Materials Research Bulletin 48 (2013) 3817–3821

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Blocking effect of crystal–glass interface in lanthanum doped barium strontium titanate glass–ceramics

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ARTICLE INFO

Article history:
Received 10 December 2012
Received in revised form 18 April 2013
Accepted 27 May 2013
Available online 4 June 2013

Keywords:
A. Ceramics
A. Interface
C. Impedance spectroscopy
D. Microstructure

ABSTRACT

The microstructures and dielectric properties in La_2O_3-doped barium strontium titanate glass–ceramics have been investigated by scanning electron microscopy (SEM) and impedance spectroscopy. SEM analysis indicated that La_2O_3 additive decreases the average crystallite size. Impedance spectroscopy revealed that the positions of Z'' and M'' peaks are close for undoped samples. When La_2O_3 concentration is 0.5 mol%, the Z'' and M'' peaks show a significant mismatch. Furthermore, these peaks separate obviously for 1.0 mol% La_2O_3 addition. With increasing La_2O_3 concentration, the contribution of the crystallite impedance becomes smaller, while the contribution of the crystal–glass interface impedance becomes larger. More interestingly, it was found that La_2O_3 additive increases blocking factor of the crystal–glass interface in the temperature range of 250–450 °C. This may be attributed to a decrease of activation energy of the crystallite and an increase of the crystal–glass interface area.

1. Introduction

Energy storage capability and reliability of capacitors are of utmost importance for various current and future demanding applications. As a result, in recent years, significant efforts have been made to develop dielectric materials with high energy storage density [1,2]. Among these materials, barium strontium titanate $Ba_xSr_{1-x}TiO_3$ (BST) ferroelectric glass–ceramics have been recognized as one of the most promising candidates in terms of their high dielectric constants and high breakdown strengths [3–5]. Generally, glass–ceramic materials have a pore-free and fine grained microstructure which is highly desirable for ceramics used in capacitors [6]. The fabrication of the ferroelectric glass–ceramics by the ferroelectric phase crystallization from the glass has proved to be a useful complement to the technology of electronic ceramics [7,8].

Of particular interest is the comparison of such ferroelectric glass–ceramics with corresponding pure ferroelectric ceramics. Although the defect chemistry of undoped and doped barium titanate ($BaTiO_3$) ceramics is well studied [9–11], many discrepancies still exist between experimental results and theoretical interpretations, especially for lanthanum doped barium titanate glass–ceramics [12,13]. Colossal dielectric permittivity was observed in $Ba_{0.95}La_{0.05}TiO_{3-x}$ ceramics [14,15]. This effective permittivity is attributed to interfacial polarization, which is formed between semiconducting grains and insulating grain boundaries in the ceramics.

In La_2O_3-doped barium titanate ceramics a replacement of Ba^{2+} on the A-site by La^{3+} (La^{3+} ion is too large to replace Ti on the B-site) leads to charge imbalance which must be compensated by either cation vacancies on the A- or B-site (ionic compensation), or electrons (electronic compensation). Three simple possible compensation mechanisms can be identified [9,10]:

$$La_2O_3 + 2TiO_2 \rightarrow 2La_{Ba}^{\bullet} + 2Ti_{Ti}^{\times} + 6O_O^{\times} + \frac{1}{2}O_2 + 2e' \quad (1)$$

$$2La_2O_3 + 3TiO_2 \rightarrow 4La_{Ba}^{\bullet} + 3Ti_{Ti}^{\times} + 12O_O^{\times} + V_{Ti}'''' \quad (2)$$

$$La_2O_3 + 3TiO_2 \rightarrow 2La_{Ba}^{\bullet} + 3Ti_{Ti}^{\times} + 9O_O^{\times} + V_{Ba}'' \quad (3)$$

In addition, a direct donor doping, especially at low donor concentration, is considered as the mechanism of the charge compensation and the appearance of semiconductive properties [16]. But the mechanism by which the normally insulating BST glass–ceramics becomes semiconducting is uncertain and has been rarely ever reported [17].

