Free Standing Tapes of Donor Doped $BaTiO_3$ for Multilayer Positive Temperature Coefficient Thermistors

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ABSTRACT

A disruptive method of fabricating free-standing tapes of La-doped (BaCaSrPb)TiO_3 thermistors is demonstrated. The greatest advantage is that the free-standing tapes do not require high temperature co-firing of electrodes or reduced environment cofiring - soft oxidation cycle to obtain thermal sensitivity. The approach thus solves the long-standing problem with the ceramic thermistor technology that eluded its compatibility with surface mount technology (SMT) and miniaturization. Stencil printing is employed that can fabricate up to 500 µm thick tapes in a single step, saving huge cost and processing steps for application requiring thicker films. The pastes suitable for free-standing tapes are reported. The method provides a novel route to integrate PTC elements into the chips of passive components and would lead to a massive reduction in cold resistivity when developed in multilayer laminated stacks.

Index Terms — **piezoelectric films, PTC, ceramics, thick films, $BaTiO_3$, thermistor**

1 INTRODUCTION

WITH the recent advances in telecommunication and high-speed electronics the demand for low power consumption, miniaturization and higher performance have become increasingly prominent. Electronic manufactures are adopting surface mount technology (SMT) [1] and interdigital capacitor technology (IDC) for advanced applications in the market. The trend has seen a rapid increase in the annual production of multilayer ceramic capacitor (MLCC) and other passive components in the modern circuitry [1–3]. On the other hand, ceramic thermistors with their huge potential in industrial applications could not be integrated into chip design due to their lack of compatibility with multilayer fabrication.

Donor doped $BaTiO_3$ is one of the smart materials with unique thermo-sensitive electrical properties. $BaTiO_3$ is a ferroelectric insulator at room temperature; however, the materials can be made ferroelectric semiconductor by suitable doping with ions La^{+3}, Sm^{+3}, Ho^{+3} or Nb^{+5}. The semiconducting property in ferroelectric BaTiO3 gives rise to a huge resistivity anomaly at the ferroelectric paraelectric transition temperature with a positive temperature coefficient of resistivity (PTCR) [4–9]. The PTC resistors have found numerous applications in industry like resettable fuses for current surge protection of sensitive electronic components, temperature sensors, time delay circuits and self-regulating heaters with inherent over-temperature protection [10, 11]. The emerging trends in the technology require low room temperature resistivity with tighter control and shorter response time at the curie temperature T_c. Several new approaches, for example, double doping schemes have been proposed to achieve this, however, it is well understood that the cold resistance below its current value cannot be further reduced by only doping or processing methods. Another challenge is the integration of PTC elements into the chips of passive components; this will not only revolutionize electronic circuitry with an onboard surge protection capability but also provides an easy route to tune and reduce resistivity substantially since it creates a parallel electric circuit. This approach, however, requires miniaturization and compatibility with surface mount technology therefore multilayer (ML) PTCR is the future of research and development in the field.

The major hurdle in the technological realization of ML-PTCR is related to the difficulties of achieving the inner metallic electrodes. The electrode material with a minimum contact resistance to the ceramic layer is required to achieve

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ohmic like behavior. Many noble metals e.g. Au, Pt, and Pd are known to form Schottky barriers with semiconducting $BaTiO_3$ and therefore not suitable. It is well established that only metals and their alloys with high oxygen affinity or shallow work function form ohmic-like contacts with $BaTiO_3$ [12–15]. Pure metals and metallic alloys are notorious for becoming oxidized during the essential high temperature (>1350°C) co-firing with the ceramic $BaTiO_3$. The oxidation disrupts their metallic nature as the oxides become highly insulating. Sintering under reducing atmosphere has been suggested as an alternative; however previous studies have shown that $BaTiO_3$ loses its desirable strong nonlinearity in resistivity with temperature in a perfect reducing environment [16]. The problem of these two opposing requirements, (i) the necessity of sintering under reducing atmosphere to achieve ohmic contacts and (ii) the indispensable need of a minimum level of oxygen for PTCR had been a major hurdle in realizing an ML PTCR using screen printing so far. Recently Niimi *et al* [17] have demonstrated BaO-rich $BaTiO_3$ material that can be sintered under a low oxidizing environment. However, in all cases the requirement of a reduced environment for ceramic process and soft-reoxidation to instill the desired PTC effect is essential [18]. Sintering in the reduced environment increases the production cost substantially and oxidation, while metal electrodes are deposited, would degrade them.

