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Contribution of an extrinsic mechanism for the electrical polarization in $BiMn_2O_5$ ceramics

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DC conductivity, frequency dependent dielectric constant and pyroelectric coefficients, obtained from thermal stimulated depolarization current curves, in $BiMn_2O_5$ ceramics in the range of temperatures from 10 K to 320 K are reported. The data could be explained if it is assumed that a dipole defect is formed due to an oxygen vacancy and two manganese ions which have their valence changed to accept an electron. *Copyright 2012 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License*. [http://dx.doi.org/10.1063/1.4769752]

I. INTRODUCTION

$BiMn_2O_5$ is part of type II multiferroic class of materials, also called magnetism driven ferroelectrics.[1] In type II multiferroics, ferroelectricity occurs only in the magnetically ordered state,[2] with the most accepted mechanism proposed to explain ferroelectricity in these materials being exchange striction.[1–3] In a recent article[4] some of us have reported in $BiMn_2O_5$ samples, pyroelectric coefficients and relaxor behavior at temperatures well above the ferroelectric-paraelectric transition reported in literature, around the Néel temperature of the antiferromagnetic transition $T_N = 38$ K.[3] In that article it is also proposed that the ferroelectric behavior could be extended to higher temperatures if the sample conductivity could be kept low enough at those temperatures. However, an increase in the conductivity of the sample allows the contribution of an extrinsic mechanism, which is related to dipoles formed in the structure due to oxygen vacancies, to be revealed. For oxides, in particular those with perovskite and related structures, a common source of oxygen vacancies is the presence of a net excess of acceptor impurities.[5,6] $BiMn_2O_5$ crystallizes in the centrosymmetrical orthorhombic space group *Pbam* structure[7,8] and have two types of magnetic ions, Mn^{4+} in distorted oxygen $Mn^{4+}O_6$ octahedra and Mn^{3+} in distorted square pyramids $Mn^{3+}O_5$. For simplicity, we assume that the oxygen vacancy is created removing one of the oxygen ions shared by two Mn^{3+} pyramids in the $BiMn_2O_5$ lattice as shown in Figure 1, following reference.[9] In order to keep charge neutrality, if an electron is accepted by two Mn^{3+} ions connected to the vacancy, they become Mn^{2+}, and a dipole defect ($\mathbf{P_D}$ in Figure 1) results. Therefore, such defect involves an oxygen vacancy and two Mn^{2+} ions. This hypothesis takes into account that there is a covalent bond between manganese and oxygens.[10] In $CaCu_3Ti_4O_{12}$ Ramirez *et al.*[11] have found a large low frequency dielectric response, (around 10^4) in the range 100–400 K, which suddenly decreases below 100 K. Ferroelectricy was excluded by X-ray and thermodynamic data, although infrared measurements suggested relaxor-like dynamics.[12] The evidence of a defect similar to the one described in Figure 1 has been reported in $CaCu_3Ti_4O_{12}$[13] with the identification of the defect due to the oxygen vacancy with the change of valence of Ti^{4+} to Ti^{3+}. Besides, the authors suggest in reference[3] that smaller effects observed in the dielectric constant and ESR line broadening of $CdCu_3Ti_4O_{12}$ could be due to the difficulty of creation of oxygen vacancies in that material. In fact this hypothesis has been confirmed by a tight binding calculation with overlap method[3] which found a significant difference in the calculated bond strength of Ca-O and Cd-O pairs, driven by

