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Ceramics International 38S (2012) S37–S40

CERAMICS INTERNATIONAL

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Dielectric properties of barium titanate–molybdenum composite

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Abstract

The barium titanate–molybdenum composites were prepared through solid state reaction method in argon atmosphere. The microstructure, resistivity, and dielectric properties of the composites were investigated. XRD results indicated that chemical reactions between barium titanate ($BaTiO_3$:BT) and molybdenum (Mo) have taken place during sintering, resulting in the formation of $BaMoO_4$ (BM) and $BaTi_2O_5$ (BT_2). The resistivity decreased with the increasing amount of Mo in the composites. The composites (when $x = 5$ and 20 wt.%) showed lower dielectric constant than pure $BaTiO_3$, especially, the dielectric constant (when $x = 20$ wt.%) reached a minimum value ($<10^4$), while composites (when $x = 10$ and 15 wt.%) showed rather high dielectric constant at temperatures range from 25 °C to 160 °C. The dielectric constant of the composite gradually decreased with increase in frequency at the room temperature. The dielectric constant of composite (when $x = 5$ wt.%) comes up to 10^4, and the T_c (Curie temperature) of the composite was relatively higher than that of BT (120 °C).

Key words : B. Composites; B. Electron microscopy; C. Dielectric properties; Barium molybdate

1. Introduction

BT is one of the most used ferroelectric ceramic in electronics, especially in the design of electronic devices such as capacitors, dielectrics or electroactive materials [1] due to its high dielectric constant. Because of its extensive use, it has been widely studied and several methods have been proposed to enhance its dielectric constant. Panteny et al. [2] reported an increase in the relative permittivity, conductivity, coercive field and remnant polarization measured for lead zirconate titanate–platinum, BT–Ag, composites. Cho et al. [3] found the $SrTiO_3$–Pt composites exhibited high values of dielectric constant at low frequencies. Many researchers had added other metals such as Ni, Cu [1,4], into BT. These researches indicated that these composites reveal some common and excellent properties such as elevated dielectric constant, enough electrical conductivity, and superior toughness.

In this study, a novel composite was prepared by adding metal molybdenum into BT. The polycrystalline phases and dielectric behavior of barium titanate–molybdenum composites were investigated.

2. Experimental

The BT powder was mixed with Mo powder in a nylon container with ethanol and pestle for 4 h according to the composites of the BT–xMo (when $x = 5$, 10, 15 and 20 wt.%). Mixed powders were compacted by a cold-isostatic pressing (CIP) at 60 MPa for 3 min to fabricate a 13.6 mm diameter and 1.7 mm thick green disk. The disk samples were sintered at 1280, 1290, 1300 and 1310 °C for 2 h in an argon atmosphere with a heating and cooling rates of 5–6 °C/min. Some of them were calcined at 750 °C in air for 2 h again.

The crystalline phases of the sintered samples were characterized by X-ray diffraction (XRD; Cu Kα, 50 kV, 100 mA, Model Rad; Rigaku, Tokyo, Japan). The scan rate (2θ) was 3°/min at a step size of 0.02°, and the scan range was 0–70°. The microstructures of the sintered samples were observed by scanning electron microscopy (SEM; JEOL JSM-T330).

For the electrical and dielectric measurements the sintered samples were plated with In–Ga electrodes. The temperature dependence of permittivity was carried out in the temperature range 25–160 °C by the HP4284A impedance tester. The resistance, frequency dependence of permittivity were measured in frequency range of 20–10^6 Hz using the Agilent E4980A impedance tester.

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doi:10.1016/j.ceramint.2011.04.044

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of BT ceramics with different proportion of Mo addition. Based on XRD analysis, it is found that BT and BM are presented as the major phases in association with BT_2 and $BaTi_4O_9$ (BT_4) as minor phases in the composites. The intensity of BM increases with increasing amount of Mo, meanwhile the intensity of BT decreases gradually. In addition, the intensity of BT_4 increases with the decrease of the intensity of BT_2 ($x \geq 10$ wt.%).

It is indicated that a chemical reaction have occurred between BT and Mo during sintering, so BM and BT_2 as the products of the chemical reaction generate in these composites. BT_4 can be observed in the X-ray diffraction pattern of pure BT too, so it may be resulted from the decomposition of BT which was sintered in argon atmosphere.

