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Magnetoelectric effect in $(BiFeO_3)_x$–$(BaTiO_3)_{1-x}$ solid solutions

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The aim of the present work was to study magnetoelectric effect (ME) in $(BiFeO_3)_x$–$(BaTiO_3)_{1-x}$ solid solutions in terms of technological conditions applied in the samples fabrication process. The rapidly growing interest in these materials is caused by their multiferroic behaviour, i.e. coexistence of both electric and magnetic ordering. It creates possibility for many innovative applications, e.g. in steering the magnetic memory by electric field and vice versa. The investigated samples of various chemical compositions (i.e. x = 0.7, 0.8 and 0.9) were prepared by the solid-state sintering method under three sets of technological conditions differing in the applied temperature and soaking time. Measurements of the magnetoelectric voltage coefficient α_{ME} were performed using a dynamic lock-in technique. The highest value of α_{ME} was observed for $0.7BiFeO_3$–$0.3BaTiO_3$ solid solution sintered at the highest temperature (T = 1153 K) after initial electrical poling despite that the soaking time was reduced 10 times in this case.

Keywords: *magnetoelectric effect; multiferroic materials; magnetoelectric voltage coefficient*

1. Introduction

There are many practical applications of materials, which exhibit ferro-(antiferro)electric or ferro-(antiferro)magnetic ordering. Ferroelectric materials possess a spontaneous polarization that is stable and switchable by an applied electric field. By analogy, ferromagnetic crystals possess a spontaneous magnetization that is stable and can be switched by an applied magnetic field. There is also a group of magnetoelectric materials exhibiting both of these properties simultaneously [1]. The coupling between magnetic and electrical order parameters enables induction of magnetization by an applied electric field and vice versa, which creates possibility for many innovative applications in microelectronics, spintronics and sensor technique [2]. The mutual control of the electric and magnetic properties, termed the magnetoelectric (ME) effect, is characterized by the magnetoelectric voltage coefficient α_{ME} describing the change in the induced electric field E per unit of the applied magnetic field H [3]:

$$\alpha_{ME} = \frac{dE}{dH} \tag{1}$$

The practical application of the magnetoelectric materials is strongly dependent on the α_{ME} value. Therefore, extensive efforts are made to optimize both the composition of the materials and technological conditions of their production in order to maximize the magnetoelectric effect.

2. Measurement of α_{ME} coefficient

Since the pioneering works on the ME effect several methods for measurement of α_{ME} coefficient have been developed [4]. In the present study a dynamic lock-in technique has been

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applied in order to investigate the room temperature ME effect in $(\mathrm{BiFeO_3})_x$–$(\mathrm{BaTiO_3})_{1-x}$ solid solutions. The samples of various chemical compositions (x = 0.7, 0.8, 0.9) fabricated under different technological conditions were placed in a time-varying DC magnetic field created by an electromagnet and controlled by a programmable DC power source (Fig. 1).

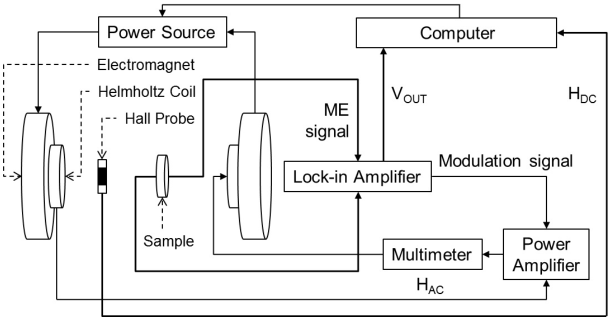

Fig. 1. The experimental setup for the dynamic measurement of the α_{ME} coefficient [3].

The field direction was perpendicular to the sample surfaces and the actual value of its magnitude H_{DC} was measured by a Hall probe. The expected voltage V induced between the sample surfaces due to the ME effect was assumed as a polynomial function of H_{DC}:

$$V = f(H_{DC}) = \mathrm{Const.} + \alpha H_{DC} + \beta H_{DC}^2 + \ldots \quad (2)$$

where α and β are the coefficients of the linear and quadratic components of the ME effect. Then, knowing the thickness of the sample d, it can determine the α_{ME} coefficient as [3]:

$$\begin{aligned}\alpha_{ME} &= \frac{\mathrm{d}E}{\mathrm{d}H_{DC}} = \frac{1}{d}\frac{\mathrm{d}V}{\mathrm{d}H_{DC}} \\ &= \frac{1}{d}(\alpha + 2\beta H_{DC} + \ldots) \end{aligned} \quad (3)$$

