

# Semi-oxalate synthesis of $(1-x)\text{BaTiO}_3-x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ) PTCR materials

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**Abstract:**  $(1-x)\text{BaTiO}_3-x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ) solid solutions were prepared using  $\text{BaTiO}_3$  pre-synthesized by oxalate method. The stability limits of  $(1-x)\text{BaTiO}_3-x\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  solid solutions have been established. It was shown that increase in  $\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  concentration results in reduction of ceramic grain size in the  $(1-x)\text{BaTiO}_3-x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ) system. It was found that the positive temperature coefficient of resistance (PTCR) effect in lead-free materials is due to the presence of a semiconductor core, which is formed by sintering under reducing atmosphere, and dielectric grain boundaries, formed on additional oxidation in air. The use of barium titanate, pre-synthesized by oxalate method, in the synthesis of solid solutions reduced the sintering temperature of ceramics compared with solid state reaction technique. By comparing the electrical properties of the synthesized lead-containing and lead-free materials, it has been shown that lead-free materials exhibit better electrical properties for practical use compared with lead-containing materials.

**Keywords:** lead-free ceramic;  $\text{BaTiO}_3$ ; semi-oxalate method; positive temperature coefficient of resistance (PTCR) effect

## 1 Introduction

Oxide materials with perovskite structure are widely used in various fields of modern technology. Materials with positive temperature coefficient of resistance (PTCR) [1–4] based on ferroelectrics–semiconductors are of particular interest. These materials are characterized by the presence of semiconductor cores and dielectric boundaries of ceramic grains. This effect is observed in donor-doped barium titanate based solid solutions and is characterized by a significant increase in resistance above the phase transition temperature 120 °C [5,6]. In order to shift the PTCR region to higher temperatures, a small amount of lead titanate is added to barium titanate. With increase in lead titanate

concentration in  $(1-x)(\text{Ba},\text{Y})\text{TiO}_3-x\text{PbTiO}_3$  system, the phase transition temperature increases from 120 ( $x=0$ ) to 490 °C ( $x=1$ ) [7,8]. However, the use of lead-containing materials is restricted in the European Union [9]. Therefore, it is urgent to develop lead-free PTCR ferroelectric materials with high Curie temperatures above 120 °C. Some of the most promising materials are  $(1-x)\text{BaTiO}_3-x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ) solid solutions [10–12]. Substitution of sodium/potassium and bismuth ions for barium ions in  $(1-x)\text{BaTiO}_3-x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $\text{M} = \text{Na}, \text{K}$ ) leads to an increase in Curie temperature [13]. It was found that in  $(1-x)\text{BaTiO}_3-x\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  solid solutions where  $x=0.1, 0.2$ , there are three components of the ceramic grains which differ in electrical properties: semiconductor core, insulating grain boundary, and outer layer region [14]. In contrast to previous data, the authors of Ref. [15] claimed

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that there are two electrically heterogeneous regions in ceramic grain in  $(1-x)\text{BaTiO}_3-x\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ : a semiconductor core and a dielectric grain boundary. In this case, the highest resistance was observed at the boundary between grains due to the higher density of acceptor levels at these points.

$(1-x)\text{BaTiO}_3-x\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $0.05 \leq x \leq 0.1$ ) PTCR materials were sintered in inert nitrogen atmosphere in order to provide semiconductor properties [16]. It was found that semiconductor properties in  $(1-x)\text{BaTiO}_3-x\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $x=0.05$ ) are due to the partial reduction of titanium ion ( $\text{Ti}^{4+} \rightarrow \text{Ti}^{3+}$ ) during sintering of ceramics in reducing atmosphere [17,18].

There is no literature data about the existence of individual compound of lithium–bismuth titanate  $\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ . The authors of Ref. [19] showed the possibility of formation of niobium-containing PTCR  $(1-x)\text{Ba}(\text{Ti},\text{Nb})\text{O}_3-x\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $0 \leq x \leq 0.03$ ) solid solutions. It was found that increasing the concentration  $x$  leads to an increase in resistance and Curie temperature from 120 to 150 °C in the range  $0 \leq x \leq 0.03$  [19].

However, today many questions associated with these systems remain unclear. In particular, there is no information about the possibility of obtaining undoped PTCR  $(1-x)\text{BaTiO}_3-x\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  materials. There is no comparative analysis of the PTCR characteristics of lead-containing and lead-free materials.

The sintering temperatures of  $(1-x)\text{BaTiO}_3-x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $\text{M}=\text{Li}, \text{Na}, \text{K}$ ) solid solutions are higher than 1300 °C, and considerable losses of alkali metals and bismuth are observed, which lower the Curie temperature of solid solutions [20,21]. Compared to the traditional solid state reaction technique, oxalate coprecipitation method can significantly reduce the sintering temperature of  $\text{BaTiO}_3$  powders [22–25] and metal losses in  $(1-x)\text{BaTiO}_3-x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $\text{M}=\text{Li}, \text{Na}, \text{K}$ ) solid solutions.

