Electrical and maagnetic properties of lead nickel titanate synthesized by sol-gel method and microwave processing

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ARTICLE INFO

ABSTRACT

The $Pb_{1-x}Ni_xTiO_3$ (x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0) nanoparticles are synthesized by sol-gel method and microwave sintering technique. Samples calcinated at 730 °C exhibit pseudo-cubic crystal structure, further sintering at 1000 °C the samples exhibited tetragonal structure except x = 0.8. The crystallite size is found to be 47–39 nm. Fourier Transfer-Infra Red studies confirm the Pb—Ti—O, Ti—O and Ni—O bond formation of prepared samples. The optical excitation spectrum reveals that the samples have direct allowed energy bandgap values of 2.81 to 2.82 eV. Synthesized samples particle size found to be 1 μm to 31 nm from High-Resolution Scanning Electron Microscope analysis. The particle size is found to be decreasing on increasing the nickel concentration. X-ray powder diffraction and electron microscope profiles confirmed single phase behaviour of the compounds in lower concentration of nickel. The prepared compounds show nearly spherical shape morphology with an average particle size of 1 μm to 31 nm which is close to crystallite size determined from the XRPD. The temperature dependent dielectric constant (ε) measurement show low values at room temperature and were nominally changes with increasing temperature upto 350 K. The ac electrical study of synthesized samples confirms the negative temperature coefficient of resistance and thermally activated charge carriers are responsible for the high-temperature behaviour. At room temperature prepared samples exhibited superparamagnetic nature. The saturation magnetization (M_s) and coercivity values are found to be 0.08–15.9 emu/g and 236–195 Oe at 15 kG field strength.

1. Introduction

Ferroelectrics are a class of ceramics mostly in ABO_3 form. ABO_3 exhibit different crystal structures viz. perovskite, ilmenite, corundum and $LiNbO_3$ structures [1]. Lead titanate exhibits perovskite structure while $NiTiO_3$ is ilmenite. Lead nickel titanate has exhibited both the structures partially. Furthermore, a systematic transformation from perovskite to ilmenite through a pseudo-cubic phase is distinctly demonstrated in the present series.

Lead titanate is a commercially important electroceramic material for its wide application as ferroelectric with high ε_r and T_c, piezoelectric with high d33 and as electromechanical transducers [2,3]. On the other hand, nickel titanate is antiferromagnetic in nature with high Néel temperature [1] and has a range of applications as gas sensors, organic degraders, photocatalyst, non-volatile memory storage device and microwave dielectric materials [1,4,5]. Nickel titanate is also a potential candidate as a n-type or, rectifiers, electrodes for solid oxide fuel cell, hydrocarbonate catalyst etc. [6]. Nickel titanate is also used as a tribological lubricant under high temperatures [7].

The present series of $Pb_{1-x}Ni_xTiO_3$ (PNT) is multifunctional ceramics. Further, it is studied for the effect of Ni^{2+} on the dielectric response of PT. Conversely, the influence of Pb^{2+} on the magnetization of nickel titanate is explored. The photoresponse of PNT leads to a new avenue of the application as optoelectronic devices. The present series of PNT couples magnetic, dielectric and optical properties.

There are many reports on lead nickel niobates (PNN), lead titanate nickel (PTN), lead zirconium titanate (PZT), lead strontium titanate (PST), lead cerium titanate (PCT) and calcium lead titanate (CPT) ceramics. To the best of authors knowledge, there is no detailed report of $Pb_{(1-x)}Ni_xTiO_3$ (PNT) electrical and magnetic properties till date. This is the first to report the PNT ceramic phase, bond formation, optical, dielectric and magnetic characterizations [3,8–17].

2. Experimental details

2.1. Materials and reagents

Lead acetate $Pb(CH_3COOH)_2.3H_2O$ (Sigma-Aldrich, 99%), Nickel

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nitrate $Ni(NO_3)_2.6H_2O$ (Sigma-Aldrich, 99%), Titanium Butoxide Ti $(C_4H_9O)_4$(Sigma-Aldrich, 99%), Glacial acetic acid CH_3COOH (Sigma-Aldrich, 99%) and Ethanol C_2H_6O (Sigma-Aldrich, 99%) are used as starting reagents.

2.2. Synthesis of nanoparticles

$Pb_{(1-x)}Ni_xTiO_3$ where (x = 0.0,0.2,0.4,0.5,0.6,0.8 and 1.0) nanoparticles are prepared by sol-gel method and microwave processing technique. Initially, Lead acetate and nickel nitrate are dissolved in pure glacial acetic acid. After the prepared solution is dehydrated at 100 °C for 10 min and cooled to room temperature. After cooling, Titanium Butoxide is added slowly to the solution under continuous stirring. Then the mixture of deionized water and ethanol are added at a slow rate so as to initiate hydrolysis and prevent fast gelation of the solution. Thus prepared gel is heated at 100 °C for 5 h in a hot air oven to obtain the PNT powder. For the calcination step, microwave furnace is used at 730 °C at a heating rate of 30 °C per min. The obtained green powder sample was grinded for 8 h using agate mortar. Using uniaxial hydraulic press the grinded powders are made into circular discs of 10 mm diameter. The circular disc is sintered at 1000 °C using microwave furnace.

