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Donor- and acceptor-cosubstituted $BaTiO_3$ for nonreducible multilayer ceramic capacitors

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Abstract

Donor- and acceptor-cosubstituted $BaTiO_3$ pellets with the composition of $[((Ba,Sr)Pb_x)_{0.98}La_{0.02}](Ti_{0.99}Mg_{0.01})O_3$ are under investigation for the purpose of developing nonreducible dielectric layers for the applications of multilayered ceramic capacitors (MLCCs) with the base-metal electrodes. The added La and Mg in this composition behaved as donors and acceptors, respectively. The Pb addition changed the Curie temperature and grain size. The dielectric performance was dependent upon the Pb content and the re-oxidation treatment. These 1150 °C-annealed pellets demonstrates a satisfying dielectric performance with a grain size of 0.8–1.5 μm, dielectric constant of 48,500, loss tangent of 0.13, TCC of −12% at 85 °C, and leakage current of 9×10^{-9} A at 5 V (∼20 V/cm). The 5% Pb-doped $BaTiO_3$ pellets are most prospective.

Keywords: A. Sintering; C. Dielectric properties; D. Barium titanate; E. Capacitors

1. Introduction

Multilayer ceramic capacitors (MLCCs) possessing high capacitance of 1–100 μF can be engineered into passive components in circuits for LSI, replacing the widely used tantalum capacitors and aluminum electrolytic capacitors. To meet the growing requirements of miniaturization, higher performance, and lower electric power consumption, the number and the dielectric constant of the dielectric active layers are expected to increase, the layer thickness to be less than 2 μm, and the grain size of dielectric layers to be small for the consideration of reliability.

The most popular dielectric material for MLCCs is barium titanate ($BaTiO_3$). Its dielectric maximum shifted towards room temperature by the compositional substitution and its dielectrics were sensitive to temperature, field strength and frequency, especially near the Curie temperature. $BaTiO_3$ has demonstrated its high dielectric maxima of $\varepsilon_r \approx 15{,}000$ in the Y5V materials and of $\varepsilon_r \approx 3000$ in the X7R specification [1]. For both specifications, the ferroelectric ceramics with the higher dielectric constants have demonstrated a higher temperature coefficient of capacitance (TCC). To reduce the cost of MLCCs, the use of base metals such as nickel (Ni) and copper (Cu) as internal electrodes in the place of the precious Ag–Pd has been commercialized. The so-called base metal-electrode (BME) process requires a nonreducible $BaTiO_3$ dielectric that can be fired in a reducing atmosphere to prevent the electrodes from oxidation.

The study on nonreducible $BaTiO_3$-based dielectrics for producing MLCC products with Ni electrodes (Ni-MLCCs) was initiated by Herbert in the early 1960s [2]. MnO and Cr_2O_3 were used as acceptors for nonreducible dielectrics [3,4]. Sakabe et al. obtained nonreducible $BaTiO_3$ at excess BaO in the BaO/TiO_2 ratio and the addition of CaO [5,6]. Nowadays, nonreducible and large-capacitance Ni-MLCCs have been mass produced, which are composed of 500 or more laminated thin dielectric layers of ∼2 μm. Donor- and acceptor-cosubstituted $BaTiO_3$ has been proved to have a high insulation resistance and life stability [7,8]. The most recognized system is $BaTiO_3$–MgO–R_2O_3, where R_2O_3 is

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the rare-earth oxide with R representing La, Sm, Gd, Dy, Ho, Er, Yb, etc. in the order of decreasing ionic size. Saito et al. used the $BaTiO_3$–MgO–Ho_2O_3-based dielectrics to obtain reliable and nonreducible Ni-MLCCs conforming to X7R specification [9]. A review paper given by Kishi et al. elucidates the $BaTiO_3$–MgO–R_2O_3 system in terms of microstructure and dielectric behaviors [10]. A formula based on a model partially substituting the rare-earth donor for Ba and the Mg acceptor for Ti in $BaTiO_3$ (ABO_3), is expressed below:

