Phase transitions study in Ba_{(1-x)}Mn_{x}TiO_{3} and BaMn_{x}Ti_{(1-x)}O_{3} ceramics

E D Rumyantseva\(^1\), V G Zalessky\(^2\) and N V Zaitseva\(^2\)
\(^1\)Student, University ITMO (National Research University), Kronverksky prospect 49, Saint-Petersburg, 197101, Russia
\(^2\)Ioffe Physical-Technical Institute RAS, Politekhnicheskaya 26, Saint-Petersburg, 194021, Russia

E-mail: ska-kotya@mail.ru

Abstract. Dielectric properties of the ceramics Ba\(_{(1-x)}\)Mn\(_x\)TiO\(_3\) and BaMn\(_x\)Ti\(_{(1-x)}\)O\(_3\) of the compositions \(x=0.01, 0.03, \) and 0.1 have been studied at temperatures 77 – 450 K and at frequencies 10 Hz -100 kHz. The phase transitions diagram and parameters of the both system have been presented and compared. Dielectric relaxations in BaMn\(_x\)Ti\(_{(1-x)}\)O\(_3\) with \(x=0.1\) have been shown.

1. Introduction

Barium titanate (BT) solid solutions, BaTiO\(_3\) -ABO\(_3\) (where A = Ba, Ca, Sr, Pb, Mn and B = Ti, Zr, Sn, Hf, Mn), have been intensively studied due to very interesting electric, piezoelectric, and optic properties [1]. Every solid solution is characterized by a phase diagram \(T - x\), as a phase transition temperature versus second component concentration. The \(T - x\) diagrams of barium titanate solid solutions consist of the three lines phase transitions: \(O_h^1\) - \(C_{4v}^1\), \(C_{4v}^1\) – \(C_{2v}^{14}\), and \(C_{2v}^{14}\) - \(C_{3v}^5\). In SrTiO\(_3\)-BaTiO\(_3\) [2] and CoTiO\(_3\)-BaTiO\(_3\) [3] where ions Sr\(^{2+}\) and Co\(^{2+}\) substitute for Ba\(^{2+}\) (A-substitution) the three lines converge to a multiphase point. The multiphase points are also observed for solid solutions with B-substitution: BaZrO\(_3\) [4, 5], BaSnO\(_3\) [6], Ba(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\), and Ba(Mg\(_{1/3}\)Ta\(_{2/3}\))O\(_3\) [7], and both with A- and B-substitution: KTaO\(_3\) [8], and KNbO\(_3\) [6]. However, the \(T - x\) diagrams with non converged lines are known in the system CaTiO\(_3\), PbTiO\(_3\) [6], and MnTiO\(_3\) [9]. All of them are the solid solutions with the A-substitution excepting MnTiO\(_3\), where Mn ions can occupy the both A- and B- sites.

The studies of the system Ba\(_{(1-x)}\)Mn\(_x\)TiO\(_3\) with concentration \(x<0.01\) were reported in [10, 11]. However the \(T - x\) diagram of this solid solution still remains indefinite because technological difficulties of the sample preparation. It is also known that Mn\(^{2+}\) ions with concentration \(x>0.15 - 0.18\) produce the hexagon phase in BT [10, 11]. We decided to fabricate the specimens of solid solutions both with A- and B- substitutions: Ba\(_{(1-x)}\)Mn\(_x\)TiO\(_3\) and BaMn\(_x\)Ti\(_{(1-x)}\)O\(_3\) with \(x>0.01\), study their phase transitions, and compare dielectric properties.

2. Experimental techniques and results

Samples of Ba\(_{(1-x)}\)Mn\(_x\)TiO\(_3\) and BaMn\(_x\)Ti\(_{(1-x)}\)O\(_3\) solid solutions with \(x=0.01, 0.03, \) and 0.1 were prepared by standard ceramic technology [7, 8]. The starting materials were high purity BaCO\(_3\), TiO\(_2\), and MnO. There were the two step of the solid solution preparation. Primary, it was synthesized BT. After pressing, the mixture of the powdered BaTiO\(_3\) and MnO was calcined at 1200 - 1400°C for 2-3 days.
The material was reground and the pellets were formed by pressing for 9 mm diameter discs at 50 MPa. After pressing, the samples were fired at 1370-1420°C for 1 hour. The phase content was monitored by X-ray diffraction study (CuKα and CoKα lines) and indicated the tetragonal perovskite single phase. Relative density of the samples was measured to be 90-93%.

The samples were coated with silver-burned electrodes for dielectric measurements. The dielectric spectroscopy study was performed by impedance meter Goodwill LCR – 819 at the frequency range 12 Hz -100 kHz and amplitude of ac electric field 1 V. Temperature dependence of dielectric parameters measurement was performed by heating or cooling at a constant rate 1 K/min between 77 K and 450 K.