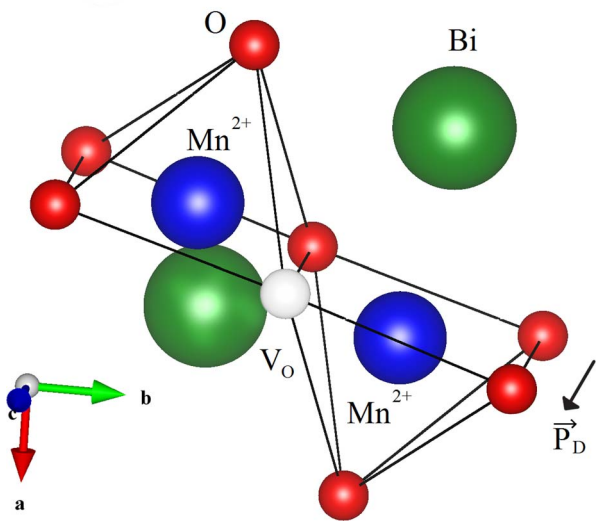

FIG. 1. Suggested defect dipole due to oxygen vacancy in $BiMn_2O_5$.

the presence of Ti, with the Ca-O interaction in $CaCu_3Ti_4O_{12}$ loosened with respect to the Cd-O interaction in $CdCu_3Ti_4O_{12}$. In the present work we will use this defect dipoles model to explain features in the pyroelectric coefficient and in the frequency dependence of the dielectric constant.

II. EXPERIMENTAL

$BiMn_2O_5$ was synthesized by a modified Pechini route, which required stoichiometric proportions of Bismuth Nitrate (Aldrich) and Manganese Acetate (Aldrich) to be mixed in a solution of 16:45 Citric Acid (Aldrich) and Ethylenglycol (Aldrich). Before the dissolution of the salts, the solution was acidified to pH = 0.5 with dropwise addition of Nitric Acid (Cromoline) under constant stirring at 80 °C to facilitate the formation of the metallic chelates. After one hour of stirring at the same temperature, the solution was poured into a vitrified porcelain crucible and heated up to 110 °C for one hour in order to polymerize. The pyrolysis of the organic material was achieved by calcinating the polymer at 600 °C for 2 hours. A black-greyish powder was obtained and hand-grounded for 20 min in Agate mortar. The powder was heat treated at 850 °C for 12 hours in an open Alumina crucible. Rietveld refinement of the X-Ray powder diffraction pattern revealed a pure material with no spurious phases. The powder was again pressed into a flat round pellet of 5 mm in diameter and 200 μm of thickness with 6 tons and later sintered at 900 °C in an open Zirconia crucible. Silver pasted contacts have been used with wires attached to the cold finger of a Janis CCS-150 cryostat with a custom designed sample holder. Impedance spectra were obtained with a Solartron Model 1260A Impedance Analyzer, applying 500 mV (25 V/cm) at several frequencies from 1 MHz to 10 Hz. DC resistivity was obtained using a Keithley Model 617 Electrometer with a fixed current of 1 nA through the entire range of 320 K to 10 K. For the pyroelectric measurements, the poling procedure was performed by field-cooling the sample applying an electric field of 2.5 kV/cm, down to 10 K, with the sample placed in a Janis CCS-150 cryostat. The sample was then short-circuited for one hour. Pyroelectric current and temperature data were taken at 3 s intervals, while the cryogenic refrigerator and heater have been both turned off, allowing the natural warm-up of the cryostat. The same procedure was repeated a second time, but poling, with the same electric field, was performed in the reverse direction.

III. RESULTS AND DISCUSSION

In Figure 2 the dc conductivity *versus* inverse temperature is shown in the range 320 K–10 K. In the inset dc conductivity *versus* temperature data is shown. Three regions with different behavior as

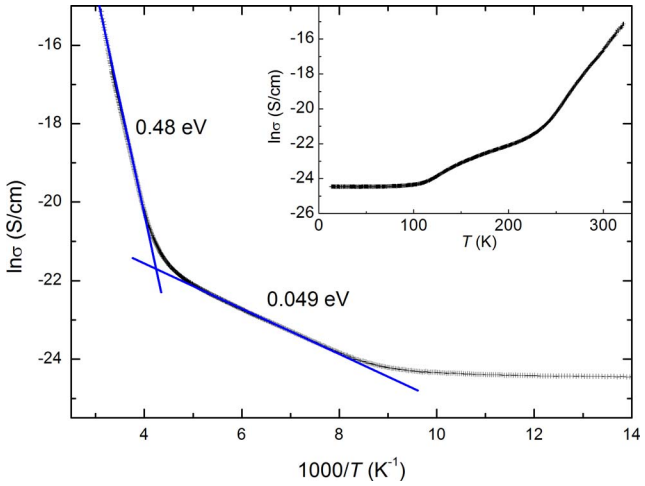

FIG. 2. DC conductivity versus inverse of temperature in the range 320 K to 10 K. Inset: The same data shown as function of temperature. Full blue lines are data fitted to equation (1).