$$(Ba_{1-2x}R_{2x})(Ti_{1-x}Mg_x)O_3, \quad x = 0{-}0.15$$

It has been confirmed that larger rare-earth ions (La, Sm) predominantly occupied the *A*-site (donor dopants), smaller ions (Yb) predominantly occupied the *B*-site (acceptor dopant) and intermediate ions (Dy, Ho, Er) occupied both *A*- and *B*-sites (donor and acceptor dopants). The electrical properties of the La- and Sm-doped samples were improved to a level near those of Dy- and Ho-doped samples when the MgO element was increased to form the core-shell structure. To obtain Ni-MLCCs, a commercialization process is conducted to weakly oxidize a sample during the cooling stage, after it has been sintered in a reduced atmosphere (re-oxidation).

In this study, the Pb-doped $(Ba,Sr)TiO_3$–MgO–La_2O_3 system or the multi-doped $BaTiO_3$ system with the formula of $[((Ba,Sr)Pb_x)_{0.98}La_{0.02}](Ti_{0.99}Mg_{0.01})O_3$, x = 0, 0.05, 0.1, and 0.2, was investigated for the purpose of modifying the dielectric properties of large-capacitance dielectric layers in Ni-MLCCs. The $[((Ba,Sr)Pb_x)_{0.98}La_{0.02}](Ti_{0.99}Mg_{0.01})O_3$ composition was cosubstituted with the donor of La and the acceptor of Mg. The defect incorporation reaction, based upon the Kröger and Vink notation [11], for the La and Mg doping can be expressed as:

$$La_2O_3 + MgO + TiO_3 \rightarrow 2La^{\bullet}_{Ba} + Mg''_{Ti} + 6O^{\times}_{O}$$

The 1% negatively charged defect can electrically balance the 2% positively charged defect in this study, i.e. $[La^{\bullet}{}_{Ba}] = 2\,[Mg''_{Ti}]$. The air-sintered, Ar-sintered, and the annealed pellets were prepared and their dielectric properties were measured.

2. Experimental procedure

Multi-doped $BaTiO_3$ ceramic powder was prepared by a conventional ceramic process. Four kinds of the investigated $[((Ba,Sr)Pb_x)_{0.98}La_{0.02}](Ti_{0.99}Mg_{0.01})O_3$ composition with the lead ratios of 0 (Pb-0), 0.05 (Pb-0.05), 0.1 (Pb-0.1), and 0.2 (Pb-0.2) were prepared. After calcination at 900 °C and ball milling, the pressed ceramic pellets were underwent different treatments. These pellets were sintered at 1350 °C in air and in argon (Ar). The Ar-sintered pellets were annealed at 800, 1000, 1050, 1100, 1150, and 1200 °C in air for 1 h (the re-oxidized pellets).

Crystal structure of the fired $BaTiO_3$ was analyzed using an X-ray diffractometer (XRD, Bruker D8, Germany). Surface morphology was examined by a scanning electron microscope (SEM, Hitachi model S-3500H, Japan). Relative dielectric constant and loss tangent were measured from 25 °C to 150 °C by employing HP 4285A LCR meter (Model 4284A, Agilent Technologies, USA) at a frequency of 100 kHz and an average voltage of 1 V. The relation of leakage current and electric field was obtained by using an electrometer/high-resistance meter (Model 6517a, Keithley Instruments, Inc., USA).

3. Results and discussion

3.1. Structure and microstructure

Fig. 1 illustrates the XRD patterns of $[((Ba,Sr)Pb_{0.05})_{0.98}La_{0.02}](Ti_{0.99}Mg_{0.01})O_3$ pellets after air annealing, argon sintering, and re-oxidation. XRD peaks of multi-doped $BaTiO_3$ displayed a single-phase structure for pellets processed at different environments. SEM micrographs of those air-sintered $[((Ba,Sr)Pb_x)_{0.98}La_{0.02}](Ti_{0.99}Mg_{0.01})O_3$ pellets are shown in Fig. 2. The grain size was 3–5 μm for pellets without the Pb addition. The grain size decreased with the addition of the Pb contents and reached a minimum of 0.8–1.5 μm at x = 0.05 and 0.1 after firing at 1350 °C. The microstructural characterization explains the Pb effect on the grain size. For the $(Ba,Sr)TiO_3$–MgO–La_2O_3 system, the addition of Pb to decrease grain size is advantageous for the advanced thin dielectric layers in Ni-MLCCs for ensuring better quality.

