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Effects of MnO_2 concentration on dielectric properties of barium strontium titanate glass ceramics

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Abstract

The phase development, microstructural evolution and dielectric properties of manganese-doped barium strontium titanate glass ceramics have been studied. The specimens with (Ba,Sr)TiO_3 (BST) as the major crystalline phase were prepared by bulk crystallization process. The results show that the dielectric constant and the dielectric loss measured at room temperature pass through a maximum with increasing MnO_2 concentration. This MnO_2 concentration dependence of dielectric properties was also investigated by impedance analyses. The evidence of impedance spectroscopy indicates that the activation energy values of grain and grain boundary coincide with the change in dielectric properties.

Keywords: C. Dielectric properties; C. Impedance; D. Glass ceramics; MnO_2

1. Introduction

Ferroelectric glass ceramics, such as barium strontium titanate (BST), have attracted much attention because they have been recognized as the most promising candidates for the application in high energy storage density capacitors [1]. It is generally accepted that the composition and processing of BST glass ceramics must be carefully controlled to provide both homogeneous microstructures and good dielectric properties. So far, much work has been done to study the effect of dopants (such as SrO [2], B_2O_3 [3], BaF_2 [4,5], AlF_3 [6]) on the microstructures and dielectric properties of barium titanate glass ceramics. In spite of extensive studies on manganese doped $BaTiO_3$ or $SrTiO_3$ ceramic systems [7–11], there are few reports that studied the effect of MnO_2 concentration on the dielectric properties of BST glass ceramics. The underlying physical mechanisms involved in the variation of dielectric properties caused by the MnO_2 addition in ferroelectric glass ceramics are not yet fully understood.

Impedance spectroscopy is a powerful tool for the investigation of the electrical properties of electronic ceramics. It has already been used to separate the contribution of each electrical component in ceramics. Typical impedance spectrum for the $BaTiO_3$ ceramics consists of two components: grain bulk and grain boundary. Here, this paper deals with MnO_2 doping behavior of barium strontium titanate glass ceramics, stressing the effect of MnO_2 on dielectric properties in an attempt to explain MnO_2 concentration dependence of dielectric properties by impedance analyses.

2. Experimental procedures

Glass samples used in this study were prepared from well-mixed powders of $BaCO_3$, $SrCO_3$, TiO_2, Al_2O_3, SiO_2, BaF_2, and MnO_2 to achieve the different compositions listed in Table 1. The powders were melted in a platinum crucible at 1550 °C for 2–3 h. The as-quenched glass was annealed at 650 °C for 10 h to remove residual stresses. Finally these samples with different MnO_2 concentrations were heated in air at 1000 °C for 2 h to convert the glasses to glass ceramics. The crystallized samples were painted with silver paste and fired at 550 °C for 30 min to prepare electrodes for dielectric measurements.

X-ray diffraction (Model-D8 Advance, Bruker AXS, Karlsruhe, Germany) and field emission scanning electron microscopy (FESEM, Model Quanta 200 FEG, FEI, Eindhoven, the Netherlands) were used to investigate the phase evolution and microstructures. The measurements of dielectric constant and dielectric loss for glass ceramics were performed

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Table 1
Compositions for barium strontium titanate glass-ceramics with different MnO_2 additions (mol%).

$BaCO_3$	$SrCO_3$	TiO_2	SiO_2	Al_2O_3	BaF_2	MnO_2
25.95	8.65	29.4	22	12	2	–
25.95	8.65	29.3	22	12	2	0.1
25.95	8.65	29.2	22	12	2	0.2
25.95	8.65	29.0	22	12	2	0.4
25.95	8.65	28.9	22	12	2	0.5

using an inductance-capacitance-resistance meter (HP4284). Complex impedance spectra were carried out at an input signal level of 2 V in a wide temperature range of 300–450 °C using a computer-controlled impedance analyzer in the frequency range of 20 Hz to1 MHz.

