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REGULAR PAPER

Fabrication of lead-free piezoelectric Li_2CO_3-added (Ba,Ca)(Ti,Sn)O_3 ceramics under controlled low oxygen partial pressure and their properties

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Reduction-resistant lead-free (Ba,Ca)(Ti,Sn)O_3 piezoceramics with high piezoelectric constants were fabricated by optimizing the amount of Li_2CO_3 added. Oxygen partial pressure was controlled during the sintering of (Ba,Ca)(Ti,Sn)O_3 ceramics in a reducing atmosphere using H_2–CO_2 gas. Enhanced grain growth and a high-polarization state after poling treatment were achieved by adding Li_2CO_3. Optimizing the amount of Li_2CO_3 added to $(Ba_{0.95}Ca_{0.05})(Ti_{0.95}Sn_{0.05})O_3$ ceramics sintered under a low oxygen partial pressure resulted in improved piezoelectric properties while maintaining the high sintered density. The prepared Li_2CO_3-added ceramic samples had homogeneous microstructures with a uniform dispersion of each major constituent element. However, the residual Li content in the 3 mol % Li_2CO_3-added $(Ba_{0.95}Ca_{0.05})(Ti_{0.95}Sn_{0.05})O_3$ ceramics after sintering was less than 0.3 mol %. Sintered bodies of this ceramic prepared in a CO_2 (1.5%)–H_2 (0.3%)/Ar reducing atmosphere ($PO_2 = 10^{-8}$ atm at 1350 °C), exhibited sufficient electrical resistivity and a piezoelectric constant (d_{33}) exceeding 500 pC/N. The piezoelectric properties of this nonreducible ceramic were comparable or superior to those of the same ceramic sintered in air.

1. Introduction

Piezoelectric ceramic materials and electronic components that contain such materials are currently used in various electronic devices. Multilayer technology is indispensable for achieving the miniaturization of electronic devices while lowering the working voltage of their piezoelectric components. However, the noble metal electrodes commonly used in current multilayer-type piezoelectric ceramic components increase the electrode cost. Therefore, similar to the fabrication of multilayer chip capacitors, that of piezoelectric materials by cofiring with base-metal electrodes under a low oxygen partial pressure has been applied to reduce cost.[1–5] Because of its electrical conductivity and high melting point, Ni is commonly used for base-metal electrodes. In a cosintering process, the oxygen partial pressure at the sintering temperature should be precisely controlled to suppress the oxidation of Ni electrodes. The major problem encountered when using perovskite-oxide-based materials (e.g., $BaTiO_3$) is their low endurance in reducing atmospheres, which results in a low insulating resistance (n-type semiconductor characteristics) and makes the achievement of the desired electrical properties difficult. In perovskite titanates, the generation of conductive electrons accompanied by the reduction of titanium ions (Ti^{4+}) during the sintering process underlies this problem.[1,6,7] Many studies have been conducted on the multilayer capacitor applications of nonreducible $BaTiO_3$-based ceramics.[1,6–8] In addition, the authors previously reported on the fabrication and characterization of reduction-resistant (Ba,Ca)TiO_3 piezoelectric ceramics and control of their grain orientation.[9–12] However, the piezoelectric properties were not sufficient. Therefore, further investigation, such as solid solution formation with other perovskite oxides (e.g., $BaZrO_3$ or $BaSnO_3$) is needed to enhance the piezoelectric properties.

With growing concerns about the global environment, the development of materials that do not contain toxic elements has been receiving considerable attention. In practical piezoelectric devices, Pb(Zr,Ti)O_3 (PZT)-based perovskite oxides have long been applied as piezoelectric materials.[13] As these compounds contain toxic PbO as a major component, lead-free piezoelectric materials have been intensively studied.[14,15] However, thermodynamic data[16] indicates that PZT-based materials may exhibit remarkably low resistance to sintering in a reducing atmosphere compared with the (Ba,Ca)TiO_3-based piezoceramics developed by the authors.[9,11,12] Lead-free (Ba,Ca)TiO_3-based piezoelectric materials are expected to partly replace PZT-based ceramics if satisfactory properties can be achieved. Recently, (Ba,Ca)-(Ti,Sn)O_3 ceramics with excellent piezoelectric properties have been reported.[17–19] In general, (Ba,Ca)(Ti,Sn)O_3 ceramics have a relatively high sintering temperature near or above the melting point of Ni metal. However, this sintering temperature can be lowered while maintaining piezoelectric properties, by adding Li_2O or Li_2CO_3 to $BaTiO_3$ or (Ba,Ca)(Ti,Sn)O_3, as recently reported by several researchers.[20–24]

In this paper, we describe the fabrication and characterization of nonreducible lead-free (Ba,Ca)(Ti,Sn)O_3 piezoceramics with electrical properties comparable to those of samples sintered in air. In particular, the effects of the addition of Li_2CO_3 on several properties were investigated to determine the processing conditions needed to prepare reduction-resistant (Ba,Ca)(Ti,Sn)O_3 ceramics with high piezoelectric constants. Precise control of oxygen partial pressure using an Ar–H_2–CO_2 mixed gas was also examined. The $(Ba_{0.95}Ca_{0.05})(Ti_{0.95}Sn_{0.05})TiO_3$ composition was selected on the basis of previously reported data[19,25] to ensure that the orthorhombic–tetragonal phase transition temperature was near room temperature.

2. Experimental procedure

2.1 Fabrication of Li_2CO_3-added (Ba,Ca)(Ti,Sn)O_3 ceramics

The starting materials used for the preparation of the (Ba,Ca)(Ti,Sn)O_3 ceramic samples were $BaTiO_3$ (Sakai Chemical BT-01), $CaTiO_3$ (Kojundo Chemical), $BaSnO_3$ (Kojundo Chemical), Li_2CO_3 (Kojundo Chemical), and $BaCO_3$ (Kojundo Chemical). In the powder compaction method, all the starting materials used to prepare $(Ba_{0.95}Ca_{0.05})(Ti_{0.95}Sn_{0.05})O_3$ containing 1 mol % $BaCO_3$ and various amounts of Li_2CO_3 were weighed and then ball-