In this paper, the properties of  $(1-x)\text{BaTiO}_3-x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $\text{M}=\text{Li}, \text{Na}, \text{K}$ ) prepared by the solid state reaction technique with  $\text{BaTiO}_3$  pre-synthesized by oxalate method are presented. The effect of different synthesis methods on the microstructure and electrical properties is discussed. A comparative analysis of PTCR characteristics for lead-containing and lead-free solid solutions is presented.

## 2 Experimental procedures

The starting chemicals used in the preparation of

$\text{BaTiO}_3$  by oxalate method were reagent grade  $\text{TiCl}_4$ ,  $\text{BaCl}_2$ , and  $\text{H}_2\text{C}_2\text{O}_4$ . Aqueous  $\text{BaCl}_2$  and  $\text{TiCl}_4$  solutions were mixed, and then oxalic acid was added to the resultant solution with constant stirring. The solution was heated to boiling and left to stand for 2 h. The resultant white  $\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$  precipitate was filtered off and thoroughly washed with distilled water. The precipitate was dried at 150 °C for 2 h.  $\text{BaTiO}_3$  was prepared by calcining  $\text{BaTiO}(\text{C}_2\text{O}_4)_2$  at above 800 °C for 2 h. In the second step of the synthesis process, extra-pure  $\text{M}_2\text{CO}_3$  ( $\text{M}=\text{Li}, \text{Na}, \text{K}$ ),  $\text{Bi}_2\text{O}_3$ , and  $\text{TiO}_2$  were added to  $\text{BaTiO}_3$  in order to obtain solid solutions (semi-oxalate (SO) method). The powders were mixed by ball milling with ethanol for 4 h. The resultant mixtures were fired for 4 h at temperatures from 800 to 870 °C.

To assess the effect of the synthesis procedure on the electrical properties of  $(1-x)\text{BaTiO}_3-x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $\text{M}=\text{Li}, \text{Na}, \text{K}$ ), the solid solutions were also prepared by solid state reaction technique (SS method) using extra-pure  $\text{M}_2\text{CO}_3$  ( $\text{M}=\text{Li}, \text{Na}, \text{K}$ ),  $\text{Bi}_2\text{O}_3$ , and  $\text{TiO}_2$  and  $\text{BaCO}_3$  as starting reagents. The powders were mixed by ball milling with ethanol for 4 h. The resultant mixtures were dried at 100–120 °C, passed through a nylon sieve, and then fired for 4 h at temperatures from 900 to 1100 °C.

The particle size distributions and the average particle size ( $d_{50}$ ) for all powders were determined using a laser light scattering particle sizer (Mastersizer 2000, Malvern Instruments, UK). The testing scope was 0.02–2000 µm, the dispersant was deionized water, and the particle and dispersant refraction indexes were 2.41 and 1.33 respectively. The gas sorption/desorption measurements were performed using an automated micropore gas analyzer Autosorb-3 (Quantachrome Instruments, Boyton Beach, FL, USA) with an automated gas sorption data acquisition and reduction software, AsiQWin. The  $\text{N}_2$  desorption isotherms collected at 77.4 K were analyzed using the Brunauer–Emmet–Teller (BET) equation to determine the specific surface area (SSA) of the produced ceramics. The micropores ( $r_{\text{pore}} < 2 \text{ nm}$ ) and mesopores ( $2 \text{ nm} \leq r_{\text{pore}} \leq 50 \text{ nm}$ ) of powder samples were characterized by the Saito–Foley (SF) and Barret–Joyner–Halenda (BJH) methods, respectively. The morphology of particles and macropores ( $r_{\text{pore}} > 50 \text{ nm}$ ) was studied by transmission electron microscope (TEM) JEOL JEM-1400.

After firing, the powders prepared by both methods were pressed at 150 MPa in the presence of polyvinyl

alcohol into pellets (10 mm in diameter and 2 mm in thickness), which were sintered in a flowing  $N_2 + H_2$  (99.5:0.5) gas mixture in the temperature range 1100–1310 °C and then oxidized in air at 700 °C. The heating/cooling rate was 300 °C/h in all of our preparations. Electrical contacts with the surface of the samples thus prepared were made by firing an aluminum paste.

The lithium, sodium, and potassium contents of the ceramic samples were determined by flame photometry on a Pye Unicam SP9 spectrophotometer using an air-acetylene flame. Bismuth was determined by trilon titration with xylenol orange as an indicator.