In order to determine $\mathrm{d}V/\mathrm{d}H_{DC}$, a small sinusoidal AC magnetic field (perpendicular to the sample surfaces) produced by Helmholtz coils driven by the lock-in amplifier was superimposed onto the DC field. The amplitude of the AC field, H_{AC} was calculated from the driving current that was measured by a multimeter. Thus, the total field H was a superposition of both the DC and AC component:

$$H = H_{DC} + H_{AC}\sin\omega t \quad (4)$$

Therefore, the total voltage V induced between the sample surfaces due to the ME effect has been also determined as a function of H_{DC} and H_{AC} according to the following equation:

$$\begin{aligned} V = {} & \mathrm{Const.} + \alpha H_{DC} + \beta H_{DC}^2 + \frac{1}{2}\beta H_{AC}^2 \\ & + H_{AC}(\alpha + 2\beta H_{DC})\sin\omega t \\ & - \frac{1}{2}\beta H_{AC}^2 \cos 2\omega t + \ldots \end{aligned} \quad (5)$$

However, the lock-in amplifier used in this experiment in order to measure the ME output voltage V_{OUT} was tuned to the well-defined frequency ω according to the modulation signal. Thus, the voltage V_{OUT} measured by the lock-in amplifier contained only these components of the voltage V which were in-phase with the modulation signal:

$$V_{OUT} = H_{AC}(\alpha + 2\beta H_{DC} + \ldots) = H_{AC}\frac{\mathrm{d}V}{\mathrm{d}H_{DC}} \quad (6)$$

When comparing equations (6) and (3) one can find out that $\mathrm{d}V/\mathrm{d}H_{DC}$ can be determined by measurement of V_{OUT} and H_{AC}. Thus, the α_{ME} coefficient can be described as:

$$\alpha_{ME} = \frac{\mathrm{d}E}{\mathrm{d}H_{DC}} = \frac{1}{d}\frac{\mathrm{d}V}{\mathrm{d}H_{DC}} = \frac{1}{d}\frac{V_{OUT}}{H_{AC}} \quad (7)$$

In the present study, the measurements of the α_{ME} coefficient were performed by recording the voltage V_{OUT} under various magnitudes of the applied DC magnetic field. The magnitude H_{DC} was varied within the range of values from 0.1 to 4.5 kOe (8 to 358 kA/m), while the amplitude H_{AC} was constant during the experiment and it was equal to 5 Oe (398 A/m, which is significantly lower than H_{DC}). The frequency of the AC modulation field was equal to 1 kHz.

3. Magnetoelectric effect in $\mathrm{BiFeO_3}$–$\mathrm{BaTiO_3}$

Production of multiferroic ceramic materials is based on a complex technology requiring a special

Table 1. Technological conditions of the samples fabrication [5].

Methods	Synthesis I	Synthesis II	Sintering	Annealing
Variant 1	1023 K/20 h	1023 K/20 h	1053 K/40 h	823 K/10 h
Variant 2	1073 K/10 h	1073 K/10 h	1103 K/20 h	823 K/10 h
Variant 3	1123 K/2 h	1123 K/2 h	1153 K/4 h	823 K/10 h

care and accuracy in choosing conditions of the processing. In this study a three-stage process of thermal treatment (including double synthesis, final sintering, and annealing in air) was chosen to obtain the $BiFeO_3$–$BaTiO_3$ solid solutions from precursor oxides Bi_2O_3 and Fe_2O_3, and a commercial compound $BaTiO_3$. The following stoichiometric formula with x values 0.7, 0.8 and 0.9 has been used:

$$(Bi_2O_3)_{x/2} + (Fe_2O_3)_{x/2} + (BaTiO_3)_{1-x} \rightarrow \\ \rightarrow (BiFeO_3)_x - (BaTiO_3)_{1-x} \quad (8)$$

Moreover, three different samples of each composition were prepared by applying three variants of the solid-state reaction differing in the sintering temperature T and the soaking time t (Table 1) [5]. The precursors were synthesized by means of mixed-oxide-method. Moreover, our experiences have shown that better results of the phase formation can be obtained when the process of synthesis is repeated twice. That is why the double synthesis was applied. After the first heat-treatment (synthesis I) the material was ground into powder and homogenized. Later on, the second heat-treatment process (synthesis II) was performed and the resultant material was powdered and homogenized once again. Finally, the materials were sintered.

