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MICROCALORIMETRY STUDIES OF PHASE TRANSITIONS IN $(Ba_XSr_{1-X})TiO_3$

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Both temperatures, T_C, (T_C –Curie temperature) and heat of the phase transition: ferroelectric-paraelectric, ΔH, in the $Ba_xSr_{1-x}TiO_3$ materials have been studied by means of the microcalorimetric method. The determined parameters were verified by either temperature dependence of the dielectric permittivity (Curie-Weiss law) or thermodynamic method. The effect of strontium content on T_C has been discussed. It was found that microcalorimetry is useful tool studying phase transition phenomena in ferroelectric perovskites.

Keywords: *barium titanate, ferroelectric materials, microcalorimetry, perovskite, phase transition, strontium titanate*

Introduction

Ferrolectrics are a special group of advanced electronic materials. They are dielectrics which are spontaneously polarized and possess the ability to switch their internal polarization with an applied field. Barium titanate, $BaTiO_3$ (BT), among ferroelectric materials barium titanate, attracted most interest due to simple crystal structure, high stability and extremely high dielectric constant, low leakage current and anisotropic optical behavior [1, 2]. At room temperature BT shows a tetragonal structure. Above 403 K the stable structure is cubic. The phase transition from tetragonal to cubic corresponds is known as ferroelectric to paraelectric transition and its transition temperature is named ferroelectric Curie temperature, T_C. A sharp peak in the permittivity of $BaTiO_3$ is observed at T_C. A number of practical applications of ferroelectric materials need some modifications of the $BaTiO_3$ properties such as Curie temperature or character of changes permittivity with temperature and frequency. BT has been widely used for high dielectric constant capacitors because of its very high dielectric constant at the Curie temperature (T_C=120°C). Some corrective modifications are required for practical application [3–5]. In order to move the T_C to lower temperatures, $SrTiO_3$, $BaZrO_3$ and $SnTiO_3$ were usually added as shifters.

A sharp peak of the dielectric constant at the T_C can be easily flattened, and, therefore, the temperature coefficient of the ε' can be reduced, by adding the depressor material, such as $CaTiO_3$ and $MgTiO_3$. Addition of strontium titanate to BT matrix was frequently used in order to reduce of the Curie temperature.

It is well established that the Curie point of BT decreases when Sr^{2+} ions replace Ba^{2+} ions in the crystal lattice. However, it is not fully understood yet, how the strontium concentration effects on the peak value of the relative dielectric permittivity, $\varepsilon'_{max,}$ at the ferroelectric Curie point in BST solid solutions. Smolenski and Rozgachev [6] as well as Zhou *et al.* [7] reported that the ε'_{max} of the BST increased with the Sr concentration from up to $Ba_{0.4}Sr_{0.6}TiO_3$ (reaching values $1.5\cdot10^4$ [6] and $3.2\cdot10^4$ [7]) and then decreases for higher concentrations of strontium. Lemanov *et al.* [8] observed the maximum value of ε'_{max} for $Ba_{0.2}Sr_{0.8}TiO_3$ ($2.5\cdot10^4$). On the other hand Ota *et al.* [9] claimed that the maximum dielectric permittivity decreased with strontium content. Recently, Jeon [10] reported that in the BST materials sintered at 1350°C the ε'_{max} decreased with an increase in the Sr, reaching the highest value for around $Ba_{0.6}Sr_{0.4}TiO_3$ and then decreased. As the sintering temperature increased to 1450°C ε_{max} increased with increasing Sr concentration up to composition $Ba_{0.4}Sr_{0.6}TiO_3$. Also, the nature of the phase transformation from ferroelectric to paraelectric state in BST is not fully understood yet. Fu *et al.* [11] suggested the first-order phase transitions in BST solid solutions. According to Lemanov *et al.* [8] the cubic-tetragonal phase transition is of the first order in $BaTiO_3$, whereas it transforms to the second order at x close to 0.2 in $Ba_xSr_{1-x}TiO_3$. Benguigi and Bethe [12] and Barb *et al.* [13] reported diffuse phase transition for $x<0.6$ in $Ba_{1-x}Sr_xTiO_3$. Recently, differential scanning calorimetry (DSC) technique was used to study phase transition in different ferroelectric materials [14–20].