Here we report the synthesis, spark plasma sintering of synthesized powders and tape casting of donor doped PTCR $BaTiO_3$ ceramics. We present an alternative route to realize a printable strategy for PTC thermistors. The focus of the present study is the preparation and development of free-standing precursor ceramic tapes of a thickness (0.1–1 mm) that will not require co-firing of electrodes with the ceramic $BaTiO_3$. Tape casting method has been used in the production process of ceramic capacitors, substrates for electronics, piezoelectric devices, and sensors. However, to the best of our knowledge has not been reported for obtaining PTCR with $BaTiO_3$.

The greatest advantage of this approach is the ability to form a laminated structure to build a multilayer PTCR, which would offer up to a 1000-fold reduction in resistance compared to present disc devices of the same volume. This is due to the internal structure of these components with alternating metallic and ceramic layers, electrically equivalent to resistors in parallel. Ohm's law predicts the total resistivity R_M of a multilayer thermistor composed of N active layers as:

$$R_M = \frac{R_T}{N} \quad (1)$$

where R_T is the resistance of the free-standing tape before lamination.

2 MATERIALS AND METHODS

Ceramic powders are the most important ingredient in the PTC tape since the final thick film only consists of ceramics constituent. The powders were prepared via solid-state reactions using mixed carbonates. The stoichiometry ratios of the powders were selected to give curie temperature Tc~130-150°C. La_2O_3 was used as a donor dopant to reduce room temperature resistivity of the mixture. The La^{+3} ions will replace Ba^{+2} on A site of the perovskite $BaTiO_3$ structure at low doping levels (typically ~0.4 atomic %). The main raw ingredients were $BaCO_3$, $SrCO_3$, $CaCO_3$, $PbCO_3$, and TiO_2. The mixed powders were ball milled for 8h in ethanol using yttrium stabilized zirconia balls and calcined in air at 1150°C for 4 hours. The calcined powder was ball milled again for 8h to break the agglomeration. The powders are then sieved with a 90 μm sieve.

The prepared powders of BaTiO3 were sintered in SPS furnace (Dr. Sinter, SPS-515S, SPS Syntex Inc., Kawasaki, Japan). Pellets of average diameter 10±0.05 mm and 2±0.01mm thickness were produced by sintering in a vacuum of 5×10^{-3}MPa and at a temperature of 950°C for 5 min under uniaxial pressure of 50 MPa. A heating rate of 50ºC/min was used and after sintering the electric power supply was switched off and the pressure was slowly released at 700°C. The sintered pellets samples (HAp-pe, SHA-10pe) had a milky gray/brown color.

The requirement for thick films and tape casting is that the paste must have a thixotropic flow, high functional particle loading to achieve high density, low porosity, good homogeneity and long shelf-life. Calcined $BaTiO_3$ powders were taken as the starting material. The powders were sieved in the 90μm sieve and dried in the oven at 100°C for 2h to remove any moisture present. An organic vehicle consisting of toluene/ethanol (ratio: 60/40 weight %) or turpentine oil solvent and phosphate ester or Hypermer KD1-SO (AP) dispersant was prepared by stirring. The hot powder was introduced in the organic vehicle in small amounts while continuously stirring the slurry. The introduction of the hot powder directly from the oven to the solvent is to reduce the interaction time between the powder and the atmosphere which important to control the slip rheology. The mixture was then ball-milled for 24h using 5mm yttrium stabilized zirconium balls. This procedure ensures the well-dispersed suspension of particles. After 24h of ball milling a mixture of polyvinyl butyral (PVB) or ethyl cellulose binder and butyl benzyl phthalate plasticizer respectively was added to the slurry and ball-milled again for another 24 hours to acquire a stable and homogenous paste with a long shelf life and good green mechanical strength and flexibility during drying and handling. The weight percentage composition of the components used in paste making is shown in Table 1. The paste was de-aired and then printed onto sacrificial substrates Cellulose $C_6H_{10}O_5)n$ and Polypropylene substrates $(C_3H_6)n$ for tape casting using Essemtee Fino Semiautomatic Stencil Printer. The green tapes and films were sintered in a box furnace at 1360°C for 30 min.