The phase composition of the samples was determined by X-ray diffraction (XRD) on a DRON 4-07 powder diffractometer (Cu  $K\alpha$  radiation, 40 kV, 20 mA). Structural parameters were evaluated by the Rietveld full profile analysis method. Intensity data were collected in the angular range  $2\theta = 10^\circ$ – $150^\circ$  with a step size  $\Delta 2\theta = 0.02^\circ$  and a counting time of 10 s per data point. As external standards, we used  $SiO_2$  ( $2\theta$  calibration) and  $Al_2O_3$  (NIST SRM 1976 intensity standard).

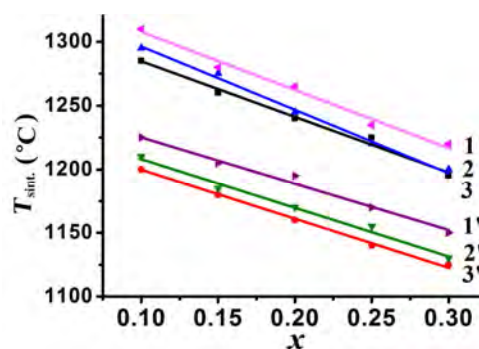
The electrical resistivity of our samples was measured as a function of temperature in the range 20 to 500 °C. In impedance measurements, we used a Solartron Analytical 1260 impedance/gain phase analyzer in the range 1 Hz to 1 MHz. The components of the equivalent electrical circuit were identified using ZView software (Scribner Associates).

### 3 Results and discussion

We have previously shown that the formation of solid solutions by solid state reaction technique occurs during the interaction of the two phases  $BaTiO_3$  and  $M_{0.5}Bi_{0.5}TiO_3$  ( $M = Li, Na, K$ ) [26]. Therefore, in order to reduce the synthesis temperature, we synthesize these materials by solid state reaction technique with the use of barium titanate pre-synthesized by oxalate method. The use of the proposed method makes it possible to

simplify the synthesis technology and to reduce the synthesis and sintering temperature of ceramics. The number of intermediate phases is also decreased in comparison with classical solid state reaction technique.

Figure 1 demonstrates that the powders prepared by SO method can be sintered in the temperature range 1100–1220 °C, whereas the powders prepared by SS method can be sintered in the range 1210–1310 °C. The temperature at which the relative density of ceramic samples is 85%–96% is used as the sintering temperature. The sintering temperature of ceramics depends on the driving force, which in the case of solid state sintering is the reduction in the surface free energy. The free energy is interconnected with the grain diameter and pore radius [27]. Powders synthesized by both SS and SO methods have unimodal (single peaked) distribution of grain size (Fig. 2(a)). The average grain size  $d_{50}$  for powders prepared by SO method is slightly larger as compared with that for SS method (Table 1). Therefore, the lower sintering temperature of the ceramic sintered from powders synthesized by SO method cannot be caused by a change in the grain size. Note that the largest and the smallest differences in the characteristics of powders synthesized by various methods are observed in samples containing Li and K respectively; Li is the most volatile and K the least volatile element among the studied alkali elements.

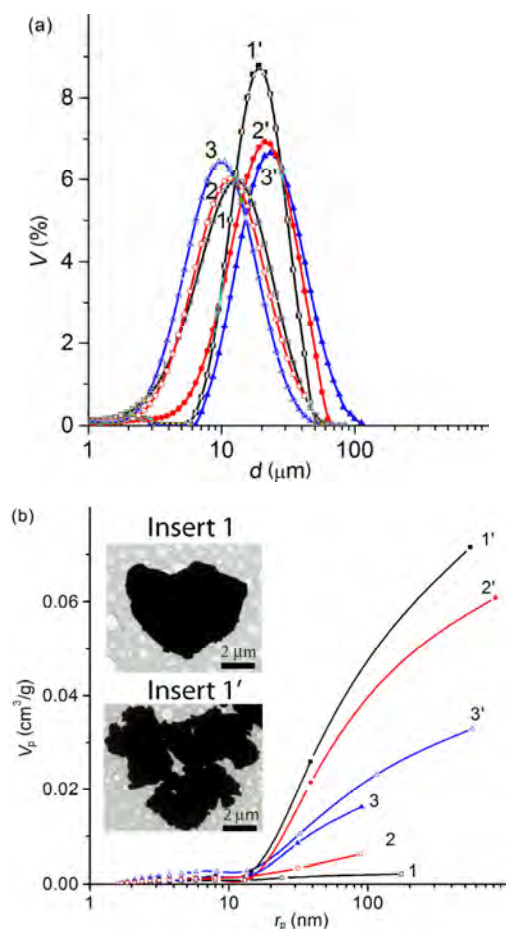


**Fig. 1** Sintering temperature as a function of  $x$  for  $(1-x)BaTiO_3-xM_{0.5}Bi_{0.5}TiO_3$  ( $M = Li$  (1, 1'),  $Na$  (2, 2'),  $K$  (3, 3')) solid solutions prepared by solid state reaction technique (1, 2, 3) and solid state reaction technique with pre-synthesized  $BaTiO_3$  (1', 2', 3').

