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Enhanced pyroelectric figure of merits of porous $BaSn_{0.05}Ti_{0.95}O_3$ ceramics

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ABSTRACT

Porous $BaSn_{0.05}Ti_{0.95}O_3$ (BTS) ceramics were prepared by sintering compacts consisting of BTS and Poly (methyl methacrylate)(PMMA)as pore former. Porous BTS ceramics were systematically characterized for microstructural, ferroelectric, dielectric and pyroelectric properties. Porosity increased from 4% to 22.5% with increasing PMMA content. Dielectric constant decreases and loss increases with porosity. At 22.5% porosity, relative dielectric constant of BTS decreased by 47% (from 2525 to 1335) at 1 MHz/303K. Porosity leads to significant reduction in dielectric constant and volume specific heat capacity, which are of great interest for improving pyroelectric figure of merits (FOMs). Further, FOMs for current responsivity (F_i), voltage responsivity (F_v), detectivity (F_d) and energy harvesting (F_e and F_e^*) are calculated. Compared with dense ceramic, 2% PMMA specimen showed an improvement of F_e by 166% and F_e^* by 177%. F_v increased by 77%, F_d by 73% and F_i by 56% at 303K. All of these advancements are favorable for pyroelectric device applications.

1. Introduction

The pyroelectric materials are well-known for their unique thermo-electric conversion ability as these materials have very high sensitivity towards temporal change in temperature and hence have large market for sensors, detectors and thermal imaging applications [1–3]. Many ceramic materials have been documented in literature from past few decades which have proved to be useful in many pyroelectric applications to date [4,5]. Researchers have been still exploring new applications and cost effective materials for efficient usage of these materials. In order to derive best performance out of pyroelectric materials, there should be optimum tradeoff between pyroelectric coefficient, dielectric constant, dielectric loss and specific heat which plays a detrimental role in enhancing their figure of merits (FOMs). The physical or chemical compositional modifications technique is one such method which has been adopted in the past to chemically tune their pyroelectric performance [6–8]. In this direction, porous ceramics have generated scientific interest since they can be promising materials for pyroelectric device applications as density and dielectric constant decrease drastically due to the incorporation of pores which are of scientific interest for many pyroelectric applications. Great efforts have been put in by many academic groups/researchers on innovative processing technologies of porous ceramics, resulting in better control of the porous structures and substantial enhancements of the properties [9]. One such processing technique is by partial sintering route. The partial sintering route manifests many experiments to be conducted to look for an appropriate sintering procedure so as to achieve the desirable porosity [10]. In addition, a dense ceramic matrix is not obtained for the sake of partial sintering. The other innovative and easy method is by adding a pore-forming agent (PFA), usually some pyrolyzable particulates to the ceramic matrix [9,10]. In this method, desirable porosity can be easily obtained when contrasted with the former method, and the PFA-derived porous ceramics also possess built-in sites of pores for some selective applications [9,11]. Literature presents copious instances of dielectric, piezoelectric and pyroelectric properties of porous lead zirconate titanate (PZT) ceramics [12]. Zhang et al. used stearic acid (SA) and Poly(methyl methacrylate)(PMMA) as the pore former to fabricate porous PZT ceramics and demonstrated the difference in both porosity and pore morphology between PMMA and SA derived porous PZT ceramics and evaluated the dependence of electrical properties on these pore microstructures [11]. It has been reported that porous PZT materials have a higher figure of merit which is a method of quantifying the performance of materials for many pyroelectric device applications [13,14]. However, owing to the toxicity of lead (Pb), these materials are facing global restriction and therefore there is an increasing demand to replace

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Table 1
FOMs of well-known porous ceramics near room temperature.

Material	PFA/ method	% porosity	P ($\mu C/m^2$ K)	F_d ($10^{-5}Pa^{-0.5}$)	F_v ($\mu C/m^2$ K)	F_e (J/m^3K^2)	F_e^* (pm^3/J)	Ref.
$Ba_{0.67}Sr_{0.33}TiO_3$	(i) PMMA	9.6	7000	26	–	–	–	[15]
	(ii) CNT	9.5	7100	27.5	–	–	–	[15]
$Ba_{0.67}Sr_{0.33}TiO_3$	PMMA	9.6	7100	26	–	–	–	[8]
$Pb(Zr_{0.3}Ti_{0.7})O_3$ (140 nm thick)	Thickness variation	–	236	1.62	–	–	–	[14]
$PbZr_{0.45}Ti_{0.55}O_3$	(i) High M.W.	25	119	–	0.94	–	–	[13]
(thin film)	Polymer	21	150	–	1	–	–	[13]
	(ii) Low M.W. Polymer							
PZT	Freeze Cast (Ice)	45	269	–	–	1.41	6.57	[31]
$Pb_{1-x}Ca_xTiO_3$	Heating rate	–	–	–	0.5–3.2	–	–	[32]
(x = 0 0.3)		–	–	80–140	–	–	–	[33]
(Thin film)								
$Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}TiO_3$ (Thick films)	Ethyl cellulose	32	420	3.8	–	–	–	[34]

Table 2
Comparison of pyroelectric FOMs for well-known lead-free ceramics with porous BTS ceramics at room temperature.

