Bulk and conductive mode investigations of Pb free PTCR ceramics with high switch temperature

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Lead free positive temperature coefficient of resistivity (PTCR) thermistors with switching temperature T_S of 155°C were synthesized from 0.95BaTiO₃–0.05(Bi_{1/2}K_{1/2})TiO₃ solid solution for high temperature applications, utilizing the conventional ceramic fabrication technique, which involved sintering ceramics in N₂ flow followed by air annealing. Addition of sintering aid AST (Al₂O₃:SiO₂:TiO₂ with 4:9:3 molar ratio) and Mn improved the bulk PTCR response. Impedance spectroscopy analysis confirmed the bulk T_S and revealed a third ferroelectric resistance-capacitance (RC) element along with a semiconducting grain and PTCR active ferroelectric grain boundary. The investigation of local electrical activity adopting hot-stage conductive mode microscopy revealed the existence of type-I grain boundary-electron beam induced current (GB-EBIC) contrast pertinent to the presence of negatively charged interfaces neighbored with compensating positive space-charge layers typical of double Schottky barrier within the Pb free PTCR system.

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1. Introduction

PTCR (positive temperature coefficient of resistivity) thermistors based on polycrystalline n-type BaTiO₃ (BT) show a large, reproducible increase in grain boundary (GB) resistivity at temperatures just above Curie temperature $T_C \approx 130^\circ\text{C}$.^{1),2)} This characteristic is exploited in applications, including current surge protection devices, self-regulating heater elements and temperature/current sensors.³⁾ For high temperature applications ($>130^\circ\text{C}$) an isovalent A-site substitution of Pb²⁺ (added as PbTiO₃ with $T_C = 490^\circ\text{C}$) for Ba²⁺ cation is the conventional practice to achieve high T_C PTCR ceramics.⁴⁾ However, lead poisoning has become common, to such an extent world-wide that it is considered the most common of health related occupational and environmental hazards.⁵⁾ Therefore Pb bearing components should be prohibited in manufacturing of electronic devices. Recently, semiconducting $(1-x)\text{BaTiO}_3$ – $x(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ abbreviated as BBNT100 x [where T_C of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ or BNT is 320°C] with PTC switch temperature (T_S)⁶⁾ $> 130^\circ\text{C}$ has been proposed as a promising candidate material for Pb free PTCR devices for high temperature applications.^{7)–9)} Therefore, incorporation of high T_C ferroelectric Perovskite BNT as an end member to low T_C BT has been proven to be an effective way of shifting T_S towards higher temperature. The resistivity jump above T_C is associated with development of potential barrier, formed from a 2D layer of adsorbed oxygen^{1),2)} or segregated acceptor ions (e.g. V, Cr, Fe, Mn)¹⁰⁾ at the grain boundaries (GBs). Recent studies have reported variability in the nature of GB electrical structure in PTC thermistors through local R-T¹¹⁾ and conductive mode (CM) studies.¹²⁾ Such variations were

linked with inhomogeneous dopant segregation and differences in misorientations¹³⁾ at the interfaces.

CM microscopy is a mode of operation used to study the local electrical activity at GBs of polycrystalline semiconductors and electroceramics complementing more established techniques like impedance spectroscopy (IS). Three forms of CM signal-contrasts sensitive to the electrical makeup of the interfaces in electroceramics are: 1) Resistive contrast arising from specimen acting as a current divider for e-beam to travel to earth and any non-linear resistance variation, giving rise to a signal step at the resistive barrier.¹⁴⁾ 2) β -conductivity contrast arising from localized injection of charge carriers by e-beam, resulting in enhanced local conductivity under a voltage bias.¹⁵⁾ 3) Electron beam induced current (EBIC) contrast arising from separation and collection of beam generated electron-hole pair by the built-in depletion layer field on either side of a charged GB interface.¹²⁾ CM microscopic technique has previously been used for observing the GB electrical activities in Pb containing BT based commercial PTC thermistors^{12),14),15)} and ZnO varistors.¹⁶⁾

In the present contribution, we reported the bulk low field electrical properties of conventionally synthesized Pb free 0.95BaTiO₃–0.05(Bi_{1/2}K_{1/2})TiO₃ PTCR system (abbreviated as BBKT5) along with an analysis of local electrical structures of individual GBs using the hot stage CM microscopy technique to probe into the origin of bulk averaged PTCR responses of the material.

