PZT/PLZT - elastomer composites with improved piezoelectric voltage coefficient

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Abstract: Lead Zirconate Titanate (PZT) and Lanthanum-modified Lead Zirconate Titanate (PLZT) ceramic sensor materials are widely used because of their excellent piezoelectric coefficients. These materials are brittle, high density and have low achievable piezoelectric voltage coefficients. The density of the sintered ceramics shall be reduced by burnable polymeric sponge method. The achievable porosity level in this case is nearly 60 – 90%. However, the porous ceramic structure with 3-3 connectivity produced by this method is very fragile in nature. The strength of the porous structure is improved with Sylgard®-184 (silicone elastomer) by vacuum impregnation method maintaining the dynamic vacuum level in the range of -650 mm Hg. The elastomer Sylgard®-184 is having low density, low dielectric constant and high compliance (as a resultant stiffness of the composites is increased). To obtain a net dipole moment, the impregnated ceramic composites were subjected to poling treatment with varying conditions of D.C. field and temperature. The properties of the poled PZT/ PLZT - elastomer composites were characterized with LCR meter for measuring the dielectric constant values (k), d_{33} meter used for measuring piezo-electric charge coefficient values (d_{33}) and piezo-electric voltage coefficient (g_{33}) values which were derived from d_{33} values. The voltage coefficient (g_{33}) values of these composites are increased by 10 fold as compared to the conventional solid ceramics demonstrates that it is possible to fabricate a conformable detector.

Key Words: Dielectric constant, Composites and Sintering

1 Introduction

Piezoceramics are the modern ceramics which, in present-day technology, find many interesting applications due to the unique electro-mechanical coupling associated with these materials. The various applications include pressure sensor, acoustic sensor, accelerometer, gas lighter, ultrasound, sonar, buzzer, actuator etc. The piezoelectric materials are characterized using parameters like d_{33}, d_{31}, g_{33} etc. The d_{33} parameter is the piezoelectric strain coefficient which gives the electric charge per unit area generated by a unit mechanical stress. It also measures the strain induced by a unit electric field in these materials. The 1st and 2nd numbers of suffix 33 or 31 show the direction of electrical and mechanical stimuli respectively, 3 being the direction parallel to electric field applied during poling and 1   being other perpendicular direction. The g_{33} (piezoelectric voltage coefficient) gives the amount of electric field generated on the application of unit stress in these materials. This value is derived by using the relation $g_{33}=d_{33}/(k*\varepsilon_o)$, where ε_o - the permittivity of the material- 8.854×10^{-12} C.V^{-1}m^{-1}. This value is used as a figure of merit for the passive piezoelectric devices [1, 2].

The g_{33} value which can be achieved in poled PZT ceramics by varying their composition is of the order of 20-40 $\times 10^{-3}$ V-m/N [1]. This value can be enhanced by an order of magnitude by using composites made of piezoceramics & polymer. The other advantages of composites are their low density, good compliance and flexibility. Lower density makes them suitable for devices like ultrasound and sonar due to their better coupling with human tissues and water respectively. Better compliance provides damping (lower mechanical Q) in these materials. Due to this, acoustic sensor, pressure sensor etc. using these materials may not require any back up materials. Their flexibility offers the interesting possibility of fabricating a conformable detector [3, 4].

In this study polymeric sponge method was used to make porous ceramic with 3-3 connectivity as it was easier to obtain large amount of porosity using this method [5, 6]. Pores were filled with silicone elastomer by vacuum impregnation. Poling parameters like D.C. field strength, temperature were varied to find their effect on the d_{33} and g_{33} values of the composites.