An examination of the X-ray diffraction patterns performed with the help of X'Pert High Score Plus software has shown the presence of only one phase for all technological methods utilized in this study (Fig. 2). The diffraction lines for all samples can be indexed only to the rhombohedral structure of $BiFeO_3$ (space group R3c, card number ICSD 01-071-2494). The one exception is the sample with x = 0.9 sintered in T = 1053 K, for which the presence of a small amount (about 5 wt.%) of

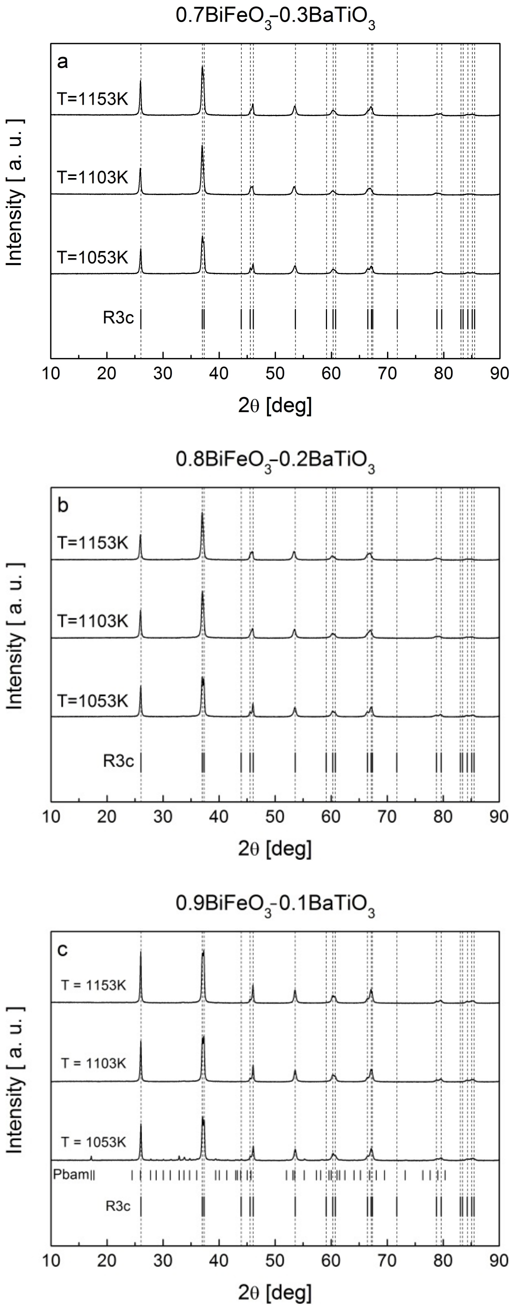

Fig. 2. X-ray diffraction patterns of $(BiFeO_3)_x$–$(BaTiO_3)_{1-x}$; (a) x = 0.7; (b) x = 0.8; (c) x = 0.9.

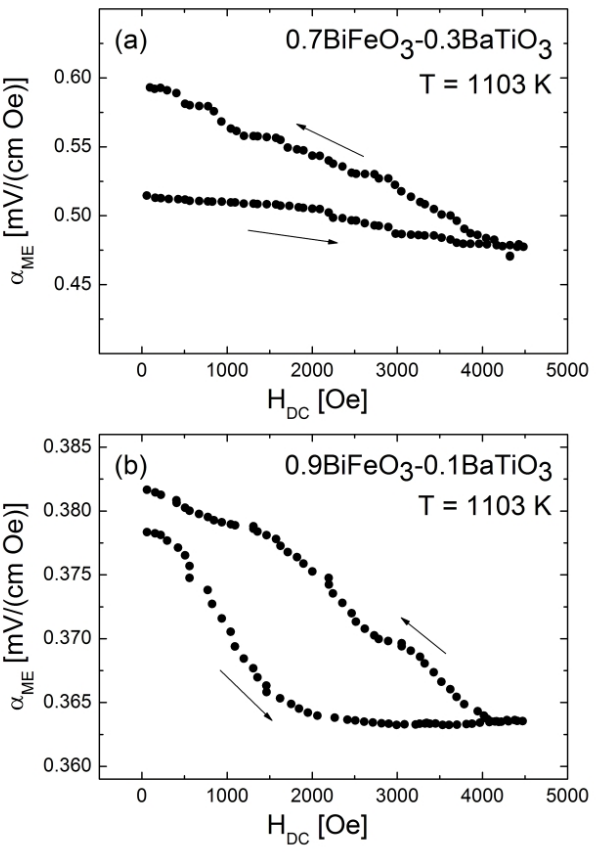

Fig. 3. Variation of α_{ME} with H_{DC} for the samples sintered at T = 1103 K; (a) x = 0.7; (b) x = 0.9 [6].