3.2. Dielectric properties of the air-sintered pellets

The variation of dielectric properties of air-sintered $[((Ba,Sr)Pb_x)_{0.98}La_{0.02}](Ti_{0.99}Mg_{0.01})O_3$ pellets with test temperature is shown in Fig. 3. Dielectric constants measured at 25 °C were 9000, 6000, 2900, and 1400 for the Pb-0, Pb-0.05, Pb-0.1, and Pb-0.2 pellets, respectively. The addition of Pb increased the Curie temperature and

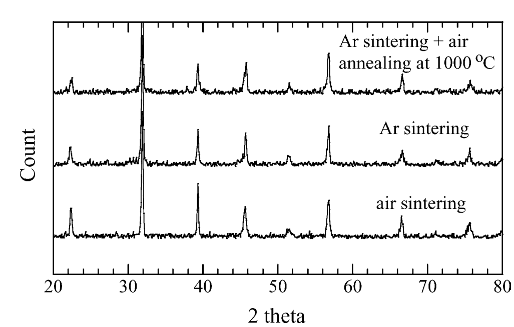

Fig. 1. XRD of the multi-doped $BaTiO_3$ with a Pb content of 0.05, processed by sintering at 1350 °C in air, sintering at 1350 °C in argon, and annealing at 1000 °C in air after sintering in argon.

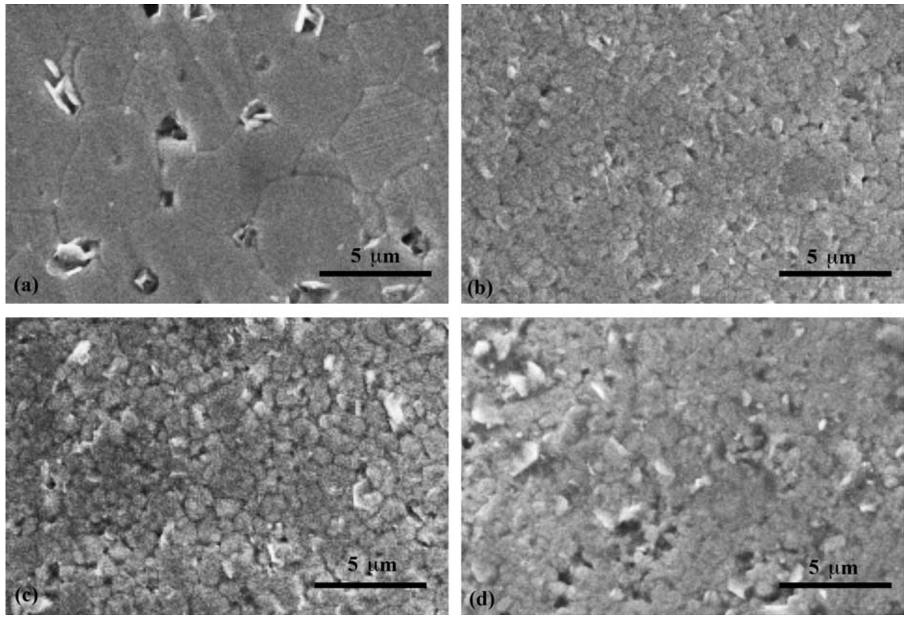

Fig. 2. SEM surface morphologies of the multi-doped $BaTiO_3$ with the Pb content of (a) 0, (b) 0.05, (c) 0.1, and (d) 0.2, after sintered at 1350 °C in air for 1 h.