2 Experimental methods

2.1.Synthesis of ceramics

Two ceramics of the following stoichiometry $Pb_{0.95}La_{0.05}(Zr_{0.58}Ti_{0.42})O_3$ [PLZT] and $Pb(Zr_{0.55}Ti_{0.45})O_3$ [PZT] were prepared by the solid state route. The starting powders, AR grade PbO, ZrO_2, TiO_2, La_2O_3 (Aldrich Corp.) were ball milled for 6 hours, followed by calcination at 800^0C for 1 hour. The calcined powders were analysed by X-ray diffraction analysis (Philips make) with the target of Cu-Kα and the radiation wavelength (λ)-1.54A^o. Data collection was performed in the 2 θ range of 20°–60° with a step scan with a step size of 0.02° and counting time of 2s/step. Fig.1 and 2 illustrates the XRD pattern of PZT and PLZT respectively showing the pure perovskite phase formation in these materials. The theoretical density of PLZT and PZT ceramics calculated by XRD analysis were found to be 8.18 g/cc and 7.98 g/cc, respectively. The powders were pressed into 10 mm diameter pellets at 200 MPa using a hydraulic press.
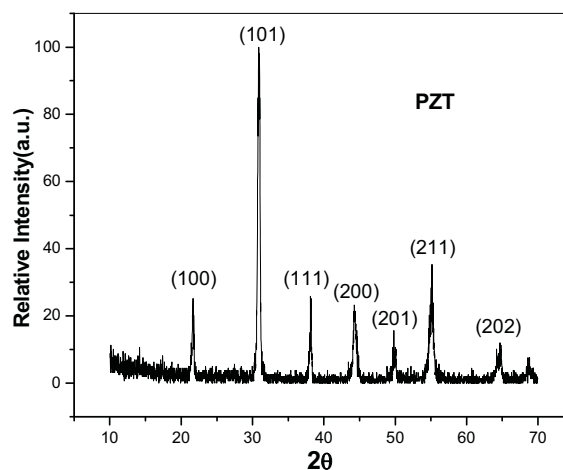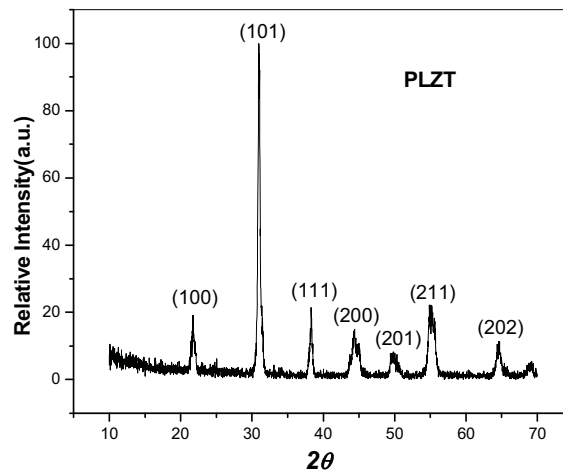

Fig.1 XRD pattern of PZT

Fig.2 XRD pattern of PLZT.

2.2. Preparation of porous ceramics

To make porous ceramics, slurry of the powders was first prepared. In this preparation 2 g of PVA (Polyvinyl alcohol) was dissolved in 100 cc of hot distilled water. About 25 cc of this solution was added to 45 g of ceramic powder and ball milled for 2 hours to get slurry of good consistency. Round pieces of sponge were dipped in the slurry and ball milled for 2 minutes to ensure the voids of the sponge are filled with slurry. Slurry dipped sponge pieces of each ceramic formulation were further divided into two lots. One lot of each formulation was spun in a centrifuge to remove excess of slurry. In this way four lots, two spun and two non-spun were prepared. Porous ceramics and composites prepared from the spun samples are referred as spun ceramics/composites in this work. Other two lots are referred as non-spun ceramics/composites. The slurry loaded sponge was dried in an oven at 80^0C. The green ceramic pellets and slurry loaded sponge pieces were sintered at 900^0C, 1000^oC and 1200^oC for an hour in PbO atmosphere. The rate of heating and cooling in the sintering schedule was kept at 1^oC/minute to avoid cracking in the fragile porous structure. The polymeric sponge was burned out during sintering leaving a porous ceramic structure. The density and porosity of the bulk and porous ceramics were calculated using Archimedes Principle. The sintered density of non-spun porous ceramic sintered at 900-1200^oC ranged between 40-60% T.D. The density of spun porous ceramic samples varied between 8.5 to 12.5% T.D. The magnified pictures of the porous ceramics are given in Fig. 3 and 4.