**Table 1** Characteristics of powders of barium titanate based solid solutions

No.	Chemical composition	Synthesis	Particle size $d_{50}$ ( $\mu m$ )	BET surface area ( $m^2/g$ )	Total pore volume ( $10^{-3} cm^3/g$ )	Average pore radius (nm)
1	$0.9BaTiO_3-0.1Li_{0.5}Bi_{0.5}TiO_3$	SS	11.25	0.8477	2.328	5.491
2	$0.9BaTiO_3-0.1Na_{0.5}Bi_{0.5}TiO_3$	SS	11.12	1.414	6.825	9.657
3	$0.9BaTiO_3-0.1K_{0.5}Bi_{0.5}TiO_3$	SS	9.166	1.822	19.43	21.33
1'	$0.9BaTiO_3-0.1Li_{0.5}Bi_{0.5}TiO_3$	SO	17.76	1.344	72.07	107.3
2'	$0.9BaTiO_3-0.1Na_{0.5}Bi_{0.5}TiO_3$	SO	18.92	0.8932	61.26	137.2
3'	$0.9BaTiO_3-0.1K_{0.5}Bi_{0.5}TiO_3$	SO	21.62	0.2387	23.62	19.79

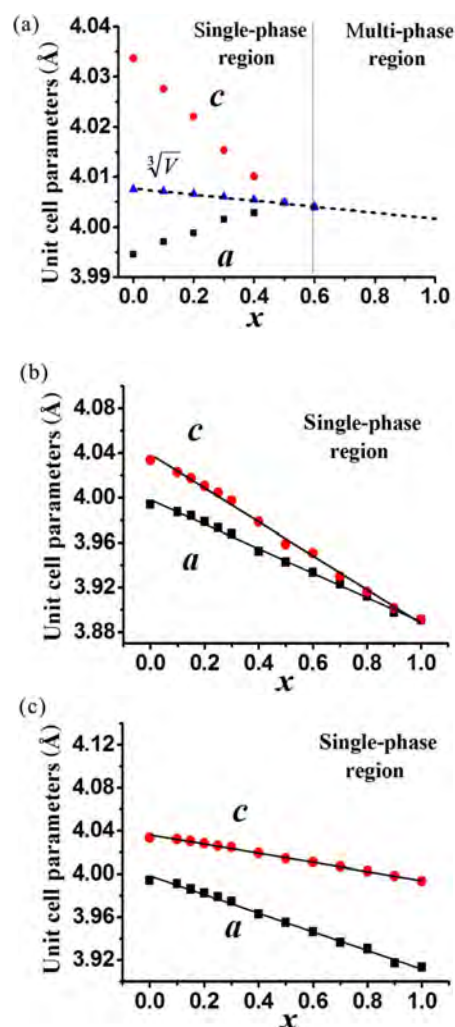
In all the samples studied, there are macropores ( $r_{\text{pore}} > 50$  nm), where capillary condensation does not occur. As a result, hysteresis is absent in adsorption isotherms at  $P/P_0 \approx 1$ , where  $P$  is partial vapour pressure of nitrogen in equilibrium with the surface at 77.4 K, and  $P_0$  is saturated pressure of nitrogen. TEM shows significant porosity of SO samples compared to SS (see inserts 1 and 1' in Fig. 2(b)). Micropores ( $r_{\text{pore}} < 2$  nm) make a small contribution to porosity in all samples (Fig. 2(b)). The distribution of mesopores ( $2 \text{ nm} \leq r_{\text{pore}} \leq 50$  nm) is significantly different for the samples synthesized by the SS and SO methods. Figure 2(b) shows that the pore volume is larger for all the samples synthesized by SO method. As a result, the total pore volume is also significantly larger: for  $0.9\text{BaTiO}_3\text{--}0.1\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  sample it is 35 times larger; for  $0.9\text{BaTiO}_3\text{--}0.1\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  sample it is an order of magnitude larger (see Table 1). Therefore, the high porosity of powders synthesized by SO method reduces the sintering temperature of ceramics based on them.



**Fig. 2** (a) Dependence of volume percentage of particles on their diameter and (b) dependence of pore volume on their radius. Chemical compositions of samples are shown in Table 1. Insert: TEM images of  $0.9\text{BaTiO}_3\text{--}0.1\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  sample synthesized by SS (1) and SO (1') methods.

In materials  $(1-x)\text{BaTiO}_3\text{--}x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $\text{M}=\text{Li}, \text{Na}, \text{K}$ ) with  $x=0.1, 0.2, 0.3$  prepared by the SS method, the bismuth loss is shown to be insignificant (0.8, 2.0, 2.5 wt%), whereas the lithium loss is 9.4, 15.2, 22.7 wt%, sodium loss is 12.2, 19.6, 26.4 wt%, and potassium loss is 16.1, 22.4, 28.5 wt%, respectively. At the same time, the materials prepared by SO method lose 0.4, 1.7, 2.0 wt% bismuth, 5.4, 7.6, 12.9 wt% lithium, 7.6, 10.4, 15.6 wt% sodium, and 9.4, 12.6, 17.0 wt% potassium, respectively. The lower loss of the volatile components during sintering of the powders prepared by the SO method is attributed to the fact that their sintering temperatures are lower (Fig. 1).