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The purpose of the present work was to study the phase transitions in $Ba_xSr_{1-x}TiO_3$ by means of dielectric and DSC techniques.

Experimental

Sample preparation

Both $BaTiO_3$ single crystal and polycrystalline solid solutions $Ba_xSr_{1-x}TiO_3$ were studied. The method of Remeika [21] was used to crystal growth of $BaTiO_3$. The method consists of crystallization from $BaTiO_3$ solution in KF, rectangular crystals of the dimensions: 7.4·3.6·2.4 mm were used for dielectric measurements.

Polycrystalline samples were obtained by coprecipitation. The aqueous solution of ammonium oxalate was dropped into the aqueous solution of Ba, Sr and Ti chlorates mixture. During the precipitation pH remained within 9.5–10. The precipitate was washed out till the disappearance of Cl^- ions. Then it was dried at 383 K for 8 h and then calcinated at 873 K for 1 h and at 1173 K for 2 h in air. The samples were pressed and then sintered at 1673 K for 2 h. Finally the samples were ground in an agate mortar, pressed again and sintered in the same conditions. X-ray analysis has indicated that all the samples were single-phase perovskite solid solutions. The cylindrical sintered pellets of the diameter 11.5 mm and thickness 1.5 mm were used for dielectric measurements.

Dielectric measurements

The dielectric permittivity, ε' and dielectric loss factor (tanδ) were measured at 1 kHz by use of an Automatic C Bridge (E315A) at 298–423 K. Subsequent measurements were performed during heating and cooling at every 3–5 K. Intervals at 0.95 confidence levels were about 0.1% for the permittivity and 2% for tanδ.

Microcalorimetric studies

Microcalorimetric experiments were performed by differential scanning calorimetry (DSC) at both heating and cooling cycles in air with rate of 5 K min^{-1} using a standard DSC equipment 2019 TA Instruments.

Results and discussion

Figure 1 illustrates temperature, *T*, dependencies of dielectric constant of the studied materials $Ba_xSr_{1-x}TiO_3$ with $0 \le x \le 1.00$ and 297 K≤*T*≤424 K. Single crystal of $BaTiO_3$ exhibits about five times higher ε than those of ceramic material. However, there is small difference between the positions of the peaks of ε. Materials with *x* higher than 0.50 show maximum of ε within experimental temperature range. Sharp peaks of the dielectric constant observed for $BaTiO_3$ become flattened when barium is replaced by Sr and therefore, the temperature coefficient of the ε can be reduced. Among the ceramic specimens the materials with *x* between 0.5 and 0.625 shows highest

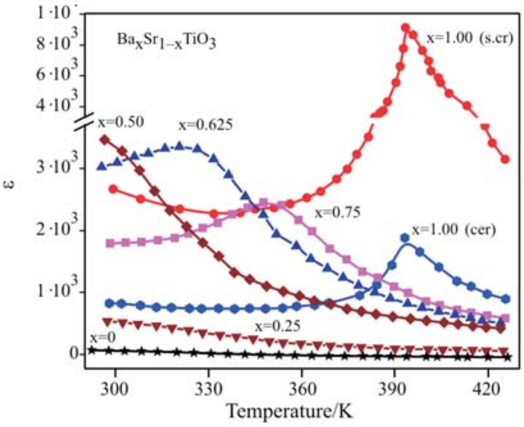

Fig. 1 Dielectric constant as a function of temperature of $Ba_xSr_{1-x}TiO_3$; s.cr – single crystal, cer– polycrystalline sample

Table 1 Curie temperature, T_C, and enthalpy of tetragonal-cubic phase transition, ΔH

Specimen	Method	T_C/K		ΔH/J mol^{-1}		Ref.
		heating	cooling	heating	cooling	
$BaTiO_3$ s.cr.	microcalor.	392.6	391.1	240.7	256.3	this work
	dielectric	392.7±1.6		–	–	this work
$BaTiO_3$ cer	microcalor.	390.3	387.1	231.4	119.2	this work
	dielectric	392.5±4.2		–	–	this work
	microcalor.	397–400		200		[25]
	thermodynamic	394.65		201		[26]
$Ba_{0.9}Sr_{0.1}TiO_3$ cer.	microcalor.	362.8	362.1	209.1	241.7	this work
	dielectric	364.3±6.3		–	–	this work