Fig. 2 shows SEM images of the morphologies and grains of BT ceramics with different addition content of Mo. Pure microcrystalline BM have rhombic shape and expose mostly (1 1 1) crystallographic planes [5], the abundant amount of rhombic shape grains can be observed in the micrographs. The grain size of BM is in range of 2–7 μm, and the grain size of BT is about 10 μm. With increasing amount of Mo, the smaller grains (BM) appear issued from the larger grains (BT). An increasing number of rod-like BT_2 [6] grains appear in these composites with increasing amount of Mo. It is suggested that the chemical reaction between BT and Mo had occurred during sintering indeed.

In order to deepen the understanding of the origin of the dielectric response in the composites, the composites which were sintered in argon gas were calcined at 750 °C again. Fig. 3 shows that the resistivity of the composite decreases with the increasing amount of Mo and the values of resistivity increase after the composites were calcined at 750 °C. In argon atmosphere BT was reduced, forming doubly ionized oxygen vacancies and free electrons in BT according to Eq. (1):

$$O \rightarrow V_O^{\bullet\bullet} + 2e + \frac{1}{2}O_2 \uparrow \quad (1)$$

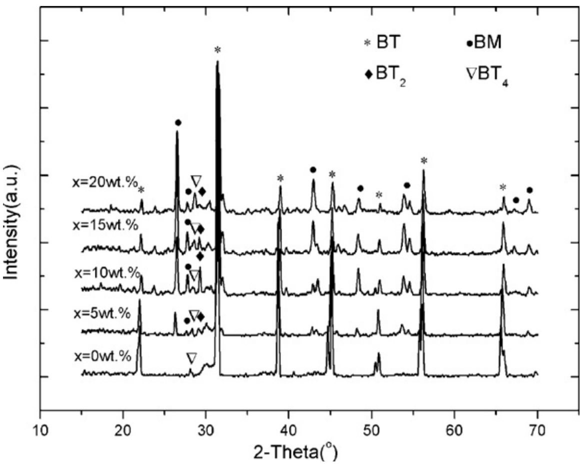

Fig. 1. X-ray diffraction patterns of the barium titanate–molybdenum composites sintered in argon atmosphere at 1300 °C for 2 h.

The electrons make the reduced perovskite material highly semiconducting. So after sintering normal BT based dielectrics in reducing atmospheres the insulation resistance (IR) decreases by 10–12 orders of magnitude [7,8]. Combining with the analysis of the XRD patterns (Fig. 1), we can deduce that a chemical reaction have occurred among BT, Mo and O_2 during sintering (low oxygen partial pressure), the O_2 may result from the decomposition of BT, so these chemical reactions promoted the formation of oxygen vacancies and free electrons during sintering. With increasing amount of Mo, more O_2 which results from the decomposition of BT is needed to finish these chemical reactions, so the increasing amount of oxygen vacancies and free electrons form in the composites and the resistivity of the composite decreases with increasing amount of Mo. Oxygen vacancies can be eliminated from dielectric materials by the way of re-oxidation [9]. The values of resistivity increase after the composites calcining at 750 °C, it is indicated that the oxygen atoms backfill to the perovskite lattice of BT, and the quantity of free electrons are trapped by oxygen vacancies.

Analysing the dielectric constant of the composites which were sintered in argon atmosphere for the temperatures range from 25 °C to 160 °C in Fig. 4, we observe that the composites (when $x = 5$ and 20 wt.%) have, lower dielectric constant than pure BT samples, especially, the dielectric constant (when $x = 20$ wt.%) reaches a minimum value ($<10^4$ at the whole temperature range). The composites (when $x = 10$ and 15 wt.%) still show rather high dielectric constant in the temperatures range from 25 °C to 160 °C. According to the present studies, Choi et al. reported that the dielectric constants of BM sintered at 800 °C were 7–11 [10], and Kumar et al. [11] had found that the dielectric constants of specimens prepared using Ba:Ti in 1:4 molar ratio were in the range of 22–37 over the temperature range of 30–100 °C, and the dielectric constants of BT_2 presented low value (230–641) [6,12], it can be deduced that the decreasing of dielectric constant is caused by the low values of dielectric constant of BM, BT_4 and BT_2, it may play a leading role of the relatively lower values of dielectric constant (when $x = 5$ and 20 wt.%). As shown in Fig. 3, doubly ionized oxygen vacancies and free electrons form in the BT, so the space charge distributions across interfaces generate in the composites [13]. The sharp rise in dielectric constant with temperature particularly in the low frequency range, is attributed to a major contribution from the space charge polarization with temperature [14], and space charge polarization has a greater effect than the low values of dielectric constant of BM, BT_4 and BT_2 on the dielectric response in the composite, so the composites (when $x = 10$ and 15 wt.%) still show rather high dielectric constant at the temperatures range from 25 °C to 160 °C with a 1 kHz/1 V signal.

