

Synthesis and characterization of porous PZT-PCN ceramics

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Porous PZT-PCN ceramics were fabricated with this formula, " $0.8 \text{Pb}(\text{Zr}_{1/2}\text{Ti}_{1/2})\text{O}_3 - 0.2 \text{Pb}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ", abbreviated as "PZTPCN" by introducing Polyvinyl chloride (PVC) and stearic acid (SA) as pore forming agents (PFA) with varied percentages (5, 10 and 15 wt%). The optimum sintering procedure was designed according to the thermogravimetric analysis of pore formers. XRD and FESEM were applied to study the formed phase and the microstructure of the system. Electrical Characterization was conducted using Piezo meter. A decrease in density reduced longitudinal piezoelectric coefficient (d_{33}) and relative dielectric constant (ϵ) and enhanced hydrostatic figure of merit (d_{hg}) of PZTPCN ceramics. The hydrostatic figure of merit (d_{hg}) of 36% porous PZTPCN ceramics was four times more than that of dense ceramic.

Key words: Porous PZT-PCN, piezoelectric properties, Hydrostatic figure of merits, SEM and XRD.

Introduction

Lead zirconate titanate (PZT) ceramics have attracted great interest because of their excellent dielectric, piezoelectric, and electrostrictive properties, which are useful in sensors, actuators besides under water and ultrasonic transducers [1-5]. The hydrostatic figure of merit, d_{hg} , is defined to evaluate the sensitivity of a piezoceramic used as underwater transducer [6, 7]. Nowadays, porous PZT ceramics have been paid huge attentions with respect to dense materials, mainly for the following several reasons. First, since piezoelectric coefficients d_{33} and d_{31} are opposite in sign, hydrostatic piezoelectric strain coefficient of dense PZT, $d_{\text{h}} (= d_{33} + 2d_{31})$, has a small value [8] but previous research [9, 10] has demonstrated that porous PZT is considered as a good substitute for dense PZT where increasing porosity can result in moderate decline in d_{33} but rapid reduction in d_{31} , contributing to the value of d_{h} . Second, inclusion of air phase reduces dielectric constant (ϵ) of the bodies considerably, leading to increase in hydrostatic piezoelectric voltage coefficient g_{h} , which can be calculated by d_{h}/ϵ . Third, porous piezoelectric ceramics are cheaper to produce than other piezoelectric composites. Finally, porous piezoelectric ceramics are very light and are thus more portable than other piezoelectric composites [11-13].

The porous PZT ceramic materials can be developed using various processing techniques such as the replica technique, direct foaming and mixing of burnable plastic spheres (BURPS). The BURPS process offers advantages such as the ability to control porosity and

pore size along with ease to manufacture at larger scale [13-16].

In the present work, porous PZT-PCN ceramics were prepared. Stearic acid (SA) and polyvinyl chloride (PVC) were used as additives for BURPS process. By varying the weight percentage of pore-forming agents, the properties of material can be monitored to meet the necessities of various applications.

Experimental Procedure

The raw materials were the reagent grade oxides PbO, CoO, Nb₂O₅, ZrO₂, and TiO₂ oxides 99% purity were purchased from Sigma-Aldrich. Polyvinyl chloride (PVC) (CHIMEI chemical industries, Ltd., Taiwan) and Stearic acid (SA) (C₁₈H₃₆O₂ with purity > 97%, Merck Co., Ltd., Germany) were used as the pore forming agents (PFAs). The size of PVC was controlled between 40 nm and 60 nm ($D_{50} = 50$ nm) and the size of SA was in the range of 160-260 nm ($D_{50} = 210$ nm) as shown in figures 1 and 2. Polyvinyl alcohol (PVA) solution was also used as a binder in the dry pressing process. All the materials described above were used directly without any further modification or treatment.

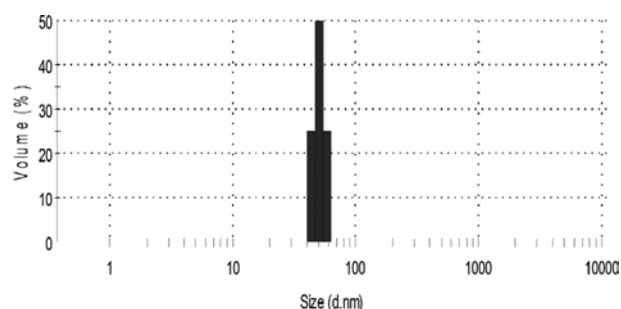


Fig. 1. Particle size distribution of poly vinyl chloride (PVC) powders.

