Journal of the European Ceramic Society **19** (1999) 1251–1254

PII: S0955-2219(98)00414-2
0955-2219/99/$ - see front matter

Electrical Conductivity of Strontium Bismuth Titanate under Controlled Oxygen Partial Pressure

Cyril Voisard,* Dragan Damjanovic and Nava Setter

Ceramics Laboratory, Material Science Department, Swiss Federal Institute of Technology, 1015 Lausanne, Switzerland

Abstract

The electrical conductivity of $SrBi_4Ti_4O_{15}$ (SBT) has been measured under controlled oxygen partial pressure. Both acceptor and donor doping effects were studied using dc conductivity and impedance measurements. In addition to the ceramic samples with random grain orientation, grain oriented samples were prepared by hot forging. It has been shown that the conductivity of SBT is electronic p type in air at low temperature and it is n type at high temperature ($\geq 700°$) up to 1 atm pO_2. The conductivity is increased by Mn doping and decreased by Nb doping at low temperatures ($\leq 220°C$) and decreased by Mn doping and increased by Nb doping at high temperatures (700–1000°C). The slope of the conductivity versus pO_2 curve is significantly decreased by Mn doping above 700°C in the pO_2 range from 1 atm to 10^{-5} atm. © *1999 Elsevier Science Limited. All rights reserved*

Keywords: bismuth titanate, electrical conductivity, ferroelectric properties.

1 Introduction

Ceramics belonging to Bismuth-based perovskites, such as $SrBi_4Ti_4O_{15}$ (SBT), are well suitable for high temperature piezoelectric applications since their ferroelectric phase transition occurs at quite high temperature ($T_c = 540°C$ for SBT).[1,2] Thin films of SBT were proposed as gate oxides for nonvolatile memory applications,[3] because of the strong anisotropy of its permittivity. SBT is orthorhombic at room temperature.[4] The dielectric constant is 100 (randomly oriented ceramic) at room temperature and the longitudinal piezoelectric coefficient is typically 15 pC N^{-1}.

In the frame of piezoelectric applications the electrical conductivity of the material is important since the ceramic needs to be poled in order to get a global piezoelectric effect. In addition, high conductivity partly shorts the sample electrically inducing charge drifts and loss of piezoelectric charge. For example the $Bi_4Ti_3O_{12}$ ceramics should be donor doped in order to decrease their conductivity,[5] otherwise their use is limited.

It is well known (e.g. $BaTiO_3$[6]) that a change of the oxygen partial pressure (pO_2) in the atmosphere will change the electrical conductivity of a material in the case of pure electronic conduction. Whether the change is an increase or a decrease depends on the type of conductivity in the observed range of temperature and pO_2. Oxygen vacancies created under oxygen deficient atmosphere provide electrons [eqn (1)], and filling oxygen vacancies under oxygen excess atmosphere brings holes, [eqn (2)].

$$O_o = V''_o + 2e' + \frac{1}{2}O_2(g) \quad (1)$$

$$V''_o + \frac{1}{2}O_2(g) = O_o + 2\,h' \quad (2)$$

In the oxygen excess region, the conductivity decreases when the oxygen partial pressure is reduced. On the contrary, in the oxygen deficient region, conductivity increases as pO_2 decreases. For many systems, the change in regime (n and p) can be observed from 1 atm down to 10^{-15} atm pO_2.[7] As pO_2 is reduced the conductivity decreases in the p type region (oxygen excess), goes through a minimum (stoichiometric region) and finally increases in the n type region (oxygen deficient). At the conductivity minimum, for $BaTiO_3$ for example, the corresponding oxygen partial pressure value, $pO^0{}_2$ may be expressed as:[8]

*To whom correspondence should be addressed. Fax: +41-21-693-5810; e-mail:cyril.voisard@epfl.ch

$$pO_2^0 = \frac{C_1}{[A']^2}\exp\left(-\frac{C_2}{kT}\right) \quad (3)$$

with the assumption that in this region, the oxygen vacancies (concentration $[V_o'']$) are compensated with natural acceptor impurities (concentration $[A']$) that is: $2[V_o''] \approx [A']$. In eqn (3), C_1 is a constant involving the electron and hole mobilities (assumed to be independent of temperature) and equilibrium constants for the reduction reaction [eqn (1)], or oxidation reaction, [eqn (2)]. C_2 is a constant containing the standard enthalpy changes associated with each reaction. From eqn (3), one can conclude that the conductivity minimum will shift towards lower pO_2 value as it is acceptor doped and towards higher pO_2 value as temperature increases.