3. Results and discussion

Fig. 1 shows the phase transformation for BaO–SrO–TiO_2–Al_2O_3–SiO_2–BaF_2 glass ceramic samples with different MnO_2 concentrations heat-treated at 1000 °C for 2 h. These XRD

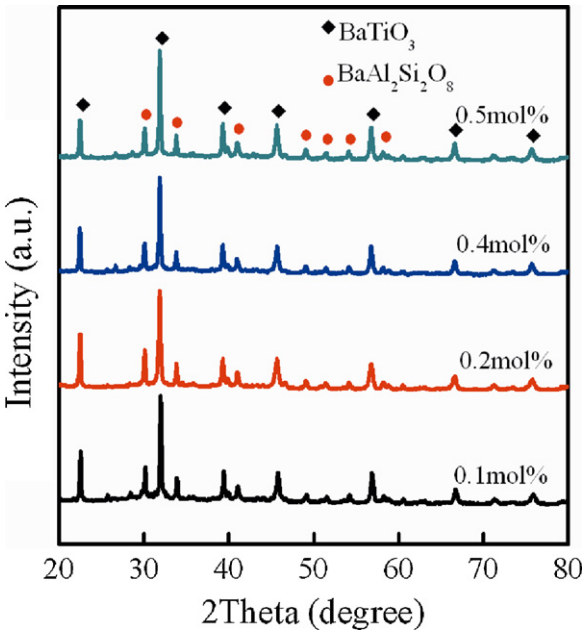

Fig. 1. XRD patterns of BST glass ceramics heat-treated at 1000 °C for 2 h with different MnO_2 concentrations.

