Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 34 (2008) 1341–1344
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Short communication

Quantitative analysis of oxidation–reduction behavior of Mn-doped $BaTiO_3$

Dong Woo Hahn, Young Ho Han [*]

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

Received 6 October 2006; received in revised form 11 January 2007; accepted 13 February 2007
Available online 6 March 2007

Abstract

Effects of Mn addition on the oxidation–reduction reaction behavior of $BaTiO_3$ have been studied as a function of oxygen partial pressure and temperature. Oxygen vacancy concentration of Mn-doped $BaTiO_3$ significantly increased as the oxygen activity was lowered. The enthalpy of reduction reaction was estimated from the oxygen vacancy contents at various temperatures and increased with increasing Mn contents. The oxygen vacancy concentration of specimens co-doped with Mg and Mn at room temperature was much lower than that of the singly Mg-doped specimen. It was confirmed that the increased enthalpy of reduction reaction could suppress the degradation behavior and improve the reliability of dielectrics with Mn.

Keywords: B. Defects; C. Electrical properties; C. Lifetime; $BaTiO_3$

1. Introduction

Effects of the valence states of manganese ions on the electrical properties of Mn-doped $BaTiO_3$ have been studied by numerous investigators [1–9]. It is well known that the valence state of Mn ion varies in $BaTiO_3$, depending on the oxygen partial pressure $P(O_2)$ [2–4,8]. The equilibrium electrical conductivity of Mn-doped $BaTiO_3$ at high temperature and the concentration of Mn^{4+} and Mn^{3+} was estimated as a function of oxygen partial pressure [2]. The valence states of Mn ions in the $BaTiO_3$ lattice was also confirmed by the magnetic susceptibility measurement [4]. The change in the valence state of metal ions leads to the formation or the annihilation of oxygen vacancies. The concentration of oxygen vacancies is also dependent on the valence state of the incorporated dopants where the ionic states of dopants as well as host elements vary with oxygen partial pressure and temperature. The condition for the electrical balance state of Mn ions can be written as

$$[\mathrm{Mn}^{4+}] \approx [\mathrm{Mn}^{3+}] + \frac{1}{2}[V_\mathrm{O}^{\bullet\bullet}] \tag{1}$$

where the valence state of manganese ions changes from tetravalent to trivalent and a half mole of oxygen vacancy is accompanied by each mole of transition in Eq. (1). The defect notation is that suggested by Kröger and Vink [10].

The change in oxygen vacancy concentrations can be measured as a function of temperature and $P(O_2)$ using thermogravimetric analysis (TGA) [11,12]. In TGA technique, the mass of a sample is monitored against time or temperature, where the temperature of the sample can be programmed in a specified atmosphere by using a TGA technique [13]. Flandermeyer et al. investigated the oxidation–reduction reaction of La-doped $SrTiO_3$ [12]. Hagemann et al. obtained the oxygen vacancy concentration of $BaTiO_3$ doped with transition metal acceptors (Cr, Mn, Fe, Co, Ni) as a function of oxygen partial pressure and reported that the valance state of Mn ion easily varies with oxygen partial pressures [3].

It has been known that the electrical degradation of acceptor doped $BaTiO_3$ could be suppressed by Mn doping [1,14]. Morita et al. studied the degradation behavior of X7R-type multilayer ceramic capacitor (MLCC) with Ni internal electrode and reported that the lifetime of MLCC during the highly accelerated lifetime testing under 20 V/μm improved as the Mn content was increased [14]. Jeong and Han also suggested that the degradation behavior of acceptor doped $BaTiO_3$ could be suppressed by Mn doping and reported that

---

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

0272-8842/$34.00 © 2007 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2007.02.005

the leakage currents of $BaTiO_3$ co-doped with Mg and Mn is lower than that of the singly Mg-doped $BaTiO_3$ [1]. However, the difference in the oxygen vacancy concentration between the two specimens was negligibly small [1].

In this paper, a thermogravimetric analysis was employed to study the reduction and oxidation behavior of Mg or/and Mn doped $BaTiO_3$. Enthalpy changes of oxidation and reduction reaction were estimated using the TGA results. Effects of Mn on the degradation behavior of acceptor doped $BaTiO_3$ was also discussed in terms of Mn contents and reduction enthalpy change.