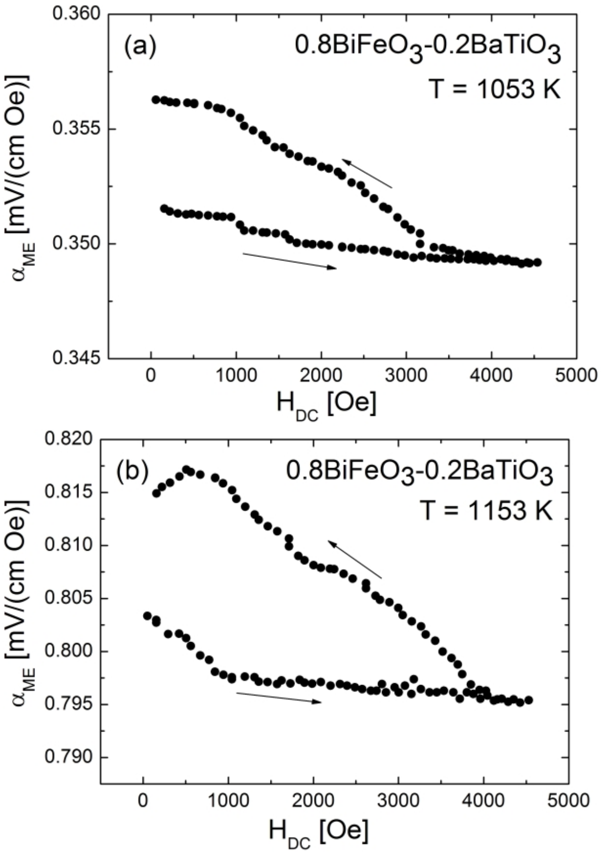

Fig. 4. Variation of α_{ME} with H_{DC} for the samples with x = 0.8, sintered under different technological conditions; (a) T = 1053 K (variant 1); (b) T = 1153 K (variant 3).

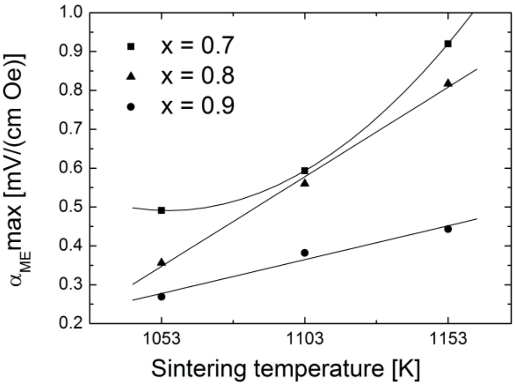

Fig. 5. Maximum value of α_{ME} in $(BiFeO_3)_x$–$(BaTiO_3)_{1-x}$ as a function of the sintering temperature T.

impurity by $Bi_2Fe_4O_9$ compound (space group Pbam, card number JCPDS 00-025-0090) has been observed (Fig. 2c).

Composition-dependent magnetoelectric properties of these materials were analyzed in terms of the technological conditions of their fabrication process. The results of measurements of the α_{ME} coefficient for various magnitudes of the applied DC magnetic field are presented in Fig. 3 and 4.

The magnitude of the ME effect for a given value of H_{DC} increases with increasing $BaTiO_3$ concentration. The maximum α_{ME} value is about 55 % higher for x = 0.7 when compared with x = 0.9 for the same variant of the samples preparation – sintering at 1103 K (Fig. 3a and 3b).

On the other hand, the maximum α_{ME} value is more than two times higher for the sintering temperature T = 1153 K when compared with 1053 K, for the same composition of the samples, i.e. x = 0.8 (Fig. 4a and 4b), despite that the soaking time was 10 times shorter in the first case. Thus,