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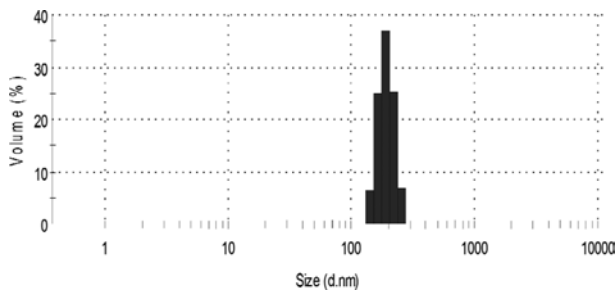


Fig. 2. Particle size distribution of stearic acid (SA) powders.

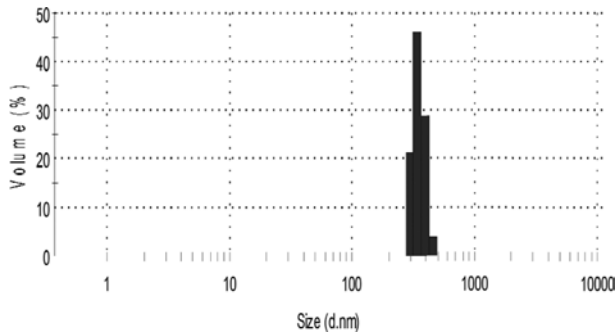


Fig. 3. Particle size distribution of PZTPCN powders.

PZT-PCN ceramic were fabricated according to the formula “0.8 Pb ($Zr_{0.5}Ti_{0.5}$) O_3 -0.2 Pb ($Co_{0.33}Nb_{0.67}$) O_3 ” by a solid-state mixed oxide technique with columbite $CoNb_2O_6$ and wolframite $ZrTiO_4$ precursors. More details of the synthesis of PCN-PZT powders can be found in Refs. [17-20]. Porous 0.8PZT-0.2PCN ceramics were prepared by mixing 0.8PZT-0.2PCN ceramic powder with pore formers. The particle size of ceramic powder prepared was approximately between 300 nm and 400 nm (D_{50} = 350 nm) as shown in Fig.3. The designed compositions of mixed powders were 0.8Pb($Zr_{0.52}Ti_{0.48}$) O_3 0.2 Pb($Co_{0.33}Nb_{0.67}$) O_3 + α PC and 0.8 Pb($Zr_{0.52}Ti_{0.48}$) O_3 0.2 Pb($Co_{0.33}Nb_{0.67}$) O_3 + β Stearic acid (SA), respectively, where α and β were in the range of 0, 5, 10, and 15 wt.%. After an appropriate amount of 7 wt% PVA aqueous solution was added, the powder was milled to ensure a homogeneous blending. Thereafter, the mixture was pressed at about 100 MPa to $\varnothing$ 20 mm disks.

Appropriate sintering procedure is of great importance because the samples are easy to crack in the sintering process, due to high porosity and other possible defects. The optimum sintering procedure depends on the thermogravimetric analysis of PFA. From the thermogravimetric analysis of PVC shown in figure 4, the optimum heating procedure was decided to begin with an initial heating rate of 120 °C/h up to 250 °C followed by 30 °C/h up to 500 °C. And then again 120 °C/h up to 1200 °C with heat preservation at 500 °C for 1h to assure the complete burn out of the PVC. A typical sintering procedure is illustrated in Fig. 5.

Figure 6 Shows that the stearic acid begin to volatilize at 200 °C and completely burn out at 450 °C therefore the heating rate was initially 120 °C/h up to

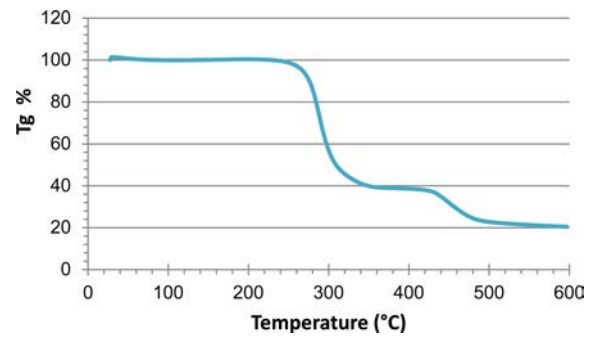


Fig. 4. TG curve of PVC at heating rate of 10 °C/min.