Figure 3 shows that  $(1-x)\text{BaTiO}_3\text{--}x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $\text{M}=\text{Na}, \text{K}$ ) solid solutions are formed in the entire concentration range  $0 \leq x \leq 1$ , whereas in the  $(1-x)\text{BaTiO}_3\text{--}x\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  system, solid solutions are



**Fig. 3** Dependence of the unit cell parameters of  $(1-x)\text{BaTiO}_3\text{--}x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $\text{M}=\text{(a) Li, (b) Na, (c) K}$ ) solid solutions on  $x$ .

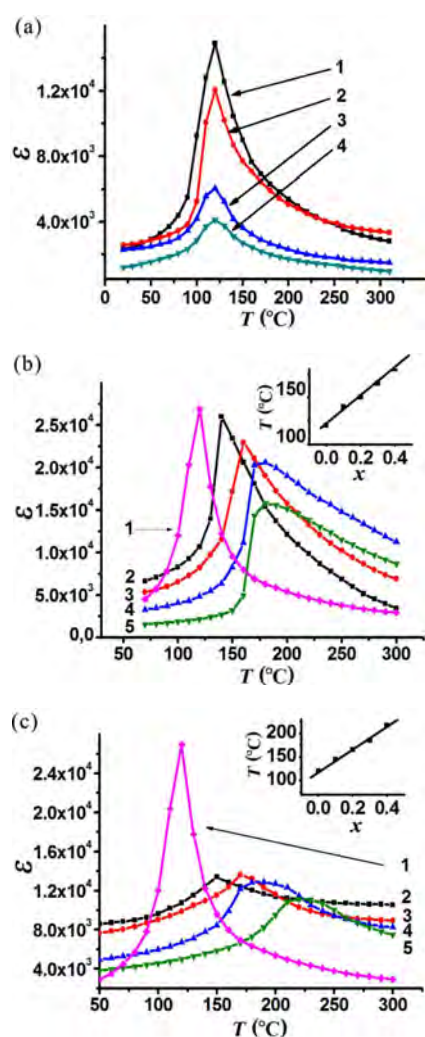


formed in the limited concentration range  $0 \leq x \leq 0.6$ . Above  $x=0.6$ , a multi-phase product with additional phases  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ,  $\text{Bi}_2\text{Ti}_2\text{O}_7$  is formed. This means that at normal conditions, lithium bismuth titanate as individual compound is unstable. Using linear extrapolation of the concentration dependence of unit cell volume, the parameters of the unit cell of the  $(1-x)\text{BaTiO}_3-x\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  solid solution with  $x=1$  have been determined. It is found that the cubic lattice parameter for individual  $\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  is  $4.0019(8) \text{ \AA}$ .

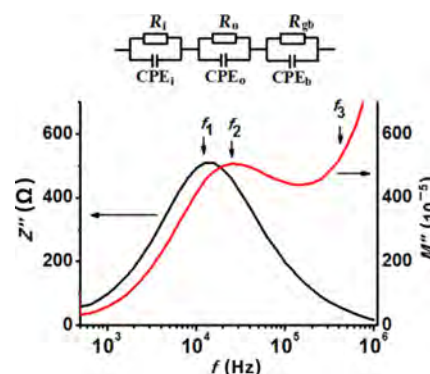
It is found that Curie temperature of materials prepared by the SS method are  $5\text{--}7^\circ\text{C}$  lower than that of materials prepared by the SO method. This can be explained by smaller loss of volatile bismuth and alkali metal components in materials prepared by the

SO method in comparison with materials prepared by the SS method. In Fig. 4, the phase transition temperature of solid solutions prepared by the SO method corresponds to the maximum of permittivity on the plot of  $\varepsilon(T)$ . As can be seen, with increase in  $x$  value, Curie temperature in  $(1-x)\text{BaTiO}_3-x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $\text{M}=\text{Na}, \text{K}$ ) solid solutions increases, whereas in  $(1-x)\text{BaTiO}_3-x\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  solid solutions Curie temperature is constant and is  $120^\circ\text{C}$ . This is due to the fact that sodium–bismuth titanate  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $T_C=320^\circ\text{C}$ ) and potassium–bismuth titanate  $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $T_C=380^\circ\text{C}$ ) are ferroelectrics with higher Curie temperatures than  $\text{BaTiO}_3$ , whereas  $\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  is perovskite with cubic symmetry and is non-ferroelectric. Increase in  $\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  concentration in solid solutions  $(1-x)\text{BaTiO}_3-x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $\text{M}=\text{Na}, \text{K}$ ) leads to blurring of dielectric constant maximum, which indicates the relaxor nature of these compounds. The relaxor nature of the solid solutions may be due to internal stresses in lattice arising from the fact that the alkali metal ions  $\text{M}^+$ ,  $\text{Ba}^{2+}$ , and  $\text{Bi}^{3+}$ , which strongly differ in radius, are statistically distributed in the A-sublattice of perovskite.