2. Experimental procedures

$BaTiO_3$ powders were synthesized using the liquid mix method developed by Pechini [15]. Samples were prepared by dissolution of precisely weighed amounts of $BaCO_3$, $MnCO_3$ and $MgCl_2$ in the Ti stock solution. Each sample with a specified composition was polymerized to a rigid gel and then calcined at 900 °C. The specimen was equilibrated in different oxygen partial pressures and its weight change was determined by a thermogravimetric analysis (TGA). Accurately weighed powder samples were suspended under a microbalance (Cahn D101) by a Pt wire in a vertically mounted tube furnace. The weight changes were then measured at 1000, 1050 and 1100 °C as a function of $P(O_2)$, where prior to the measurement, the specimen was stabilized by preheating at 1200 °C for 2 h. The weight changes were also measured as a function of temperature at $P(O_2) = 10^{-4}$ and 1 atm. Flowing gas mixtures of either O_2/N_2 or CO/CO_2 were used to establish the oxygen activity, which was monitored by a stabilized ZrO_2 oxygen sensor.

3. Results and discussion

Fig. 1 shows weight changes of undoped $BaTiO_3$ as a function of oxygen partial pressure $P(O_2)$ measured at 1000, 1050 and 1100 °C. Weight changes in the range $P(O_2) = 1$–10^{-10} atm are not significant at the temperatures studied. In this horizontal segment called the extrinsic region, the formation of oxygen vacancy due to the reduction reaction is negligibly small compared with the extrinsic oxygen vacancy concentration accompanied by the background acceptor impurities [16–18]. However, drastic weight losses were observed at lower oxygen partial pressures ($<10^{-12}$ atm). This result demonstrates that the reduction reaction has become the major source of oxygen vacancy in this region, and the oxygen vacancy concentration due to the background acceptor impurities is negligible [11,16,19]. The more weight loss occurred as the measured temperature was increased. This result indicates that the reaction is an endothermic process, which is in agreement with the previous studies [3,11]. Larger temperature dependence of the weight change at low $P(O_2)$ indicates that the enthalpy change is greater in this region. This is consistent with the previous report that the enthalpy of reduction is fairly larger than that of oxidation [21]. It also supports that the oxidation in the presence of extrinsic oxygen vacancies is much easier than the reduction at low $P(O_2)$ [16–21].

Fig. 2 shows TGA profiles of $BaTiO_3$ co-doped with 0.5 mol% Mg and 1.0 mol% Mn. A significant weight change was observed compared with the undoped $BaTiO_3$ (Fig. 1) over the same $P(O_2)$ range (1–10^{-10} atm). The valence state of Mn ions changes from tetravalent in the high $P(O_2)$ region to trivalent/divalent in the low $P(O_2)$ [2–4]. The larger weight loss of $Ba(Ti_{0.985}Mg_{0.005}Mn_{0.010})O_{2.995-y}$ results from the formation of compensating oxygen vacancies due to the easier valence change of Mn ions [3–6,8]. According to the change in the valence state of Mn ions, the charge neutrality condition can be written as follows:

$$[\mathrm{Mn}'_{\mathrm{Ti}}] \approx 2[V_{\mathrm{O}}^{\bullet\bullet}] \quad (2)$$

$$[\mathrm{Mn}''_{\mathrm{Ti}}] \approx [V_{\mathrm{O}}^{\bullet\bullet}] \quad (3)$$

The horizontal region normally occurring in undoped or inert acceptor doped $BaTiO_3$ is absent in this Mn-doped $BaTiO_3$ system, where the oxygen vacancy formation due to the change

