

Hall effect and dielectric properties of Mn-doped barium titanate

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Abstract

BaMn_xTi_{1-x}O₃ (0 ≤ x ≤ 0.01) ceramics have been prepared using a sol–gel method. The Hall coefficient, leakage conductance and dielectric constant were measured. The Hall effect confirms that the charge carriers of the ceramics are electrons, and the electronic concentration $n = 1/|eR|$ decreases with increasing Mn concentration. We propose that Mn³⁺ and Mn⁴⁺ substitution of Ti can partially trap the conductance electrons. The dielectric constant ϵ_1 of the pellets exhibited a peak at $T_c \sim 110$ °C upon heating and the height and position of this peak depends on the Mn concentration. The Mn²⁺ incorporated in the oxygen octahedron of the BaTiO₃ unit cell is in a more centered position than Ti⁴⁺ and may, therefore, modify considerably the ferroelectric property.

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1. Introduction

Barium titanate with a high dielectric constant (ϵ_1) is widely used in the production of ceramic capacitors [1–4]. However, during sintering large numbers of ionized oxygen vacancies and conduction electrons are created according to the following equation [2]:



In order to maintain an equilibrium state of electron concentration, the produced electrons are almost fully delocalized by hopping motion from one titanate site to another. These conduction electrons will lead to poor electric insulation and make the dielectric material into a semi-conductor.

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Doping with manganese is one of several ways to confine the electrons to a small region. In Mn-doped BaTiO₃ there exist three valence states for the manganese ions, Mn²⁺, Mn³⁺ and Mn⁴⁺ [3–5]. The Mn⁴⁺ is nearly exactly incorporated into Ti⁴⁺ sites and participates in the collective motion in the lattice [3]. When some titanate sites are occupied by Mn ions at the valence 3+ or 4+, the electrons will be trapped on these sites because Mn³⁺, Mn⁴⁺ are more reducible than the Ti⁴⁺ [2]. Because the Mn concentration is very low, the hopping motion of the trapped electrons from one Mn site to another is almost impossible. In other words, the electrons are effectively localized on these Mn sites. Therefore, doping with Mn into BaTiO₃ would reduce the conductance of BaTiO₃ ceramic. Two papers [3,4] using EPR and dielectric spectra have been reported to support this mechanism. Here, we may verify it directly by measuring the concentration of the charge carriers in Mn-doped BaTiO₃.

2. Experimental

The Mn-doped BaTiO₃ ceramic samples were prepared using a sol–gel method from Ba(CH₃COO)₂, Ti(OC₄H₉)₄ and Mn(CH₃COO)₂. An appropriate mixture was weighed, milled and dried, then calcined at 300 °C for 10 h. The powder was made into disk-like pellets of 8 mm in diameter and 1 mm thick, and then sintered at 1380 °C for 3 h in air. X-ray diffraction of calcined powders revealed single phase perovskite structure [6]. In the dielectric and leakage conductance studies, silver electrodes were evaporated onto the two large surfaces of the pellets under examination. For the EPR study, the powder samples were obtained from the pellets crushed in a mortar. Hall coefficient was measured at 77 K using van der Pauw method. During the experiment four electrodes were symmetrically arranged on the surface of the sample to neutralize the difference of the samples.

3. Results and discussion

EPR spectra at 9.48 GHz and 123 K are shown in Fig. 1 for the Mn-doped BaTiO₃ with Mn concentration of 0.002, 0.006 and 0.01, respectively. In the spectra, two peaks with a ‘g’ values of ~2 and ~4 were observed, which could be related to the existence of Mn²⁺ and Mn⁴⁺ [3,4]. The presence of Mn³⁺ could be inferred from the concentration of Mn⁴⁺ and Mn²⁺ since the [Mn²⁺] plus [Mn⁴⁺] is considerably less than the dopant concentration [4]. These Mn ions at the valence 2+, 3+ and 4+ partly replaced Ti ions [2].

