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Dielectric Relaxation and Conductivity of $Ba(Mg_{1/3}Ta_{2/3})O_3$ and $Ba(Zn_{1/3}Ta_{2/3})O_3$

Md. Monwar Hoque[1)], *Alo Dutta*[2)], *Sanjay Kumar*[1)*], *Tripurari Prasad Sinha*[2)]

1) Department of Physics, Jadavpur University, Raja S.C. Mullik Road, Kolkata 700032, India

2) Department of Physics, Bose Institute, 93/1, Acharya Prafulla Chandra Road, Kolkata 700009, India

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The frequency dependent dielectric properties of barium magnesium tantalate (BMT), $Ba(Mg_{1/3}Ta_{2/3})O_3$ and barium zinc tantalate (BZT), $Ba(Zn_{1/3}Ta_{2/3})O_3$ synthesized by solid state reaction technique have been investigated at various temperatures by impedance spectroscopy. BMT and BZT possess cubic structure with lattice parameter $a = 0.708$ and 0.451 nm, respectively. The resonance peaks due to dielectric relaxation processes are observed in the loss tangent of these oxides. The relaxation in the samples is polydispersive in nature. The temperature dependence of dc conductivity, the most probable relaxation frequency (ω_m) obtained from $\tan\delta$ vs $\log\omega$ plots and ω_m obtained from imaginary parts of the complex electrical modulus vs $\log\omega$ plots follow the Arrhenius behavior. According to these Arrhenius plots the activation energies of BMT and BZT are about 0.54 and 0.40 eV, respectively. Thus the results indicate that samples are semiconducting in nature. The frequency-dependent electrical data are analyzed in the framework of conductivity and electric modulus formalisms. Both these formalisms show qualitative similarities in relaxation time. Our study points that for complex perovskite oxides with general formula $A(B'B'')O_3$, the dielectric properties significantly depend on the atomic radii of both A and B type cations. BMT and BZT exhibit enhancement in dielectric property compared to their niobate counterparts. They may find several technological applications such as in capacitors, resonators and filters owing to their high dielectric constant and low loss tangent.

KEY WORDS: Perovskite oxides; Impedance spectroscopy; Dielectric properties; Electrical conductivity

1. Introduction

With the recent progress of microwave integrated circuits and developments in commercial microwave devices, the demand for low dielectric loss materials with high dielectric constant is rapidly increasing. Several types of microwave dielectric ceramics have been developed to meet these requirements[1−12]. The majority of dielectric ceramics used in microwave systems have perovskite structure. The perovskite-type oxides have the general formula ABO_3, in which A represents a large electropositive cation and B represents a small transition metal ion. The complex perovskite structures with general formula $A(B'_{1/3}B''_{2/3})O_3$ and $A(B'_{1/2}B''_{1/2})O_3$ having two B type cations (B' and B'') are widely studied due to their important technological applications.

In recent times, quite a great amount of work has been done on the microwave, radiofrequency and infrared dielectric response of $A(B'_{1/3}B''_{2/3})O_3$ type niobates[13−26]. Alternating current impedance spectroscopic studies on $A(B'_{1/3}B''_{2/3})O_3$ perovskite ceramics (where A = Ba, Sr; B' = Mg, Zn and B'' = Nb) in a frequency range, 100 Hz to 1 MHz and over a wide temperature range have provided very significant results[21−26]. Several issues like the departure of the dielectric response from ideal Debye model, separation of the role of local defects from electrode effects, contribution of grain (bulk) and grain boundary on relaxation phenomena etc. are successfully resolved by examining these results in the framework of different well established models. On the other hand, although microwave dielectric characteristics of tantalum (Ta) based $A(B'_{1/3}B''_{2/3})O_3$ perovskite systems are extensively investigated[27−32], to the best of our knowledge, there is only one report on low frequency dielectric property of this class of perovskite oxides[33]. In this context, our attention has been focused on the alternating current impedance spectroscopic study of $Ba(B'_{1/3}Ta_{2/3})O_3$ (B' = Mg and Zn) (BBT) compounds in a frequency range of 100 Hz−1 MHz and the temperature range of 393−573 K. The results have also been tested in the framework of different well established formalisms.

* Corresponding author. Assist. Prof., Ph.D.; Tel.: +91 33 24138917; Fax: +91 33 24146584; E-mail address: kumars@phys.jdvu.ac.in (S. Kumar).

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According to the literature, the complex perovskite ceramics $Ba(B'_{1/3}Ta_{2/3})O_3$ (B' = Mg and Zn) are usually hexagonal system having lattice parameters $a = 0.5782$ nm and $c = 0.7067$ nm for BMT and $a = 0.5782$ nm and $c = 0.7097$ nm for BZT[34,35]. In contrast, the disordered $Ba(B'_{1/3}B''_{2/3})O_3$ has a cubic structure e.g., bulk BZT is a cubic system with lattice parameter $a = 0.4093$ nm whereas, BZT thin film crystallizes in a cubic structure with lattice parameter $a = 0.4192$ nm[36,37]. During the last few decades, several studies are performed on microwave characteristics (dielectric loss and quality factor) of BMT, BZT, solid solution of BZT with ZrO_2 and $BaZrO_3$, BZT thin films on Pt-coated Si substrate, barium substituted $Pb(Zn_{1/3}Ta_{2/3})O_3$ synthesized by different techniques[27−32]. It is noteworthy that according to these studies the tantalum based complex perovskites $Ba(B'_{1/3}B''_{2/3})O_3$ exhibit ultra high value of quality factor Q and are very promising material having wide range of application possibilities (from mobile telephone to satellite broadcasting systems). Thus, Ta based perovskites deserve special attention. The investigation on the dielectric properties of BZT in microwave region has revealed that the increase of sintering temperature and additional annealing improve the dielectric parameters (especially dielectric loss)[38]. The quality factor Q of BZT strongly depends upon crystalline structure, cationic order and unit cell distortion[38]. The weak field dielectric ($\sim$1 V_{rms}/mm) properties of $Pb(Zn_{1/3}B''_{2/3})O_3$ (where B'' = Nb, Ta) with lead (Pb) partly/fully substituted by Ba have been widely investigated in the low frequency region (1−1000 kHz)[35,36]. The highest values of the dielectric constants in these systems have been obtained for a threshold value of Ba concentration and the maximum values of the dielectric constants for Nb based system are much higher than those in Ta based systems[36].