In the case of SBT, we observed a large conductivity increase after annealing in reducing atmosphere (''vacuum'', total pressure of 10^{-10} atm, 72 h at 400°C) Fig. 1. The observed conductivity increase (3–4 orders of magnitude) prevents the piezoelectric use of SBT in reducing atmosphere at high temperature. The goal of this paper is to investigate conductivity of SBT under changing pO_2 and for different dopants.

2 Experimental Procedure

Conventional mixed oxides technique was used to prepare pure and doped $SrBi_4Ti_4O_{15}$ powder. Proper amount of reagent grade Bi_2O_3, TiO_2, $SrCO_3$ and $MnCO_3$ or Nb_2O_5 were mixed together and reacted at elevated temperature. After calcination and milling the powder was pressed and fired above 1200°C. Hot forged samples were first presintered at lower temperature and then sintered under uniaxial pressure for a few hours. After hot forging the orthorhombic *c* axis of most of the grains are parallel to the forging axis and the *ab* planes are perpendicular to it. Grain oriented samples (*c* direction or *ab* plane) were prepared by cutting them in the desired directions. Sputtered Pt electrodes were used for the low temperature measurements and a Pt paint was used for the high temperature measurements as we observed a degradation of the sputtered electrodes at high temperature and low pO_2. The samples (discs) were around 8·5 mm in diameter and 1 mm thick. Three different methods were used to measure the electrical conductivity: (i) between 100 and 220°C, the conductivity is measured under constant voltage. The charging and discharging current are recorded with a precision electrometer (Keithley 617) and the two currents are subtracted. This method allows us to measure the conductivity down to 10^{-13} S m^{-1}. Noise level is strongly reduced by shielding the measurement surroundings and by using low noise cables. Nb doped samples were measured both in the 'as sintered' state and after annealing in Argon (purity > 99·998%, O_2 < 3 ppm) at 800°C for 15 h. (ii) Under controlled oxygen partial pressure from 600°C up to 1000°C, the conductivity is measured by a four probes technique under constant current using a multimeter (Hewlett Packard 34401). The oxygen activity is adjusted from 1 atm down to 10^{-5} atm by a gas mixture between Ar and O_2 using mass flow meters and controllers. The oxygen partial pressure is measured with a zirconia oxygen probe. (iii) The bulk conductivity is determined from the impedance plots by fitting one semi circle in the complex plane. The electrical impedance is measured by a four probes technique from 100 up to 1000°C with a precision LCR meter (Hewlett Packard 4284A).

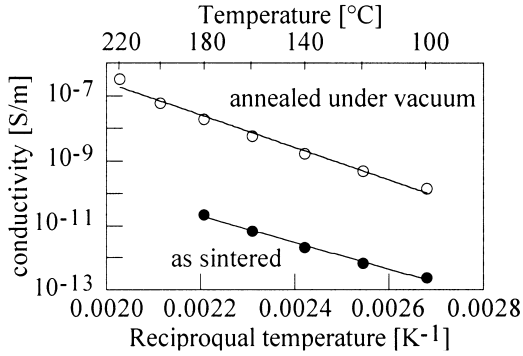

Fig. 1. Electrical conductivity of undoped SBT from 100 up to 220°C measured in air in the 'as sintered' state and after annealing under ''vacuum'' at 400°C, 10^{-10} atm, 72 h.

3 Results

3.1 Conductivity in air at low temperature

The electrical conductivity at 220°C versus dopant concentration for Mn or Nb doped samples is shown in Fig. 2. The conductivity decreases as the ceramic is donor doped (Nb) and it increases above 0·1 mol% as it is acceptor doped. Mn and Nb doping create substitutions on Ti sublattice written as: Mn_{Ti}^{x} and Nb_{Ti}^{x}. When those defects are ionized one can write: $Mn_{Ti}' + h^{\bullet}$ and $Nb_{Ti}^{\bullet} + e'$. Thus, the electrical conductivity of undoped SBT is p type up to 220°C in air since Mn doping increases it and Nb doping decreases it. The first decrease of conductivity with Mn concentration is explained by both a shift of the p type region towards lower pO_2 values as Mn is added and a change of the slope of the conductivity versus pO_2 plot, as shown in the next section [Fig. 3(b)]. Nb doping decreases the conductivity by first compensating for the natural acceptor impurities. Thus as stated by eqn (3), the p type region shifts towards higher pO_2.

