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Defect chemistry and electrical degradation of $BaTiO_3$ co-doped with Ho and Mn

Jaill Jeong, Eun Jung Lee, Young Ho Han *

Department of Materials Engineering, Sungkyunkwan University, 300 Chonchon-Dong,
Jangan-Gu, Suwon 440-746, Republic of Korea

Abstract

Defect chemistry and electrical degradation of $BaTiO_3$ co-doped with holmium (Ho) and manganese (Mn) have been studied in terms of electrical conductivity, oxygen vacancy concentration, leakage current and thermally stimulated depolarization current (TSDC). $Ba(Ti_{0.99}Ho_{0.01})O_{2.995}$ showed considerable leakage currents, compared with the un-doped $BaTiO_3$. The specimen co-doped with Ho and Mn showed a stable leakage current behavior with time, which was much lower than that of un-doped $BaTiO_3$. TSDC of $Ba(Ti_{0.99}Ho_{0.01})O_{2.995}$ increased drastically at the temperature range above 50 °C. TSDC of $(Ba_{0.99}Ho_{0.01})(Ti_{0.995}Mn_{0.005})O_3$ decreased at >150 °C, whereas a abrupt increase in TSDC was observed with the specimens of $Ba(Ti_{0.985}Ho_{0.01}Mn_{0.005})O_{2.995-\delta}$.

Keywords: $BaTiO_3$; Defects; Electrical conductivity; Life time; Thermally stimulated depolarization current (TSDC)

1. Introduction

Oxygen vacancies ($V_O^{\bullet\bullet}$) play a major role in the electrical degradation process of $BaTiO_3$-based multi-layer ceramic capacitors (MLCCs).[1–9] Oxygen vacancy is the most mobile species in $BaTiO_3$ lattice. Under dc fields, the positively charged oxygen vacancies move to the cathode and pile up nearby. This behavior causes the difference in the oxygen vacancy concentration between the anode region and the cathode. At the anode, the relatively lower concentration of oxygen vacancies gives rise to reduction of the material, resulting in the formation of oxygen vacancies and electrons. This reaction can be represented by the following equation[1,2]:

$$O_O \rightarrow \frac{1}{2}O_2 + V_O^{\bullet\bullet} + 2e' \qquad (1)$$

The defect notation is that suggested by Kröger and Vink.[10] An increase of electron leads to local dielectric breakdown processes and degradation of $BaTiO_3$ dielectrics. It is thus required to examine all of the sources and factors that determine the oxygen vacancy concentration and electro-migration.

To improve the reliability of $BaTiO_3$ dielectrics, the addition of various oxides and the re-oxidation processes have been studied by numerous researchers.[1–9,11–13] It is well known that the doping of trivalent rare earth ions (R^{3+}:Ho^{3+}, Dy^{3+}, Y^{3+}, Er^{3+}) and manganese ions are effective to improve the reliability of $BaTiO_3$ dielectrics.[2–9,11–13] Since the ionic radii of R^{3+} range from 0.08 to 0.13 nm, these dopants could be substituted for either Ba^{2+} (0.161 nm) or Ti^{4+} (0.061 nm) sites, depending on the Ba/Ti ratio and their solubilities.[2,3,13–18] When R^{3+} is substituted for Ba sites as a donor impurity, the extra oxygen of R_2O_3 fills the oxygen vacancies accompanied by acceptor impurities. However, excess BaO forces R^{3+} ions into Ti sites, resulting in an acceptor-type behavior. Within the solubility limit, R^{3+} ions on Ti sites are compensated by the oxygen vacancies. This indicates that oxygen vacancies in $BaTiO_3$ can be created or consumed by doping rare earth ions (R^{3+}), depending on the Ba/Ti ratio. Oxygen vacancies formed during the sintering process in a heavily reduced atmosphere are partially refilled by the re-oxidation process in a weakly oxidizing atmosphere.[2]

The study of dipole relaxation by thermally stimulated depolarization current (TSDC) was introduced by Bucci and Fieschi.[19] In ionic crystals such dipoles may be formed when host ions are substituted by aliovalent impurity ions. Charge compensation is usually achieved by lattice vacancies, interstitial host ions, or impurity ions of other types. If the compensating charge is near the impurity ion, a dipolar complex is

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* Corresponding author. Tel.: +82 31 290 7392; fax: +82 31 290 7410.
E-mail address: yhhan@skku.ac.kr (Y.H. Han).