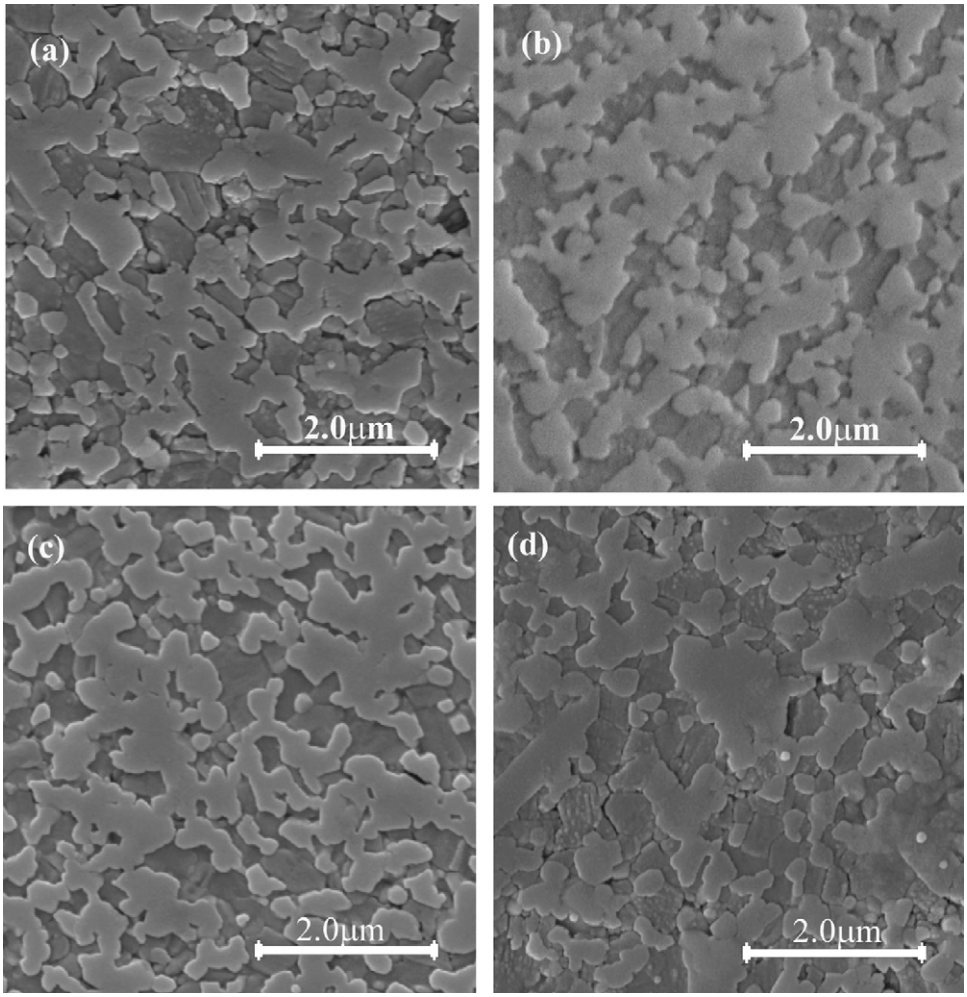

Fig. 2. SEM microstructures of BST glass ceramics heat-treated at 1000 °C for 2 h with different MnO_2 concentrations. (a) 0.1 mol%; (b) 0.2 mol%; (c) 0.4 mol%; (d) 0.5 mol%.

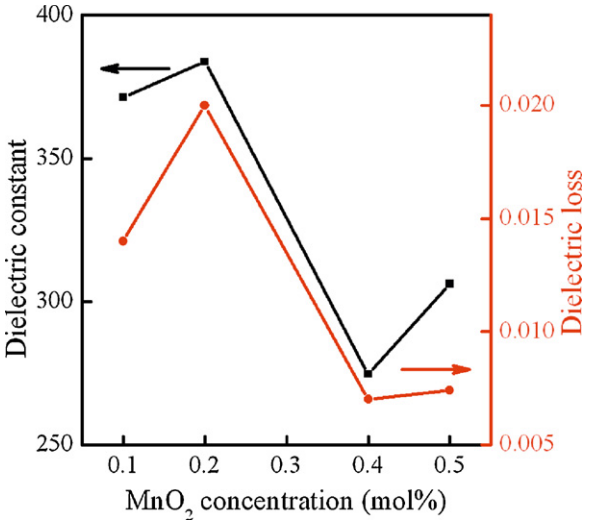

Fig. 3. Dielectric constant and dielectric loss for BST glass ceramics heat-treated at 1000 °C for 2 h as a function of MnO_2 concentrations.

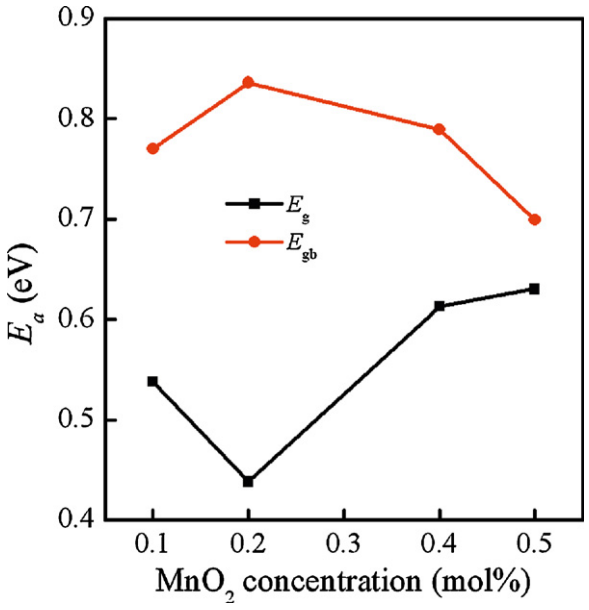

Fig. 4. Activation energy of grain E_g and grain boundary E_{gb} as a function of MnO_2 concentrations.

results indicated there are two phases, the major crystalline phase, (Ba,Sr)TiO_3, and the minor phase, $BaAl_2Si_2O_8$ feldspar in each compositions. Meanwhile, SEM microstructures of BST glass ceramics heat-treated at 1000 °C for 2 h with different MnO_2 concentrations were shown in Fig. 2. As seen from Fig. 2, a typical homogeneous structure was observed and the grains are surrounded by grain boundary (glassy silicate matrix) in all four compositions.