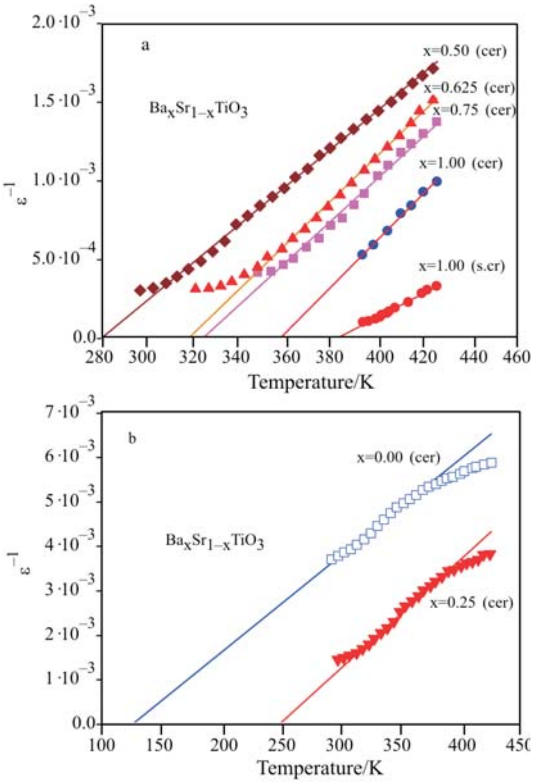

Fig. 2 Reciprocal dielectric constant *vs.* temperature of $Ba_xSr_{1-x}TiO_3$; s.cr – single crystal, cer– polycrystalline sample; a – $0.50 \le x \le 1.00$; b – $x=0$ ($SrTiO_3$) and $x=0.25$

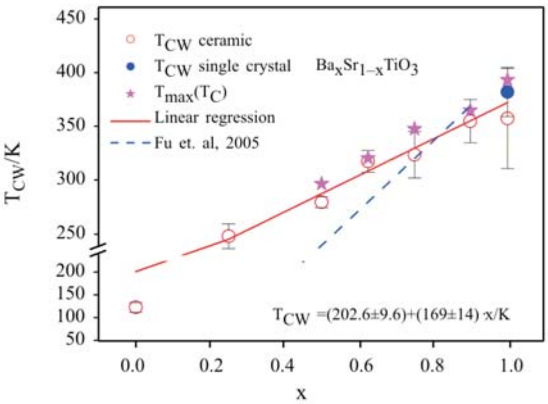

Fig. 3 Curie and Curie–Weiss temperatures as a function composition, *x*, of $Ba_xSr_{1-x}TiO_3$