It is well known that in polycrystalline $BaTiO_3$ ceramic materials grain boundaries often have a significant influence on material properties. Study of the grain boundary properties is essential to the design of the $BaTiO_3$-based ceramic materials and to the optimization of their performance. However, the preparation of the $BaTiO_3$

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0025-5408/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.materresbull.2013.05.088

glass–ceramics is generally based on total or partial conversion of silicate glasses to the $BaTiO_3$ crystalline phase. The glass composition must be chosen properly to minimize the interactions between the $BaTiO_3$ crystalline phase and the residual glass. The different doping mechanisms in $BaTiO_3$ ceramics provide a framework for conducting experiment on the $BaTiO_3$ glass–ceramics. Notably, the grain boundary models for the $BaTiO_3$ ceramics are in agreement with the experimental results [17]. However, such models are inherently incapable of elucidating the mechanisms of ionic transport phenomena for the BST glass–ceramics. Therefore, they must be supplemented by electrical continuity and blocking effect. In our previous publications it has been reported that the interfacial polarization significantly affects the dielectric and energy storage properties of the ferroelectric glass–ceramics [5,12,18].

In the present work, the complex impedance analysis is employed to obtain information about the ionic transport phenomenon in the BST glass–ceramics. The technique of complex impedance allows us to separate the individual contributions of the crystallite and the crystal–glass interface from the total impedance spectroscopy. Using this technique, the ionic transport phenomenon in each component can be understood to explain the blocking effect of the crystal–glass interface in the glass–ceramics.

2. Experimental procedure

The glass–ceramic samples with the composition of aBaO–bSrO–29TiO_2–22SiO_2–12Al_2O_3–2.4BaF_2–$x$$La_2O_3$ (x = 0, 0.5 and 1.0 mol%) were prepared by a melt-annealing technique. The ratio of BaO and SrO was kept 4:1, at the same time, the amount of A-site ions was kept 34.6 mol%, that is, $a + b + 2x$ = 34.6 mol%. The powder containing appropriate amounts of $BaCO_3$, $SrTiO_3$, TiO_2, SiO_2, Al_2O_3, BaF_2 and La_2O_3 (all with purity ≥99%) was ball-milled for 4 h using zirconia balls and ethanol as media, and then dried at 120 °C for 2 h. After drying, the mixture was melted in a platinum crucible at 1550 °C for 3 h. Cylindrical glass ingot was prepared by casting the molten glass into a copper mold with an inner cavity of 30 mm diameter and 20 mm height. Then the casted glass was immediately annealed at 650 °C for 3 h to relieve residual stresses. The as-annealed glass was cut to obtain thin slabs with the thickness of 1 mm. Finally, samples with different La_2O_3 concentrations were heated in air at 700–1000 °C for 2 h to convert the glasses into glass–ceramics. Both sides of the crystallized samples were covered with silver paint and then fired at 550 °C for 30 min in order to ensure good electrical contacts for the impedance measurements.

X-ray diffraction (Model-D8 Advance, Bruker AXS, Karlsruhe, Germany) and field emission scanning electron microscopy (Model Quanta 200 FEG, FEI, Eindhoven, The Netherlands) were used to investigate the phase evolution and microstructure, respectively. Complex impedance spectrum was obtained at an input signal level of 2 V in a wide temperature range of 250–450 °C using a computer-controlled impedance analyzer (HP4194, Hewlett-Packard, CA, USA) in the frequency range of 20 Hz to 1 MHz.