decreased the dielectric peak maximum. The shift of the Curie temperature of the $[(Ba,Sr)_{0.98}La_{0.02}](Ti_{0.99}Mg_{0.01})O_3$ composition above 0 °C is the motivation of the Pb addition to form $[((Ba,Sr)Pb_x)_{0.98}La_{0.02}](Ti_{0.99}Mg_{0.01})O_3$ with $x = 0$, 0.05, 0.1, and 0.2. The effect of the Pb addition on the Curie temperature is consistent with the prediction of Jaffe et al. on the isovalent substitutions of $BaTiO_3$ [12]. The Pb-0 pellet had a lowest dielectric loss tangent (tan δ) of ~0.02, while the Pb-0.05 sample had a highest value above 0.04.

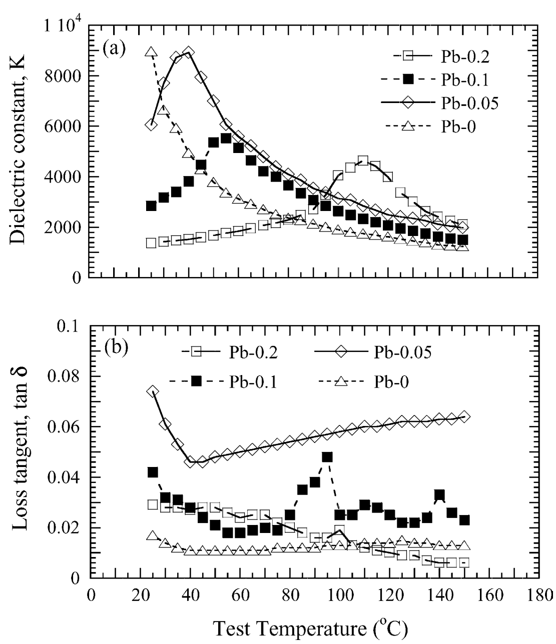

Fig. 3. Variations of (a) dielectric constant and (b) loss tangent with test temperature for multi-doped $BaTiO_3$ with different Pb contents. The pellets were sintered in air at 1350 °C for 1 h.

3.3. Dielectric properties of the argon-sintered and the re-oxidized pellets

The variation of dielectric properties of the argon-sintered and the re-oxidized $[((Ba,Sr)Pb_x)_{0.98}La_{0.02}](Ti_{0.99}Mg_{0.01})O_3$ pellets with annealing temperature is shown in Fig. 4. The Ar-sintered pellets demonstrated higher dielectric constants and loss tangents, as compared with the air-sintered pellets (Fig. 3). The room-temperature dielectric

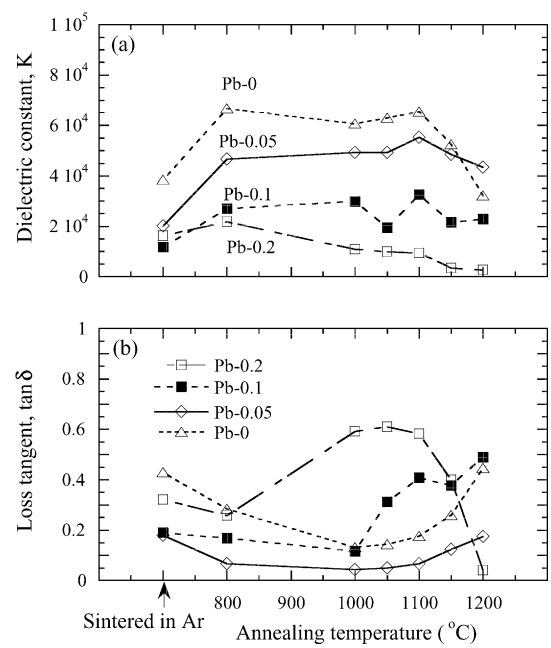

Fig. 4. Variations of (a) dielectric constant and (b) loss tangent with annealing temperature for the argon-sintered and annealed $[((Ba,Sr)Pb_x)_{0.98}La_{0.02}](Ti_{0.99}Mg_{0.01})O_3$. The pellets were sintered at 1350 °C in argon for 1 h, followed by annealing in air.