The composite (when $x = 5$ wt.%) shows superior dielectric properties. Thus, despite that addition of Mo has the effect of reducing dielectric constant, the composite (when $x = 5$ wt.%) still show rather high dielectric constant (the dielectric constant $>10^4$ at the whole temperature range), and the T_c of the composite is relatively higher than that (120 °C) of BT. The T_c of the composite (when $x = 5$ wt.%) is relatively higher than

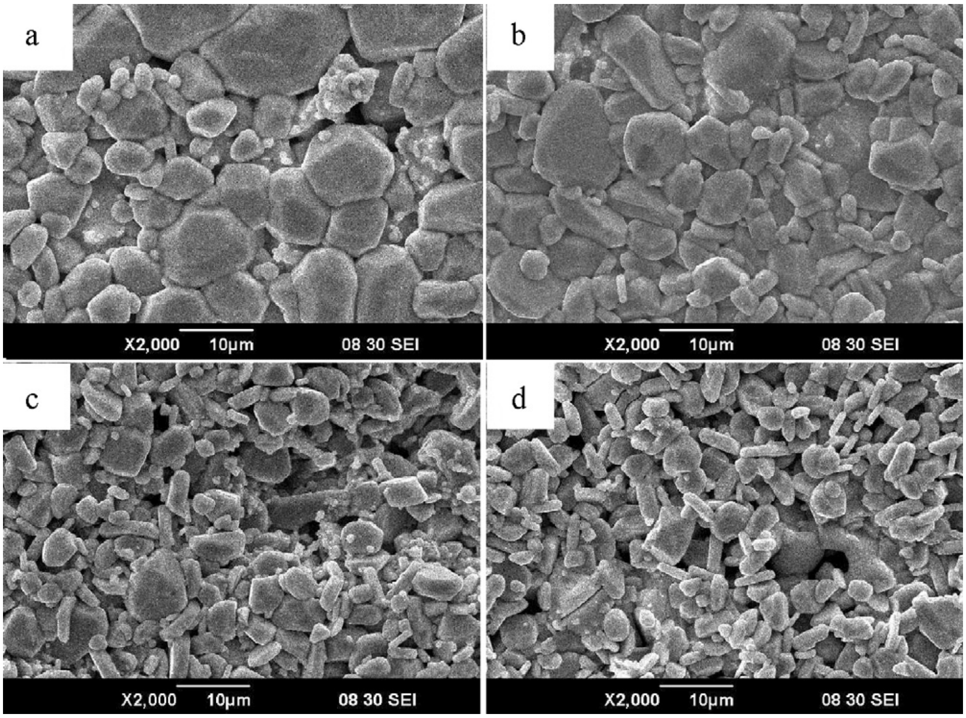

Fig. 2. SEM images of barium titanate–molybdenum composites: (a) $x = 5$ wt.%; (b) $x = 10$ wt.%; (c) $x = 15$ wt.%; (d) $x = 20$ wt.%.

that (120 °C) of BT, it may due to the higher T_c (461 °C) of BT_2 [12].

Fig. 5 shows the frequency dependence of dielectric constant of the composites which were sintered in argon atmosphere at 1300 °C. The dielectric constant gradually decreases with increase in frequency at the room temperature. First the dielectric constant increases with increasing amount of Mo (when $x = 5–15$ wt.%), then decreases (when $x = 15–20$ wt.%), when x is 20 wt.%, the dielectric constant reduces to the minimum, it is very similar to the variations of temperature dependence of dielectric constant. It is obvious that both the space charge polarization and the low values of dielectric constant of BM, BT_4 and BT_2 have effect on frequency dependence of dielectric constant of the composites. Because of the maximum chemical composition of BM, BT_4 and BT_2 in the composite (when $x = 20$ wt.%), the low values of dielectric constant of BM, BT_4 and BT_2 play a leading role of the dielectric response in the composite (when $x = 20$ wt.%), so the dielectric constant decreases with increasing amount of Mo (when $x = 15–20$ wt.%). It is found that the dielectric constant was influenced not only by grain size but also by pore morphology [15], a large proportion of pores appearing resulted in low dielectric constant for the materials [16], we can observe that the largest proportion of pores appear in the composite (when $x = 20$ wt.%) in Fig. 2, it may be another reason of the dielectric constant decreasing at $x = 20$ wt.%.

