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Preparation and dielectric properties of B_2O_3–Li_2O-doped $BaZr_{0.35}Ti_{0.65}O_3$ ceramics sintered at a low temperature

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Abstract

$BaZr_{0.35}Ti_{0.65}O_3$ (BZT) ceramics have been fabricated via a traditional ceramic process at a relatively low sintering temperature using liquid-phase sintering aids B_2O_3 and Li_2O. The dielectric properties of BZT ceramics have been investigated with the emphasis placed on the dielectric properties under an applied dc electric field. The temperature-dependent dielectric constant reveals that the pure BZT and B_2O_3–Li_2O-doped BZT ceramics all have a typical relaxor behavior and diffuse phase transition characteristics. The temperature-dependent dielectric constant under the applied dc electric field shows that the Curie temperature is slightly shifted to higher temperature and the peaks are suppressed and broadened. The dielectric loss is still under 0.005 and tunability is above 20% at an applied dc electric field of 30 kV/cm.

Keywords: C. Dielectric properties; Liquid-phase sintering; Tunability; BZT

1. Introduction

Barium zirconium titanate ($BaZr_xTi_{1-x}O_3$) ceramics have recently received extensive attention due to high-dielectric tunability and low-dielectric loss. They have been chosen as an alternative to $Ba_{1-x}Sr_xTiO_3$ solid solution for potential applications in tunable filters, phase shifters, antennas, etc. [1–4]. In addition, the results indicate that the system of $BaZr_xTi_{1-x}O_3$ exhibits high-voltage resistance characteristic. This is possible because the Zr^{4+} ion has larger ionic size (0.087 nm) than Ti^{4+} (0.068 nm) while the Zr^{4+} ion is chemically more stable than Ti^{4+} ion [5,6].

Low-temperature co-fired ceramics (LTCC) with high-electrical-conductivity metallization, i.e., Cu and Ag, have been widely used to fabricate wireless communication components and modules [7,8]. Application of microwave tunable devices based on $BaZr_xTi_{1-x}O_3$ with a LTCC module provides a route to more integrated, miniaturized and reconfigurable microwave systems. However, the sintering temperature of pure $BaZr_xTi_{1-x}O_3$ ceramics is relatively high, >1500 °C, and not suitable for base-metal electrodes. Therefore, reducing the sintering temperature of $BaZr_xTi_{1-x}O_3$ ceramics, in order to be compatible with LTCC technology, has become an attractive challenge.

Currently, many researchers have already reported attempts to decrease the sintering temperature of $Ba_{1-x}Sr_xTiO_3$ ceramics to the vicinity of 900 °C through the use of various sintering aids such as B_2O_3, Li_2O, SiO_2, etc. [9–11]. However, very few works have been reported on the preparation and dielectric properties of $BaZr_xTi_{1-x}O_3$ ceramic sintered at low temperature. The purpose of this study is to decrease the sintering temperature of $BaZr_{0.35}Ti_{0.65}O_3$ ceramics via the additions of sintering aids, i.e., B_2O_3 and Li_2O and hence to obtain a kind of microwave tunable materials which can be sintered at a relatively low temperature. The dielectric properties of $BaZr_{0.35}Ti_{0.65}O_3$ ceramics with the aids of B_2O_3 and Li_2O sintered at a low temperature have also been investigated.

2. Experimental procedure

$BaZr_{0.35}Ti_{0.65}O_3$ (BZT) powder was prepared by the conventional solid-state reaction method. Starting raw chemicals were $BaCO_3$ (99.7%), ZrO_2 (99.0%) and TiO_2 (99.9%) powders. According to the stoichiometric composition of $BaZr_{0.35}Ti_{0.65}O_3$, all carbonate and oxide powders were weighed and mixed with alcohol and zirconia milling media

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Table 1
Experimental compositions and heat-treating condition of samples

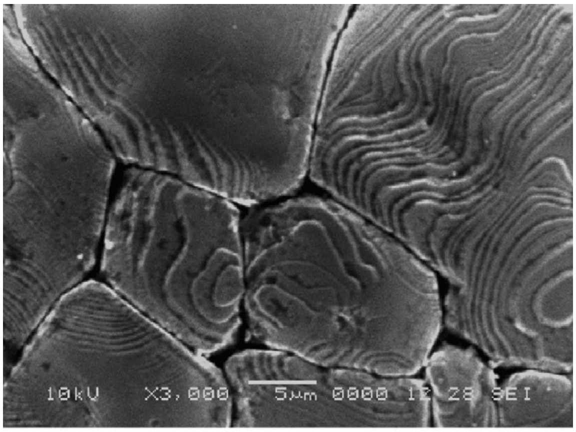
Sample	$BaZr_{0.35}Ti_{0.65}O_3$ (wt%)	Li_2O (wt%)	B_2O_3 (wt%)	Sintering temperature (°C)
A	100.00	0	0	1500
B	96.00	4.00	0	1000
C	95.25	4.00	0.75	1000

for 24 h. After drying, the mixtures were calcined in an alumina crucible at 1200 °C for 5 h in air atmosphere. Then various amounts of Li_2O and B_2O_3 were added to the BZT powder. The calcined powders were again milled and dried. The obtained powders with the addition of 8 wt% polyvinyl alcohol (PVA) binder were pressed into disc-shaped pellets at 100 MPa. The green pellets were covered by Al_2O_3 powder in alumina crucibles and then sintered at different temperatures for 4 h in air atmosphere. The detail experimental compositions and sintering conditions are shown in Table 1.