2. Experimental

The BBKT5 ceramics with 5 mol % (Bi_{1/2}K_{1/2})TiO₃ (abbreviated as BKT) in BT were synthesized by adopting a conventional ceramic fabrication route. BaCO₃, TiO₂ and K₂CO₃ powders with +99.99% purity, Bi₂O₃ with 99.999% purity, 5 mol % of AST (Al₂O₃:SiO₂:TiO₂ with 4:9:3 molar ratio as sintering aid)

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Table 1. Summary of sintering and annealing schedules

Sample specification	Sintering conditions			Air annealing conditions	
	Sintering temperature (°C)	Soaking time (h)	O ₂ concentration (%)	Annealing temperature (°C)	Soaking time (h)
BBKT5	1350	2	0.15	1250	5
BBKT5-Mn	1350	2	0.15	1200	5
BBKT5-AST	1300	2	0.15	1200	5
BBKT5-ASTMn	1300	2	0.15	1200	5
Nb-doped BT	1400	2	0.15	1400	2

and 0.1 wt % MnCO₃ were used as starting raw materials. The powders were ball milled for 10 h in acetone, followed by drying and then calcining at 800 and 1000°C for 2 h in alumina crucible. The calcined powders were re-milled in acetone for 20 h followed by drying and uniaxially pressing into disks of 13 mm diameter and 1 mm thickness at 190 MPa. A series of compositions was prepared with or without Mn and/or AST additions (Table 1). The green samples were sintered at 1300–1350°C for 2 h in N₂ flow and subsequently annealed in air over 1200–1250°C for 5 h. A pure BT based composition BaTi_{0.999}Nb_{0.001}TiO₃ was prepared by sintering in N₂ flow followed by annealing in air, both at 1400°C for 2 h.

Sample densities were measured by Archimedes method using distilled water. Microstructures were observed in SEM (TOPCON, SM-300). For bulk electrical property measurement, In–Ga eutectic alloy electrode was applied to both polished surfaces of the ceramics. Bulk resistivity vs. temperature [$\rho(T)$] was measured from RT to 350°C using a digital resistance meter (ADVANTEST, R8340). IS and Z* measurements were carried out from RT to 250°C over a frequency range 100 Hz–1.5 MHz using impedance analyzer (Agilent HP4194A). The quantitative chemical analysis was carried out using electron probe micro-analyser (SHIMADZU, EPMA-1610). Cross section of BBKT5-ASTMn sample was prepared for CM imaging by cutting and polishing in colloidal Silica. Pairs of Ag/Ti 80 × 80 μm² current collecting electrodes with 20 μm inter electrode spacing were deposited using photolithographic technique. The sample was mounted on a GATAN HC1001 heating stage in SEM (JEOL JSM-6300) and imaged using SE and BSE modes of operations. The CM signals generated by impinging PE beam from sample area in between the electrodes were collected by Tungsten micromanipulator probes and were manipulated to generate CM contrasts.

3. Results and discussions

3.1 Electrical property and microstructure

Figures 1(a)–1(d) depict the bulk $\rho(T)$ responses of BBKT5 based ceramics prepared with/without Mn and/or AST additions. The corresponding detailed processing conditions and electrical properties [room temperature resistivity/ ρ_{RT} , PTCR switching temperature/ T_S ($\approx T_C$),⁶ temperature coefficient of resistivity/ α ⁶ and PTC ratio (ρ_{max}/ρ_{min})] are tabulated in Tables 1 and 2 respectively. BBKT5 ceramic sintered at 1350°C under N₂ flow exhibited 10¹–10² Ω.cm ρ_{RT} with a negligible PTCR anomaly at 155°C. Alike BT based PTC thermistors, as sintered BBKT5, BBKT5-AST and BBKT5-ASTMn ceramics under 0.15% O₂ conc., when annealed in air at 1200–1250°C for 5 h, they exhibited well developed PTCR anomalies with $\rho_{RT} \leq 3.1 \times 10^2$ Ω.cm, $T_S \geq 153^\circ\text{C}$ and $\alpha \geq 8.3\%/^\circ\text{C}$, with BBKT5-ASTMn ceramics having the highest T_S ($=156^\circ\text{C}$), ρ_{max}/ρ_{min} ($\approx 10^{4.5}$) and

