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The effect of rare earth Dy^{3+} ions on structural, dielectric and electrical behavior of new nanocrystalline $PbZrO_3$ perovskites

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ABSTRACT

Dy^{3+} metal ions doped nanocrystalline lead zirconate perovskite with nominal composition $Pb_{1-1.5x}Dy_xZrO_3$ (x=0, 0.01, 0.02, 0.03, 0.04 and 0.05) were fabricated by wet chemical micro-emulsion technique. The annealing of all the samples was done at 700 °C for 3 h. The prepared nanocrystalline powder was characterized by different techniques such as X-ray powder diffraction (XRD), Fourier transforms infra-red spectroscopy (FTIR), dielectric response and dc-electrical resistivity. The powder XRD pattern confirmed the development of orthorhombic perovskite structure and the size of crystallite was calculated in the range of 45–135 nm. The lattice parameters and the crystallite size were demonstrated a nonlinear trend. The FTIR spectra were represented the intrinsic cation's vibration in the characteristic perovskite orthorhombic structure which observed in the range of 500–4000 cm^{-1}. The dielectric properties of all the prepared samples were measured in the range of 1×10^6 to 1×10^9 Hz at room temperature. The decreasing trend in dielectric characteristics was observed with the incorporation of Dy^{3+} metal ions in $PbZrO_3$ and also in these dielectric parameters, the damping effect was observed due to the replacement of Pb^{2+} ions with Dy^{3+} ions in the region of higher frequency. The ac conductivity was measured in the range of 6.94×10^{-5}–2.73×10^{-5} $(\Omega\ cm)^{-1}$ by using dielectric results at 1.5 MHz frequency. Such results revealed that the ac conductivity have decreasing behavior with the doping of Dy^{3+} ions in $PbZrO_3$ nanocrystals. The current voltage (I-V) measurements depicted the increase in DC-electrical resistivity with increase of Dy^{3+} content in lead zirconate. The minimum and maximum resistivities were observed as 1.315×10^{11} Ω cm for $PbZrO_3$ and 2.206×10^{11} Ω cm for $Pb_{0.955}Dy_{0.03}ZrO_3$ nanocrystals, hence two fold increase in DC-electrical resistivity was found. The dominating influence of doping on dielectric and electric parameters is highly encouraging for the manufacturing of high frequency memory devices.

1. Introduction

Since 1940s the compounds with perovskite type structure have been studied widely due to their importance in advance researches for high-tech applications. The perovskite compounds have a general formula like ABO_3 (where A=Pb, Ba, Ca, or Sr, and B=Zr or Ti). Such materials are highly utilized due to their significant characteristics like dielectric, ferroelectric, optical and electronic properties [1–6]. A perovskite material lead zirconate ($PbZrO_3$) has great importance in advance technology. This material has an anti-ferroelectric characteristic which has been extensively studied in the large strain actuator applications. It has electric field induced phase transformation behavior from anti-ferroelectric to ferroelectric, due to this behavior its utilization is encouraged [7–9]. The $PbZrO_3$ material is a significant part of a series of lead zirconate titanate (PZT) that has been widely used in advance research due to its constructive electro-optical and piezoelectric characteristics. The anti-ferroelectric lead zirconate material is used in the fabrication of electronic devices such as high energy density capacitors [10–13]. In the literature, the lead zirconate ($PbZrO_3$) material has lattice constants of a=5.87 Å, b=11.74 Å,

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c=8.20 Å and has an orthorhombic crystal structure at room temperature. It is reported that the dielectric constant of lead zirconate nano material revealed a maximum transition at about 230 °C curie point temperature, due to this transition the orthorhombic phase changed to cubic phase [14,15]. The characteristics of lead zirconate can be modified by different approaches which have already been studied in the literature like the fabrication techniques, selection of dopant materials and the size of grown nano particles. To attain such characteristics various approaches have been studied already in the literature. For example, by combining other oxides with $PbZrO_3$, different solid solutions were made like $Pb(Zr_{1-x}Ti_x)O_3$, (Pb,La)(Zr,Ti)O_3, $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbZrO_3$ and $Pb(Fe_{1/3}W_{2/3})O_3$–$PbZrO_3$. Such compositions are highly applicable in the development of micro actuators, electro-optic devices, nonvolatile memories, ultrasonic transducers and multilayer capacitors [16–19]. To achieve particular stoichiometry and desired characteristics, the fabrication technique of nanocrystals was found complex; it depends upon various factors like temperature, processing history, nature and purity of starting materials, stirring etc. To attain the nano sized $PbZrO_3$ crystals, a wide study have been done on many fabrication techniques based on chemistry like micro-emulsion [12], sol-gel technique [20–22], co-precipitation method [9], conventional solid state reaction technique [23,24]. The goal of such growing techniques is to reduce the formation temperature and the particle size of prepared samples [16]. In the present research work, we used the micro-emulsion technique for synthesize of Dy^{3+} ions substituted lead zirconate "$Pb_{1-1.5x}Dy_xZrO_3$" nanocrystals to improve the dielectric and electrical characteristics. A facile and economic wet chemical micro-emulsion method is used for the fabrication process of nanocrystals. This method does not demand a very high temperature like other growing methods; it requires a low temperature for nanocrystal growth process. The reduction in the temperature is occurred due to uniformly incorporation of reactant precipitations. In this method the processing temperature should not exceed than 60 °C. As in this method size of nanocrystals can be modified by controlling pH, stirring rate, stirring time and stoichiometric ratio of precursors; hence it greatly attracts the researchers.

