



# Phase transitions in the $(\text{BaTiO}_3)_x/(\text{BiFeO}_3)_{1-x}$ composite ceramics: Dielectric studies



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## ABSTRACT

Dielectric studies were carried out for composite ceramics  $(\text{BaTiO}_3)_x/(\text{BiFeO}_3)_{1-x}$  ( $0 < x < 1$ ) within a temperature range 23–450 °C. Linear permittivity studies at various frequencies showed the emergence of peaks near the temperatures of the ferroelectric phase transition in the  $\text{BaTiO}_3$  grains and of the antiferromagnetic phase transition in the  $\text{BiFeO}_3$  grains. The positions of the peaks did not depend visibly on frequency. The permittivity peaks near the antiferromagnetic phase transition shifted to low temperature with increasing the barium titanate fraction which suggests the reduction of the Neel temperature. The decrease in the Neel temperature in the composite ceramics was confirmed by measurements of the temperature dependence of the third harmonic generation.

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## 1. Introduction

Multiferroics combine two or more ferroic orderings (ferroelectricity, ferromagnetism, and ferroelasticity) within some temperature ranges [1] which make them promising functional materials for various applications. The greatest attention is focused on multiferroics–magnetolectrics as they can be used to switch the magnetic state by electric field and vice versa [2–6]. In a broader sense, the multiferroics–magnetolectrics comprise materials with the ferroelectric and ferro- or antiferromagnetic properties. A review of crystalline substances which show multiferroicity and magnetolectricity can be found, for instance, in Ref. [2]. The only “intrinsic” room-temperature multiferroic found till recently is  $\text{BiFeO}_3$  while the magnetolectric coupling in it is not strong. To find magnetolectrics with more appropriate parameters, many efforts were made to design various new multiferroics including ceramic materials, in particular, on the basis of  $\text{BiFeO}_3$  (see, for instance, Refs. [7–15]). Spontaneous polarization and other properties were found to be changed remarkably in many such ceramic samples: substituted ceramics which composition can be written as  $\text{Bi}_{1-x}\text{A}_x\text{Fe}_{1-y}\text{B}_y\text{O}_3$  [7,9–13] and composite ceramics with

composition  $x\text{P}/(1-x)\text{BiFeO}_3$  [8,14,15]. A characteristic which influences strongly the magnetolectric coupling in ceramics is the temperature of the antiferromagnetic phase transition. For substituted  $\text{BiFeO}_3$  ceramics the pronounced decrease of the Neel temperature from the value 370 °C for pure  $\text{BiFeO}_3$  was observed [16–19]. For composite ceramics the problem of the Neel temperature shift was not discussed and it was assumed a priori that this temperature remains equal to the bulk value for big enough grains. Here we present results of dielectric studies of composite ceramics  $(\text{BaTiO}_3)_x/(\text{BiFeO}_3)_{1-x}$  for  $x = 0, 0.25, 0.5, 0.75$ , and 1. Temperature dependences of the dielectric permittivity and coefficient of third harmonic generation were obtained in a range of 23–450 °C. The results give unambiguous evidence of the regular decrease in the Neel temperature with increasing  $x$  from 0 to 0.75.

## 2. Samples and experiment

$\text{BiFeO}_3$  was prepared by the solid state reaction of the  $\text{Bi}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  precursors at 860 °C during 3 h. The mixture of oxides was taken in a non-stoichiometric ratio (with excess of  $\text{Bi}_2\text{O}_3$ ) to minimize the emergence of the impurity phase  $\text{Bi}_2\text{Fe}_4\text{O}_9$ . The X-ray diffraction of the as prepared powder showed only the pattern for  $\text{BiFeO}_3$ . To get the pure  $\text{BiFeO}_3$  ceramic the powder was pressed into about 12 mm diameter pellets with the polyvinyl alcohol

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binder and sintered at 960 °C for 3 h. The thickness of the pellets was 2–3 mm. BaTiO<sub>3</sub> was obtained by calcination of the TiO<sub>2</sub> and BaO oxides at 1250 °C for 3 h. The prepared powder was pressed with the polyvinyl alcohol into pellets and sintered at 1250 °C for 3 h to get the BaTiO<sub>3</sub> ceramic samples. To get the composite (BaTiO<sub>3</sub>)<sub>x</sub>/(BiFeO<sub>3</sub>)<sub>1-x</sub> ( $x = 0.25, 0.5, \text{ and } 0.75$ ) ceramics the prepared BaTiO<sub>3</sub> and BiFeO<sub>3</sub> powders were mixed in appropriate ratios with the polyvinyl alcohol, pressed into pellets, and sintered at 1100 °C for 3 h.

The electron images of the ceramic samples are shown in Fig. 1. The ceramic grains in BiFeO<sub>3</sub> have rather regular shape. The composite ceramics are denser with irregular shape of grains. The grain size increased for  $x = 0.25$  compared to the pure bismuth ferrite ceramic and then decreased for higher  $x$ . Similar influence of mixing was reported earlier [20,21].

The room temperature X-ray diffraction patterns of the composite ceramics displayed the superposition of peaks for BaTiO<sub>3</sub> and BiFeO<sub>3</sub>. Fig. 2 shows the X-ray pattern for  $x = 0.5$ . As it was obtained recently [22–24], BaTiO<sub>3</sub> and BiFeO<sub>3</sub> can form solid solutions as a result of the solid-state reaction under special conditions. The crystalline symmetry of such solid solutions varies with  $x$ . The cubic structure dominates for solid solutions with  $0.3 < x < 0.9$ , while the composite ceramics keep the structures of pure BaTiO<sub>3</sub> and BiFeO<sub>3</sub>. Fig. 2 confirms that the symmetry of the ceramic samples under study is not cubic. In contrast, the X-ray pattern of the composites preserves features of the BaTiO<sub>3</sub> and BiFeO<sub>3</sub> patterns in agreement with the sample preparation procedure. For comparison, the X-ray pattern of the Ba<sub>1/2</sub>Bi<sub>1/2</sub>Fe<sub>1/2</sub>Ti<sub>1/2</sub>O<sub>3</sub> solid solution obtained by solid state reaction of appropriate monoxides is also shown in Fig. 2. To make the comparison clearer (as the X-ray patterns of composite ceramics and solid solutions are rather similar) the extended patterns near 32° are shown in the inset to Fig. 2.