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formed. Such dipolar defects are the main origin of TSDC in ionic crystals.[9,19] In this paper, the defect chemistry and electrical degradation of $BaTiO_3$ co-doped with holmium (Ho^{3+}) and manganese (Mn^{3+}) have been studied in terms of electrical conductivity, oxygen vacancy concentration, leakage current and thermally stimulated depolarization current (TSDC).

2. Experimental procedure

Powders of precisely determined compositions were prepared by the liquid mix method developed by Pechini.[20] $BaTiO_3$ samples were prepared by dissolution of weighted amounts of $BaCO_3$ (99.999%) dried by ignition in CO_2, in weighted portions of the Ti stock solution, containing weighted amounts of the dopant solution. Dopants were added as weighted amounts of solutions of $MnCl_2$ (99.99%, Aldrich) and $HoCl_3$ (99.999%, Aldrich) in deionized water. Dissolution of carbonate, by reaction with citric acid, was achieved by heating over a period of several hours. This solution was poured into platinum crucible and heated to polymerize thermally to a glassy gel by raising temperature of the hot plate. This was calcined in the same platinum crucible at 900 °C. The calcined powders were pulverized into fine powders and pressed into a shape of disk and rectangular bar at 150 MPa. The samples were then sintered at 1320 °C for 5 h in air. The conductivity was measured using a four-point dc method. The desired oxygen partial pressures were obtained from mixtures of N_2–O_2 and CO–CO_2. Leakage currents were measured in a dc field at 150 °C. For measurement of a thermally stimulated depolarization current (TSDC), the specimen was polarized by applying dc field (V_p) at polarization temperature (T_p) for a polarization time (t_p). After polarization, the specimen was cooled to −120 °C with an electric field and then heated at a constant rate of 2 °C/min without a field. The TSDC was detected using a picoammeter (KEITHLEY 487) for heating process.

3. Results and discussion

Figs. 1 and 2 show the equilibrium electrical conductivities of $BaTiO_3$ doped with 1.0 mol% Ho either in excess TiO_2 or in excess BaO, respectively. The conductivity of $(Ba_{0.99}Ho_{0.01})TiO_3$ in Fig. 1 follows the −1/4th power dependence of Po_2 at higher oxygen activities, approaching the undoped $BaTiO_3$ curve as Po_2 is decreased, where the equilibrium electrical conductivity was measured at 1300 °C due to the sluggish oxidation–reduction. This result is in agreement with the previous studies of heavily donor doped $BaTiO_3$ (>0.5 mol.%).[21,22] The Po_2 dependence with a slope of −1/4 in conductivity of $(Ba_{0.99}Ho_{0.01})TiO_3$ indicates that the donor impurity $\mathrm{Ho_{Ba}}^{\bullet}$ is compensated by cation vacancies V''_{Ba} and V''''_{Ti}.

At excess BaO composition (Ba/Ti > 1), the oxygen vacancy is formed according to the incorporation reaction of Ho_2O_3:

$$2\mathrm{BaO} + \mathrm{Ho_2O_3} \rightarrow 2\mathrm{Ba_{Ba}} + 2\mathrm{Ho}'_{\mathrm{Ti}} + 5\mathrm{O_O} + V_{\mathrm{O}}^{\bullet\bullet} \qquad (2)$$