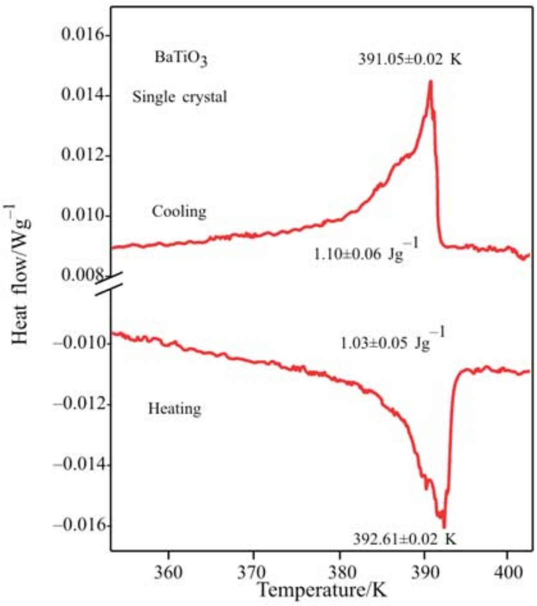

Fig. 4 DSC curves (heating and cooling) of $BaTiO_3$ single crystal

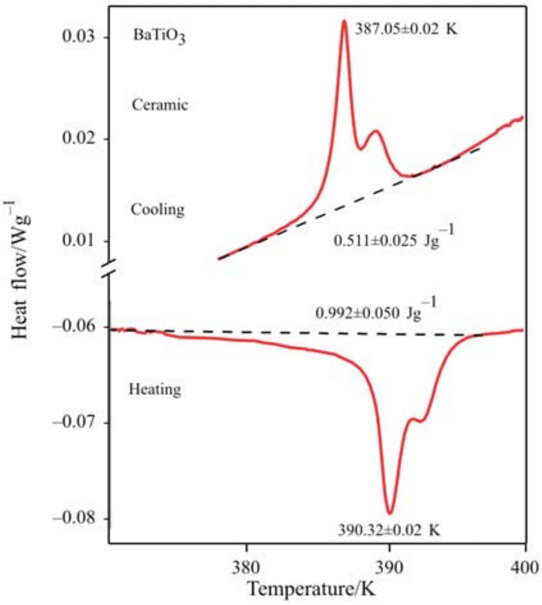

Fig. 5 DSC curves (heating and cooling) of ceramic $BaTiO_3$

values of the dielectric constant. The temperature corresponding to these maximum points can be identified with the ferroelectric Curie temperature, T_C. On the other hand, the Curie–Weiss law is expected for the studied materials in paraelectric state ($T > T_C$):

$$\varepsilon = \frac{C}{T - T_{CW}} \tag{1}$$

where: C – constant, T_{CW} is named Curie–Weiss temperature. According to Curie–Weiss law, the Curie–Weiss temperature (T_{CW}) can be obtained from linear extrapolation of inverse dielectric constants in the paraelectric region.

Figure 2 (a and b) show the dependence ε^{-1} *vs.* T, the Curie–Weiss temperature is calculated from the intersection of the linear fit to the experimental data with the temperature axis. The determined T_{CW} and T_C are presented in Fig. 3 as a function of x in $Ba_xSr_{1-x}TiO_3$. As can be seen, the experimental points well obey straight-line dependencies. However, the difference in slopes between linear fit data in this

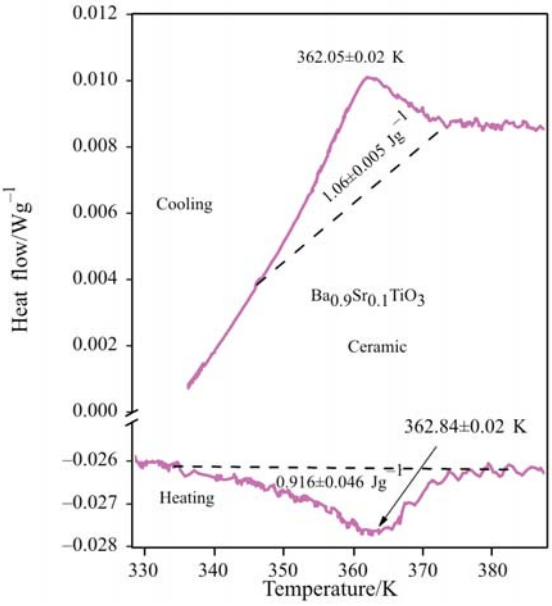

Fig. 6 DSC curves (heating and cooling) of ceramic $Ba_{0.9}Sr_{0.1}TiO_3$

work and literature reported by Fu *et al.* [23] can be observed. The ferroelectric-paraelectric phase transition is of first order when $T_C > T_{CW}$ and of second order when $T_C = T_{CW}$ [24]. According to Fig. 3 all studied samples exhibit first order of the ferroelectric-paraelectric phase transition.

Figures 4–6 illustrate Differential Scanning Calorimetry, DSC, curves monitored during both heating and cooling cycles of single crystal $BaTiO_3$, ceramic $BaTiO_3$ and $Ba_{0.9}Sr_{0.1}TiO_3$, respectively. The presented results clearly show an endothermic effect. This effect corresponds to the tetragonal to cubic phase transition at the Curie point. Table 1 summarizes both Curie temperature, T_C, and change of enthalpy, ΔH, corresponding to the tetragonal-cubic phase transition.

Conclusions

Barium-strontium titanate is a solid solution with ferroelectric Curie temperature covering a wide range. When strontium ions were introduced into the A site in a perovskite structure replacing barium ions the Curie temperature decreases. It gives an opportunity to prepare a ferroelectric material exhibiting Curie temperature at room temperature. Such composition may be use as environment-friendly material in various practical applications. DSC technique is a very useful tool for the characterization of ferroelectric-paraelectric phase transitions. It enables to determine not only the heat of the phase transition but also it can be use to precise determination of the transition temperature.

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