Prepared pellets and films were characterized by X-ray diffraction using a PANalytical diffractometer (PANalytical, Netherlands). The copper anode operating at a voltage of 40 kV and a current of 40 mA generated CuKα radiation of wavelength 1.5405600 Å. Data were collected using a 2θ scan

through a range of angles from 20° to 60° with a step size of 0.0167°. The resulting diffraction patterns were analyzed using analytical software HighScore Plus, PANalytical.

Table 1. Components weight composition in thick film/tape casting.

Material	Sample 1 (wt%)	Sample 2 (wt %)	Sample 3 (wt %)	Sample 4 (wt %)
$BaTiO_3$	65.5	70	60	70
Toluene-ethanol (60:40)%	24.5	-	33	-
Turpentine oil	-	20	-	26.7
Phosphate Ester	-	-	0.20	-
Menhaden Fish oil	-	-	1.00	0.90
PVB-98	10	10	4	-
Ethyl Celloluse	-	-	-	2.10
Di-octyl Phthalate	-	-	0.8	0.90
Di-butyl Phthalate	-	-	0.8	-

The samples were gold coated for 1 min using a sputter coater (Emitech K550, USA) to prevent charging during SEM imaging. A Hitachi Su-70 field emission gun scanning electron microscope (FEG-SEM) was employed to image topography and morphology of the powder samples, films and tapes using a voltage of 10kV and current of 30 mA and a working distance of 10–15mm.

Electrical measurements were performed in a tube furnace (Lenton Thermal Designs) without external voltage. The temperature was recorded in a thermocouple monitor [Stanford Research Systems; model: SR630 and electrical resistance was recorded in digital multimeter (Keysight 3458A).

3 RESULTS AND DISCUSSION

Figure 1a shows the XRD pattern of spark plasma sintered pellets from the solid-state reactions route. To confirm that SPS sintered pellets have a similar structure as conventionally sintered pellets, the XRD pattern of commercial PTC stone sample, which was conventionally sintered is shown in Fig 1b. The XRD pattern indicates that our synthesized material and SPS sintered reveal a good agreement with the conventional tetragonal $BaTiO_3$ structure with the P4mm space group (JCPDS data No. 05-0626), with no impurity peak appearing in the diffractogram. The XRD analysis also confirms that there is no structural difference between commercial and SPS sintering process. The pellets were then characterized with XRD at elevated temperatures to follow the variation in the structure as a function of temperature. XRD pattern of SPS sintered pellet and commercial sample show peak splitting at 45°. The peak splitting in the XRD patterns at 45° is generally attributed to the tetragonal BaTiO3 corresponding (002) and (200) planes, whereas cubic $BaTiO_3$ shows a single peak at 45° corresponding to (002) [19]. X-ray diffraction analysis at elevated temperatures confirmed the formation of the desired tetragonal crystalline structure from room temperature to 100°C

