Evolution of Phase Transitions in SrTiO₃—BiFeO₃ Solid Solutions

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1. INTRODUCTION

Phase transitions in multiferroics (which undergo at least two of the possible transitions, namely, (anti)ferrodistortive and (anti)ferroelectric or (anti)ferromagnetic) [1], have been attracting considerable interest during the recent several decades. The family of perovskites with the general formula ABO₃ was found to include multiferroics with both ferroelectric and antiferrodistortive (AFD) ordering and with ferroelectric and (anti)ferromagnetic (ferroelectric magnets) ordering [2–4]. The ferroelectric instability observed in perovskites is driven by polar displacement in B–O bonds, while the antiferrodistortive instability originates from rotation of the BO₆ octahedra. As a rule, these instabilities compete [5]. SrTiO₃ (STO) is an incipient ferroelectric whose dielectric permittivity grows to a fairly high level with decreasing temperature and reaches saturation at cryogenic temperatures. It is commonly supposed that quantum fluctuations (zero-point motion) play a significant part in suppression of the ferroelectric state at a temperature approaching 0 K [6–9]. It is assumed that, in addition to quantum fluctuations, tetragonal distortions of the lattice driven by the AFD transition from the cubic Pm3m phase into the nonpolar tetragonal I4/mcm phase also contribute to suppression of the ferroelectric transition [10]. Because the energies of the paraelectric phase and incipient ferroelectric phase are close in magnitude, small perturbations, such as relatively weak electric field and pressure, are capable of inducing a ferroelectric transition. Isovalent impurities present in low concentrations can likewise induce a low-temperature ferroelectric transition or transition to a glassy polar state. It is assumed that any perturbations, including impurities which stabilize the STO cubic structure and prevent rotation of TiO₆ octahedra, can favor formation of just the ferroelectric state in its competition with antiferrodistortive instability. The substitution of Sr in the STO lattice with Ba [11–13], Pb [14], Ca [15–18], Cd [19], and Bi [20] leads to the conventional ferroelectric transition or to the formation of a relaxor ferroelectric state. The critical impurity concentration x_r, at which the ferroelectric phase emerges, is practically the same for all the impurities, except for Ba [11, 13], and is about 0.002. Substitution of Sr with Ba and Pb ions was shown to decrease the temperature of the AFD transition, and at impurity concentrations above 0.03 the ferroelectric instability suppresses completely the antiferrodistortive factor [21]. The decrease of the temperature of the AFD transition in strontium titanate with Ba and Pb ions lends support to the hypothesis of the role of the antiferrodistortive instability in suppression of the ferroelectric transition in the incipient ferroelectric STO [10], the fact that this temperature remains unchanged in substitution of the 18O isotope by the 16O isotope and the observed increase of the temperature of the AFD transition in STO:Ca are in conflict with such assumption [22]. Suppression of the AFD transition observed to occur when its temperature approaches that of formation of polar regions in the paraelectric matrix (the Burns temperature) was demonstrated for the SrTiO₃–PbZrO₃ solid solutions in which the relaxor state sets in already at low PbZrO₃ concentrations [23]. As follows from published data, the understanding of the processes involved in coexistence and mutual influence of the antiferrodistortive transition and induced polar states requires further experimental studies.

BiFeO₃ (BFO) stands out in the family of ferroelectric magnets with high Curie (T_C ≈ 1093 K) and Néel (T_N ≈ 637 K) temperatures [24–26]. At room temperature, single crystals of this compound demonstrated
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extremely high values of spontaneous polarization about 60–100 μC cm\(^{-2}\), for a low coercive field of 12 kV/cm [27, 28]. High values of spontaneous polarization of the ceramics (40 μC cm\(^{-2}\)) [29] and films of bismuth ferrite (up to 158 μC cm\(^{-2}\)) [30, 31] were reported. The magnetic subsystem of BFO has a \(G\)-type structure, which is a spatially modulated spin cycloid with a period of 62 nm [25, 32]. Spin modulation brings about absence of the linear magnetoelectric effect. Synthesis of BiFeO\(_3\)-based ceramic solid solutions, in particular, incorporation of rare-earth magnetically active ions in Bi position, initiates a weak ferromagnetism accompanied by the linear magnetoelectric effect [33–35]. It was reported also that substitution of Fe with ions of transition metals in polycrystalline films of bismuth ferrite results in an increase of polarization and magnetization [36]. The results presented here suggest promising potential applications of BFO as a basic component of solid solutions employed in development of new materials with attractive properties for the field of applications.