Fig.3 Photograph of porous spun ceramics sintered at 1100^0C (sample dia= 8.8mm)
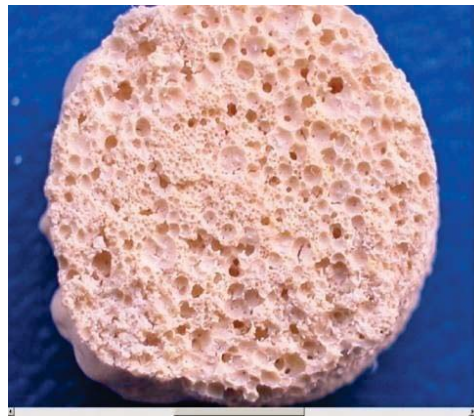
Fig. 4 Photograph of porous non-spun ceramics sintered at 1100^0C (sample dia = 8.8 mm)

2.3. Impregnation of porous ceramics

The epoxy and hardener of the silicone elastomer (Sylgard®184, Dow Corning Corp., U.S.A) were mixed in the required ratios. The porous samples were placed in a flask and a vacuum of -670 mm column of Hg was created by a rotary pump. The liquid elastomer was then poured into the flask and vacuum was maintained for ½ - 1 hour. The impregnated samples were then cured at 100^oC for 1 hour. The density of the samples was measured by Archimedes Principle. By comparing the density difference between the impregnated composites and density of porous ceramics, the volume fractions of ceramics, elastomer and air in composites were calculated. There were considerable variations in the volume fraction of these phases. For example, the variations in volume fractions of ceramics, elastomer and air phase of composite made from porous PLZT ceramics (non-spun) sintered at 1100^oC ranged between 33-35%, 22-39% and 26-44% respectively.

2.4. Electroding

Flat surfaces of sintered bulk ceramics were coated with air-fired silver and heated at 550^0C for 30 minutes. For composites, round pieces of aluminum foil of 5 mm and 8 mm diameter were pasted on opposite surface of composite with the help of an epoxy (5 Minute Epoxy, Devcon, USA).

2.5. Poling

Electroded samples of bulk ceramics and composites were given poling treatment to align the dipoles of each domain in a particular direction, so as to get a net dipole moment. Each sample was fixed in a suitable jig and then heated in a stirred silicone oil bath to a temperature ranging from 120^0C to 140^0C. After reaching the temperature a D.C. field of 3-7 kV/mm was applied for 15 minutes. Then the oil bath was allowed to cool to 70^0C with D.C. field on, after which the field was removed.

2.6. Dielectric and piezoelectric constant measurement of composites

The dielectric constant (k) values of the samples were determined using a LCR meter (Stanford Research System 715). The d_{33} values of the bulk ceramics and composites were measured with the help of a d_{33} meter (S5865 APC Inc.). The g_{33} values were derived using the relation $g_{33} = d_{33}/(\varepsilon_0 * k)$.

3 Results and discussions

The properties of the PZT/PLZT- elastomer composites were analyzed with LCR meter used for measuring the dielectric constant values (k), d_{33} meter used for measuring piezo-electric charge coefficient values (d_{33}) and piezo-electric voltage coefficient (g_{33}) values which were derived from d_{33} values prepared in the different processing conditions were given in the Table 1 and 2.

Table1 Dielectric, piezoelectric properties & density of PLZT ceramics & their composites.