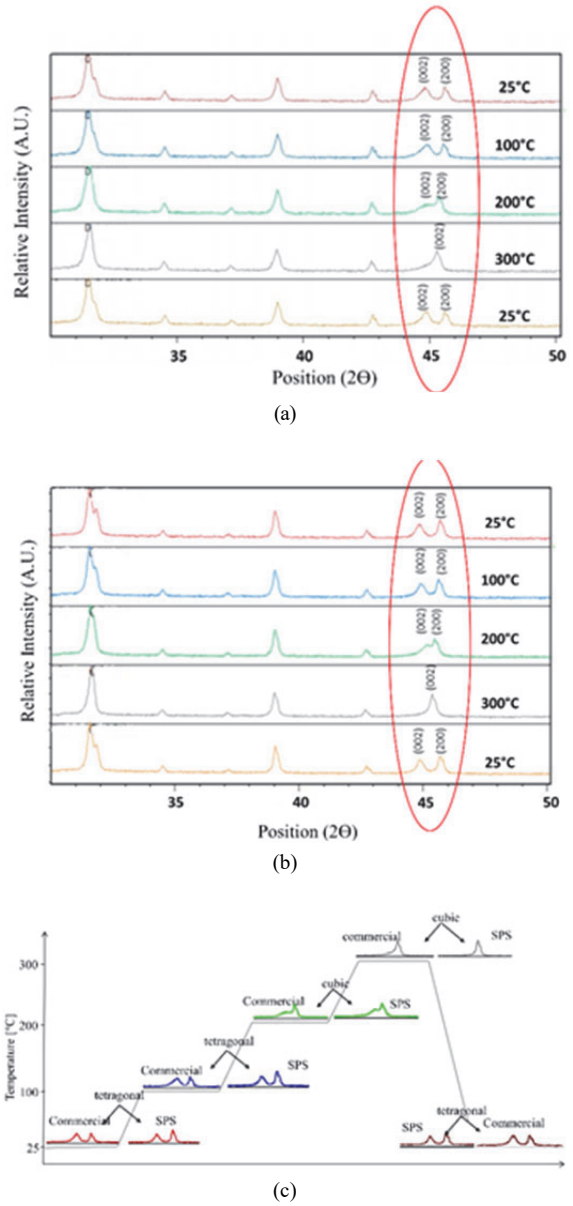

Figure 1. (a) Comparison of XRD analysis of the SPS sintered pellet and (b) commercial sample conventionally sintered in the temperature range of 25-300°C. (c)Zoom in of peak at 2Θ ~45°; the splitting in the peak at RT-100°C is due to the tetragonal phase and higher temperature the splitting diminished an indication of change to cubic phase.

and then changes to the cubic phase above this temperature. The PTCR behavior is strongly linked to the phase transition between two crystalline polymorphs of $BaTiO_3$: a room temperature tetragonal phase to a high-temperature cubic phase [Figure 1a,b]. A careful examination of the XRD reflection intensities further revealed that both commercial and our synthesized samples had no preferred orientation. Representative SEM images of an SPS sintered surface are shown in Figure 2a. The image shows that the surface is densely packed with grains of the size of 1–2 µm. The corresponding particle size distribution histogram in Figure 2b shows that the grains have a narrow size distribution range with an average particle size of 1.2 µm. The images also show that there is no preferred orientation of the grains. The

measured density of the SPS sintered pellets using the Archimedes method was 5.88 g/cm^3 which is 97.6% of the predicted theoretical density for $BaTiO_3$ showing that SPS sintered pellets are highly dense.