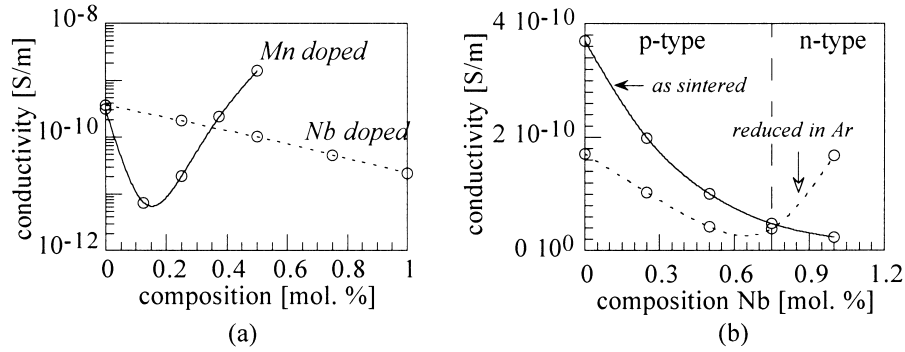

Fig. 2. (a) Electrical conductivity at 220°C of SBT versus composition for both Nb and Mn doping at 220°C, 'as sintered'. (b) Electrical conductivity at 220°C versus composition for Nb doped SBT at 220°C for both 'as sintered' state and after annealing under reducing atmosphere.

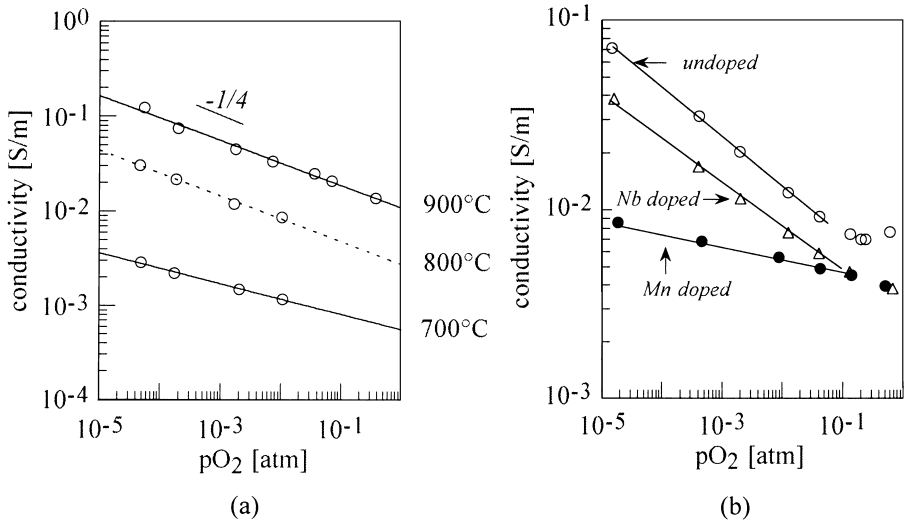

Fig. 3. (a) Electrical conductivity versus oxygen partial pressure for undoped SBT at several temperature. (b) Electrical conductivity versus oxygen partial pressure for undoped (770°C), Mn doped (0·5 mol% Mn, 765°C) and Nb doped SBT (1 mol% Nb, 740°C).

It is proposed that Nb doping with 1 mol% Nb/Ti changes the electrical conductivity from p type (undoped) to n type, because the conductivity of samples annealed in Ar [eqn (1)] is greater than the conductivity of 'as sintered' samples [Fig. 2(b)]. For other concentrations, the conductivity is still p type, since the conductivity decreases after annealing in Ar [Fig. 2(b)].

3.2 Conductivity measurements under controlled pO_2

The electrical conductivity as a function of oxygen partial pressure for undoped SBT is shown in Fig. 3(a) for undoped SBT at 700, 800 and 900°C. It is assumed that the conductivity is n type as it increases when pO_2 is decreased. At 900 and 800°C, the slope of the conductivity versus pO_2 curve (log–log scale) is close to −0·25 (m(900°C) = −0·23, m(800°C) = −0·24), at 700°C this slope is lower (m(700°C) = −0·16). The value of −0·25 is predicted[6,8] using conventional point defects models, if one assumes a direct compensation of the oxygen vacancies by the acceptor centers. The conductivity is n type in the observed range (600–900°C and 1–10^{-5} atm pO_2) and the p type region is no longer visible. Similar low temperature (around 200°C) measurements are much more difficult since at those temperatures, the diffusion rates are very slow.