Two $\mathrm{Ho}'_{\mathrm{Ti}}$ accompany an oxygen vacancy as expressed in Eq. (2) and behave as an acceptor impurity. The conductivity of $Ba(Ti_{0.99}Ho_{0.01})O_{2.995}$ in Fig. 2 has a conductivity minimum separating the n-type and the p-type region, which is similar to the previous reports of acceptor-doped $BaTiO_3$.[4,18,23,24] Conductivity minimum of $Ba(Ti_{0.99}Ho_{0.01})O_{2.995}$ moved to lower Po_2 by 3.4 orders of magnitude, compared with that of the undoped $BaTiO_3$. Smyth suggested that the conductivity minimum moves to lower oxygen activities (Po_2) by two orders of magnitude for each order of magnitude increase in acceptor content and this shift serves as a measure of the relative contents of oxygen vacancies.[23,24] The oxygen vacancy concentration of $Ba(Ti_{0.99}Ho_{0.01})O_{2.995}$ was estimated to be ∼50 times greater than that of un-doped $BaTiO_3$ according to the relationship proposed by Smyth and co-workers.[23,24]

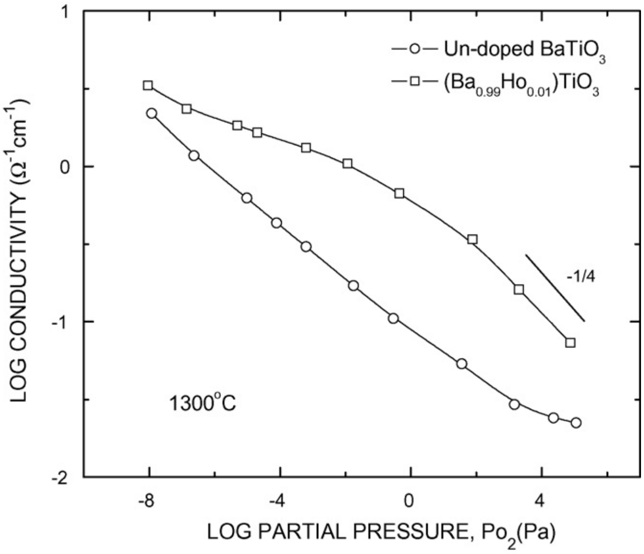

Fig. 1. Equilibrium electrical conductivities of un-doped $BaTiO_3$ and $(Ba_{0.99}Ho_{0.01})TiO_3$ (Ba/Ti < 1) at 1300 °C.

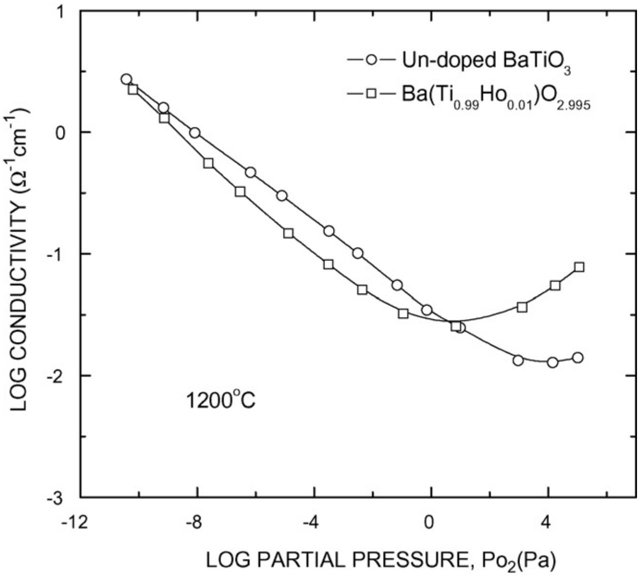

Fig. 2. Equilibrium electrical conductivities of un-doped $BaTiO_3$ and $Ba(Ti_{0.99}Ho_{0.01})O_{2.995}$ (Ba/Ti > 1) at 1200 °C.