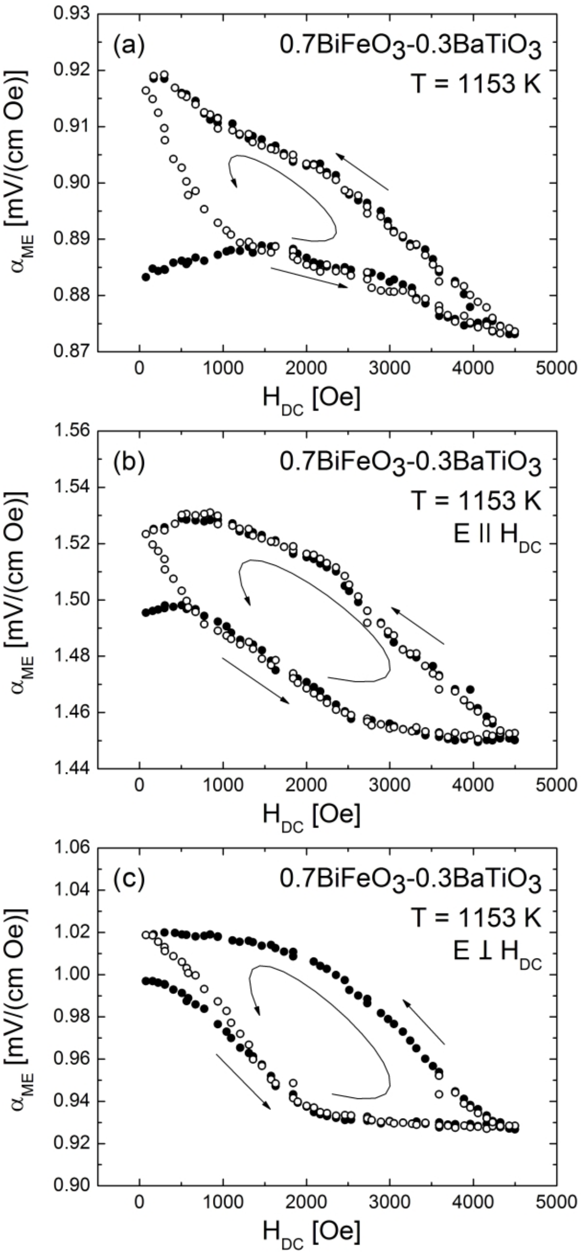

Fig. 6. Variation of α_{ME} with H_{DC} for the sample with $x = 0.7$, sintered at $T = 1153$ K; solid symbols represent the first hysteresis loop, and open symbols are for the second course; (a) before poling; (b) after poling in E parallel to H_{DC}; (c) after poling in E perpendicular to H_{DC}.

the ME properties of the investigated materials are strongly dependent on both the chemical composition and the technological conditions applied during their preparation process.

Fig. 5 shows the maximum α_{ME} values as a function of the sintering temperature T for various compositions of the $(BiFeO_3)_x$–$(BaTiO_3)_{1-x}$ solid solutions.

The highest ME effect in this set of materials was observed for the sample with $x = 0.7$, prepared using the third variant of the fabrication method (Table 1). Therefore, for this sample (the most promising one) the initial electrical poling was performed and the measurements of α_{ME} were repeated in order to compare the results after that.

Poling is a process, by which a strong electric field is applied across a material to align the randomly oriented dipoles into one direction (parallel or perpendicular to the magnetic field). The sample with $x = 0.7$ was poled in a field of 3 kV/mm at 368 K for 1 h. Moreover, the α_{ME} measurements for this sample (before and after poling) were performed twice in order to verify if the hysteresis of the resultant curve is recurrent (Fig. 6).

4. Remarks and conclusions

The magnetoelectric voltage coefficient has been measured for the samples of $(BiFeO_3)_x$–$(BaTiO_3)_{1-x}$ solid solutions with various compositions, sintered at different temperatures. The α_{ME} value decreases with increasing DC magnetic field for all the samples investigated in the present work, which is not consistent with the results of studies performed for very similar materials and reported by Kumar et al. [7]. This may, however, be attributed to the differences in samples composition, structure, or preparation conditions.

For all the samples the curves $\alpha_{ME}(H_{DC})$ do not retrace the same path on reversal magnetic field, but exhibit the hysteretic nature, which may be related to the hysteresis behavior of the solid solution constituents. The highest magnetoelectric effect was observed for the sample with $x = 0.7$ sintered at $T = 1153$ K. Moreover, the experiment showed that the maximum α_{ME} value which was observed for this material can be higher even up to 66 % when the initial electrical poling of the sample is applied. The value $\alpha_{ME} = 1.53$ $mV{\cdot}cm^{-1}{\cdot}Oe^{-1}$ obtained for $0.7BiFeO_3$–$0.3BaTiO_3$ sintered at

1153 K and electrically poled in E parallel to H_{DC} is larger than that obtained very recently for $0.725BiFeO_3$–$0.275BaTiO_3$ solid solution, i.e. $\alpha_{ME} = 0.87$ mV·cm^{-1}·Oe^{-1}, as reported by Yang et al. [8]. Currently, extensive efforts are being made in further optimizing both the composition of the investigated $(BiFeO_3)_x$–$(BaTiO_3)_{1-x}$ solid solutions and the technological conditions of their fabrication in order to maximize their magnetoelectric effect.

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