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Phase transformation, morphology, DC electrical resistivity and dielectric properties investigations of properties of manganese doped barium titanate nanoparticles

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Highlights

- Mn substituted BaTiO₃ lattice is achieved by the sol-gel auto-combustion method.
- The resistivity decreases with increase in Mn doping.
- The ϵ' , ϵ'' and tan δ get decreases with increasing frequency at room temperature.
- The AC-conductivity increases with frequency.

Abstract

In this work, manganese (Mn) doped barium titanate BaTi_{1-x}Mn_xO₃ nanoparticles with varying

composition of Mn (x=0.0, 0.10 and 0.20) were prepared by using sol-gel self-ignition wet chemical route. The influence of Mn doping on crystal structure, infra-red, morphology, DC electrical resistivity and frequency dependent dielectric studies was systematically investigated. To know the crystalline nature and purity of the prepared samples, a non-destructive X-ray diffraction (XRD) tool was used. The analysis of XRD results revealed that pure $BaTiO_3$ and $BaTi_{1-x}Mn_xO_3$ with x=0.1, samples show tetragonal structure and for higher Mn content (x=0.20) shows the hexagonal structure. The values of interplanar spacing, Miller indices, etc. were used to determine the unit cell parameters, X-ray density and unit cell volume. The highest intensity peak (110) observed in XRD pattern was considered to determine the crystalline size and which is found to be in the range of 3 to 8nm. Scanning electron microscopy (SEM) technique was employed to study the surface morphology. SEM analysis confirm the dense nature of the grains with hexagonal shape for x=0.2. EDX results confirm the presence of Ba, Ti, Mn and O elements as per the stoichiometric proportion. The functional groups and chemical bonds of Mn doped BaTiO₃ were obtained by Fourier transform infrared spectroscopy (FTIR). The temperature dependant DC electrical resistivity studies were performed by standard two probe technique. The conductivity plot exhibits negative temperature coefficient (NTC). The activation energy and resistivity both decreased with Mn doping. The dielectric properties such as dielectric constant (ϵ'), dielectric loss (ϵ'') and dielectric loss tangent $(\tan \delta)$ were studied by means of LCR-O meter. The variation of these parameters as a function of frequency shows the exponential decrease. The dielectric constant and dielectric loss reduces, whereas dielectric loss tangent increase on Mn doping. The ac conductivity increases with frequency.

Introduction

Now a days, ferroelectric materials are emerging as a very good class of electroceramics on account of its wide spread applications. Generally, ferroelectric materials are found into the wide variety of subgroups like perovskite, pyrochlore, compounds with a bismuth layer structure and compounds tungsten-bronze like structure. Perovskite materials exhibits very interesting ferroelectric properties and are extremely used in variously technological applications [1], [2]. Among the ferroelectric materials, BaTiO₃ (BT) possessing perovskite structure is gaining lot of interests among the various researchers. These materials show very interesting properties such as photorefratctivity, piezoelectricity, negative temperature coefficient, pyroelectricity etc. It is one of the classical example of a ferroelectric crystalline material [3], [4]. BT materials are chemically and mechanically very stable. At room temperature and above room temperature (BT) attributes ferroelectric properties. BT possesses a perovskite structure with high dielectric constant and useful in many electronic applications [5], [6]. Barium titanate (BT) can be used as electrical insulator, as a dielectric ceramic materials in capacitor, as a piezoelectric materials in microphone, nonlinear optics, photorefractive, sensors etc. [7], [8], [9]. Generally, BT belongs to the ferroelectric material of ABO₃ perovskite-type where 'A' and 'B' represents Ba and Ti respectively, and oxygen coordinates with 6fold and-12 fold are present in the structure. At different temperatures, BT exhibits different

structures such as rhombohedral at 183K, orthorhombic at 273K, tetragonal at 300K, cubic 403, and hexagonal phases at 1773K With the doping of transition metal ions at Ba or Ti sites, the various properties of BT can be efficiently controlled [10], [11]. It has been reported that the properties of BT are significantly varied on transition metal cations (Ni, Mn, Cu, Cr, Co, Fe, etc) doping at the Ti site. In particular, Mn doping in BT was extensively studied and reported at Ti site which acts as an acceptor. This results in enhancement of electrical resistivity in the regime of transition temperature. The doping of Mn ion in the lattice of BT may result in inducement of ferromagnetism which leads to its applicability as a multifunctional material. [12], [13]. From the literature, it is clear that several techniques were employed to synthesize samples of manganese doped BaTiO₃ such as hydrothermal, solid-state reaction, thin-film deposition etc. Although the sol-gel technique offers better homogeneity, purity as well as good crystallite size then also very few reports are available for the preparation of Mn-doped BT by safe as well as cost-effective eco-friendly sol-gel autocombustion methods. Therefore, it develops the interest to prepare of BaTiO₃ nanopowder by selfignition route [14], [15]. The above mentioned facts led us to investigate the influence of Mn doping on structure, infra-red, morphology, DC electrical resistivity and frequency dependent dielectric studies of BaTi_{1-x}Mn_xO₃ nanopowder synthesized by self-ignition route. This paper describes the preparation of Mn transition metal ion doped BaTiO₃ using well known wet chemical sol-gel self ignition technique. The phase purity of the prepared samples was tested by XRD technique. The determination of lattice parameters and other structural parameters was carried out by using XRD data. Fourier transform infrared spectroscopy technique to study the different absorption bands. The two-probe technique was employed to study the DC electrical resistivity as a function of temperature. Frequency dependence of real and imaginary dielectric constant and dielectric loss tangent studies were carried out using LCR-Q meter. The results are discussed in the light of Mn doping.

Section snippets

Chemicals

For the preparation of BaTi_{1-x}Mn_xO₃ (x=0.0, 0.10 and 0.20) nanoparticles following AR grade chemicals were used without further purification as shown in Table 1....

Preparation of BaTi_{1-x}Mn_xO₃ nanoceramics

For the preparation of BaTi_{1-x}Mn_xO₃ (x=0.0, 0.10, 0.20) nanoceramics, the well known wet chemical route i.e. sol-gel self ignition route was considered. The detailed preparation method was discussed in our earlier report [9]. In brief, all the precursors solutions were taken in stoichiometric proportions and mixed together. The...

X-ray diffraction (XRD)

The crystal structure, single phase formation and nanocrystalline nature of the prepared $BaTi_{1-x}Mn_xO_3$ (x=0.10 and 0.20) nanoparticles were investigated by means of X-ray diffraction technique. Room temperature X-ray diffraction patterns for typical sample x=0.10 and 0.20 are given in Fig. 2. It is seen from Fig. 2 that, no extra peak other than tetragonal structure was observed for x=0.10 which suggest the single phase structure of the prepared samples. However, for x=0.20 the XRD...

Conclusions

The successful preparation of pure BaTiO₃ (BT) and Mn doped BaTiO₃ (BaTi_{1-x}Mn_xO₃, x =0.0, 0.10 and 0.20) nanoparticles was carried out by sol–gel self ignition method. The characterizations made by X-ray diffraction technique show tetragonal structure for x=0.10 whereas for x=0.20 it shows hexagonal structure. Thus, phase transformation from tetragonal to hexagonal with increase in Mn concentration (x) is observed in the present study. The microstructure examined through scanning electron ...

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper....

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