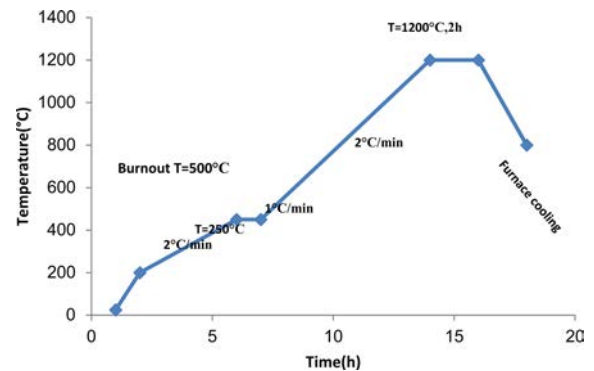


Fig. 5. A typical sintering procedure of porous PZTPCN-PVC.

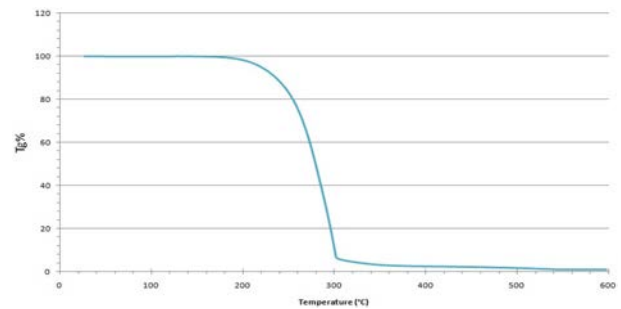


Fig. 6. TG curve of stearic acid at heating rate of 10 °C / min in air.

200 °C then 60 °C/h up to 450 °C and then again 120 °C/h up to 1200 °C with heat preservation at 450 °C to assure complete burn out of it. A typical sintering procedure is illustrated in Fig.7.

A double crucible technique using $PbZrO_3$ powders for atmospheric control was used to minimize the volatilization of PbO during sintering. The sintered samples were ground to remove surface layers, and was coated with silver electrodes in vacuum, and poled by applying a dc field of 2-3 kV/mm for 10 min in a silicone oil bath at 120 °C.

The densities of dense and porous PZTPCN were determined by the Archimedes method and the porosity P was obtained using equation (1):

$$P = (1 - \rho^* / \rho_t) \times 100\% \quad (1)$$

Where ρ^* is the density of the porous sample measured by the Archimedes method, ρ is the theoretical density

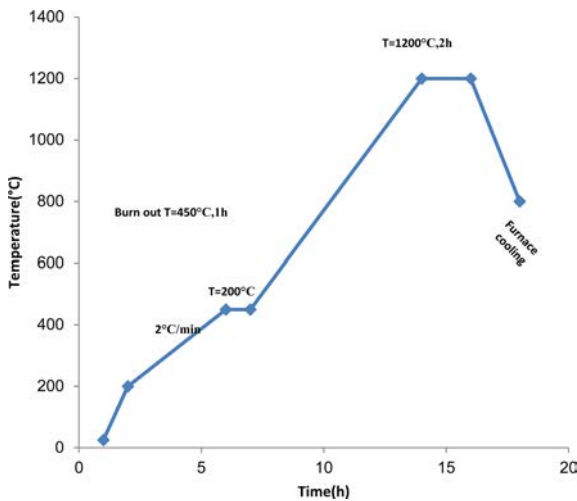


Fig. 7. A typical sintering procedure of porous 0.8 PZT-0.2-PCN-SA.

($\rho_t = 8.12 \text{ gm/cm}^3$).

The sintered samples were analyzed by X-ray diffraction (STOE, Model STADI P, Germany) using Cu α radiation at step scan of 0.015° from 5° to $120^\circ 2\theta$.

The piezoelectric coefficients, d_{33} and d_{31} , were measured by a direct method based on quasi-static d_{33}/d_{31} meters (Model ZJ-6B, Institute of Acoustics, Chinese Academy of Science) and the parameters of d_h , g_h and $d_h g_h$ were calculated.

The dielectric constant (ϵ_r) was calculated from a parallel-plate capacitor equation, using equation (2)

$$\epsilon_r = Cd/\epsilon_0 A \quad (2)$$

where C is the capacitance of the specimens was measured with a HP4284A LCR meter, d and A are, respectively, the thickness and the area of the electrode and ϵ_0 is the dielectric permittivity of vacuum ($8.854 \times 10^{-12} \text{ Fm}^{-1}$).

Gold was deposited on discs by disc sputter coater (DSC) (nano structural coating Co.), then the microstructure of dense and porous PZT-PCN ceramics were observed by Field Emission Scanning Electron Microscopy (FESEM; Model MIRA, TESCAN, IRQST).