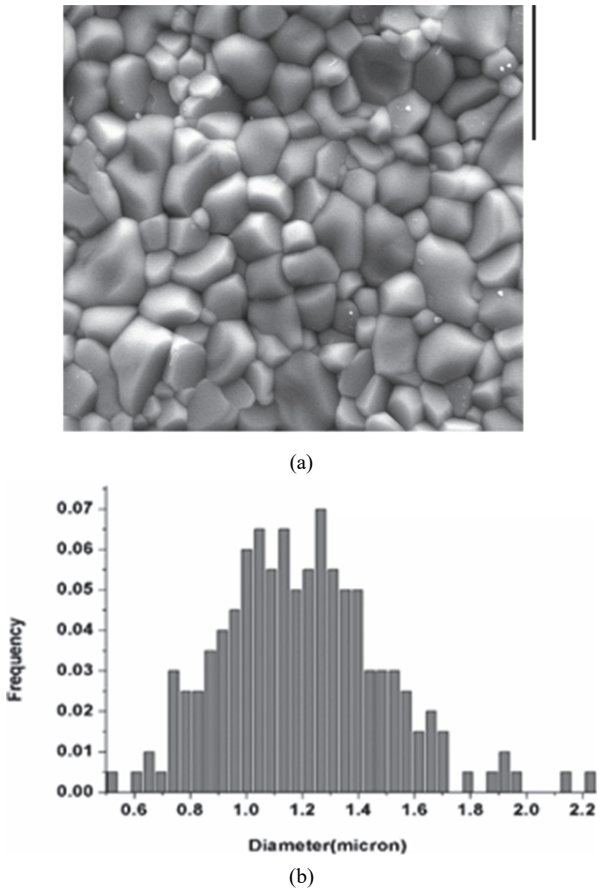

Figure 2. Representative SEM microphotographs (a) SPS sintered donor doped $BaTiO_3$, the scale bar is 2µm (b) Grain distribution of SPS sintered. sample.

Figure 3 shows typical rheological behaviors of our pastes. Four different paste samples were examined; two of these samples were prepared without any dispersant while two samples have a combination of different dispersants, details are given in Table 1. One of the important properties of the paste is that it should have shear thinning behavior. Therefore understanding and control of the rheological properties of pastes are critical for optimizing the ink formulation. The viscosity values at a given shear rate allow evaluation of the effectiveness of a given dispersant at preventing particle agglomeration in a suspension. All samples prepared here show shear thinning behavior with a typical viscosity of 1.5–15 Pa-sec at a shear of 10/sec which is the suitable rheological properties for both screen printing and tape casting. The paste without dispersant show a higher viscosity and they have severe sedimentation issues, their shelf life was short. For freestanding tapes, additional requirements are higher green strength and flexibility for a safe removal of tapes from the substrate and ease of handling. This is achieved by optimizing binder and plasticizer content until free standing tapes can be removed from the supporting substrates without any mechanical fault such as disintegration, cracks or cleavage. The typical viscosity values of processed pastes are (1–300) Pa-sec at a shear rate of 10/sec with a preferred range between 1–30 Pa-sec at a shear rate of 10/sec.

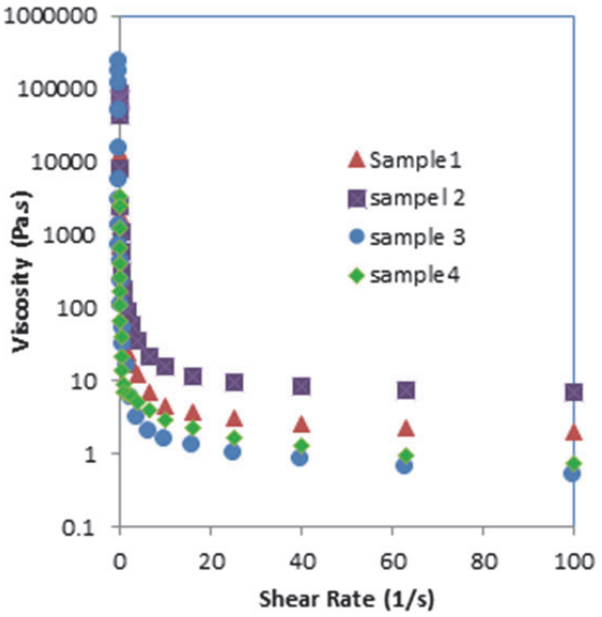

Figure 3. Rheological properties of the screen printable paste showing a shear thinning behaviour.

The paste sample 4 with higher functional material loading and longer screen life was used for stencil printing tapes. The green tapes after removal from the sacrificial substrate are shown in Figure 4. The green tapes were dried in air for 2 hours and then sintered in box furnace in the air at 1360ºC for 30 min. The sintered the thickness of our ceramic tapes is 300–400µm. Finally, the sintered tapes were sputter-coated with 1–15 µm Al layer on both sides and wire bonded for electrical characterization. A typical R(T) behavior of PTCR ceramic tape is shown in Figures 5a and 5b.