Material	Sample	Sintering Temp. ^{0}C/hr.	Poling Temp.^{o}C	Poling Field kV/mm	Dielectric constant (k)	$d_{33\,x}$ 10^{-12} C/N	g_{33} V-m/N	Density g/cc
PLZT ceramic	PL11	900/1	140	3	870	90	0.012	6.07
	PL12	1100/3	140	3	1200	335	0.032	7.26
	PL13	1200/3	140	3	1090	325	0.034	6.17
	PL21	900/1	120	3	20.5	14.9	0.063	2.31
Non-Spun Composite	PL22	900/1	120	4.5	21	23.8	0.12	2.31
	PL23	1100/3	130	7	20	40.7	0.23	3
	PL24	1100/3	120	3	18.5	27	0.17	3
	PL25	1100/3	135	3	21	51.3	0.27	3
Spun Composite	PL31	1100/3	140	4.5	13.8	14.7	0.12	1.72
	PL32	1200/3	140	4.5	14.7	14.1	0.11	1.73

Table 2 Dielectric, piezoelectric properties & density of PZT ceramics & their composites

Material	Sample ID	Sintering Temp. ^{0}C/hr.	Poling Temp. ^{o}C	Poling Field kV/mm	Dielectric constant (k)	$d_{33\,x}$ 10^{-12} C/N	g_{33} V-m/N	Density g/cc
PZT Ceramic	P11	900/1	140	3	748	117	0.017	6.65
	P12	1100/3	140	3	530	186	0.039	7.55
	P13	1200/3	140	3	463	181	0.044	7.42
Nonspun Composite	P21	1100/3	140	3	12.5	37.6	0.34	2.2
	P22	1200/3	140	3	6.9	32.9	0.54	2.22
Spun Composite	P31	900/1	140	3	6.8	4.7	0.08	1.36
	P32	1100/3	140	3	9.3	9.4	0.114	1.47
	P33	1200/3	140	3	8.7	11.5	0.15	1.68

The k, d_{33} and g_{33} values of bulk PZT and PLZT ceramics fairly matched with the values given in the literature [1, 7]. The dielectric constant (k) values of the bulk PZT samples decrease with increase in the sintering temperature, which is also reported elsewhere [8]. This trend is similar to the dependence of dielectric constant on internal stresses in barium titanate ceramics [9]. In these ceramics, the dielectric constant (k) at the room temperature decreases with increase in their grain size. However, reverse trend is noted for the PLZT ceramics. Such dielectric behavior of PLZT ceramics is similar to the dielectric behavior of PMN (Lead Magnesium Niobate) ceramics, where increase in grain size is associated with rise in the dielectric constant values [10]. The k and d_{33} values of PLZT ceramics are greater as compared to these values in PZT ceramics. However, the g_{33} values of PZT ceramics are on higher side as compared to those of PLZT ceramics. Similar trends are carried forward in composites made from PZT and PLZT ceramics. As the dielectric and piezoelectric constant values of a composite will depend on the amount of the ceramic phase present, k, d_{33} and g_{33} values of the non-spun composites are higher as compared to these values in the spun composites. Higher g_{33} values in the range of 0.34-0.54 V-m/N could be achieved in the non-spun composites made from PZT ceramics. The D.C field and temperature during poling has minor influence on the k-values of the composites, but has pronounced effect on the d_{33} and g_{33} values as is evident from the data history of the samples PL21 to PL25 shown in Table 1. The increase in D.C field strength and temperature is associated with the rise in the d_{33} and g_{33} values of the composites. Out of the two parameters, temperature has a more drastic effect on these

values as is clear on comparing the values of samples PL23 and PL25.Variation in density ranging between 1.3 g/cc to 1.7 g/cc for spun composites and 2.3 g/cc to 3.0 g/cc for non-spun composites was obtained. These values are relatively much lower than the density of the bulk ceramics.

4 Conclusions

The lower density composites of PZT/PLZT ceramics impregnated with silicone elastomer could be prepared which is having high g_{33} values about ten times greater than that of bulk ceramics demonstrate that it is possible to fabricate a conformable detector.
 PZT is a better candidate material than PLZT to make composites with higher g_{33} values. Non-spun composites have higher g_{33} values as compared to the spun composites. D.C. field and temperature during poling have important role in obtaining composites with higher g_{33} values.

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