The bismuth ferrite, BiFeO<sub>3</sub>, is the most known single-phase crystalline material which has multiferroic properties at room temperature. It has a ferroelectric Curie temperature of 830 °C and an antiferromagnetic Néel temperature of about 370 °C. At room temperature it exhibits a rhombohedral structure with space group *R3c* and canted *G*-type antiferromagnetic order.

The barium titanate, BaTiO<sub>3</sub>, is one of the most known ferroelectric crystals. It has a perovskite structure with the ferroelectric phase transition at 120 °C.

The linear complex permittivity of the (BaTiO<sub>3</sub>)<sub>x</sub>/(BiFeO<sub>3</sub>)<sub>1-x</sub> ceramics was measured with a E7-25 impedance meter at several frequencies in the range from 25 Hz to 1 MHz using silver electrodes. The measurements were carried out upon continuous warming in the range from room temperature to 450 °C with a rate of 1°/min. The applied ac voltage was 0.7 V. Temperature was monitored with accuracy of about 0.2 °C.

A setup to study the nonlinear dielectric properties of the ceramics comprised a sinusoidal generator operated at a frequency of 2 kHz. The voltage amplitude was 30 V. The signals at the fundamental and triple frequencies were picked up from a resistor connected in series with a sample under study. The experimental setup is described in more detail in Ref. [25]. From measurements the coefficient  $\gamma_3$  of the third harmonic generation at different temperatures was calculated as the ratio of the intensities of signals at the triple and fundamental frequencies.

### 3. Results and discussion

The variations with temperature of the real part of the dielectric permittivity at a frequency of 1 kHz for all samples under study are shown in Fig. 3 for a temperature range 80–240 °C which covers the ferroelectric phase transition in the BaTiO<sub>3</sub> crystals. One can see

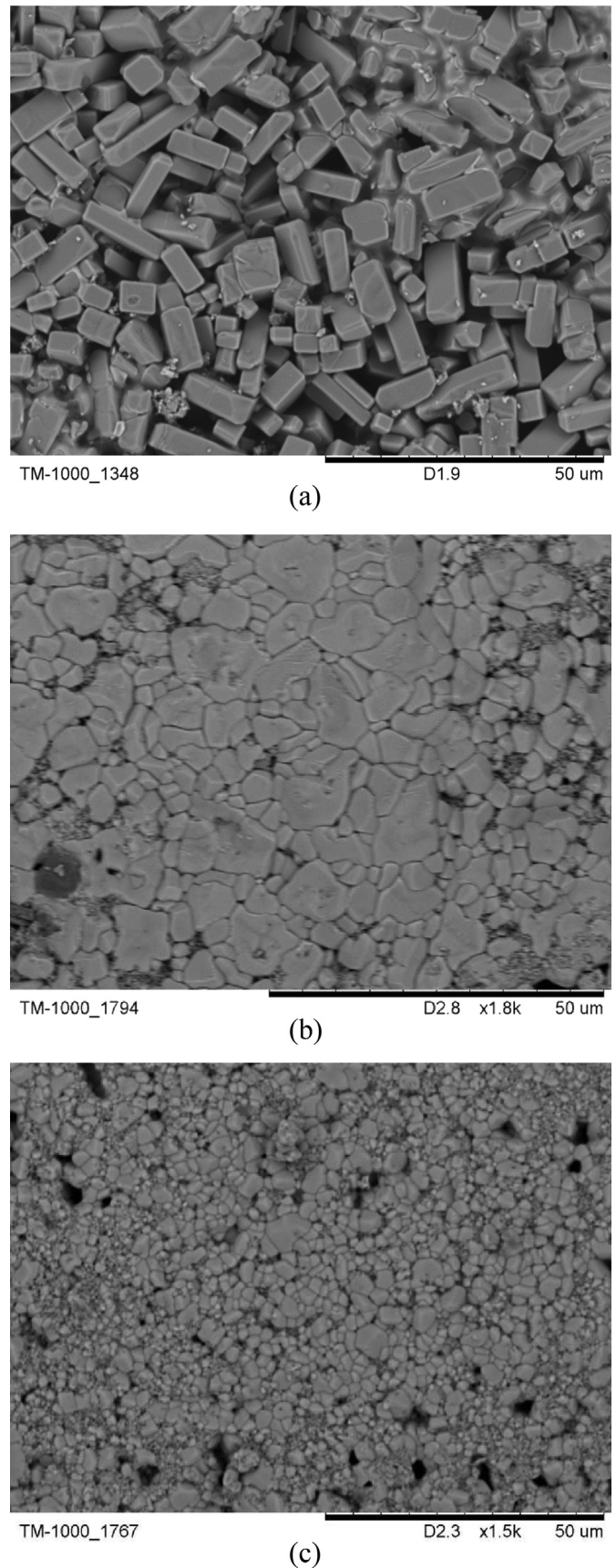


Fig. 1. Electron images of the pure BiFeO<sub>3</sub> ceramic (a) and composite ceramics with  $x = 0.25$  (b) and  $x = 0.5$  (c).

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