Figure 4. Donor doped $BaTiO_3$ tapes using 500 µm stencil printed on a sacrificial substrate.

The tapes show an unambiguous resistance anomaly at ferroelectric paraelectric transition temperature with T_c~ 115°C with an abrupt rise resistance with temperature as predicted by theoretical predictions (Figure 5a). Below Tc the material is exhibiting the negative temperature coefficient of resistivity (NTCR) behavior with temperature (Figure 5b).

Further improvement in PTC behavior especially the transition temperature and cold resistivity can be obtained by close control of the combination of the tape casting process, precursor powder chemistry, loading and viscosity, drying/ calcining/sintering profile.

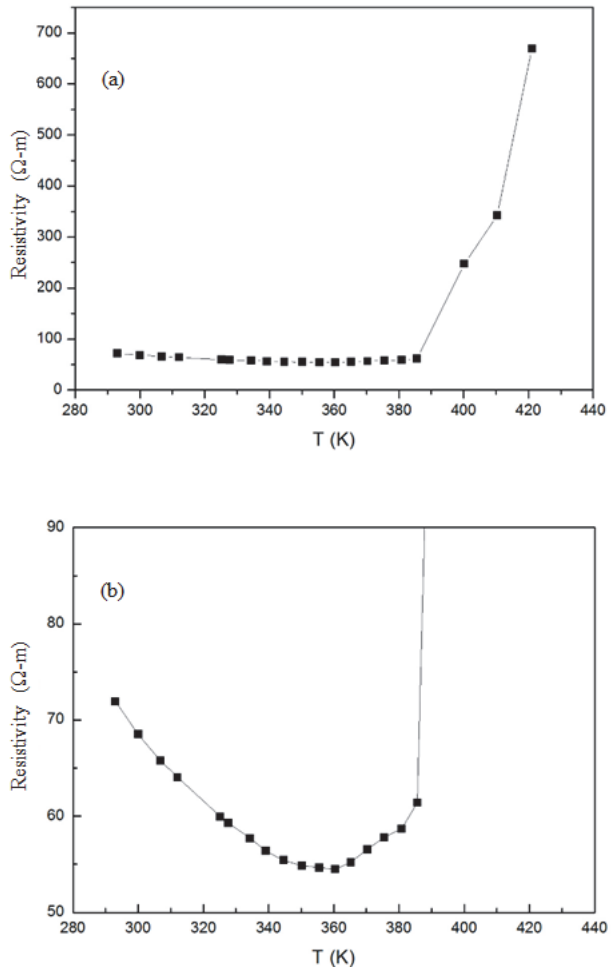

Figure 5. (a) A typical resistivity–temperature characteristic of donor doped PTC tapes. (b) A closer view of the region closer the transition temperature T_c depicting that the tapes show a typical (negative temperature co-efficient) NTC behaviour below T_c and PTC behaviour above T_c.

4 CONCLUSIONS

Synthesis, SPS sintering and tape casting of donor doped $BaTiO_3$ with a positive temperature coefficient of resistivity are reported. We have developed a disruptive solution for multilayer_PTCR with a potential 1000-fold reduction in cold resistance and compatibility with surface mount technology. Freestanding tapes of $BaSrCaPbTiO_3$ with donor doping of La were demonstrated via stencil printing. Unlike conventional printing with typical maximum film thickness ~50µm, stencil printing with film thicknesses up to 600 µm in a single print, offering a cheaper alternative for thicker films ceramic structures. The formulations of ink suitable for the stencil printing process have been demonstrated. The films show thixotropic behavior with shear-thinning with stress. The developed pastes provide excellent mechanical strength to the green film that can easily be handled after removal from the sacrificial substrate. The sintered tape shows an abrupt resistance rise at the ferroelectric paraelectric transition temperature, typical of PTC material. The approach could greatly improve the performance of PTC components in present applications with huge cost reduction and manufacturing ease. This could potentially revolutionize on-chip integration of future generation PTC components with novel device and chip designs.

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