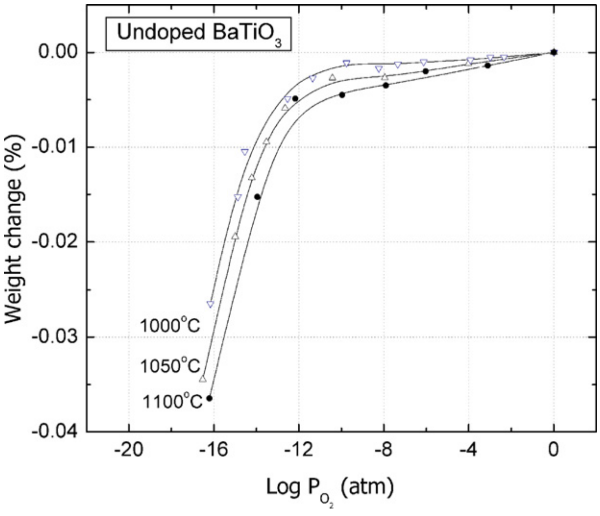

Fig. 1. Weight changes of undoped $BaTiO_3$ as a function of oxygen partial pressure measured at 1000, 1050 and 1100 °C.

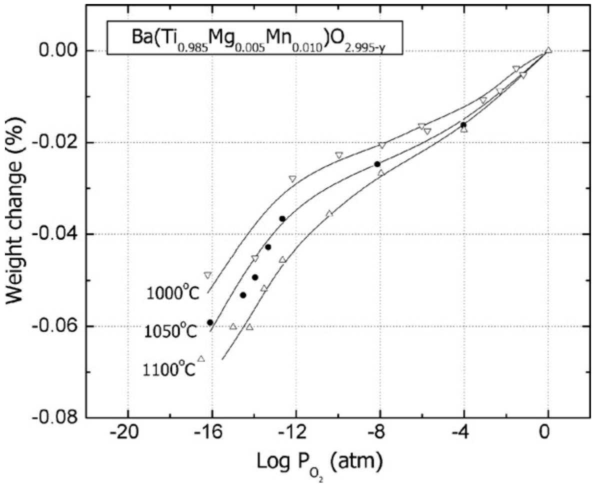

Fig. 2. Weight changes of $BaTiO_3$ co-doped with 0.5 mol% of Mg and 1.0 mol% of Mn.

in ionic states of manganese ions could surpass the extrinsic oxygen vacancies formed by Mg ions. It should be noted that as $P(O_2)$ is lowered, the temperature dependence of weight change in $Ba(Ti_{0.985}Mg_{0.005}Mn_{0.010})O_{2.995-y}$ specimen is getting larger compared with the undoped $BaTiO_3$ specimen (Fig. 1). This indicates that the reduction enthalpy of $Ba(Ti_{0.985}Mg_{0.005}Mn_{0.010})O_{2.995-y}$ for the creation of oxygen vacancy, would be larger than that of the undoped one. In order to confirm this result, the reduction enthalpies of Mg-doped, Mn-doped and (Mg + Mn)-doped $BaTiO_3$ were obtained from the TGA data measured at various temperatures.

Arrhenius plots of oxygen vacancy concentration for undoped and Mg or/and Mn doped $BaTiO_3$ are shown in Fig. 3. Weight changes of the specimen were measured from 850 to 1000 °C at $P(O_2) = 10^{-4}$ atm. The reduction reaction and its mass action expression can be written as follows:

$$O_O \Leftrightarrow V_O^{\bullet\bullet} + 2e' + \frac{1}{2}O_2 \qquad (4)$$

$$[V_O^{\bullet\bullet}]n^2 = K'e^{-\Delta H/kT}P(O_2)^{-1/2} \qquad (5)$$

where K' is the temperature independent pre-exponential factor and ΔH is the enthalpy change required for the reduction reaction in Eq. (4). The enthalpy change for the creation of doubly ionized oxygen vacancy can be calculated from the temperature dependence of oxygen vacancy concentration. For each oxygen vacancy, two electrons are formed according to Eq. (4)