a function of temperature can be observed. Two different ranges have been fitted with the equation:

$$\sigma(T) = \sigma_0 \exp(-E_a/k_B T) \tag{1}$$

suggesting activation-like behavior. For the range 320 K–275 K, we have obtained an activation energy $E_a = 0.48$ eV with the activated conductivity of holes being the most probable origin. If the trapped holes are allowed to diffuse, no defect formation is expected for this temperature range. For the second region from 275 K–120 K an activation energy $E_a = 0.049$ eV is obtained and for this range of temperatures we assume that the acceptors-vacancy dipoles described in Figure 1 are formed. Two mechanisms of polarization can be envisaged with the application of an electric field: The dipole tries to get aligned with the field direction and the hopping of the nearest neighbor oxygen to the vacancy position in response to the application of the field. Below a certain temperature denominated by T_F, no more hopping is allowed and only a constant behavior attributed to a frozen polarization is observed in Figure 2 in the range from 120 K to 10 K.

In Figure 3 the dielectric constant (ε') versus temperature is shown for some frequencies and representative temperatures can be remarked. At low temperatures, the dielectric constant is frequency independent until a temperature near T_F. It is also remarkable the temperature around 275 K in which a maximum can be observed in the low frequency dielectric constant. This is the temperature above which hopping conduction of holes can be observed in Figure 2. From 275 K–120 K the frequency dependence of the dielectric constant can be attributed to the two mechanisms of polarization described above. In this way, there is equivalence between the dc conduction information in Figure 2 and the frequency dependence regimes as a function of temperature of the dielectric constant in Figure 3.

In Figure 4 pyroelectric coefficients are shown. For both directions of the poling field, direct, curve (a) (full squares) and reverse, curve (b) (open triangles) pyroelectric coefficients have been obtained from the measured pyroelectric currents. Again, three ranges of temperature can be identified. Below 120 K the coefficients of curves (a) and (b) show remarkable differences. In the range from 120–250 K they are very similar, with features observed at the same temperatures of 125 K, 188 K and 223 K. However, above 250 K huge values of the pyroelectric coefficient of both signs start to be observed in curve (a) (inset of Figure 4). Just remarking that the applied electric field of Figure 4 is much larger than that of Figure 1, the behavior observed above 250 K can be attributed to the hopping of holes and breaking of the Mn^{2+}-oxygen vacancy dipole defect. For curve (b) the pyroelectric coefficient in this range of temperature, although showing a peak around 250 K, remains much smaller than that of curve (a). This behavior can be explained if one assumes that the diffusion of O^{2-} ions (and in consequence, of the oxygen vacancies) in curve (a) proceeds until they

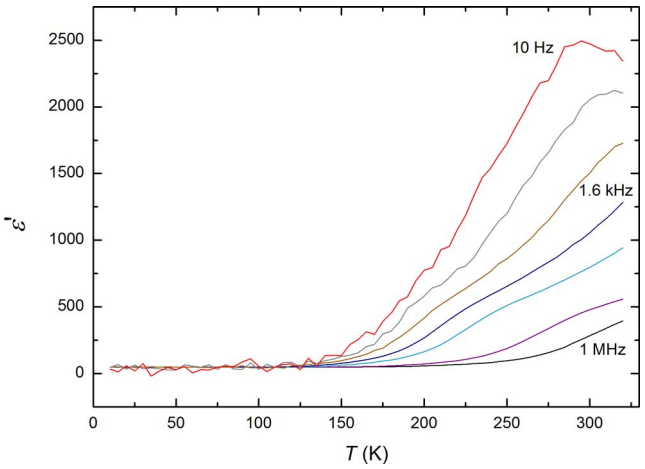

FIG. 3. Real part of the dielectric constant for several frequencies.