Material	$p(10^{-4}C/m^2K)$	F_i(p.m/V)	$F_v(m^2/C)$	$F_e(J/m^3K^2)$	F_e^* (pm^3/J)	Ref.
$BaSn_{0.05}Ti_{0.95}O_3$ (0% PMMA)	4.32	228	0.01	8.2	2.34	This work
$BaSn_{0.05}Ti_{0.95}O_3$(2% PMMA)	5.57	355	0.018	22	6.48	This work
$[(K_{0.5}Na_{0.5})_{0.96}Li_{0.04}]Nb_{0.84}Ta_{0.1}Sb_{0.06}O_3$	1.9	42	0.003	3	0.1	[3]
PVDF	0.27	100	0.147	10	1.7	[35]
$BaTiO_3$	2	80	0.008	4.2	0.6	[36]
$[Bi_{0.5}(Na_{0.95}K_{0.05})_{0.5}]_{0.95}$ $Ba_{0.05}TiO_3$	3.25	112	0.015	–	1.7	[3]
Triglycinesulphide (TGS)[a]	2.8	121	0.362	263	44.1	[35]
Mn:94.6$Na_{0.5}Bi_{0.5}TiO_3$ −5.4$BaTiO_3$ [001][a]	3.8	131	0.082	22	2.3	[28]
$LiNbO_3$	0.83	35	0.141	31	6	[36]
$Ca_{0.15}(Sr_{0.5}Ba_{0.5})Nb_2O_6$	3.61	171	0.02	17	3.4	[37]

[a] Single crystal.

such materials for device application. In this direction, few lead-free porous ceramics based on modified $BaTiO_3$ have been recently reported such as $Ba_{0.5}Sr_{0.5}TiO_3$ and $Ba_{0.67}Sr_{0.33}TiO_3$ for their excellent pyroelectric properties, figure of merits (FOMs) and superior device performance [8,15,16]. Table 1 summarizes data reported for various porous pyroelectric ceramics along with their pyroelectric properties. It is very clear from Table 1 that porous ceramics are not extensively investigated and hence needs further scrutiny (F_v was calculated without considering the effect of specific heat and hence the units are different from them in all the materials reported in Table 2). $BaTiO_3$ undergoes various phase transitions namely, rhombohedral–orthorhombic–tetragonal–cubic with the possibility of shifting either of them close to room temperature by doping. In this context, Sn doped $BaTiO_3$ has already been reported for many dielectric applications with reduction of phase transition temperature towards room temperature [17–19]. For instance, a mere 5% Sn dopant in $BaTiO_3$ not only lowers the phase transition temperature but also leads to enhancement in remnant polarization (P_r) by about 38% in comparison with pure $BaTiO_3$ which is of interest in improving the pyroelectric coefficient and hence the FOMs [17]. In another study, a mere 11% Sn in $BaTiO_3$ resulted in giant piezoelectric coefficient (d_{33}) of 697 pC/N which is highest reported value till date [20]. Such a large scale exploration on Sn doped BT suggests that they could be a promising materials for many pyroelectric applications. We selected $BaSn_{0.05}Ti_{0.95}O_3$ (BTS) as it has been reported for improved pyroelectric properties as stated above along with many other promising ferroelectric and piezoelectric properties [17–20]. In order to further explore this material and enhance its properties for device applications, we attempted to fabricate porous BTS ceramics using PMMA as pore forming agent (PFA) which was allowed to burn out during sintering in order to leave pores in the materials. The porous BTS ceramics with varied amount of PMMA were further investigated for their microstructural, dielectric and pyroelectric properties.

2. Experimental

The designated compositions of mixed powders were BTS + *y* PMMA, where *y* = 0, 2, 4, 6 and 8 wt.%. The BTS ceramic powder was fabricated using conventional solid state reaction route. High purity reagents of $BaCO_3$ (99% pure), TiO_2 (99% pure) and$SnCl_2$ (98.5% pure) powders were used as the starting precursors. Stoichiometric amounts of these powders were ball milled using acetone as the wetting agent to have physical homogeneity. Calcination was done at 1130 °C for 2 h to obtain the BTS compound. PMMA was dissolved in acetone prior to mixing with calcined BTS powder at the designated composition. The mixture was ball billed again to achieve physical homogeneity. The powders were then pressed into a disk shaped pellet with dimensions of 12 mm × 1 mm (diameter × thickness). To begin with, the optimum heating procedure was adopted from literature [16] with an initial heating rate of 2 °C/min upto 240 °C, followed by 1 °C/min upto 420 °C and then 2 °C/min upto 700 °C to assure the complete burnout of PMMA. The compacts were then sintered at 1330 °C for 2 h. The sintered samples were ground to remove the surface layers and coated with silver electrodes prior to electrical measurements.

The phase purity of the sintered ceramics was characterized by X-ray diffractometry (XRD) (Philips, Netherlands) with CuKα radiation. Scanning electron microscopy (SEM) (FEI-Technai SEM-Sirion) was used to observe the surface morphology of the samples. The density of the prepared specimens was measured employing Archimedes principle. The polarization-electric field (P-E) hysteresis loops were recorded at 50 Hz at various electric fields and temperatures using a modified Sawyer Tower circuit (Marine India). The dielectric properties of the samples were measured using impedance analyzer (Agilent E4990A, Agilent Technologies Inc., Santa Clara, CA) at a heating rate of 1°/min.

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