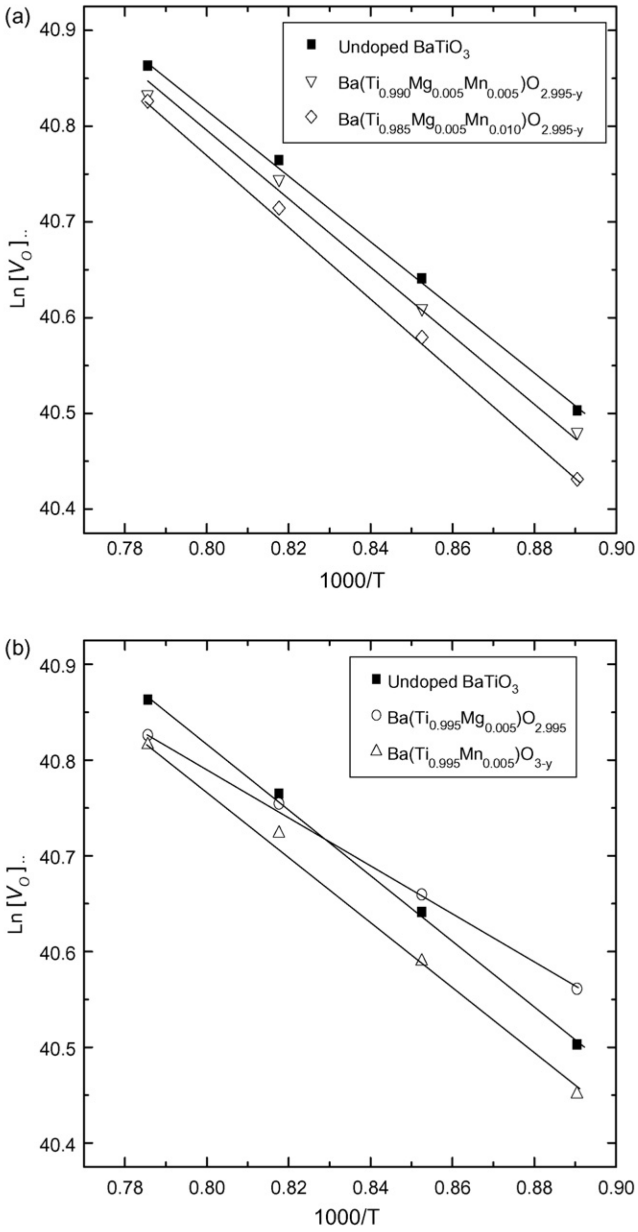

Fig. 3. Arrhenius plot of oxygen vacancy concentration of (a) undoped $BaTiO_3$ and co-doped with Mg and Mn; (b) undoped and singly Mg- or Mn-doped $BaTiO_3$.

$$n = 2[V_O^{\bullet\bullet}] \qquad (6)$$

The oxygen vacancy concentration of Eq. (5) can be written as follows:

$$[V_O^{\bullet\bullet}] = \left(\frac{K'}{4}\right)^{1/3}\exp\left(-\frac{\Delta H}{3kT}\right)P(O_2)^{-1/6} \qquad (7)$$

Enthalpy changes for the oxygen vacancy formation obtained from Eq. (7) are summarized in Table 1. The singly Mg-doped specimen exhibits the lowest value (0.66 eV at $P(O_2) = 10^{-4}$) regardless of $P(O_2)$, referring to Fig. 3(b). Enthalpy changes of Mn doped specimens increase with increasing Mn contents and the specimen co-doped with 0.5 mol% Mg and 1.0 mol% Mn shows the largest value in both $P(O_2) = 10^{-4}$ atm and 1 atm. The oxygen vacancy concentrations at 1000 and 25 °C, estimated using Eq. (7) and the enthalpy changes obtained at $P(O_2) = 1$ atm, are shown in Table 1. The difference in oxygen vacancy concentration $[V_O^{\bullet\bullet}]$ between $Ba(Ti_{0.995}Mg_{0.005})O_{2.995}$ and $Ba(Ti_{0.985}Mg_{0.005}Mn_{0.010})O_{3-y}$ is not significant at 1000 °C whereas at 25 °C, the oxygen vacancy concentration of the former is eight times greater than the latter. This result demonstrates that the creation of oxygen vacancy in $BaTiO_3$ lattice is suppressed by the incorporation of Mn ions, where the effect of Mn additions is more significant at room temperature.