Results and Discussion

Figure 8 shows porosity yield as a function of PVC and SA addition, the porosity yield by the PVC was lower than SA because of the particle size of PVC is smaller than SA therefore the SA-derived porous PZTPCN ceramics had higher porosity resulting from pore interconnection than PVC-derived ones. Relative density of samples with addition of 5, 10, 15 wt % of PVC and SA after sintering at 1200°C for 2 h are shown in figure 9. In a relative comparison, the relative density of PZTPCN sintered at the same condition, with addition of 15 wt% of pore formers, was reduced about 18.93% for PVC and 24.43% for SA, respectively.

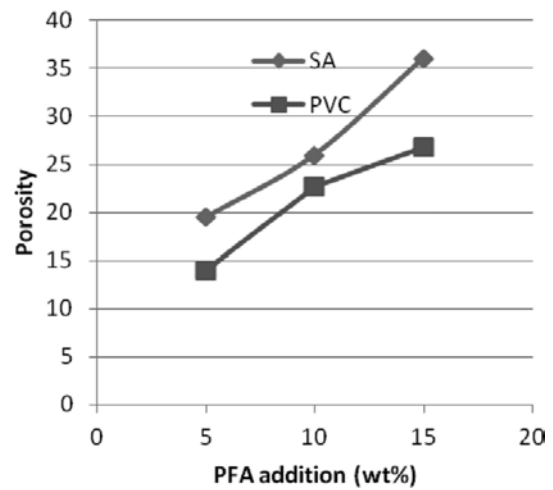


Fig. 8. Variations of porosity of porous PZTPCN with PVC and SA addition.

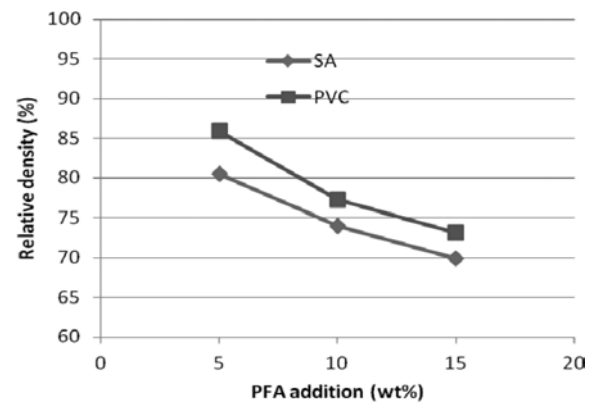


Fig. 9. Variations of relative density of porous PZTPCN with PVC and SA addition.

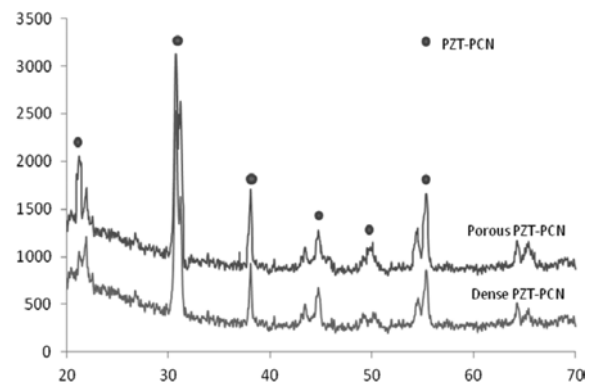


Fig. 10. XRD of the PZTPCN ceramics with different pore formers.

The relative density changes with PVC and SA content are easy to understand. During sintering, PVC or SA burnt off, leaving pores in the PZTPCN matrix. The more the added Pore forming agents, the more the porosity in the material microstructure. Many previous works have reported a similar behavior [16-18].

The phase formation behavior of the sintered ceramics is revealed by an XRD method. The XRD patterns are presented in figure 10. It is prominent that single perovskite structure was observed for both dense