Using complex impedance data and a model of PTCR for ceramic grains proposed by Sinclair and West [28,29], it is found that the grain in  $(1-x)\text{BaTiO}_3-x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $\text{M}=\text{Li}, \text{Na}, \text{K}$ ) ceramics consists of several electrically heterogeneous regions (Fig. 5): semiconducting core, dielectric outer layer, and shell. The presence of electrically heterogeneous regions manifests itself by 3 maximums on the plots of imaginary electric impedance ( $Z''$ ) and imaginary electric modulus ( $M''$ ), whose positions shift in different directions with temperature, as described in detail in Ref. [30].



**Fig. 4** Temperature dependence of the permittivity of  $(1-x)\text{BaTiO}_3-x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $\text{M}=(\text{a}) \text{Li}, (\text{b}) \text{Na}, (\text{c}) \text{K}$ ) solid solutions:  $x=0$  (1);  $0.1$  (2);  $0.2$  (3);  $0.3$  (4);  $0.4$  (5).  $f=100 \text{ kHz}$ . Insets: Curie temperature as a function of  $x$  for the  $(1-x)\text{BaTiO}_3-x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $\text{M}=(\text{b}) \text{Na}, (\text{c}) \text{K}$ ) ceramics.

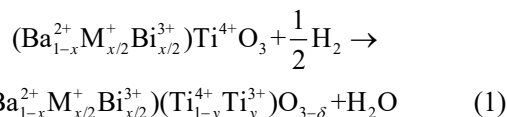


**Fig. 5** Frequency dependence of imaginary electric impedance  $Z''$  and imaginary electric modulus  $M''$  of  $0.9\text{BaTiO}_3-0.1\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  sample synthesized by SO method. Equivalent electrical scheme is shown above.

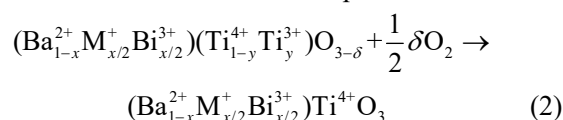
Figure 6 shows that the grain interior resistance varies a little in the investigated temperature range (Fig. 6, curve 1). At the same time, the resistance of the outer layer region and the grain boundary increases sharply in the temperature range above the Curie temperature (Fig. 6, curves 2 and 3). This indicates that the outer layer region and the grain boundary make a contribution to the PTCR effect in  $(1-x)\text{BaTiO}_3-x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $M=\text{Li, Na, K}$ ) solid solutions.

Using scanning electron microscopy, it is found that with increasing  $x$  the grain size of  $(1-x)\text{BaTiO}_3-x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $M=\text{Li, Na, K}$ ) ceramics prepared by the SS and SO methods decreases due to the segregation of bismuth and alkali metals in the outer layer region. In addition, ceramics prepared by the SO method consist

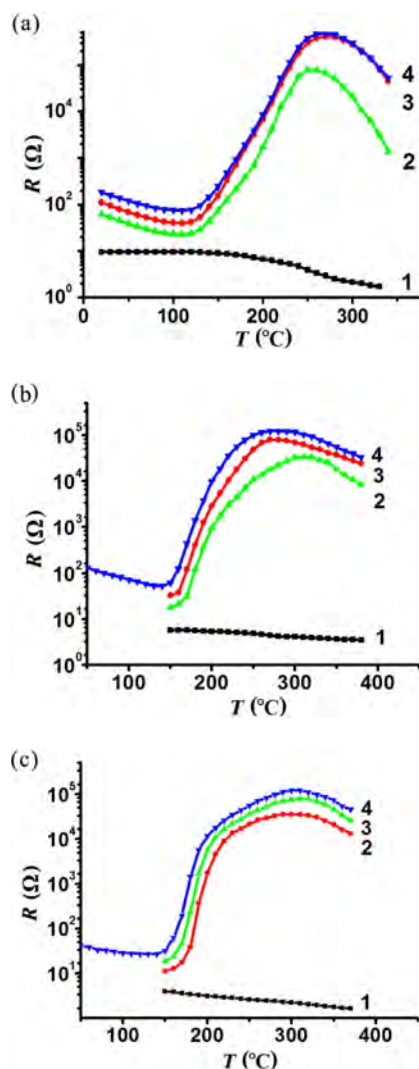
of larger grains in comparison with the SS method. This can be attributed to the higher reactivity of the barium titanate powders prepared by the oxalate method and higher mass transport rate during sintering, which contribute to grain growth. Using energy dispersive X-ray analysis, the surface of the  $(1-x)\text{BaTiO}_3-x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $M=\text{Li, Na, K}$ ) ceramics is investigated (Fig. 7). Distribution maps of the basic elements (Ba and Ti) show no significant difference in their concentration in the shell and core of ceramic grains. Oxygen concentration is shown to be higher in grain shell than in grain core, as evidenced by the presence of lighter areas in Fig. 7(b). This is due to the fact that the oxygen content of grain shell is close to stoichiometric one while the internal parts of grain core contain a considerable number of oxygen vacancies. Based on the data on the distribution of oxygen, the following mechanism of the PTCR effect for  $(1-x)\text{BaTiO}_3-x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $M=\text{Li, Na, K}$ ) solid solutions can be suggested (Eqs. (1) and (2)). The PTCR effect of the  $(1-x)\text{BaTiO}_3-x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $M=\text{Li, Na, K}$ ) materials is caused by the presence of semiconductor properties in grain core and dielectric properties in grain shell. Semiconductor properties appear in the materials on sintering in a reducing atmosphere. Partial reduction of titanium ion gives rise to semiconductor properties:



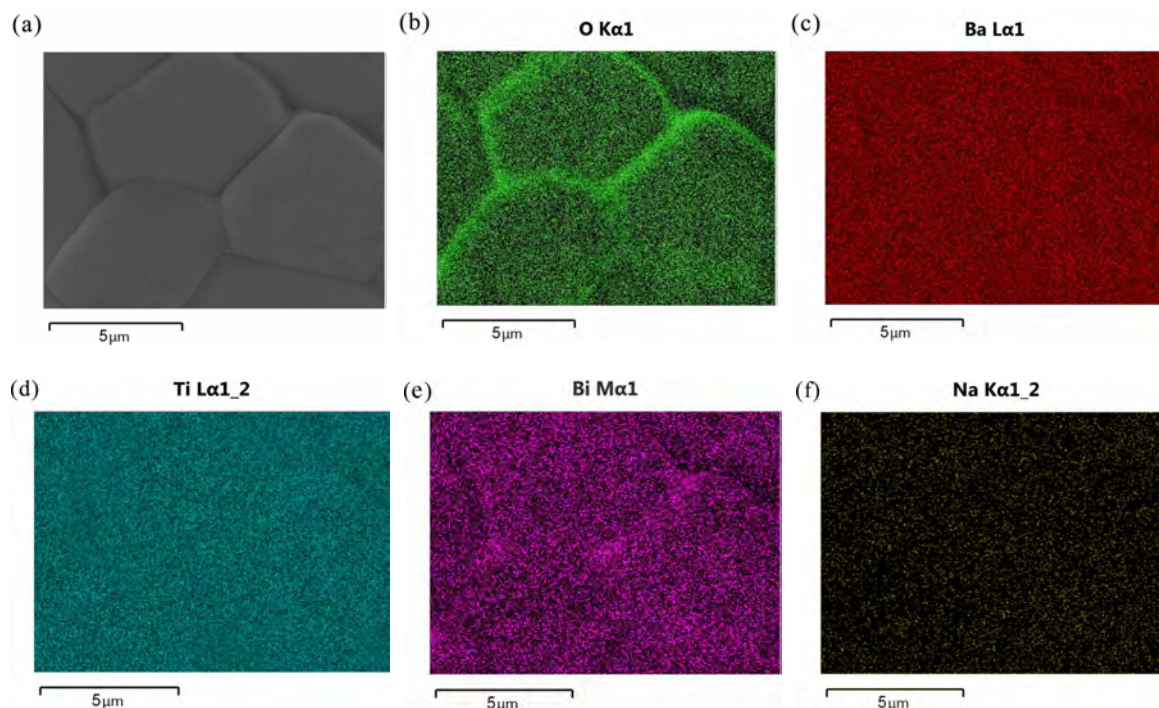
Dielectric properties in the grain shell are formed by additional oxidation of reduced samples in air:



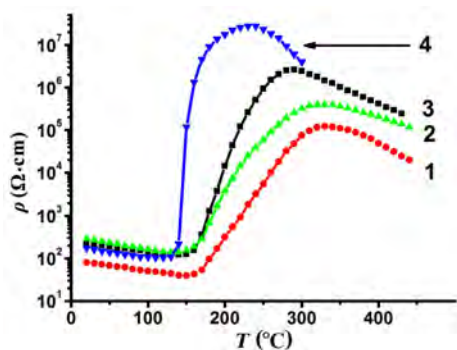
Plots of temperature against the resistance of samples of the  $(1-x)\text{BaTiO}_3-x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $M=\text{Li, Na, K}$ ) system, synthesized by the SO process, and  $(1-x)(\text{Ba,Y})\text{TiO}_3-x\text{PbTiO}_3$  are shown in Fig. 8. The minimum value of resistance for solid solutions increases in the order Li–Na–K while the maximum resistance value decreases. Growth of the minimum resistance can be attributed to a decrease in the average grain size of ceramic samples in the order Li–Na–K. Li-containing samples have the smallest temperature range of PTCR effect ( $\Delta T=70^\circ\text{C}$ ), while lead-containing and potassium-containing samples are characterized by a wide temperature range ( $\Delta T=170^\circ\text{C}$ ).