Fig. 4 shows the leakage currents at a dc field of 10,600 V/cm at 150 °C, which was published in the author's previous report [1]. The specimen of 0.5 mol% Mg-doped $BaTiO_3$ exhibited the highest leakage current and failure occurred in 6.3 h. The leakage currents of Mn-doped $BaTiO_3$ specimens

Table 1
Reduction enthalpy changes measured at various $P(O_2)$ and fractional concentrations of oxygen vacancies at 1000 and 25 °C

Composition	Reduction enthalpy (eV)		$[V_O^{\bullet\bullet}]$ (at $P(O_2)$ = 1 atm)	
	10^{-4} atm	1 atm	1000 °C	25 °C
Undoped $BaTiO_3$	0.89	0.90	6.5×10^{-2}	8.5×10^{-6}
$Ba(Ti_{0.995}Mg_{0.005})O_{2.995}$	0.66	0.78	9.4×10^{-2}	4.0×10^{-5}
$Ba(Ti_{0.995}Mn_{0.005})O_{3-y}$	0.91	0.92	6.1×10^{-2}	6.5×10^{-6}
$Ba(Ti_{0.990}Mg_{0.005}Mn_{0.005})O_{2.995-y}$	0.88	0.89	6.7×10^{-2}	9.6×10^{-6}
$Ba(Ti_{0.985}Mg_{0.005}Mn_{0.010})O_{2.995-y}$	0.98	0.94	5.8×10^{-2}	5.0×10^{-6}

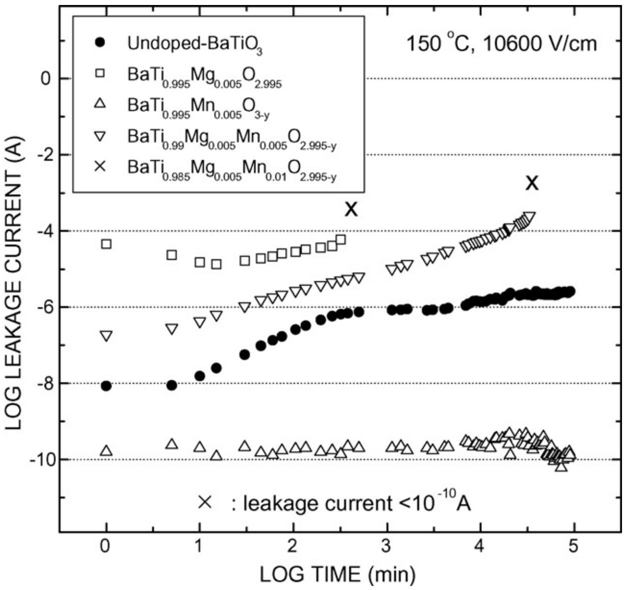

Fig. 4. Leakage currents of Mn or/and Mg-doped BaTiO$_3$ as a function of time at 150 °C, 10,600 V/cm.

were stable with time and much lower than the un-doped BaTiO$_3$, and the specimen co-doped with 0.5 mol% Mg and 1.0 mol% Mn showed the lowest leakage current below 10^{-10} A. This result is compatible with the reduction enthalpies summarized in Table 1. According to the reduction model, the main cause of the electrical degradation is the creation of oxygen vacancy and free electrons [1,5]. The concentration of oxygen vacancies at low temperatures could be considerably decreased with increasing the reduction energy as shown in Table 1. This indicates that Mn doping effectively suppresses the formation of oxygen vacancies at room temperature and thus significantly decreases the leakage currents.

4. Conclusion

Mn-doped specimens showed a significant weight loss as the oxygen activity was lowered. The amount of weight loss became larger as the temperature was increased. Reduction enthalpy of Mn doped specimens increased with Mn content. The specimen co-doped with 0.5 mol% Mg and 1.0 mol% Mn showed the highest value in all $P(O_2)$ measured. The oxygen vacancy concentration of Ba(Ti$_{0.995}$Mg$_{0.005}$)O$_{2.995}$ at room temperature was estimated to be eight times greater than Ba(Ti$_{0.985}$Mg$_{0.005}$Mn$_{0.010}$)O$_{3-y}$. Mn doping effectively suppressed the formation of oxygen vacancies at room temperature and significantly decreased the leakage currents.