Recently, the investigations on dielectric properties of Nb based 1:2 ordered perovskite oxides have undergone a rapid growth due to their promising electrical properties. Frequency dependence of the real and imaginary part of the dielectric permittivity of $A(Mg_{1/3}Nb_{2/3})O_3$ (where A = Ca, Ba and Sr) in the frequency range, 100 Hz−1 MHz and at different temperatures between 303 and 633 K has been explored in detail by Cole−Cole method[20−26]. It has been found that the values of most probable relaxation frequencies of these systems obey Arrhenius law. Moreover, the alternating current impedance spectroscopic study (ACIS) suggested that the relaxation frequency of these samples is strongly temperature dependent although relaxation in these samples follows same mechanism. Thus, detailed investigations on 1:2 ordered niobates have provided very interesting results on their dielectric relaxation behavior and conduction mechanism. It may also be noted that the ionic radii of Nb and Ta are reported to be identical (0.064 nm)[27]. It therefore emerges that in spite of several investigations in microwave range, a systematic study on dielectric property and the electrical conductivity of BBTs at low frequencies (100 Hz−1 MHz) and wide temperature range can provide interesting results on their dielectric properties, low frequency relaxation behavior and the electrical conductivity. Though the dielectric properties of barium nickel tantalate (BNT) have been studied very recently in frequency range from 100 Hz to 1 MHz and temperature range from 393 to 573 K[33], to the best of our knowledge, no such studies on BMT and BZT synthesized by solid state reaction technique have been carried out so far. In this background the systematic studies on structural, microstructural, dielectric properties at low frequencies and the electrical conductivity (ac and dc) of BMT and BZT along with comparison of the present outcomes with the results of their previously reported Nb based counterparts appear to be very interesting.

Studies on structural and microstructural properties along with electrical conductivity of ceramic oxides have also provided interesting results[39]. In this context, the ACIS is a very versatile and powerful experimental technique for examining electrical properties of materials. This method enables us to analyze the dielectric properties and obtain the correlation between electrical and structural/microstructural properties of a material. It also gives us the opportunity to separate out the contributions from various regions (i.e., grains, grain boundaries, interfaces, etc.) in the dielectric parameters of polycrystalline materials. The analysis of the dielectric data obtained by ACIS study in different formalisms allows us to extract different features of the material under investigation[20−26,33].

Thus in this paper we report the structural, microstructural, dielectric property, ac and dc conductivity of BMT and BZT synthesized by solid state reaction technique. The dielectric parameters and ac conductivity of the samples have been measured at low frequencies (50 Hz−1 MHz) over a wide range of temperature. The study of dielectric parameters, such as dielectric constant, loss tangent, electric modulus etc. in these oxides over a wide range of frequency and temperature has helped us in assessing their insulating character and application possibilities. The powder X-ray diffraction (PXRD), field emission scanning electron microscopic (FESEM), ACIS and four probe techniques have been employed to achieve our goal.

2. Experimental

The polycrystalline BMT and BZT perovskite oxides were synthesized by ceramic route. Powders of $BaCO_3$ (reagent grade), MgO (reagent grade), ZnO (99% in purity) and Ta_2O_5 (reagent grade) were taken in stoichiometric ratio and blended in an agate mortar for 10 h in the presence of acetone. The blended powder was calcined in a Pt crucible at 1623 K in air for 16 h and then brought to room temperature under controlled cooling at the rate of 100 K h^{-1}.

PXRD patterns of these samples were recorded at room temperature by a Rigaku Miniflex II X-ray powder diffractometer with a scan speed of 2° min^{-1} at scan step of 0.02° using Cu$K\alpha$ radiation over a range of Bragg angles $10° \leq 2\theta \leq 80°$. In the PXRD patterns of the samples, only the characteristic diffraction peaks for perovskite structure have been observed. There is no additional peak corresponding to any of the ingredient used or the probable impurity phases in the PXRD patterns. So, samples obtained after calcinations are single phase perovskite oxides. Now for the sake of better crystallizations the calcined samples were pelletized into a disc using polyvinyl alcohol as binder and then these discs were sintered at 1673 K for 12 h. Afterward, the samples were cooled down to room temperature at the cooling rate of 1 K min^{-1}. These sintered discs were polished thoroughly. The thickness and the diameter of these discs are 2.18 and 10.49 mm, 1.535 and 7.27 mm for BMT and BZT respectively. The electrodes were fabricated on both flat surfaces of these discs by coating them with fine silver paint followed by heating at 473 K for 2 h. The morphological and microstructural characterizations of the samples were performed by FESEM (Hitachi S-4800).

The capacitance (C) and conductance (G) were measured using an LCR meter (HIOKI 3532) in the frequency range,