2. Experimental

Dy^{3+} metal ions doped $Pb_{1-1.5x}Dy_xZrO_3$ (x=0, 0.01, 0.02, 0.03, 0.04, 0.05) nanocrystalline powder was synthesized by micro-emulsion route. The micro-emulsion method is a very cheap and facile wet chemical method used for the fabrication of nanocrystals. The following chemicals were used in the fabrication of these nanocrystalline powder: $Cl_2OZr{\cdot}8H_2O$ (98% Pure, Sigma Aldrich), $Cl_3Dy{\cdot}6H_2O$ (99.9% Pure, Sigma Aldrich), $Pb(NO_3)_2$ (99% Pure, BDH), Cetyltrimethylammonium bromide (CTAB) (99% Pure, Bio Basic Canada) and Aqueous ammonia (35%, BDH). CTAB was prepared with the concentration of 0.3 M. The appropriate volumes of above given metal salts were mixed in de-ionized water in separate beakers. These solutions were then stirred on magnetic stirrer's hotplate. When the temperature reached at 55 °C, CTAB solution was mixed in each solution as prepared above and stirring was continued. The pH of all the mixtures was increased to 10–11 by using aqueous ammonia solution (3 M). The stirring was further carried out for 5 h. All these mixtures were washed out by using de-ionized water, dried and then grinded. After that annealing of grinded samples was carried out for 3 h at 700 °C by using a programmable temperature controller furnace Nabertherm Lilienthal (Germany) Mdl. LHT 02/17 Nr.16408. Different characterization techniques were used to characterize the finally prepared nanocrystalline powder. X-ray diffraction (XRD) pattern was taken by using "Phillips X'Pert PRO 3040/60 diffractometer with radiation source CuKα", Fourier transform infra-red spectroscopy (FTIR) spectra were recorded on "Bruker FTIR Tensor 27 Spectrometer", dielectric properties were measured by LCR meter (Wayneker (WK6500B)) at room temperature and DC-resistivity was calculated by using 6487 PicoAmmeter/voltage source (Kiethley) at room temperature.

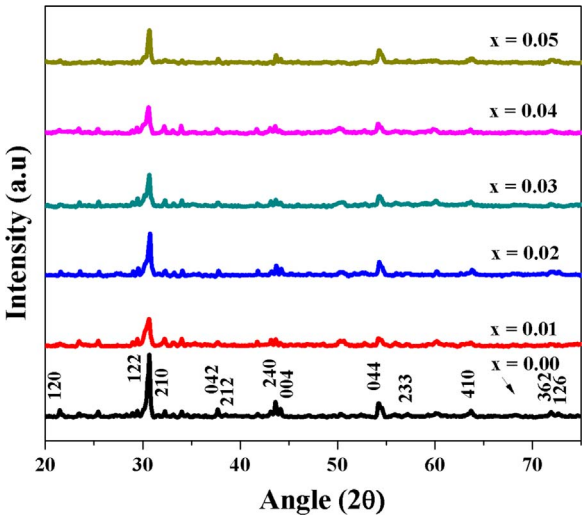

Fig. 1. X-ray powder diffraction (XRD) of "$Pb_{1-1.5x}Dy_xZrO_3$" (x=0, 0.01, 0.02, 0.03, 0.04, 0.05) nanocrystals annealed at 700 °C for 3 h.

3. Results and discussion

3.1. X-ray diffraction (XRD) analysis

XRD patterns for all the compositions of $Pb_{1-1.5x}Dy_xZrO_3$ (x=0, 0.01, 0.02, 0.03, 0.04, 0.05) were recorded at room temperature as shown in Fig. 1. The structural phase identification was successfully carried out by comparing the observed diffraction peaks with the standard diffraction pattern and also by using the Nelson Relay extrapolation method. The observed diffraction planes at different angles (2θ) were indexed as (120), (122), (210), (042), (212), (240), (044), (004), (233), (410), (362) and (126). These planes confirmed the development of body centered orthorhombic perovskite structure of lead zirconate ($PbZrO_3$) nanocrystals with space group Pba2 32. Similar diffraction peaks of lead zirconate have been reported in literature by other researchers [8,9,11,18,23,25]. These XRD spectra of $Pb_{1-1.5x}Dy_xZrO_3$ nano powder were strongly verified with the standard XRD pattern (ICSD 01-075-1607) of $PbZrO_3$. Different physical parameters like lattice constants (a, b and c), cell volume, crystallite size, bulk density, diffraction peak density and porosity for all samples of $Pb_{1-1.5x}Dy_xZrO_3$ were calculated from XRD results (Table 1). To determine the crystallite size D_m the Debye Scherrer's formula was used [26,27]:

$$D_m = \frac{K\lambda}{\beta COS\theta} \quad (1)$$

where 'K' is a constant with value 0.9 approximately, 'λ' is X-ray wavelength and here its value is 1.54 Å. 'β' is full width and half maxima (FWHM) that is an angle value of intense peak and 'θ' is a Bragg's angle of most intense peak. The lattice parameters (a, b and c) illustrate a non linear trend with the Dy^{3+} incorporation in $PbZrO_3$ as given in Table 1. Further 'ρ_x' an X-ray density was measured by using the relation given below:

$$\rho_x = \frac{ZM}{N_A V_{cell}} \quad (2)$$

where 'Z' is a constant and its value for an orthorhombic body centered crystal system is 8, 'M' represents the molecular weight, 'N_A' reveals an Avogadro's number (6.02×10^{23}), 'V_{cell}' is the volume of crystal cell that was found by the relation:

$$\text{Cell volume(vcell)} = a \times b \times c \quad (3)$$