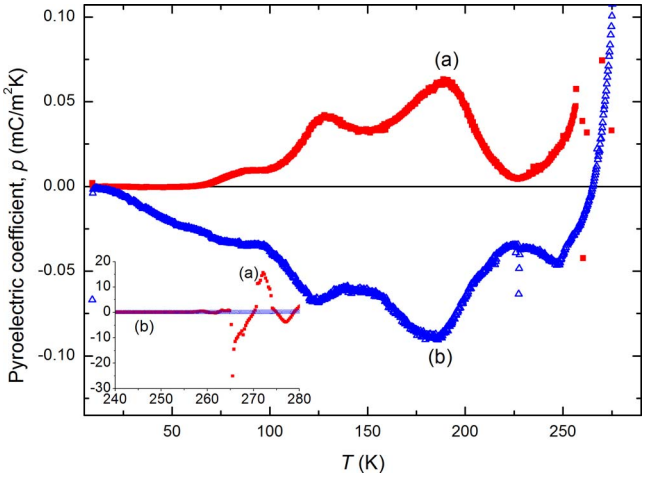

FIG. 4. (a) Pyroelectric coefficient versus temperature after a poling field of 2.5 kV/cm. (b) The same as (a) but with the poling field in the reverse direction.

find limiting obstacles, which could be inter grains regions and the blocking silver-pasted electrodes. For the second measurement, curve (b), performed in sequence to the first, more vacancies would be found at grain boundaries, with less mobility to be freed with the increase of temperature. The increased polarization of curve (b) below 250 K compared to curve (a) could be due to this increased localization.

IV. CONCLUSIONS

In summary, in this work an explanation for the behavior of the dc conductivity, frequency dependence of the dielectric constant and pyroelectric coefficients observed in the range 10–320 K is given assuming the formation of dipole defects due to the presence of oxygen vacancies in multiferroic $BiMn_2O_5$ ceramics. Three different ranges of temperature are related to different regimes of mobility of the oxygen vacancies. In the high temperature one, above around 250 K–275 K, depending on the value of the applied electric field, the dipole defects break and the vacancies diffuse. In the second temperature range, only next neighbor motion is allowed and a frequency dependent dielectric constant is observed. Below 120 K no motion is allowed and a frequency independent dielectric constant is observed. This relaxor-like dynamics, also observed for another sample in reference ,[4] has also been suggested for $CaCu_3Ti_4O_{12}$ in reference.[12] For single

crystals of $CaCu_3Ti_4O_{12}$ the number of oxygen vacancies was estimated to be around 2% from magnetic measurements.[13] The possibility of also finding such defects in single crystals can explain the pyroelectric coefficients measured close to room temperature in single crystals of $BiMn_2O_5$.[17] In this work, for simplicity, we have assumed a defect due to the change of the valence of the Mn^{3+} ions. However, other possibilities such as the change of valence of Mn^{4+} or a cation impurity substitution of one of the manganese ions must also be considered. Evidence of Mn^{2+} in films of $BiMn_2O_5$ has been determined by Near edge X-ray absorption fine structure (NEXAFS).[15] The XPS technique has been employed for the determination of Mn^{3+}/ Mn^{4+} in $BiMn_2O_5$ ceramics.[16] However, a small amount of Mn^{2+} with binding energy around 640eV ($Mn2p_{3/2}$) would also possibly fit the data, within the experimental error, suggesting that a bulk local technique like ESR would give more information about the defect or defects formed.[6,13] Further investigation is also necessary to determine in what extent these dipole defects mask the intrinsic ferroelectric properties of doped or unintentionally doped $BiMn_2O_5$ ceramics.

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