2.3. Characterization of nanoparticles

The crystal structure and crystallite size were analyzed by X-ray powder diffraction (XRPD) method using D8 Advance, Bruker diffractometer. The powder compounds are spread with a thickness of ~1 mm on the grooved polymethylmethacrylate (PMMA) compound holder. The pure K_α radiation of wavelength 0.154056 nm from the Cu target (Siemen D5000) with monochromator was permitted to decimate on the powders in Bragg-Brentano geometry. The synthesized samples weight loss and decomposition analyzed by Thermogravimetric Analysis (SDT Q600 V2 0.9 Build 20). The Fourier transform infrared (FT-IR) investigations were carried out on the samples to measure the existence of secondary crystalline phases by lattice vibration analysis as well as to signify surfactant functional bands existence on the prepared nanoparticles surface. Infrared (IR) spectroscopy is useful to investigate the vibrational velocities of molecules as various groups of atoms vibrate at different frequencies and absorb energy accordingly. The dried samples were kept in an oblong cuvette and FT-IR spectra were recorded in transmission mode from 4000 to 400 cm^{-1} energy range with 1 cm^{-1} resolution using He−Ne laser as a source in the spectrophotometer (IR Affinity-1, Shimadzu). The electron excitation characteristics of the nanoparticles were investigated by UV-Vis-NIR spectrophotometer (V-670, Jasco). The UV–Vis-NIR spectra were recorded in diffuse reflectance mode using photomultiplier tube detector in 150–2500 nm input wavelength range. The sample is kept on the compound holder and diffuse reflected radiation was calculated in the semicircular path near the compound with an integrating sphere. The relative diffuse reflectance (R) was probate with $BaSO_4$ powder as a reference. The nanoparticles morphology and particle size were investigated by High-Resolution Scanning Electron Microscope (HRSEM) in FEI Quanta FEG200 and elemental analysis studied by Energy-dispersive X-ray Spectroscopy (EDS). The electrical properties of the sample were recorded using LCR meter (LCR HiTESTER 3532–50 HIOKI) which is computer interfaced along with a tubular furnace. The samples magnetic properties were studied at 300 K in the applied field intensity up to 15000 G using vibrating sample magnetometer (Lakeshore7410). The prepared nanoparticles were taken in polychlorotrifluoroethylene (PCTFE) compound holder and were perpendicularly vibrated at 80 Hz frequency with 1 mm amplitude to calculated magnetic characteristics of the compound using the pickup coils kept at magnetic pole pieces.
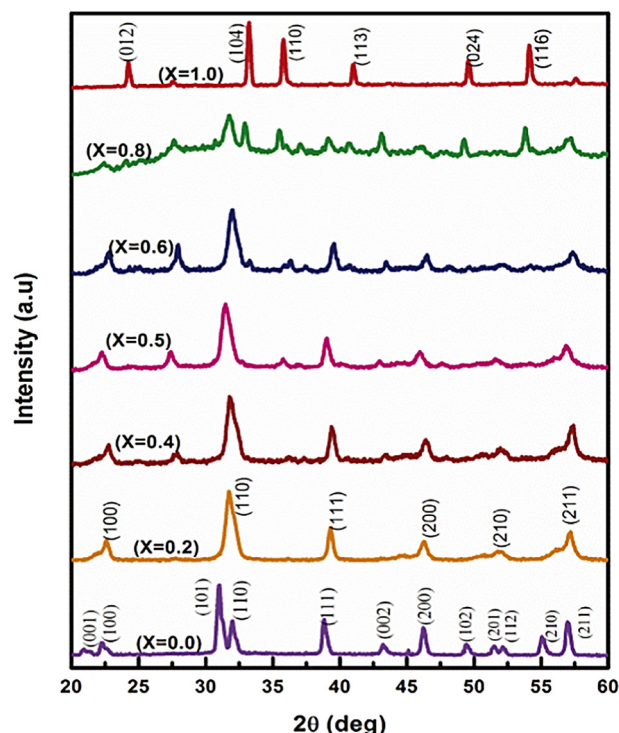

Fig. 1. XRPD profile of calcinated $Pb_{1-x}Ni_xTiO_3$ (x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0) nanoparticles.

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows the X-ray powder diffraction profile of PNT calcinated samples where x = 0.0 is lead titanate (PT) and x = 1.0 is nickel titanate (NT). XRPD analysis confirms that PT compound is tetragonal crystal structure with P4mm space group and NT compound is rhombohedral crystal structure with R3 space group. The transformation from tetrahedral to rhombohedral occurred gradually with increasing the nickel concentration. The pseudo-cubic structure can be noticed for x = 0.2 to 0.6 in agreement with earlier reports [18,19]. The co-existence of tetragonal and rhombohedral (probably-cubic [2,20]) phase is evidenced from the XRPD patterns. Fig. 2 shows the XRPD profile of PNT sintered at 1000 °C. It clearly shows the splitting of (101) and (110) maximum intense peaks of tetragonal structure in the compositions x > 0. On further heat treatment from 700 °C to 1000 °C the phase is transformed from cubic to tetragonal. Both phases (101), (110) peaks for tetragonal and (104), (110) for rhombohedral could be observed in the compositions with 0.4 ≤ x ≤ 0.8. Similar phase transformation from tetragonal to cubic is reported [16]. From this report, the minimum calcination temperature and the lower percentage of nickel(x) are required to achieve the single phase formation of the perovskite structure. The tetragonality of a perovskite defines the strength of polarization. On increasing the sintering temperature and Ni^{2+} concentration it is observed that c/a is decreasing. For increasing the x concentration from 0.2 to 0.8 the (tetragonality) c/a ratio has decreased as shown in Fig. 3. The formation of perovskite is confirmed using the Goldschmidt tolerance factor (t) as in relation (1). When't' is between 0.8 < t < 1.1 the structure forms a stable perovskite. The calculated 't' values are tabulated in Table 1. For increasing the Ni^{2+} concentration 't' value decreases eventually going below 0.8 value for x = 0.8 and 1.0 indicating that the perovskite structure is not stable in these compositions. This is in accordance with the literature reports on the formation of perovskite [21]. From the above exercise, it is surmised that Ni^{2+} at lower concentrations (< 0.8) alone facilitate