3. Results and discussion

The typical X-ray diffraction (XRD) patterns for the studied glass-ceramic samples with different La_2O_3 concentrations indicate that perovskite (Ba,Sr)TiO_3 is a major crystalline phase and feldspar $BaAl_2Si_2O_8$ is a minor phase in all the glass-ceramic samples, as shown in Fig. 1. As can be seen in Fig. 1, the intensity of XRD peaks of the (Ba,Sr)TiO_3 crystalline phase increases with increasing La_2O_3 concentration. When the La_2O_3 concentration is increased to 1.0 mol%, the intensity of the major diffraction peaks of the (Ba,Sr)TiO_3 crystalline phase significantly increases, which illustrates the trend in the relative content of (Ba,Sr)TiO_3 crystalline phase. And this also shows that La_2O_3 acts as a nucleating agent and promotes the crystallization of the major crystalline phase from the glass matrix. Therefore, in this glass system, phase separation took place when the appropriate concentration of La_2O_3 was added. It is well known that there is a large difference in ionic radius between Ba^{2+} and La^{3+}, being 0.161 and 0.136 nm, respectively. The substitution of La^{3+} for Ba^{2+} ion creates lattice distortion, which could lead to limited solubility of La^{3+} on the A-site for the perovskite (Ba,Sr)TiO_3. This tendency is consistent with the influence of La_2O_3 concentration on the average crystallite size shown in Fig. 2.

SEM investigations have been conducted to ascertain the effect of La_2O_3 concentration on the microstructures of the BST glass–ceramics. The specimens were prepared by polishing and etching with 0.5 wt% HF solution. Fig. 2 shows the microstructures of the BST glass–ceramics with different La_2O_3 concentrations. Addition of small amount of La_2O_3 does not change the microstructural morphology of the BST glass–ceramics. Submicrometer crystallites are uniformly distributed in the glass matrix. On the other hand, an increase of La_2O_3 concentration up to 1.0 mol% leads to an abrupt decrease of the average crystallite size [Fig. 2(c)]. Such behavior could be related to the limited solid solubility of lanthanum in the BST lattice. The addition of 1.0 mol% La_2O_3 may go beyond the solid solubility limit of La_2O_3 in the BST lattice. Thus this will probably result in the segregation at the crystal–glass interface thereby inhibiting a growth of the crystallites and hence leading to the decrease of the average crystallite size.

The impedance analysis combined with the modulus spectroscopy is a powerful technique, which provides important information about the contribution of different electroactive regions such as crystalline phase, crystal–glass interface and glass matrix to the relaxation process. Combined impedance Z'' and modulus M'' plots are particularly useful to understand the heterogeneity of the electrical properties. Fig. 3 shows the variation of both Z'' and M'' with the frequency for the La_2O_3-doped glass-ceramic samples at different measurement temperatures. It can be seen that both Z'' and M'' peaks for all samples appear in the studied frequency and temperature ranges. All peaks shift toward higher frequencies with the increase of measurement temperature. This indicates that high temperatures trigger the relaxation processes for the La_2O_3-doped glass–ceramics. Additionally, it can be shown that the Z'' maximum decreases with the increase of the temperature, while the change

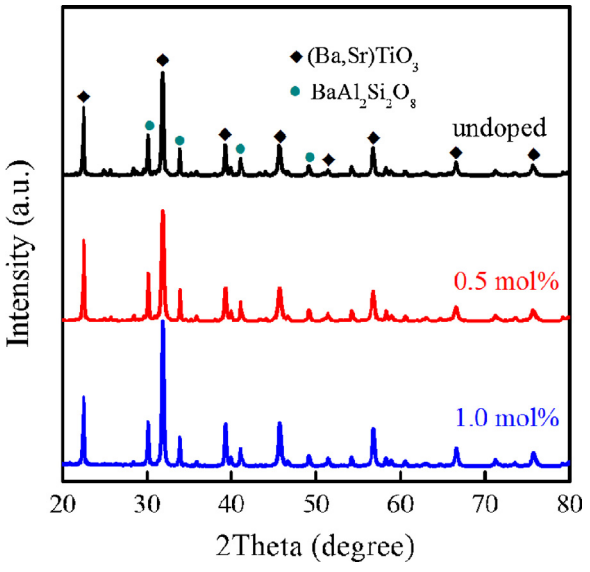

Fig. 1. X-ray diffraction patterns for the BST glass–ceramics with different La_2O_3 concentrations.