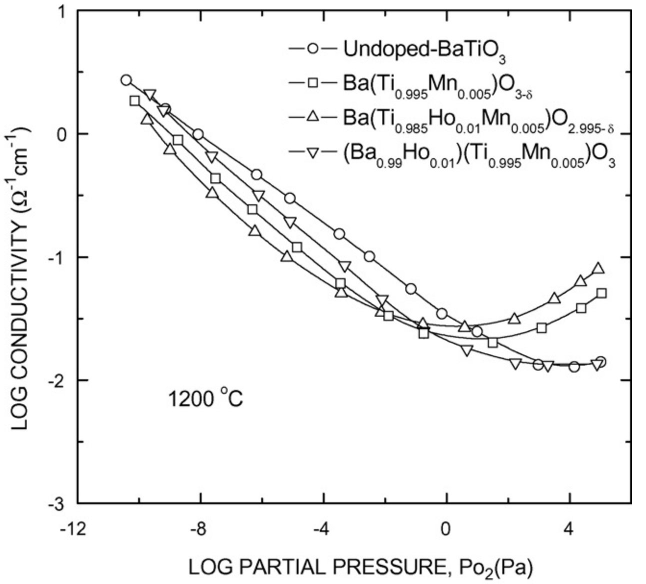

Fig. 3. Equilibrium electrical conductivities of $BaTiO_3$ co-doped with Ho and Mn at 1200 °C.

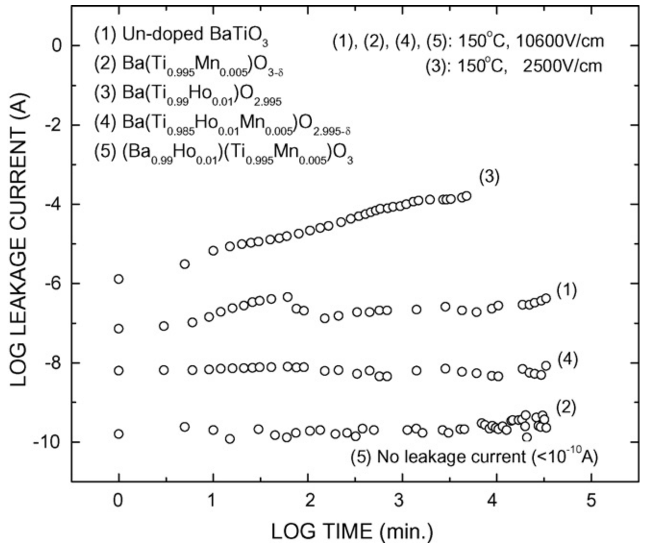

Fig. 4. Time dependence of leakage currents of $BaTiO_3$ co-doped with Ho and Mn.