**Fig. 6** Grain core (1), outer layer (2), grain shell (3), and total resistance (4) as a function of temperature for (a)  $\text{Ba}_{0.7}\text{Li}_{0.15}\text{Bi}_{0.15}\text{TiO}_3$ , (b)  $\text{Ba}_{0.8}\text{Na}_{0.1}\text{Bi}_{0.1}\text{TiO}_3$ , and (c)  $\text{Ba}_{0.9}\text{K}_{0.05}\text{Bi}_{0.05}\text{TiO}_3$ .



**Fig. 7** (a) Microstructure and distribution maps of (b) oxygen, (c) barium, (d) titanium, (e) bismuth, and (f) sodium in  $\text{Ba}_{0.8}\text{Na}_{0.1}\text{Bi}_{0.1}\text{TiO}_3$  ceramic.



**Fig. 8** Temperature dependence of resistance for ceramic samples:  $0.925(\text{Ba},\text{Y})\text{TiO}_3\text{--}0.075\text{PbTiO}_3$  (1),  $0.9\text{BaTiO}_3\text{--}0.1\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  (2),  $0.85\text{BaTiO}_3\text{--}0.15\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  (3), and  $0.9\text{BaTiO}_3\text{--}0.1\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  (4).

The  $T_C$  of the Li-containing sample is relatively low ( $\sim 120^\circ\text{C}$ ), though the value of  $\rho_{\max}/\rho_{\min}$  of this sample is rather high. Figure 8 and Table 2 show that among high- $T$  ( $T > 150^\circ\text{C}$ ) PTCR materials investigated, sodium-containing  $(1-x)\text{BaTiO}_3\text{--}x\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  samples have the best PTCR

characteristics (maximum  $\rho_{\max}/\rho_{\min}$  ratio and maximum resistance  $\rho_{\max}$ ).

## 4 Conclusions

Materials prepared by the SO method are characterized by lower sintering temperatures, bismuth and alkali metal losses, and higher Curie temperatures in comparison with materials prepared by the SS method. With increase in  $x$  value, phase transition temperature in  $(1-x)\text{BaTiO}_3\text{--}x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $\text{M} = \text{Na}, \text{K}$ ) solid solutions increases, whereas in the  $(1-x)\text{BaTiO}_3\text{--}x\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  system it is constant and is  $120^\circ\text{C}$ . It is shown that the outer layer region and the grain boundary make a contribution to the PTCR effect in  $(1-x)\text{BaTiO}_3\text{--}x\text{M}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ) solid solutions. PTCR effect in lead-free materials is caused by the presence of semiconductor properties in grain core, which contains a considerable number of oxygen

**Table 2** Characteristics of PTCR effect in barium titanate based solid solutions

Chemical composition	$T_C$ ( $^\circ\text{C}$ )	$T$ of PTCR ( $^\circ\text{C}$ )	$\rho_{\max}/\rho_{\min}$	$\rho_{\min}$ ( $\Omega\cdot\text{cm}$ )	$\rho_{\max}$ ( $\Omega\cdot\text{cm}$ )
$0.925(\text{Ba},\text{Y})\text{TiO}_3\text{--}0.075\text{PbTiO}_3$	150	150–320	$2.9 \times 10^3$	38	$1.1 \times 10^5$
$0.9\text{BaTiO}_3\text{--}0.1\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$	120	120–190	$2.5 \times 10^5$	108	$2.7 \times 10^7$
$0.85\text{BaTiO}_3\text{--}0.15\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$	150	150–290	$2.0 \times 10^4$	127	$2.6 \times 10^6$
$0.9\text{BaTiO}_3\text{--}0.1\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$	150	150–320	$2.8 \times 10^3$	140	$4.0 \times 10^5$



vacancies, and dielectric properties in grain shell, where oxygen content is close to stoichiometric one. A comparative analysis of lead-containing and lead-free solid solutions shows that among high- $T$  ( $T > 150\text{ }^{\circ}\text{C}$ ) PTCR materials investigated, sodium-containing  $(1-x)\text{BaTiO}_3-x\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  samples have the best PTCR characteristics (maximum  $\rho_{\text{max}}/\rho_{\text{min}}$  ratio and maximum resistance  $\rho_{\text{max}}$ ).

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