constants were 38,500, 20,000, 11,500, and 16,000 for the Pb-0, Pb-0.05, Pb-0.1, and Pb-0.2 pellets, respectively. The dielectric constants of these Pb-0.05 and Pb-0.1 pellets remained high after air annealing, but declined at higher annealing temperatures for the Pb-0 and Pb-0.2 pellets. The room-temperature dielectric constants for the Pb-0.05 pellets were 49,000, 48,500, and 43,500 after air annealed at 1000, 1150, and 1200 °C, respectively. Furthermore, these Pb-0.05 pellets also had a relatively lower loss tangent. The lowest loss tangent of 0.05 was obtained for the Ar-sintered Pb-0.05 pellet after air annealing at 1000 °C. From the above results in dielectric properties of the Ar-sintered and re-oxidized $[((Ba,Sr)Pb_x)_{0.98}La_{0.02}](Ti_{0.99}Mg_{0.01})O_3$, the pellets with the Pb ratio of 0.05 had the best composition suitable for the re-oxidation process to obtain the good dielectric performance. Therefore, other properties of the Pb-0.05 pellets were further investigated as shown below.

Fig. 5 displays the variation of temperature coefficients of (a) capacitance (TCC) and (b) tan δ (TCT) with annealing temperature in the range of 25–150 °C for the Ar-sintered Pb-0.05 pellets. TCC and TCT are defined as $[(C_T - C_{25})/C_{25}]$ and $[(\tan\delta_T - \tan\delta_{25})/\tan\delta_{25}]$, respectively, where C represents the capacitance and the subscript number the test temperature. The TCC values had larger scatters at higher test temperatures for the Pb-0.05 pellets annealed at higher temperatures, while few scatters were for pellets annealed at low temperatures. The absolute TCC values at 85 °C were 2.5, 25, and 42% for the Pb-0.05 pellets after annealed at 1000, 1150, and 1200 °C. The effects of annealing temperature on TCT were opposite to those on TCC, i.e.

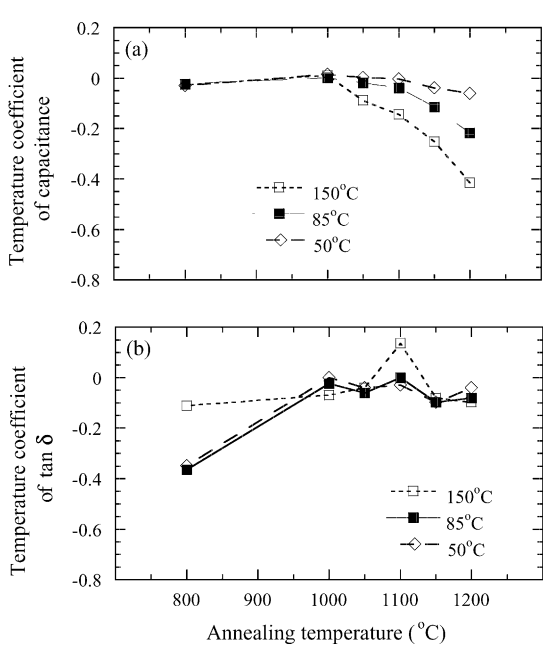

Fig. 5. Variations of the temperature coefficients of (a) capacitance and (b) loss tangent with annealing temperature for the argon-sintered and annealed $[((Ba,Sr)Pb_x)_{0.98}La_{0.02}](Ti_{0.99}Mg_{0.01})O_3$. The pellets were sintered at 1350 °C in argon for 1 h, followed by annealing in air.