Equilibrium electrical conductivity curves at 1200 °C for $BaTiO_3$ co-doped with Ho and Mn are shown in Fig. 3. The conductivities of $\mathrm{Ba(Ti_{0.995}Mn_{0.005})O_{3-\delta}}$ and $\mathrm{Ba(Ti_{0.985}Ho_{0.01}Mn_{0.005})O_{2.995-\delta}}$ show an acceptor-doped behavior such as typical n-type and p-type behavior with a conductivity minimum. The conductivity minimum of $\mathrm{Ba(Ti_{0.985}Ho_{0.01}Mn_{0.005})O_{2.995-\delta}}$ moves to lower $\mathrm{Po_2}$ by about one order of magnitude than that of $\mathrm{Ba(Ti_{0.995}Mn_{0.005})O_{3-\delta}}$, implying that the former includes more oxygen vacancies than the latter. The equilibrium electrical conductivity of $\mathrm{(Ba_{0.99}Ho_{0.01})(Ti_{0.995}Mn_{0.005})O_3}$ shows a typical n-type conductivity behavior and a flat $\mathrm{Po_2}$ independent conductivity minimum, which is similar to the previous result on $BaTiO_3$ co-doped with Y and Mn.[22] At low $\mathrm{Po_2}$ ($<10^{-1}$ Pa), $\mathrm{(Ba_{0.99}Ho_{0.01})(Ti_{0.995}Mn_{0.005})O_3}$ reveals higher n-type conductivity than the $\mathrm{Ba(Ti_{0.995}Mn_{0.005})O_{3-\delta}}$. However, the suppression of p-type conductivity in $\mathrm{(Ba_{0.99}Ho_{0.01})(Ti_{0.995}Mn_{0.005})_3}$ was observed at high $\mathrm{Po_2}$ ($>10^3$ Pa). The nominal composition, $\mathrm{(Ba_{0.99}Ho_{0.01})(Ti_{0.995}Mn_{0.005})O_3}$ has two times more donor impurities $[\mathrm{Ho_{Ba}}^{\bullet}]$ than acceptors $[\mathrm{Mn}'_{\mathrm{Ti}}]$. Thus, the electrical conductivity data is compatible with the chemical formula that Ho ions would substitute for Ba sites as long as the ratio of Ba to Ti is less than unity. When $\mathrm{Ho^{3+}}$ is substituted for $\mathrm{Ba^{2+}}$ as a donor impurity, the extra oxygen carried by $\mathrm{Ho_2O_3}$ fills the oxygen vacancy accompanied by acceptor ($\mathrm{Mn^{2+}}$, $\mathrm{Mn^{3+}}$) ions. Mn ions change valence states from tetravalent in the higher $\mathrm{Po_2}$ region to trivalent or divalent in the low $\mathrm{Po_2}$ region. The oxygen vacancies originated from $\mathrm{Mn^{2+}}$ and $\mathrm{Mn^{3+}}$ ions decrease with increasing $\mathrm{Po_2}$. Therefore, the p-type conductivity of $\mathrm{(Ba_{0.99}Ho_{0.01})(Ti_{0.995}Mn_{0.005})_3}$ is suppressed due to the decrease of oxygen vacancies.

Leakage currents at 150 °C under a continuously applied dc field are plotted as a function of time in Fig. 4. $\mathrm{Ba(Ti_{0.99}Ho_{0.01})O_{2.995}}$ showed the highest leakage current, where the oxygen vacancy concentration is ∼5000 ppm and much greater than that of the un-doped. The un-doped $BaTiO_3$ is assumed to have ∼100 ppm oxygen vacancy, which stems from the background acceptor impurities naturally present even in pure materials.[25] However, the leakage current of $\mathrm{Ba(Ti_{0.985}Ho_{0.01}Mn_{0.005})O_{2.995-\delta}}$ was stable with time and lower even than that of the un-doped $BaTiO_3$, and $\mathrm{(Ba_{0.99}Ho_{0.01})(Ti_{0.995}Mn_{0.005})O_3}$ showed the lowest leakage current. Higher leakage currents of $\mathrm{Ba(Ti_{0.99}Ho_{0.01})O_{2.995}}$ could be due to the electro-migration of oxygen vacancies. It should be noted that regardless of the occupation site of Ho ions the manganese doping significantly suppresses leakage currents. The shift of the conductivity minimum of $\mathrm{Ba(Ti_{0.995}Mn_{0.005})O_{3-\delta}}$ to lower temperature in Fig. 3 indicates that the manganese substitution for Ti sites accompanies corresponding amount oxygen vacancies to compensate negatively charged defects $\mathrm{Mn}'_{\mathrm{Ti}}$ and/or $\mathrm{Mn}''_{\mathrm{Ti}}$. The increase in oxygen vacancy concentration would give rise to the increase in leakage currents, leading to the degradation of insulating resistance. It is of interest that the oxygen vacancies accompanied by manganese ions do not contribute the leakage currents. However, the oxygen vacancies originated for the Ho substitution for Ti sites significantly increase leakage currents and give failures early time.