Fig. 2 shows the Hall coefficient R of Mn-doped BaTiO₃. The charge carrier is obviously electron because R is negative. The carrier concentration n equals to $1/|eR|$. In Fig. 2, the n value decreases with increasing Mn concentration. Because Mn³⁺ and Mn⁴⁺ are more reducible than the Ti⁴⁺ [2], the electrons were trapped at these sites. The hopping motion of the trapped electrons from one Mn site to another was almost prohibited. In other words, the conduction electrons were effectively localized on these Mn sites, which resulted in a drop of carrier’s concentration.

The resistivity of Mn-doped BaTiO₃ has been obtained from its leakage conductance, and the relationship of resistivity versus Mn concentration is shown in Fig. 3. The resistivity increases with the Mn dopant concentration. The enhancement of resistivity in BaTiO₃ can be attributed to a drop of carrier concentration.

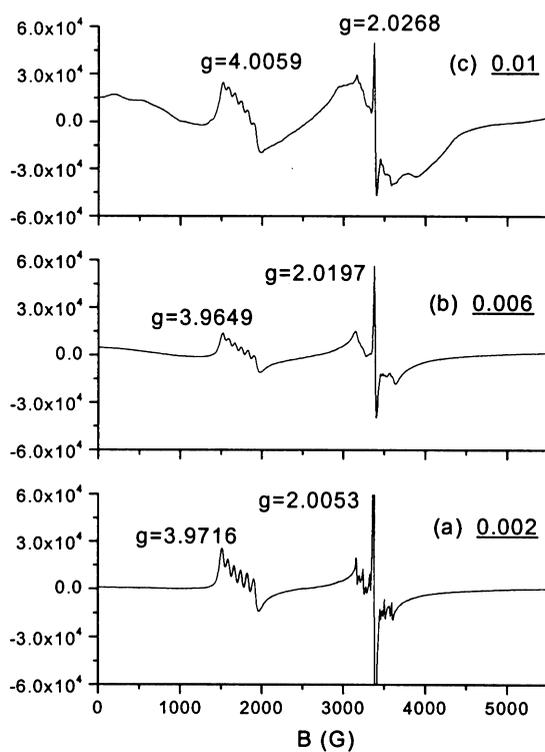


Fig. 1. EPR spectra of the Mn-doped BaTiO₃ with Mn concentration of (a) 0.002, (b) 0.006 and (c) 0.01 at 9.48 GHz and 123 K.

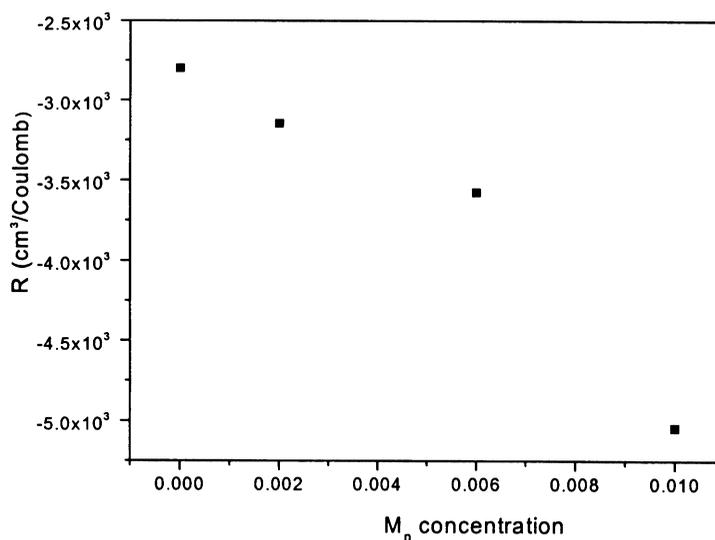


Fig. 2. Hall coefficient R of Mn-doped BaTiO₃ at 77 K.

