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The effect of bimodal model on the ultra-broad temperature stable $BaTiO_3$–$Na_{0.5}Bi_{0.5}TiO_3$–Nb_2O_5 system

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ABSTRACT

A new lead-free, high dielectric constant, wide temperature stable dielectric ceramics was prepared by traditional solid-state method. The phase contribution, electric and dielectric properties of the $BaTiO_3$–$Na_{0.5}Bi_{0.5}TiO_3$–Nb_2O_5 ceramics were investigated. The bimodal model was proposed to explain the phenomenon of ultra-broad temperature stable. The doping of CoO played a decisive role in the realization of a wide temperature range of −50–350 °C stability. In addition, a relative higher dielectric constant and lower dielectric loss ($\varepsilon_r = 1365 \pm 15\%$, $\tan\delta = 1.513\%$) were obtained. These features suggest that the ceramics system can be considered as a promising candidate material for the next generation of MLCC.

1. Introduction

The rapid development of the electronics industry puts forward higher requirements for the next generation of dielectric ceramic materials. With the increasing integration of components, more circuits and devices are integrated in a limited space. A high dielectric constant is required for the capacitor, so that it can meet the requirements of miniaturization. What's more, the needs for short circuit length force us to make the circuit module near or directly in the work environment. Harsh working conditions, such as automobile engines, rocket, as well as outer space, require that the components should be stable in the ultra-broad temperature scope [1–4]. It is not enough for the device to be stable only in high temperature (HTCC) or low temperature (EIA X7R, X8R) respectively. A wide temperature range from a low (−55 °C) to a higher temperature (~300 °C) is needed [5–9].

Generally, there are two ideas for preparing wide temperature, that is the single dielectric peak such as relaxation ferroelectric dielectric [10,11], and double dielectric peaks such as core–shell structure in the X7R and X8R ceramics [12]. There is only one dielectric peak in the relaxation ferroelectric dielectric. The height and position of the dielectric peak need to be adjusted, so that the dielectric material can be kept stable in a wide temperature range. In this process, some of the modified materials are added to form a solid solution, which is bound to make the dielectric constant deteriorate. Thus, using a single dielectric peak method, the obtained dielectric material is either high temperature stable only, or wide-temperature stable but small dielectric constant [13]. In contrast, bimodal method works by interference of the double dielectric peaks. It can be wide temperature stable and a higher dielectric constant at the same time, which is very significant for the next generation of MLCC.

Double dielectric peaks had been discovered in many ceramics [14–18]. However, double dielectric peaks have not yet attracted much attention in the ultra-temperature stable ceramic. In this paper, the $BaTiO_3$–$Na_{0.5}Bi_{0.5}TiO_3$–Nb_2O_5 (referred to as BNN) system doped with CoO was investigated. Moreover, the bimodal model is proposed and the microscopic mechanism of the model is analyzed.

2. Experimental procedure

Reagent-grade $BaTiO_3$, Na_2CO_3, Bi_2O_3, TiO_2, CoO and CeO_2 were used as raw materials. Firstly, reagent-grade oxides and carbonate of Na_2CO_3, Bi_2O_3, and TiO_2 were weighed with a mole ratio of 1:1:4 and mixed using ball-milling in deionized water for 4 h. Then the mixture was calcined in air at 800 °C to synthesize $Na_{0.5}Bi_{0.5}TiO_3$(NBT) phase. Secondly, $BaTiO_3$(BT), NBT and Nb_2O_5 were weigh according to the mole ratio of BT:NBT:Nb_2O_5 = 85:15:2 and mixed by ball milling in deionized water for 4 h. The mixture was dried and calcined at 1000 °C in covered alumina crucible for 2 h. Then various amounts of CoO, 5 wt.% glass flux (synthesized by Bi_2O_3, TiO_2, ZnO, H_3BO_3), and 0.4 mol% CeO_2 were added and mixed by ball milling in deionized water for 2 h. The final powders were pressed into pellets with 15 mm in diameter and 1 mm in thickness with 7 wt.% wax as a binder. Then, the pellets were sintered at 1130 °C–1145 °C for 1 h in air. The samples with 3.5 wt.%, 4.25 wt.%, 5 wt.% and 5.75 wt.% were named C1, C2, C3 and C4 respectively.

Crystal structure of the samples was indentified at room temperature using an X-ray diffractometer (D8-Focus; Bruker AXS GmbH, Karlsruhe, Germany). Microstructure of the ceramic samples was

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observed by field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Ltd. Japan). Both sides of the samples were coated with silver paste and sintered at 800 °C. Dielectric constant was measured by the use of capacitance meter (HP4278A) at 1KHz–1 MHz. Insulation resistance was measured by using a high resistance meter (Agilent 4339B) at room temperature.

3. Results and discussion

3.1. Discussion of dielectric properties

3.1.1. The bimodal model

Two dielectric permittivity anomalies were observed in all of the samples in Fig. 1(a). One is in the high temperature zone, the other is in the low temperature region. The presence of double dielectric peaks makes the dielectric ceramics stable in the wide temperature zone.

3.1.2. Analysis of the dielectric peak in the high temperature

The dielectric peak in the high temperature was caused by defects ($Co''_{Ti}-V_o^{\cdot\cdot}$, $Bi^{\cdot}_{Ba}-V''_{Ba}$, $Nb^{\cdot}_{Ti}-e$, mainly it is the $Co''_{Ti}-V_o^{\cdot}$ in this paper) [19,20]. Defect equations are as follows:

$$CoO \rightarrow Co''_{Ti} + O_o + V_o^{\cdot\cdot}$$
$$Bi_2O_3 \rightarrow Bi^{\cdot}_{Ba} + O_o + \frac{1}{2}V''''_{Ti}$$
$$Nb_2O_5 \rightarrow Nb^{\cdot}_{Ti} + O_o + e.$$

In this paper, only the content of CoO was changed. According to the defect equations, the variation of the dielectric properties in the high-temperature region is mainly related with the defects $CoTi'' - Vö$.