The valence state of Mn ion is known to change from $\mathrm{Mn^{2+}}$ to $\mathrm{Mn^{3+}}$ or $\mathrm{Mn^{4+}}$ with increasing oxygen activity.[3–8] At low oxygen activities, $\mathrm{Mn^{2+}}$ ions are compensated by oxygen vacancies, leading to the suppression of oxygen vacancy creation in low oxygen activities:

$$\mathrm{BaO} + \mathrm{MnO} \rightarrow \mathrm{Ba_{Ba}} + \mathrm{Mn}''_{\mathrm{Ti}} + 2\mathrm{O_O} + V_{\mathrm{O}}^{\bullet\bullet} \tag{3}$$

The valence change of Mn ions to trivalent ($\mathrm{Mn^{3+}}$) and tetravalent ($\mathrm{Mn^{4+}}$) is effective to decrease oxygen vacancy concentration during the re-oxidation process as follows:

$$2\mathrm{Mn}''_{\mathrm{Ti}} + V_{\mathrm{O}}^{\bullet\bullet} + \frac{1}{2}\mathrm{O_2} \rightarrow 2\mathrm{Mn}'_{\mathrm{Ti}} + \mathrm{O_O} \tag{4}$$

$$\mathrm{Mn}_{\mathrm{Ti}}'' + V_{\mathrm{O}}^{\bullet\bullet} + \frac{1}{2}\mathrm{O}_2 \rightarrow \mathrm{Mn}_{\mathrm{Ti}}^{x} + \mathrm{O}_{\mathrm{O}} \quad (5)$$

The decrease in oxygen vacancies would significantly reduce the ionic conduction of $BaTiO_3$. Rödel suggested that an increasing amount of Mn^{2+} is created from Mn^{3+} or Mn^{4+} during the degradation process.[7] This seems to occur close to the anode rather than near the cathode. As oxygen ions move to the anode, the oxygen vacancy concentration will decrease nearby, and to maintain the equilibrium oxygen vacancy concentration, oxygen ions are expelled from the lattice sites, doubly ionized oxygen vacancies and corresponding electrons being left behind. Those electrons could be consumed for the manganese reduction. This would be expressed as an oxygen vacancy injection from the anode. Consequently, positively charged oxygen vacancies would move towards the cathode, where they could be captured by the negatively charged manganese ions on Ti sites, forming a neutral defect complex ($\mathrm{Mn}_{\mathrm{Ti}}''$–$V_{\mathrm{O}}^{\bullet\bullet}$). Merkle et al. also reported that the defect complex ($\mathrm{Mn}_{\mathrm{Ti}}''$–$V_{\mathrm{O}}^{\bullet\bullet}$) could significantly reduce the ionic conductivity of $SrTiO_3$ at temperatures up to 270 °C.[26]

Thermally stimulated depolarization currents (TSDC) of $Ba(Ti_{0.995}Mn_{0.005})O_{3-\delta}$ and $Ba(Ti_{0.99}Ho_{0.01})O_{2.995}$ are shown in Figs. 5 and 6, respectively. TSDC spectrum of $Ba(Ti_{0.995}Mn_{0.005})O_{3-\delta}$ showed sharp peaks around phase transition temperatures of $BaTiO_3$. Huebner reported that the un-doped $BaTiO_3$ exhibits typically three TSDC peaks around the phase transition temperatures.[9] The sharp peaks of $Ba(Ti_{0.995}Mn_{0.005})O_{3-\delta}$ may be due to the abrupt depolarization currents accompanied by the phase transition. The TSDC of $Ba(Ti_{0.99}Ho_{0.01})O_{2.995}$ in Fig. 6 increases drastically at the temperature range above 150 °C and reaches a maximum point, and then decreases above 225 °C. The main conduction mechanism at the temperature range studied can be considered as an ionic conduction by oxygen vacancy. Thus, the increase in TSDC of $Ba(Ti_{0.99}Ho_{0.01})O_{2.995}$ could be due to the migration of oxygen vacancies during the polarization and depolarization process. It is compatible with the result of leakage current shown in Fig. 4.