In view of the unique characteristics of the starting components, one might suggest that STO–BFO solid solutions should reveal an interesting evolution involving coexistence and interaction of the antiferromagnetic transition and an STO-induced polar state, as well as of the BFO-supported antiferromagnetic and ferroelectric transitions. This suggests that this system may serve as a model object for the relevant studies. Apart from this, investigation of this system may be considered as the next step in development of bismuth ferrite-based materials.

Acoustic studies combined with dielectric measurements offer a possibility of classifying the various phase transitions and follow their evolution and, as an important aspect for the field of applications, determine the elastic constants of the material.

2. EXPERIMENT

Ceramic samples of the \((1 – x)\)STO–xBFO \((0 \leq x \leq 1)\) solid solutions were prepared by conventional technique. The starting reagents were the oxides TiO\(_2\), Fe\(_2\)O\(_3\), Bi\(_2\)O\(_3\), and strontium carbonate SrCO\(_3\). One mostly used high-purity reagents (HPR). Preliminary annealing of the samples was performed in platinum crucibles at a temperature from 1155 to 780°C for 21–4 h, with the temperature and annealing time reduced with increasing bismuth ferrite concentration. The batch thus prepared was pressed in pellets 8 mm in diameter and 1.5–2 mm thick and bars 8 × 5 × 5 mm in size at 50 MPa. Final annealing of the samples with BFO concentration \((0 \leq x \leq 0.9)\) was performed at temperatures of 1350–900°C for one hour; the annealing temperature was also lowered with increasing \(x\). To obtain nominally pure BFO, final annealing was carried out at 850°C for 10 min, with subsequent fast cooling to room temperature [37]. The density of the samples obtained was 90–96% of the X-ray diffraction-evaluated density.

X-ray diffraction (XRD) studies of the synthesized samples were performed with a DRON-3 X-ray diffractometer operating with CuK\(_\alpha\), \(\lambda = 1.54178\) Å radiation, Ni filter, 38 kV, 18 mA. Scanning covered the 20 angle interval from 10° to 160° in 0.1° steps, 2 s. Germanium served as reference in measurements of the lattice parameters.

Dielectric permittivity spectra were measured with a Solartron SI 1260 impedance analyzer at frequencies from 10 to 1 MHz and temperatures ranging from 4.2 to 600 K. The field amplitude was 1 V/cm. The samples were shaped as pellets 8 mm in diameter and 0.5–1 mm thick. The electrodes were silver pads prepared by firing silver paste into the samples at a temperature of about 500°C. The velocity of the longitudinal acoustic wave \(V_L\) was evaluated as a function of temperature by the ultrasonic echo-pulse method with RITEC Advanced Ultrasonic Measurement System RAM-5000 at the frequency 10 MHz. In these measurements one employed ceramic bars 5 × 5 × 8 mm in size. Temperature measurements in the interval from 4.2 to 350 K were performed in an Oxford Instruments cryostat, and at 300 to 850 K, in a Carbolite furnace, with the temperature stabilized to within 0.1 K, or in a cooling mode with a rate of 1 K/min.

3. EXPERIMENTAL RESULTS

AND DISCUSSION

Plotted in Fig. 1 are temperature dependences of the dielectric permittivity \(\varepsilon'\) for compositions with bismuth ferrite concentrations up to 0.08. The maxima of \(\varepsilon'(T)\) observed at temperature \(T_m\) shift into the high temperature region, and their smearing grows with increasing \(x\). The onset of the polar state characterized by maxima of dielectric permittivity, its dispersion and polarization loops in the \((1 – x)\)STO–xBFO was reported in [38]. At the lowest concentrations studied, the \(T_m(\varepsilon)\) dependence is fitted by the relation \(T_m = A(x – x_c)^{1/2}\), with the critical concentration \(x_c \approx 0.002\), a value typical of incipient ferroelectrics in which the ferroelectric phase transition is induced by impurities [11, 13, 16]. The dielectric permittivity spectra measured at different temperatures and the dependences \(\varepsilon'(T)\) plotted from these data for different frequencies demonstrate a behavior typical of relaxors (Fig. 2), more specifically, smeared maxima of dielectric permittivity, with the temperature of the maximum shifting toward higher temperatures with increasing measurement frequency. Note the growth of the sample conductivity observed to occur at low frequencies already at room temperature. The \(\varepsilon'(T)\) dependence is fitted by the Curie–Weiss relation at temperatures higher than \(T_m\) by about 100–150 K, a feature also characteristic of relaxors. The temperature at which the \(1/\varepsilon'(T)\) curve starts to deviate from the linear graph.