The electrical conductivity under oxygen partial pressure for undoped Mn (0·5 mol% Mn/Ti) and Nb (1 mol% Nb/Ti) doped SBT is shown in Fig. 3(b). Mn doping has a significant effect and it decreases the slope of the curve (m(undoped) = −0·25, m(Nb doped) = −0·23, m(Mn doped) = −0·06). This indicates a change of the compensation mechanisms that could be explained[9] by the shift of the ionization equilibrium of the Mn substitutions:

$$Mn_{Ti}^{x} = Mn_{Ti}^{'} + h^{\bullet} \qquad (4)$$

The defects are fully ionized at low pO_2 and not at all at high pO_2.[9] Another explanation is that Mn doping could induce a large ionic conductivity which is independent of pO_2. Donor doping does not affect the trend of the conductivity versus pO_2 curve in the selected range. In Fig. 3(b), as the

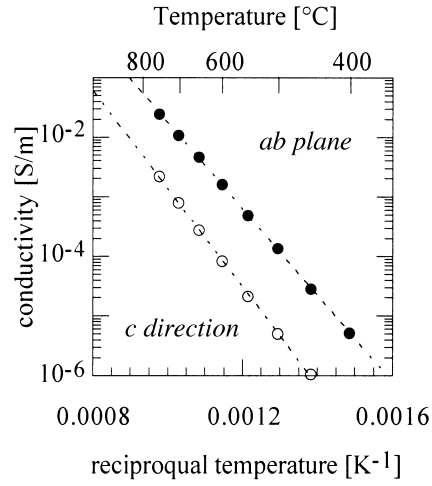

Fig. 4. Electrical conductivity of Mn doped SBT (0·5 mol% Mn/Ti) for a hot forged sample in the *c* direction and in the *ab* plane.

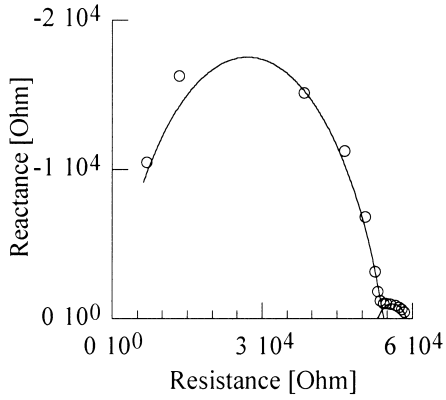

Fig. 5. Impedance plot for hot forged Mn doped SBT in the *ab* direction at 700°C.

measurement temperature is lower for the Nb doped sample, the conductivity is lower for Nb doped than for undoped sample.

3.3 Anisotropy of the electrical conductivity

The electrical conductivity has been measured for Mn doped SBT along the *ab* planes and along the *c* direction, using the impedance method. It can be seen that the electrical conductivity is one order of magnitude higher in the *ab* plane than in the *c* direction. The activation energy is similar for the two directions: 1·4 eV (*ab* plane) and 1·6 eV (*c* direction).

One of the impedance plots (complex plane) used to calculate the conductivity presented in Fig. 4 is shown in Fig. 5. Up to 700°C, only one semi-circle is visible, but at higher temperature, a second semi-circle is observed. This second contribution is of lower conductivity and higher permittivity.

4 Conclusion

We have shown that undoped $SrBi_4Ti_4O_{15}$ is a p type electronic conductor in air up to 220°C, because acceptor doping increases the conductivity and donor doping decreases it. Due to the transition from p type to n type, the conductivity strongly increases after annealing under reducing atmosphere. Mn doping (acceptor) stabilizes the electrical conductivity because of (i) the shift of the ionization equilibrium of the Mn_{Ti}^{x} defect or (ii) a change from electronic to ionic type conductivity. This significantly reduces the conductivity increase after annealing under low pO_2 atmosphere compared to undoped material.

References

1. Subbarao, E. C., *J. Phys. Chem. Sol.,* 1962, **23**, 665–676.
2. Damjanovic, D., *et al.*, *Sens. Act. A*, 1996, **53**, 353–360.
3. Yamamuro, K., *et al.*, *Mat. Sc. Eng.,* 1996, **B41**, 174–177.
4. Reaney, I. M., *et al.*, *Appl. Phys.*, 1996, **80**(7), 4223–4225.
5. Shulman, H. S., PhD. Thesis, EPFL, Lausanne, Switzerland, 1997.
6. Chan, N.-H., *et al.*, *J. Am. Ceram. Soc.,* 1981, **64**(9), 556–562.
7. Smyth, D. M., Prog. *Sol. State Chem.*, 1984, **15**, 145–171.
8. Chan, N.-H., *et al.*, *J. Am. Ceram. Soc.*, 1982, **65**(3), 167–170.
9. Kim, J.-Y., *et al.*, *J. Electroceram.*, 1997, **1**(1), 27–39.