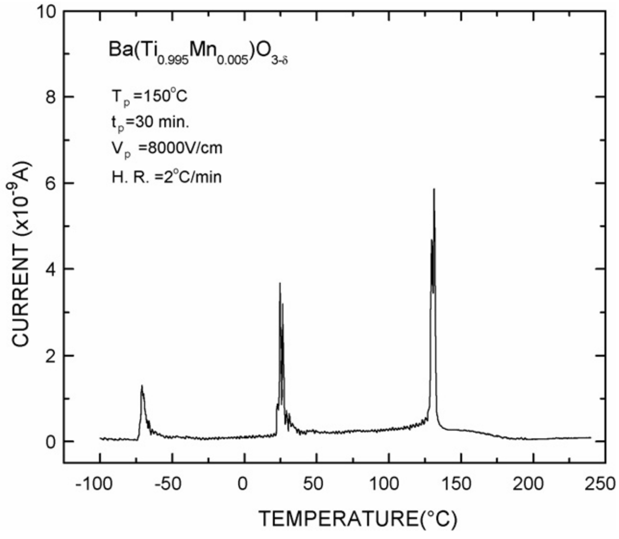

Fig. 5. TSDC spectrum of $Ba(Ti_{0.995}Mn_{0.005})O_{3-\delta}$.

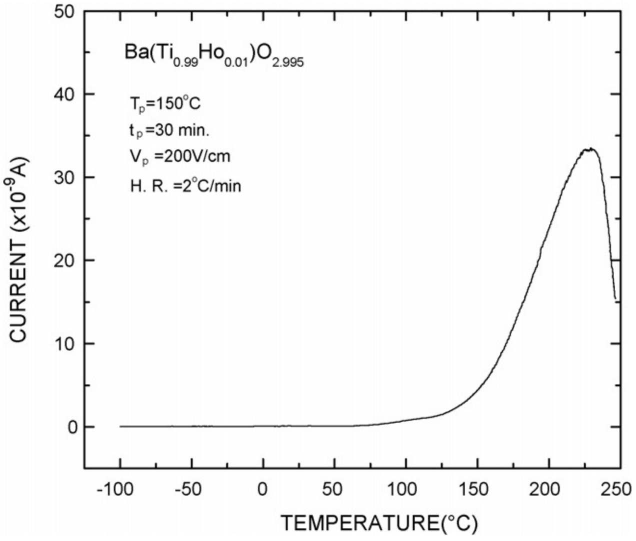

Fig. 6. TSDC spectrum of $Ba(Ti_{0.99}Ho_{0.01})O_{2.995}$.

TSDC of $BaTiO_3$ co-doped with Ho and Mn is shown in Figs. 7 and 8. TSDC of $(Ba_{1-x}Ho_x)(Ti_{1-y}Mn_y)O_3$ decreased at the temperature range above 150 °C, whereas a abrupt increase in TSDC was observed at the specimens of $Ba(Ti_{1-x-y}Ho_xMn_y)O_{3-0.5x-\delta}$. The oxygen vacancy of $(Ba_{0.99}Ho_{0.01})(Ti_{0.995}Mn_{0.005})O_3$ specimen can be significantly reduced by excess oxygen with donor (Ho) doping and by valence change of Mn ions. Although the $Ba(Ti_{0.985}Ho_{0.01}Mn_{0.005})O_{2.995-\delta}$ has plenty of oxygen vacancies, the defect association of ($\mathrm{Mn}_{\mathrm{Ti}}''$–$V_{\mathrm{O}}^{\bullet\bullet}$) could effectively suppress the migration of oxygen vacancies during polarization and depolarization process.[26] However, a abrupt increase in TSDC with $Ba(Ti_{0.985}Ho_{0.01}Mn_{0.005})O_{2.995-\delta}$ above 150 °C implies that the defect association ($\mathrm{Mn}_{\mathrm{Ti}}''$–$V_{\mathrm{O}}^{\bullet\bullet}$) could be dissociated by reasonable amount of thermal energy.