With the amount of CoO increasing, $CoTi'' - Vö$ increased. At low temperature, *Vö* is bound by a weak barrier. Just as Fig. 2(a) shows it. The thermal vibration energy of *Vö* increased along with the increasing temperature. When the energy of the thermal vibrations is higher than the barrier, the transition occurs. When no external electric field existed, the probability of transition is equal in all directions.

$$\omega 0 = \frac{\upsilon}{6}\exp\left(-\frac{U}{kT}\right) \quad (1)$$

υ: Thermal vibration frequency, 6: six vibration directions in three-dimensional space, U: the barrier and k: Boltzmann constant.

When there was an external electric field, the on of the barrier changed. Transitions along the electric field direction become relative easily. The details were as follows.

When an external electric field existed, the probability of *Vö* staying in position 2 increased. While, the chance of *Vö* staying in the equilibrium position 1 decreased.

$$\frac{dn1}{dt} = -n1\omega 12 + n2\omega 21 \quad (2)$$

$$\frac{dn2}{dt} = n1\omega 12 - n2\omega 21 \quad (3)$$

When there is a presence of an external electric field, the state of the uniform distribution of the charge was destroyed. Dipole formed and

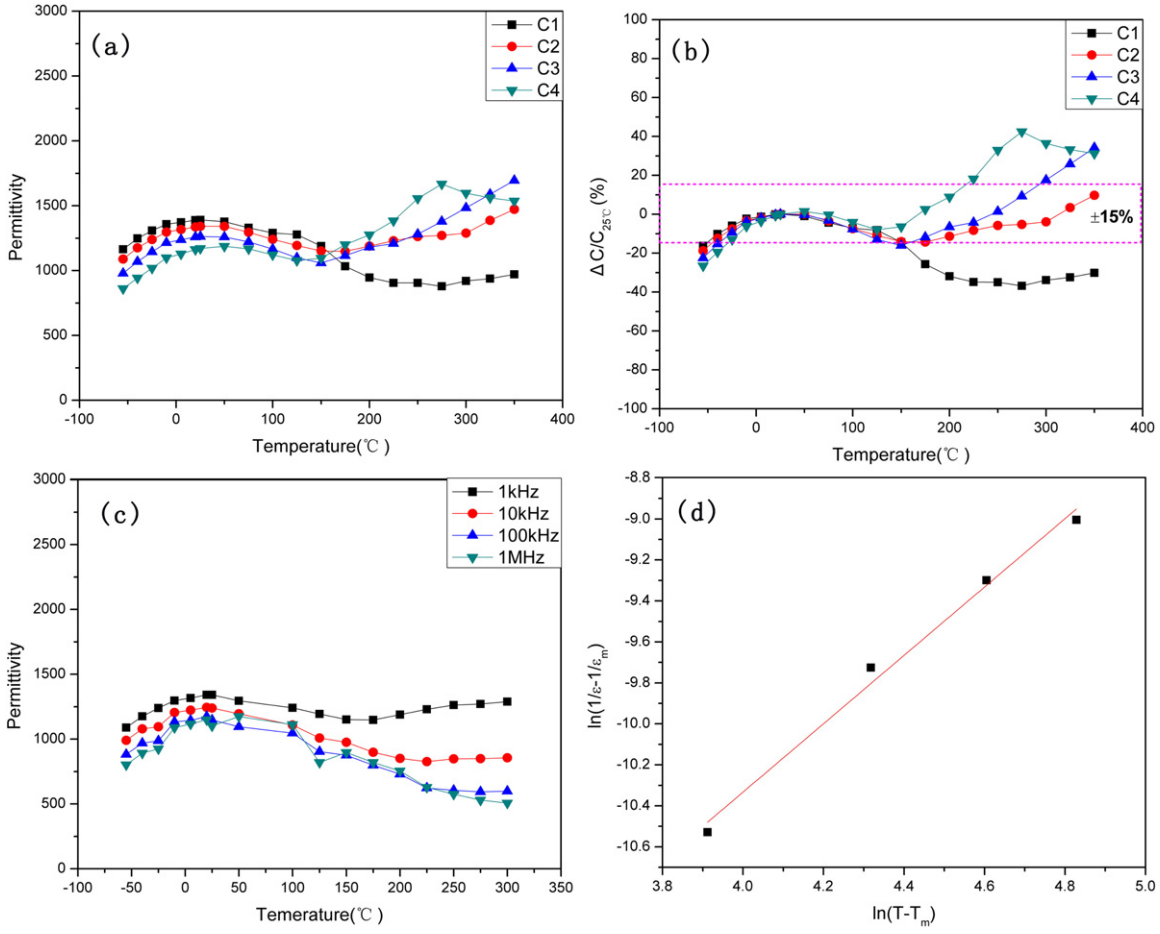

Fig. 1. (a)–(b) Temperature dependence of dielectric constant and capacitance variation rate based on $C_{25\,°C}$ for samples with various amounts of CoO, sintered at 1140 °C; (c) The sample doped with 4.25% CoO, sintered at 1140 °C, measured at 1 kHz–1 MHz (d) Plot of $\ln(1/\varepsilon - 1/\varepsilon_m)$ as a function of $\ln(T - Tm)$ for BNN-xCoO (x = 4.25%, sintered at 1140 °C) at 1 kHz.