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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:

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

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

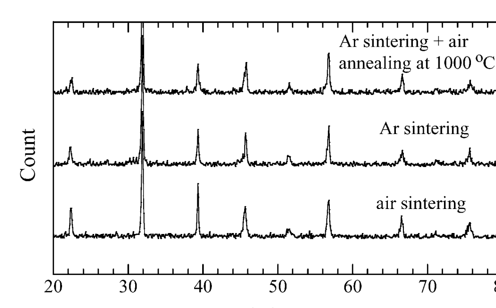

Fig. 1. XRD of the multi-doped $BaTiO_3$ with a Pb content of 0.05, processed by sintering at 1350 °C in air, sintering at 1350 °C in argon, and annealing at 1000 °C in air after sintering in argon.