Fig. 1. Variations in PTCR characteristics for annealed ceramics with 5 mol % BKT content, specified as (a) BBKT5 (b) BBKT5-AST (c) BBKT5-ASTMn (d) BBKT5-Mn (e) Nb-doped BT.

Table 2. Variations in ρ_{RT} , T_S , α , ρ_{max}/ρ_{min} and grain size of annealed samples

Sample specification	ρ_{RT} (Ω.cm)	T_S (°C)	α (%/°C)	ρ_{max}/ρ_{min}	Grain size (μm)
BBKT5	3.1×10^1	153	9.1	$10^{2.50}$	49.2 ± 18.0
BBKT5-Mn	5.0×10^{12}	—	—	$10^{0.50}$	—
BBKT5-AST	8.0×10^1	155	8.3	$10^{3.00}$	39.0 ± 10.9
BBKT5-ASTMn	3.1×10^2	156	10.3	$10^{4.50}$	19.8 ± 5.6
Nb-doped BT	3.3×10^2	131	5.6	$10^{1.75}$	—

α ($=10.3\%/^\circ\text{C}$) values. In contrast, Nb-doped BT [Fig. 1(e)] exhibited a PTCR anomaly at a lower T_S ($=131^\circ\text{C}$) with a lower α ($=5.1\%/^\circ\text{C}$) value. Following Nikahara and Murakami¹⁷⁾ the observed reduction in ρ_{RT} of insulating BBKT5-Mn approximately by 10 orders of magnitude to 3.1×10^2 Ω.cm due to addition of AST sintering aid can be attributed to preferential segregation of trap forming Mn at the GBs from a homogeneously distributed state. T_S has shifted by 22, 24 and 25°C towards higher temperatures in comparison to that of Nb-doped BT for BBKT5, BBKT5-AST and BBKT5-ASTMn respectively. In our previous study,¹⁸⁾ as sintered BBKT5 ceramic was found to remain as single phase and exhibited a tetragonal symmetry with perovskite structure with a -axis reduced by 0.08% from that of pure BT, indicating that 5 mol % BKT forms a solid solution with BT and explains the observed shift in T_S with BKT addition.

The microstructures of all BBKT5 based annealed PTCR ceramics in Figs. 2(a)–2(c) exhibit randomly oriented grains with irregular shapes. Inter-granular and triple junction second phases could be observed in both BBKT5-AST and BBKT5-ASTMn

Fig. 2. SEM micrographs of samples (a) BBKT5 (b) BBKT5-AST, (c) BBKT5-ASTMn.

Fig. 3. Temperature dependence of (a) resistance and (b) capacitance of the RC elements of annealed BBKT5-ASTMn PTCR ceramics.

samples. The average grain size has reduced by 21 and 60% respectively with consecutive additions of AST and Mn (Table 2) indicating both acting as grain grown inhibitors. Addition of ASTMn to BBKT5 composition reduced relative density from 93 to 83.2%.

3.2 Complex impedance study

For probing the PTCR responses specific to individual microstructural region, BBKT5-ASTMn ceramic was chosen. **Figure 3** depicts the resistance and capacitance of each RC element obtained from Cole-Cole and combined Z'' and M'' spectroscopic plots¹⁹⁾ respectively over RT-250°C temperature range. In Fig. 3(a), among the observed resistances of GB (R_A), grain core (R_B) and an additional 3rd component (R_C), only the GB component can be found to have significant contribution to the PTCR effect above T_S , whereas, the grain interior remains semiconducting, indirectly indicating that the resistance of GB element originates from a potential barrier. The grain core semiconductivity mostly arises from reduction in Ti^{4+} by $V_O^{\bullet\bullet}$ generated while sintering under N_2 flow as follows:

The third component (R_C), which was not observed below 170°C is believed to be originated from a $V_{Ba}^{\bullet\bullet}$ rich thin shell¹⁹⁾ in between grain core and GB formed during cooling from annealing temperature. Formation of a frozen in $V_{Ba}^{\bullet\bullet}$ rich layer has previously been reported for BBNT system due to a transition from electronic to vacancy compensation mechanism by an excess Bi^{3+} (generated from preferential evaporation of Na over Bi), for more than 1 mol % BNT.²⁰⁾ From our chemical analysis,

the Ba:Bi:K:Ti molar ratios for BBKT5 ceramics sintered in air and in N_2 flow were found to be 0.95:0.020:0.017:1 and 0.95:0.017:0.015:1 respectively, also indicating a preferential evaporation of K over Bi. Capacitance data corresponding to GB (C_A) and shell type region (C_C) depicted in Fig. 3(b) exhibit ferroelectric behavior with similar values. So, a stronger PTCR response of the GB over the grain shell indicates a more prominent trap activity at the GB than $V_{Ba}^{\bullet\bullet}$ at the shell type region. The peak GB capacitance occurs at $160 \pm 10^\circ\text{C}$, which fairly agrees with the T_S value of the corresponding ceramic in Table 2. For the reason that grain possesses lowest R and C values, the corresponding M'' peak can fairly be assumed to fall outside the measured frequency range and no information corresponding to grain core capacitance could be obtained.

3.3 Conductive mode (CM) study

The BBKT5-ASTMn ceramic was chosen to study GB electrical activity for having the strongest PTC effect and hence the most prominent interface electrical activity. **Figure 4** depicts the sample on a Cu hot-stage inside an SEM vacuum chamber along with a series of square electrodes and a pair of contact probes, which collect CM signals generated by e-beam impinging the sample in between electrode pads. The hot-stage BSE images in **Figs. 5(a)** and **5(b)** demonstrate the disappearance of ferroelectric domains inside individual grains as the temperature is raised from 140 to 160°C, indicating the existence of T_C within the temperature range $150 \pm 10^\circ\text{C}$. This agrees well with the T_S value of BBKT5-ASTMn in Table 2. So, for CM study, temperature was raised to above T_C to $T_{\rho_{\max}}$ ($=250^\circ\text{C}$) where GB resistance is maximum [Fig. 3(a)], due to maximization of GB potential barrier, according to the most widely accepted PTCR model.^{1),2),21)}

Fig. 4. Real-time specimen configuration for CM microscopy.

Fig. 5. Hot-stage back scatter electron (BSE) images of BBKT5-ASTMn PTCR ceramic at (a) 140°C, (b) 160°C.

Figure 6(a) is an SE image of a typical area of the ceramic randomly selected for detailed study, which shows inter-granular porosities. The edges of the electrodes are spaced 20 μm apart, which is approximately equal to average grain size. **Figure 6(b)** shows the zero bias CM image of the same area at 250°C under 15 nA beam current. Typical EBIC contrasts can be observed parallel to GBs ('A' and 'B') as bright-dark contrasts which are consistent with it being formed from a back to back interface double Schottky barrier (DSB) layer. Ideally, DSB layer in thermistors is formed from a negatively charged GB plane compensated by positive space charge layers, consisting of opposed electric fields extended into the grains on either side of the interface. As the e-beam rasters across a GB plane, the opposed electric fields cause the EBIC signals generated by electron-hole pair separation to flow firstly in one direction and then in the other. In CM image, this appears as bright-dark contrasts running parallel to GB or as symmetric positive-negative current peaks in EBIC line scan and is known as type-I EBIC contrast.¹⁶⁾ Such contrast is similar to that observed for commercial Pb containing BT based thermistors,¹²⁾ but differs from those observed in ZnO, where internal field generated by crystal anisotropy suppresses EBIC signal generation from one side of the GB at zero bias and are known as type-II EBIC contrast.¹⁶⁾ Under sufficient positive [Fig. 6(c)] or negative [Fig. 6(d)] bias applied across GBs 'A' and 'B' through the electrode pads, a single bright or dark contrast apparently resembling type-II EBIC contrast appears. **Figure 6(e)** depicts the EBIC line scans across GB 'A' along 'XY'. Zero bias produces symmetric +ve and -ve peaks in current profile which is typical for symmetric band bending on either side of the interface. With +0.5 V bias, the current profile shows a single positive current

