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Electrical properties of rare earth-doped Barium Titanate

Adil Ahmad Al Shoaibi

King Faisal University, Saudi Arabia
adshoaibi@kfu.edu.sa

Samples of undoped $BaTiO_3$, BT were prepared by three mixed oxide routes; hand mixing, *HM* using a pestle and mortar, ball milling, *BM* using Y_2O_3-stabilised zirconia balls and planetary ball milling, *PBM* using tungsten carbide balls. The electrical properties of slow cooled (SC) and quenched (Q) BT material for *HM*, *BM* and *PBM* samples were studied by impedance spectroscopy, IS after heat treatments in air at different temperatures. IS measurements with application of applied voltage and in atmospheres of different oxygen partial pressure were used to determine the conduction mechanism. The application of bias voltage was used during IS measurements to separate Schottky barrier interfacial impedances from sample impedances. In general, two types of Schottky barrier can be detected: (i) barriers at electrode-sample interfaces due to Fermi level mismatch and (ii) barriers between grains associated with partial oxidation of sample surfaces. In-Ga electrodes were considered to yield *ohmic* contacts and associated with partial oxidation that also produced the positive temperature coefficient of resistance, PTCR effect. A methodology has been developed to understand the effect of an applied voltage and changing oxygen partial pressure on electrical properties and possible explanations. Rare earth dopants can occupy either Ba or Ti sites or a mixture of Ba and Ti sites depending on their size. This requires charge compensation mechanisms which can be ionic or electronic. The ionic mechanism can involve either cation or oxygen vacancies. A survey has been carried out of the charge compensation mechanism for different rare earth ions (Gd, Dy, Ho, Y, Er and Yb). It was found that Y^{3+} preferentially occupied the Ti^{4+} site with charge compensation by oxygen vacancies and therefore, Y behaved as an acceptor with solid solubility limit of ~ 15%. Y^{3+} can also simultaneously occupy both Ba and Ti sites with a solubility limit of ~ 7.5%, but exclusive occupancy of Ba sites is limited to ~ 1.5%. A partial phase diagram $BaO-TiO_2-Y_2O_3$ can been presented showing the different solid solutions and the polymorphism of doped $BaTiO_3$. Several parameters affected the electrical properties of pure and doped BT ceramics: the charge compensation mechanism, whether ionic or electronic; the sample preparation methods; the cooling rate at the end of sample heat treatment because many samples lost a small amount of oxygen at high temperature and showed n-type semiconductivity. A common observation was that many slow cooled samples showed weak p-type behaviour attributed to uptake of oxygen on cooling. The holes may be associated with either underbonded oxide (O^-) ions or unavoidable impurities such as Fe^{3+}. Leaky dielectric properties were observed for extrinsic n-type region whereas, normal dielectric properties were observed for extrinsic p-type region. The electrical properties of $BaTi_{1-x}Y_xO_{3-x/2}$ samples fired and cooled in air were ferroelectric insulators at $x \leq 0.05$ and relaxor ferroelectrics at higher x with no evidence of semiconductivity in any of the samples, whether they were cooled slowly or quenched from high temperatures (1200-1600 °C). The possible occurrence of a resistivity minimum in rare earth doped BT was investigated. Three possible mechanisms for semiconductivity were considered for generating Ti^{3+} ions: direct donor doping, oxygen loss at high temperatures and a more complex double doping mechanism involving Y^{3+} and Ti^{3+} ions to charge-balance the oxygen vacancies. No semiconductivity and resistivity minimum were observed for Yb-BT for all three joins and Er-BT. Semiconductivity was observed for other RE dopants and the total resistivity passed through a minimum at 0.1% RE substitution then increased generally for > 1% Y, Ho, Dy and Gd substitution on all three joins.

Keyword: Rare Earth doped; Barium Titanate