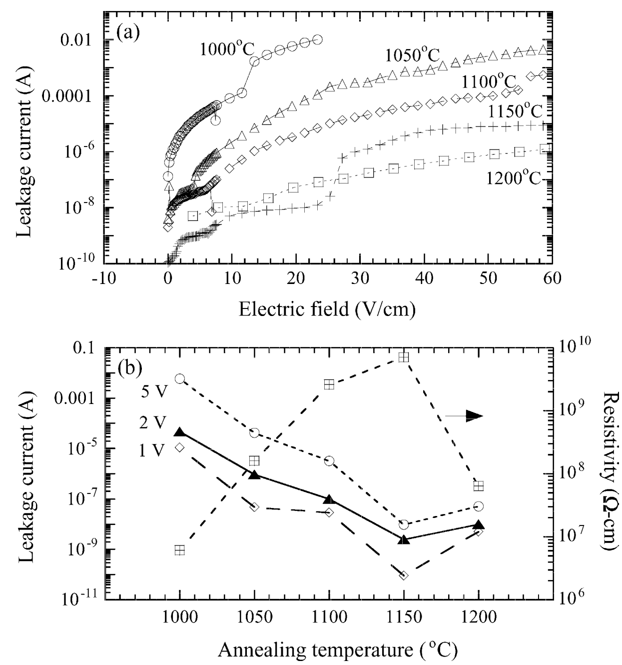

Fig. 6. (a) The variation of leakage current with electric field at different annealing temperatures and (b) the variations of leakage current with annealing temperature at different applied voltages and resistivity with annealing temperature, for multi-doped $BaTiO_3$ with the Pb ratio of 0.05. The pellets were sintered at 1350 °C in argon for 1 h.

the TCT values were lower at higher annealing temperatures.

Fig. 6 demonstrates the variations of leakage current and electrical resistivity with applied field and annealing temperature for the Ar-sintered Pb-0.05 pellets. Fig. 6a shows the relation between leakage current and electric field at different annealing temperatures. Fig. 6b displays the effects of applied voltage and annealing temperature on the leakage current and electrical resistivity. The low temperature-annealed Pb-0.05 pellets lost their insulation at higher electric field, although they had extremely low TCCs. The leakage current was lower for pellets annealed at higher temperatures. Nevertheless, the 1150 °C-annealed pellet had a lower value at the electric field less than 25 V/cm, as compared with the 1200 °C-annealed pellet. The minimum leakage current was 9×10^{-9} A at 5 V (~20 V/cm). Resistivity measured at low voltage increased with annealing temperature and reached a maximum of $7 \times 10^{9}\ \Omega$ cm at 1150 °C (Fig. 6b). After different compositions and heat treatments have been analyzed, it is clear that the Ar-sintered $[((Ba,Sr)Pb_x)_{0.98}La_{0.02}](Ti_{0.99}Mg_{0.01})O_3$ pellets with the Pb ratio of 0.05 can give the best dielectric results unless they are air annealed at 1150 °C.

4. Conclusions

Donor- and acceptor-cosubstituted $BaTiO_3$ pellets of the modified $(Ba,Sr)TiO_3$–MgO–La_2O_3 system, Pb-doped

$[((Ba,Sr)Pb_x)_{0.98}La_{0.02}](Ti_{0.99}Mg_{0.01})O_3$, have been synthesized and investigated for the nonreducible dielectric layers of Ni-MLCCs. The Pb addition controlled the grain size and Curie temperature. The re-oxidized pellets with the Pb ratio of 0.05 had not only higher dielectric constants but also lower loss tangents, as compared with other compositions. These Pb-0.05 pellets demonstrated a better insulation after they were annealed at 1150 °C in air. The 1150 °C-annealed $[((Ba,Sr)Pb_{0.05})_{0.98}La_{0.02}](Ti_{0.99}Mg_{0.01})O_3$ pellet demonstrates a satisfying dielectric performance at low applied voltage with a grain size of 0.8–1.5 μm, high dielectric constant of 48,500, medium loss tangent of 0.13, low TCC of −12% at 85 °C, and low leakage current of 9×10^{-9} A at 5 V (∼20 V/cm).

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