Fig. 6. (a) SE image of inter-electrode area. (b-d) CM images of the same area at 250°C under the condition of (b) 0 V (c) -0.5 V and (d) +0.5 V, (e) EBIC current line scans along 'XY' showing a change in EBIC profile under different voltage bias conditions, (f) variations in EBIC current with e-beam current at the EBIC active GB.

peak corresponding to bright contrast, whereas a reversal in bias polarity produces a negative current peak corresponding to dark contrast. Under sufficient bias voltage, the barrier in one side of the GB plane reduces to zero due to band-flattening by compensation of space charge field in one side of the interface while leaving a large band bending in the other. Under such flat band condition, charge separating field is lost and EBIC signal from that side disappears leaving only a single EBIC peak. A bias reversal reverses the situation as depicted in insets of Fig. 6(e) for +0.5 V and -0.5 V line scan profiles. This transition from type-I to type-II contrast confirms the existence of back to back DSB layer along GBs of Pb free thermistor and explains the PTCR effects in our sample based on DSB model.²²⁾ A further confirmation of the fact that the observed contrasts in Figs. 6(b)-6(d) correspond to DSB layer is that the contrast reversal with change in bias polarity would be accompanied by a lateral shift equal to the width of e-beam excitation volume (γ)²³⁾ which is approximately 1.38 μm calculated for an accelerating voltage of 20 keV and sample density of 4.99 g/cc. We obtained a peak shift of $\sim 1.4 \mu\text{m}$ in EBIC profile upon contrast reversal [Fig. 6(e)], which is similar to γ value. A linear variation in peak EBIC current (I_{EBIC}) with beam current (I_{beam}) in Fig. 6(f) with an EBIC gain ($I_{\text{EBIC}}/I_{\text{beam}}$) just under unity ($=0.90 \pm 0.05$) also agrees with a previous observation of EBIC gain for type-I contrast in PTC thermistor GB.¹²⁾ In BBKT5-ASTMn ceramics

the EBIC contrast forming charge traps could form from adsorption of atmospheric O_2 at the grain surfaces while annealing, which activates Mn^{2+} at the GBs to higher oxidation states forming deep electron traps with energy depth as high as 1.59 ± 0.01 eV.²²⁾ The absence of any GB-EBIC contrast at 140°C , i.e. below T_C suggests the suppression of Schottky barrier by their interaction with spontaneous polarization charges of the ferroelectric domains in tetragonal phase as predicted by the DSB model.^{2),21)}

4. Summary

In this study, Pb free PTC thermistors with T_S higher than 130°C were processed by using a base composition of 5 mol% BKT in BT. Conventional ceramic processing route was adopted which involved sintering under O_2 conc. $\approx 0.15\%$ followed by air annealing. A maximum T_S , $\rho_{\max}/\rho_{\min}$ and α of 156°C , $10^{4.5}$ and $10.3\%/^\circ\text{C}$ were obtained by a combined addition of 5 mol% AST and 1 wt% $MnCO_3$. AST was believed to reduce ρ_{RT} by segregating Mn at the GBs. IS analysis revealed $V_O^{''}$ rich semi-conducting grain core, $V_{Ba}^{//}$ rich outer grain shell and deep trap rich GB with the most prominent PTCR effect. CM study at 250°C , revealed type-I EBIC contrast at the GB consistent with the existence of charge separating electrostatic barrier formed from Mn traps and confirmed the formation of interface back to back DSB layer. The disappearance of GB-EBIC signals with concurrent appearance of ferroelectric domains below T_C directly supported the surface charge compensation phenomenon by spontaneous polarization, proposed by DSB model.

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