2.1. \( \text{Ba}(1-x)\text{Mn}_x\text{TiO}_3 \) (A -substitution)

The temperature dependences of real \( \varepsilon'(T) \) and imaginary \( \varepsilon''(T) \) part of the dielectric permittivity in \( \text{Ba}(1-x)\text{Mn}_x\text{TiO}_3 \) solid solution with \( x = 0.01, 0.03, \) and \( 0.1 \) are shown in figures 1 and 2. One can see that composition at the range from \( x = 0 \) to 0.03 changes the high temperature phase transition parameters such as: Curie temperature \( T_C \), Curie-Weiss temperature \( T_{CW} \), and Curie-Weiss constant \( C_{CW} \) (see table 1 and inset figure 1). The sequence of the low temperature phase transitions at \( T_1 \) and \( T_2 \) are also shifted down to lower values (figure 1). The \( T - x \) diagram in figure 3 shows the three non converged lines.

| \( x \)     | \( T_C \) (K) | \( T_{CW} \) (K) | \( C_{CW} \) (K) |
|-------------|--------------|-----------------|-----------------|
| 0           | 392          | 378             | 1.2 \times 10^5 |
| 0.01        | 387          | 358             | 1.3 \times 10^5 |
| 0.03        | 383          | 340             | 9 \times 10^4   |

The composition with the concentration \( x = 0.1 \) changes the temperature dependence \( \varepsilon'(T) \) drastically. All the peaks disappear excepting smeared maximum at \( T_2 = 186 \) K, that is 4 K below the temperature upon the orthorhombic-rhombohedral phase transition in pure BT.

The temperature dependence \( \sigma(T) \) in \( \text{Ba}(1-x)\text{Mn}_x\text{TiO}_3 \) solid solutions doesn’t show an evidence of a dielectric relaxation (figures 1 and 2). Increasing of real and imaginary parts of the dielectric permittivity in the case \( x = 0.1 \) is related to the thermal activated conductivity in the sample (Figure 2). The ac conductivity can be described using the relationship \( \sigma = \sigma_0 \exp(E_a/kT) \), where \( E_a \) is the activation energy and \( k \) is the Boltzmann constant. The activation energy is estimated to be \( E_a = 0.46 \) eV. This value can be characterized the acceptors or donors charge carriers activated in the energy gap bound.

2.2. \( \text{BaMn}_x\text{Ti}(1-x)\text{O}_3 \) (B -substitution)

The temperature dependence of the real part of the dielectric permittivity \( \varepsilon'(T) \) of \( \text{BaMn}_x\text{Ti}(1-x)\text{O}_3 \) with \( x = 0.01, 0.03, \) and 0.1 is shown in figure 4. One can see that the high temperature phase transition parameters are also changed by manganese doping at the range \( x = 0 - 0.01 \) (see table 2 and inset figure 4). The rest two phase transitions peaks at low temperatures \( T_1 \) and \( T_2 \) are also shifted down to lower value. The \( T - x \) diagram in figure 3 shows the three non converged lines. Despite the diffuseness, this material does not exhibit the strong frequency dispersion of the dielectric permittivity as the evidence of the relaxor behavior [1].
Figure 1. The temperature dependence of the real part of the dielectric permittivity \( \varepsilon' (T) \) at 1kHz in Ba\(_{1-x}\)Mn\(_x\)TiO\(_3\) solid solution with \( x=0.01, 0.03, \) and \( 0.1 \). Inset reciprocal permittivity fitted by the Curie-Weiss law.

Figure 2. The temperature and frequency dependence of the imaginary part of the dielectric permittivity \( \varepsilon'' (T) \) in Ba\(_{1-x}\)Mn\(_x\)TiO\(_3\) with \( x = 0.1 \). Dashed line is the imaginary permittivity fitted by the thermal activated conductivity.

Figure 3. Phase transition temperatures vs. second component concentration \( x \) in Ba\(_{1-x}\)Mn\(_x\)TiO\(_3\) and BaMn\(_x\)Ti\(_{1-x}\)O\(_3\) solid solutions (phase transition diagram).
In comparison to BT with A-substitution, the concentration $x = 0.03$ makes the significant changes in the temperature dependence $\varepsilon'(T)$ (figure 4). All the peaks disappear excepting smeared maximum $T_2$ that is 14 K below the temperature upon the orthorhombic-rhombohedral phase transition in pure BT.