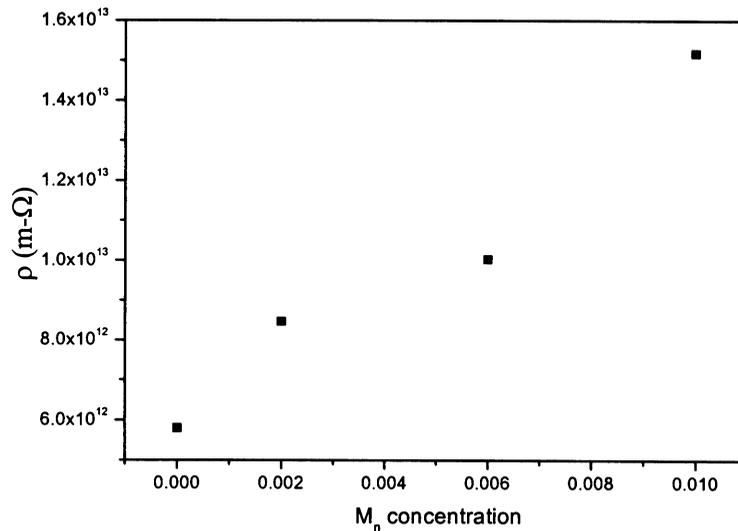


Fig. 3. Resistivity versus Mn concentration for Mn-doped BaTiO₃.

Fig. 4 depicts the dielectric constants of the Mn-doped BaTiO₃ with Mn concentrations of 0.002, 0.006 and 0.01, respectively, and in its pristine state. The dielectric constants ϵ_1 of the pellets exhibited a peak at $T_c \sim 110^\circ\text{C}$ upon heating, which is related to a ferroelectric–paraelectric phase transition. The height and position of the peak depends on Mn concentration. Mn²⁺ incorporated in the oxygen octahedron of the BaTiO₃ unit cell is in a more centered position than Ti⁴⁺ and may therefore modify considerably the ferroelectricity. Therefore, the amount of Mn ions and their valence state will affect the phase transition temperature T_c [7]. Furthermore, there exist oxygen vacancies in Mn-doped BaTiO₃, some of oxygen vacancies produced from sintering and others from the

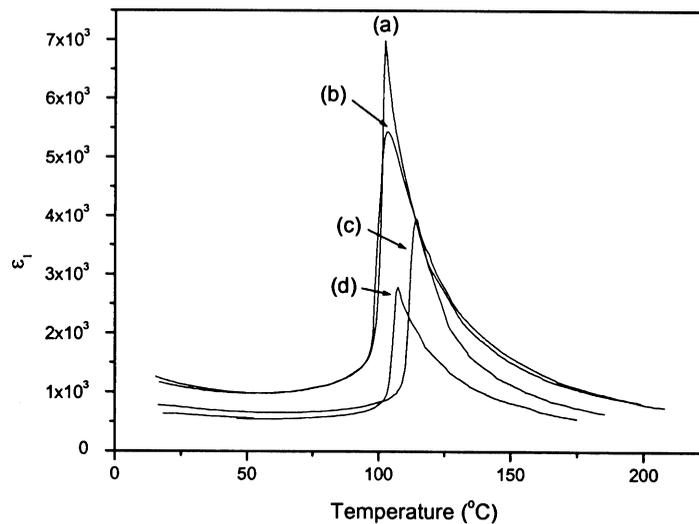


Fig. 4. Dielectric constant at 10 kHz measured for pristine BaTiO₃ (curve a) and samples doped with 0.002, 0.006 and 0.01 Mn (curves b–d).

replacement of Ti^{4+} by Mn^{2+} . A mobility of these oxygen vacancies would enhance the electric conductance.

4. Conclusion

Hall coefficient R has been measured for Mn-doped BaTiO_3 of various Mn concentrations. We found that the charge carrier is electron, and its concentration $n = 1/|eR|$ decreases with increasing Mn concentration, which indicates that Mn^{3+} and Mn^{4+} on the Ti sites will effectively trap the conduction electrons, causing the decrease of carrier concentration in the material.

Acknowledgements

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