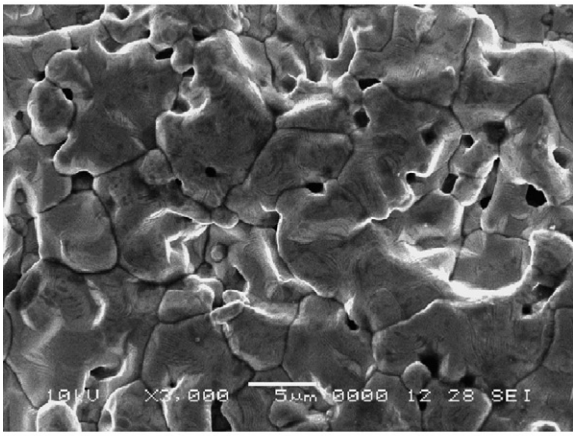
Microstructures of the sintered samples were examined by scanning electron microscope (SEM, JSM EMP-800). X-ray diffraction (XRD, Rigaku, Japan) with Cu Kα radiation was employed to examine the phase identification. In order to determine the dielectric properties of the samples, the disc samples were polished, electroded with silver paste and, then, fired at 600 °C for 10 min. The temperature dependences of the dielectric constant and loss were measured in the temperature range of −160 to 120 °C at frequencies of 1, 2, 5, 10, 20, 50, 100, 200 and 500 kHz using a high-precision LCR meter (HP 4284A). The tunability was measured at 10 kHz and room temperature up to the maximum bias voltage of 30 kV/cm by a Keithley Model 6517A Electrometer coupled with a TH2613A LCR meter. The temperature dependences of the dielectric constant under different applied electric field were also measured from −160 to 140 °C at the frequency of 10 kHz.

3. Results and discussion

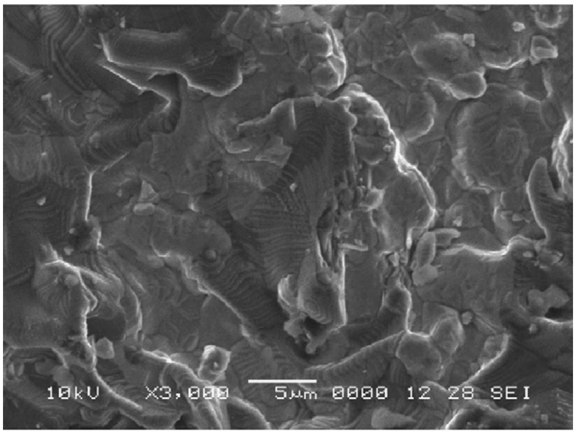
The SEM micrographs of BZT ceramic samples are shown in Fig. 1. Sample A, the pure BZT without any additives sintered at 1500 °C (Fig. 1(a)), had a relatively dense microstructure and the grain sizes were in a range of 8–25 μm. Compared with sample A, sample B, the BZT with 4.0 wt%Li_2O (Fig. 1(b)) and sample C, the BZT with 0.75 wt% B_2O_3 and 4.0 wt% Li_2O (Fig. 1(c)) can be sintered at 1000 °C and the grain sizes were obviously decreased. Sample C had much denser microstructure than samples A and B. Within the microstructure of sample B, some pores were trapped in grains. The results indicate that with Li_2O and B_2O_3, as sintering aids, the sintering temperature of co-doped BZT ceramics can be dramatically decreased and dense microstructures of BZT ceramics obtained by means of liquid-phase sintering.



(a) Sample A



(b) Sample B



(c) Sample C

Fig. 1. Scanning electron microscope (SEM) photographs of ceramic samples—(a) sample A: pure BZT sintered at 1500 °C, (b) sample B: BZT with 4.0 wt% Li_2O sintered at 1000 °C and (c) sample C: BZT with 0.75 wt% B_2O_3 and 4.0 wt% Li_2O sintered at 1000 °C.

Fig. 2 shows the XRD patterns of BZT ceramic samples with different sintering aids. It is evident that the main phase in all ceramic samples is the perovskite structure, and no obviously secondary phase was observed in XRD patterns. It can be seen that with the addition of Li_2O and B_2O_3 additives, all diffraction peaks of sample B and C were shifted to the higher two-theta when compared with those of sample A. This shift of diffraction peaks reveals that the lattice constant of samples B and C decreases. It is possible because the Li^+ ion incorporates into the crystal lattice of $BaZr_{0.35}Ti_{0.65}O_3$ and occupies the A-site ions. The ionic radius of Li (0.076 nm) is much smaller than that of Ba (0.161 nm). Accordingly, the lattice constants of samples B and C decrease and diffraction peaks shift to the high-angle side.