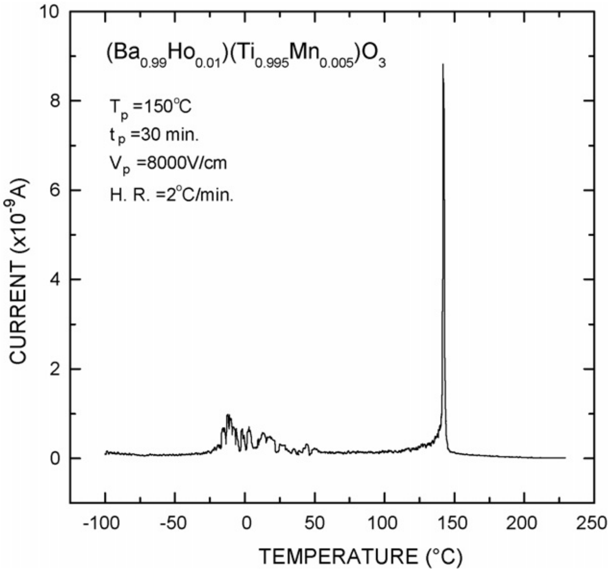

Fig. 7. TSDC spectrum of $(Ba_{0.99}Ho_{0.01})(Ti_{0.995}Mn_{0.005})O_3$.

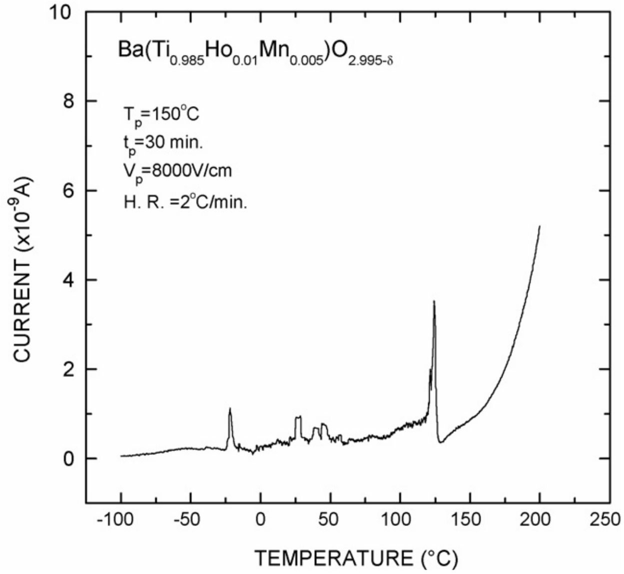

Fig. 8. TSDC spectrum of $Ba(Ti_{0.985}Ho_{0.01}Mn_{0.005})O_{2.995-\delta}$.

4. Conclusions

The electrical conductivities of $Ba(Ti_{0.99}Ho_{0.01})O_{2.995}$, $Ba(Ti_{0.995}Mn_{0.005})O_{3-\delta}$ and $Ba(Ti_{0.985}Ho_{0.01}Mn_{0.005})O_{2.995-\delta}$ showed a typical n-type and p-type behaviors with a conductivity minimum and an acceptor-doped behavior. However, the conductivity $(Ba_{0.99}Ho_{0.01})(Ti_{0.995}Mn_{0.005})O_3$ exhibited a flat Po_2 independent conductivity minimum with a suppression of p-type conductivity. The highest leakage current was confirmed at the $Ba(Ti_{0.99}Ho_{0.01})O_{2.995}$ with the oxygen vacancy concentration ~5000 ppm, whereas the $BaTiO_3$ co-doped with Ho and Mn showed negligibly low leakage currents. Above 50 °C, a continuous increase in TSDC was confirmed at the specimen of $Ba(Ti_{0.99}Ho_{0.01})O_{2.995}$. The abrupt increase in TSDC at the temperature range above 150 °C was observed at the specimen of $Ba(Ti_{0.985}Ho_{0.01}Mn_{0.005})O_{2.995-\delta}$.

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