For the composition with concentration $x = 0.1$ any maxima at the temperature dependence of the real permittivity $\varepsilon'(T)$ (figure 5) cannot be recognized. However, the temperature dependence of the imaginary part $\varepsilon''(T)$ shows an evidence of a dielectric relaxation. At the low temperatures range 150-250 K it can be recognized the maximum $\varepsilon''(T)$ that shifts up to higher temperature with frequency increasing. In the other range 250-450 K one can also see the maximum upon monotonic increased background curve (figure 5). The maximum is also shifted to higher temperatures as the frequency increases. The relationship between the frequency $f$ (or cycling frequency $\omega = 2\pi f$) and the temperature of maximum can be described using the Arrhenius relationship $\omega = \omega_0 \exp (-E_a/kT_m)$, where $\omega_0$ is Debye frequency, $T_m$ is the temperature of the imaginary dielectric maximum at the given frequency, $E_a$ is the activation energy, and $k$ is the Boltzmann constant. As a result, we estimate the values for both relaxations: for low temperatures $\omega_0 = 1.4 \cdot 10^{12}$ s$^{-1}$ and $E_a = 0.3$ eV, and for high temperatures $\omega_0 = 4 \cdot 10^{15}$ s$^{-1}$ and $E_a = 0.8$ eV.

| $x$       | $T_C$ (K) | $T_CW$ (K) | $C_{CW}$ (K) |
|-----------|-----------|------------|--------------|
| 0         | 392       | 378        | 1.2 \cdot 10^5 |
| 0.01      | 385       | 370        | 7.1 \cdot 10^4 |

In comparison to BT with A-substitution, the concentration $x = 0.03$ makes the significant changes in the temperature dependence $\varepsilon'(T)$ (figure 4). All the peaks disappear excepting smeared maximum $T_2$ that is 14 K below the temperature upon the orthorhombic-rhombohedral phase transition in pure BT.

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**Figure 4.** The temperature dependence of the real part of the dielectric permittivity $\varepsilon'(T)$ at 1 kHz in BaMn$_x$Ti$_{1-x}$O$_3$ solid solution with $x=0.01$, 0.03, and 0.1. Inset reciprocal permittivity fitted by the Curie-Weiss low.

**Figure 5.** The temperature and frequency dependence of the imaginary part of the dielectric permittivity $\varepsilon''(T)$ in BaMn$_x$Ti$_{1-x}$O$_3$ with $x=0.1$. 

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**Table 2.** BaMn$_x$Ti$_{1-x}$O$_3$ (B -substitution).

| $x$       | $T_C$ (K) | $T_CW$ (K) | $C_{CW}$ (K) |
|-----------|-----------|------------|--------------|
| 0         | 392       | 378        | 1.2 \cdot 10^5 |
| 0.01      | 385       | 370        | 7.1 \cdot 10^4 |
We attribute the low temperature relaxation to impurity centers \{\text{Mn}^{2+} - \text{Vo}\} in BT as well as in SrTiO$_3$ [12, 13]. In strontium titanate the Mn$^{2+}$ impurity ion substitutes the Ti$^{4+}$ ion and produces oxygen vacancy \text{Vo} in oxygen rhombohedra to compensate the charge. As a result, the dipole impurity centers \{\text{Mn}^{2+} - \text{Vo}\} is formed. It is known [12-14] that the thermally activated dipole reorientation via the vacancy jumping in SrTiO$_3$ is observed with $E_a \approx 0.1 - 0.3$ eV and $\tau_0 \approx 10^{-10} - 10^{-12}$ s. Therefore, the estimated parameters $E_a = 0.3$ eV and $\omega_0 = 1.4 \cdot 10^{12}$ s$^{-1}$ evidence for the same relaxation mechanism in BT.

The high temperature relaxation can be related to electronic subsystem because the high value of Debye frequency $\omega_0 = 4 \cdot 10^{15}$ s$^{-1}$. The estimated activation energy $E_a = 0.8$ eV is of the same order as in SrTiO$_3$ $E_a = 0.8$ eV [14] and can be determined by energy of donor or acceptors in the band gap. On the other hand, it is well known [14, 15] that the thermal activated conductivity in ceramic grains and boundaries produces a strong dielectric relaxation. Therefore, we can associate the high temperature relaxation with the Maxwell-Wagner mechanism due to the heterogeneous nature of the ceramics with grain and boundary layers.

3. Conclusion
We studied the BT ceramic with A and B substitution: Ba$_{(1-x)}$Mn$_x$TiO$_3$ and BaMn$_x$Ti$_{(1-x)}$O$_3$ with manganese concentration $x = 0.01, 0.03$ and $0.1$. The phase diagrams ($T-x$) was plotted according to the temperature dependence of the dielectric permittivity Compositions dependences of the phase transition parameters were obtained. Debye relaxation associated with impurity polar centers and relaxation Maxwell - Wagner due to grain and boundary layers in ceramic BaMn$_x$Ti$_{(1-x)}$O$_3$ with $x = 0.1$ were investigated.

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