b) very broad and intense absorption bands are

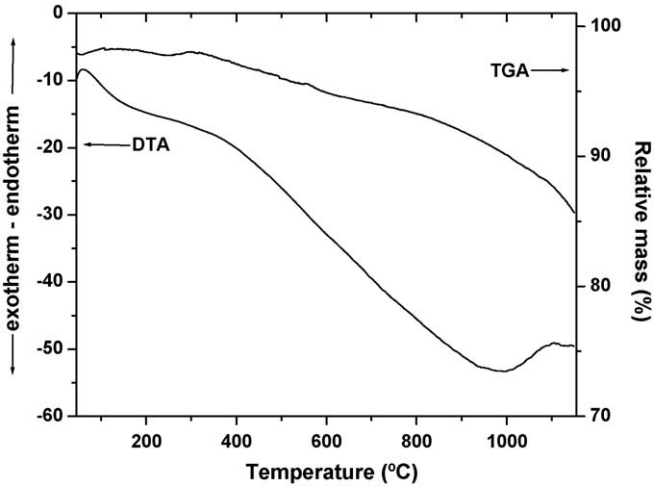

Fig. 2. DTA/TGA trace of $MgTiO_3$ nanocrystals.

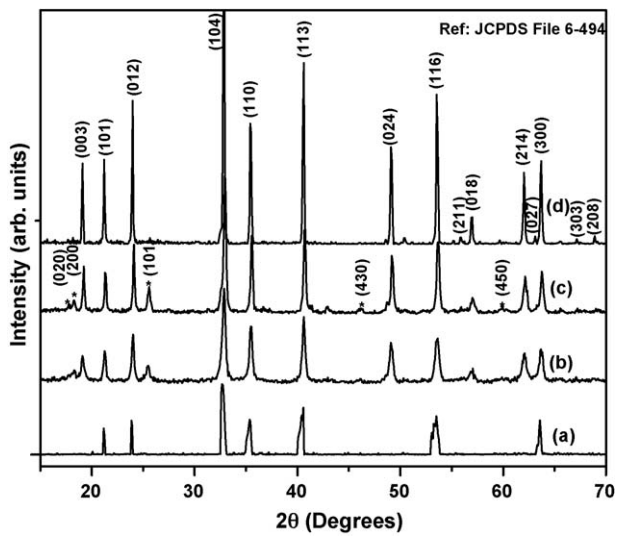

Fig. 1. XRD patterns of $MgTiO_3$ nanopowder: (a) as-prepared, (b) heated a 600 °C, (c) heated at 800 °C, and (d) heated at 1000 °C for 1 h.

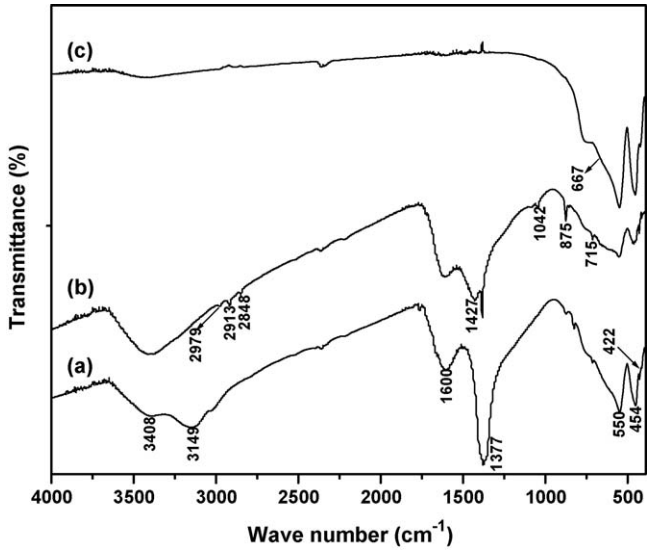

Fig. 3. FT-IR spectra of $MgTiO_3$ nanoparticles: (a) as-prepared, (b) heated at 400 °C, and (c) heated at 800 °C.