Acknowledgement

This research was supported by a grant from the Center for Advanced Materials Processing (CAMP) of the 21st Century Frontier R&D Program funded by the Ministry of Commerce, Inustry and Energy(MOCIE), Republic of Korea.

References

[1] J. Jeong, Y.H. Han, Defect chemistry of Y doped BaTiO$_3$, J. Electroceram. 13 (2004) 549–553.

[2] S. Osawa, A. Furuzawa, N. Fujikawa, Effect of the manganese valence state on the electrical conductivity of barium titanate, J. Am. Ceram. Soc. 76 (5) (1993) 1191–1194.

[3] H.J. Hagemann, D. Hennings, Reversible weight change of acceptor-doped BaTiO$_3$, J. Am. Ceram. Soc. 64 (10) (1981) 590–594.

[4] H.J. Hagemann, H. Ihrig, Valence change and phase stability of 3d-doped BaTiO$_3$ annealed in oxygen and hydrogen, Phys. Rev. 20 (9) (1979) 3871–3878.

[5] E.J. Lee, J. Jeong, Y.H. Han, Defect and degradation of BaTiO$_3$ co-doped with Dy and Mn, Japan. J. Appl. Phys. 45 (2A) (2006) 822–825.

[6] J. Rödel, G. Tomandl, Degradation of Mn-doped BaTiO$_3$ ceramic under a high dc electric field, J. Mater. Sci. 19 (1984) 3515–3523.

[7] S.B. Desu, E.C. Sabbarao, Effect of oxidation states of Mn on the phase stability of Mn-doped BaTiO$_3$, Ferroelectrics 37 (1981) 665–668.

[8] I. Burn, Mn-doped polycrystalline BaTiO$_3$, J. Mater. Sci. 14 (1979) 2453–2458.

[9] H. Kishi, Y. Okino, M. Honda, Y. Iguchi, M. Imaeda, Y. Takahashi, H. Ohsata, T. Okuta, The effect of MgO and rare-earth oxide on formation behavior of core-shell structure in BaTiO$_3$, Japan. J. Appl. Phys. 36 (1997) 5954–5957.

[10] F.A. Kröger, H.J. Vink, in: F. Seitz, D. Turnbull (Eds.), Solid State Physics, Academic Press, New York, 1956.

[11] B.F. Flandermeyer, A.K. Agarwal, H.U. Anderson, M.M. Nasrallah, Oxidation–reduction behaviour of La-Doped SrTiO$_3$, J. Mater. Sci. 19 (1984) 2593–2598.

[12] D. Hennings, Part III. Thermogravimetric investigations, Philips Res. Reports 31 (1976) 516–525.

[13] P.J. Haines, Thermal Method of Analysis, Chapman & Hall, London, 1995.

[14] K. Morita, Y. Mizuno, H. Chazono, H. Kishi, Effect of Mn addition on dc-electrical degradation of multilayer ceramics capacitor with Ni internal electrode, Japan. J. Appl. Phys. 41 (2002) 6957–6961.

[15] M. Pechini, U.S. Pat. No. 3,330,697 (1967).

[16] N.H. Chan, R.K. Sharma, D.M. Smyth, Nonstoichiometry in aceptor doped BaTiO$_3$, J. Am. Ceram. Soc. 65 (3) (1982) 167–169.

[17] Y.H. Han, J.B. Appleby, D.M. Smyth, Calcium as an acceptor impurity in BaTiO$_3$, J. Am. Ceram. Soc. 70 (2) (1987) 96–100.

[18] N.H. Chan, D.M. Smyth, Defect chemistry of BaTiO$_3$, J. Electroceram. 123 (10) (1987) 1584–1585.

[19] N.H. Chan, R.K. Sharma, D.M. Smyth, Nonstoichiometry in undoped BaTiO$_3$, J. Am. Ceram. Soc. 64 (90) (1981) 556–562.

[20] Y.M. Chiang, D.P. Birnie III, W.D. Kingery, Physical Ceramics, John Wiley & Sons, 1997.

[21] D.M. Smyth, The Defect Chemistry of Metal Oxides, Oxford University Press, 2000.