Fig. 3 shows the dielectric constant and the dielectric loss measured at room temperature as a function of MnO_2 concentration for the glass ceramic samples heat-treated at 1000 °C for 2 h. As can be seen, when the amount of MnO_2 is lower than 0.2 mol%, the dielectric constant is slightly increased with increasing MnO_2 concentration. Further addition of MnO_2 above 0.2 mol% leads to a rapid decrease in the dielectric constant. When the amount of MnO_2 is 0.5 mol%, the dielectric constant is slightly increased. According to Fig. 3, the average dielectric loss for MnO_2-doped BST glass-ceramics varies between 0.005 and 0.02. When the amount of MnO_2 is 0.2 mol%, both the dielectric constant and the dielectric loss have the maximum values.

Impedance analysis is performed to study the effect of MnO_2 concentration on the dielectric properties. The samples are tested at different measuring temperatures at every 20 °C interval in order to get series of cole–cole images. For fitting purposes, a constant phase element (Q) may be included in the equivalent circuit consisting of two parallel elements, resistor–capacitor element and resistor–constant phase element. Thus the capacitance value can also be obtained from the following equation [12]

$$C = (R^{1-n}Q)^{1/n} \tag{1}$$

where C is capacitance, R is resistance, Q can be interpreted as a nonideal capacitance. The parameter n is the relaxation distribution parameter. $n = 1$ for a pure capacitor, $n = 0$ for a pure resistor and $n = 0.5$ for a Warburg impedance (pure diffusion).

According to the Arrhenius relationship

$$\tau = \tau_0 \exp\left(-\frac{E_a}{kT}\right) \tag{2}$$

where τ is the relaxation time, τ_0 is the preexponential factor, E_a is the activation energy, k is Boltzmann's constant, and T is the absolute temperature.

According to Eq. (2), the values of E_a for grain and grain boundary can be obtained from the slope of the function between relaxation time and measuring temperature, respectively. Fig. 4 gives the MnO_2 concentration dependence of the activation energy of both grain bulk and grain boundary.

As seen from Fig. 4, the activation energy of grain boundary increases in the MnO_2 concentration range of 0.1–0.2 mol%, and then decreases gradually with the increase of MnO_2 concentration. However, the activation energy of grain bulk changes in the opposite. In the manganese-doped BST, there exist three valence states for the manganese ions, Mn^{2+}, Mn^{3+} and Mn^{4+}, respectively. Electrons may bond to Ti^{4+} and Mn^{3+} in the form:

$$Ti^{4+} + e' \leftrightarrow Ti^{3+} \tag{3}$$

$$Mn^{3+} + Ti^{3+} \rightarrow Mn^{2+} + Ti^{4+} \tag{4}$$

Because electrons trapped by Ti^{4+} are weakly bounded, the hopping motion of the trapped electrons from one Ti site to another is possible. However, when some Ti sites are occupied by Mn ions at the valence 3+ or 4+, the electrons will be trapped on these sites in order to avoid the reduction of Ti^{4+} ions. At the same time, the hopping motion of the trapped electron from one Mn site to another is impossible. For less than 0.2 mol% MnO_2 addition, electron conductivity is predominant. The activation energy of the grain decreases

and dielectric loss increases. At higher MnO_2 concentration, electrons trapped by Mn^{3+} or Mn^{2+} weaken the conductivity of the specimens which was evidenced by the increase of the activation energy for the grain and the decrease of the dielectric loss. On the other hand, the higher E_a values for grain boundary than that for grain bulk indicate that it is more difficult to activate the conducting electrons without any applied field, and hence the carrier-conducting access is blocked by the insulating grain boundary layer. Thus, the opposite charges will accumulate at the two edges of the insulator layer to form many microcapacitors, which result in the high dielectric constant. This factor is believed to contribute to the observed maximum value of dielectric constant at 0.2 mol% MnO_2 addition.

4. Conclusions

The effects of different MnO_2 concentrations on the dielectric properties of BST glass ceramics are examined. The experimental results indicate that the dielectric constant and the dielectric loss measured at room temperature pass through a maximum with increasing MnO_2 concentration. Additionally, different MnO_2 concentration dependences of the activation energy for the grain bulk and the grain boundary have been observed. The dielectric properties are correlated to the variation of activation energy.

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