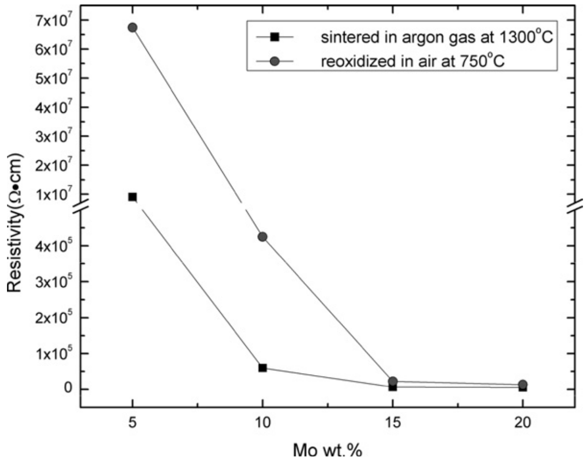

Fig. 3. Resistivity of barium the sintered titanate–molybdenum composites sintered in argon atmosphere at 1300 °C for 2 h and resistivity of the composites reoxidized in air at 750 °C for 2 h.

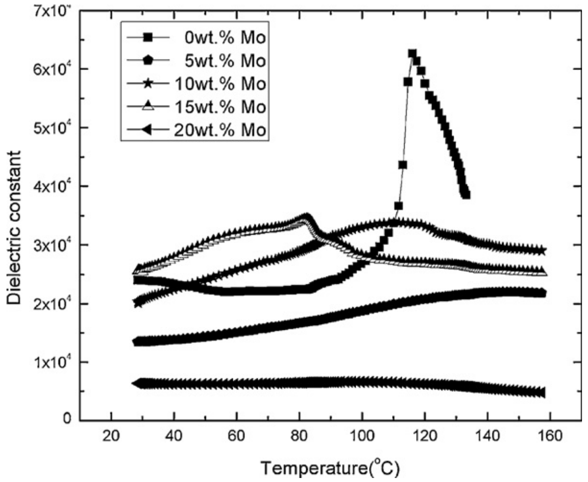

Fig. 4. Temperature dependence of dielectric constant of the barium titanate–molybdenum composites sintered in argon atmosphere at 1300 °C for 2 h.

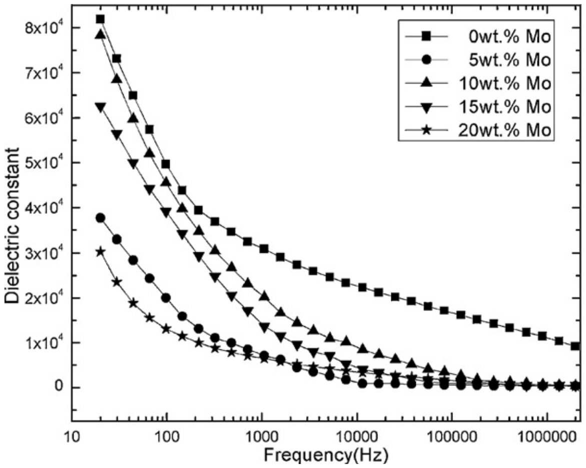

Fig. 5. Frequency dependence of dielectric constant of the barium titanate–molybdenum composites sintered in argon atmosphere at 1300 °C for 2 h.

4. Conclusions

A novel composite of barium titanate–molybdenum were sintered in argon atmosphere by solid state reaction method. XRD and SEM results support the idea that a chemical reaction has occurred between BT and Mo during sintering, BM and BT_2 as the products of the chemical reaction generate in these composites, and the composites (when $x = 5$ and 10 wt.%) have the more dense microstructures in these composites. The resistivity of the composites decreases with increasing amount of Mo, it results from the increase of amount of oxygen vacancies and free electrons. The composite (when $x = 5$ wt.%) shows superior dielectric properties and the dielectric constant reaches to 10^4, and the T_c value of the composites is relatively higher than that (120 °C) of BT.

Acknowledgements

This research has been supported by the Key Project of Chinese Ministry of Education (209126), Research projects of Science and Technology Division, Shaanxi (2010K10–14), Foundation of Shaanxi Educational Committee (112H011). This project was supported by the Graduate Innovation Fund of Shaanxi University of Science and Technology.

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