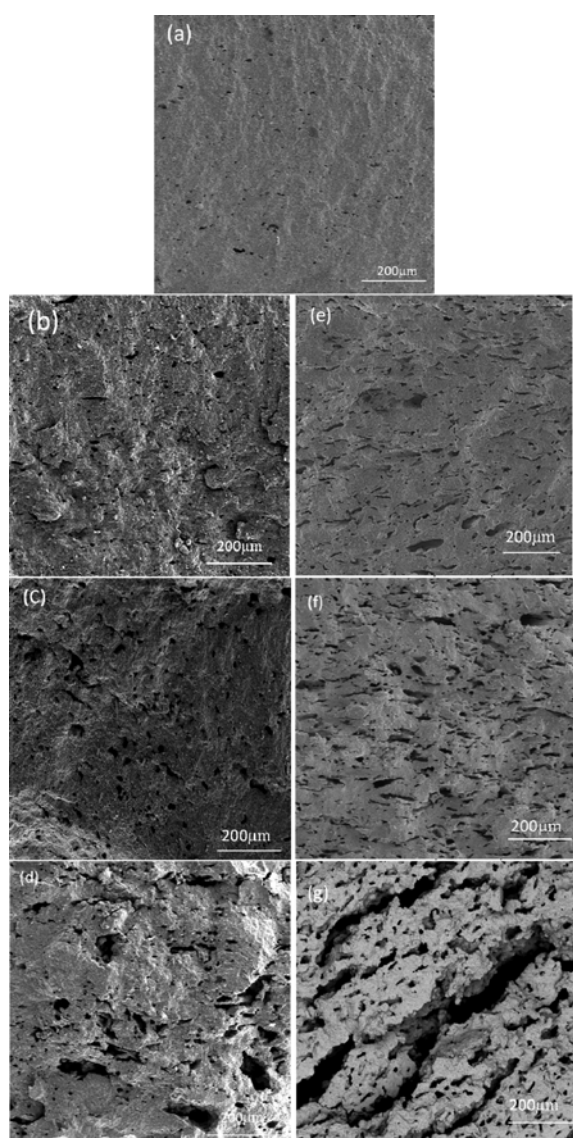


Fig. 11. Fracture surfaces of porous PZTPCN ceramics: (a–d) ceramics fabricated with 0, 5, 10, and 15 wt% PVC additions, (e–g) ceramics fabricated with 5, 10, and 15 wt% SA addition respectively.

and porous PZTPCN and no secondary phase was detected. This demonstrated that the PVC and SA as

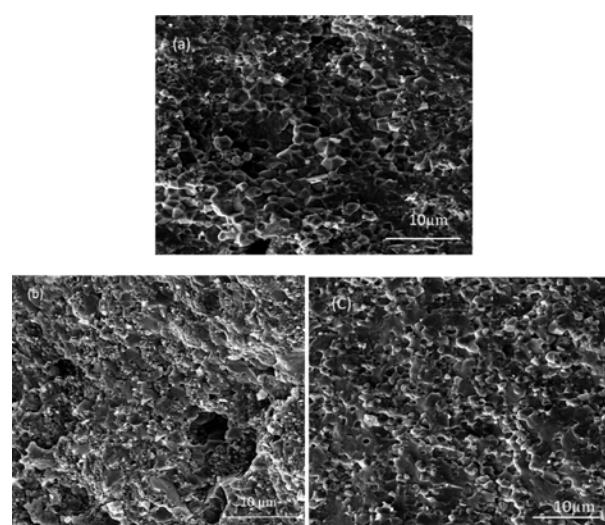


Fig.12. FESEM micrographs of the cross section of PZTPCN ceramics fabricated with (a) 0% PFA, (b) 10% PVC (C) 10%SA addition respectively.

pore forming agents did not influence the phase of PZTPCN ceramics.

Figure 11 shows FESEM images of samples fabricated by the BURPS process with different PVC and SA additions. The cross sections were made by fracture of the samples. The resultant pores are mostly macropores and with the increase of PFA addition, the porosity increased and the pores became densely distributed. The observations were consistent with those of earlier research [14–17]

Figure 12 Shows that the PVC- derived pores were irregularly but the SA-derived pores were approximately oval-like. The difference in pore morphology arises mainly from the different characteristics of PVC and SA as the PFA, which in turn influences the porosity obtained. This porosity discrepancy could be related to the difference in particle size between the PVC and SA.

As stated above, the SA and PVC used as PFAs have resulted in different pore morphologies and porosities, and the difference in the porous microstructures could in turn lead to different properties for porous PZT-PCN

Table1. Summary of the samples prepared in this study.

Sample	PVC content (wt %)	Sintered density (gm/cm^3)	Porosity%	Relative density (%)	ϵ	d_{33} (pC/N)	d_h	$\frac{g_h}{(10^{-3} \text{Vm/N})}$	Figure of merit $\frac{d_h g_h}{(10^{-15} \text{m}^2/\text{N})}$
A	0	7.10	12.56	87	1137	356	74	6.5	481
B	5	6.98	14.04	85.96	346	231	46	13.30	612
C	10	6.27	22.70	77.22	340	226	55	16.20	891
D	15	5.94	26.85	73.15	311	213	57	18.33	1045
SA content (wt %)									
E	5	6.54	19.46	80.54	336	230	64	19.00	1216
F	10	6.01	25.98	74.01	264	206	66	25.00	1650
G	15	5.19	36.08	69.92	256	185	74	28.89	2138

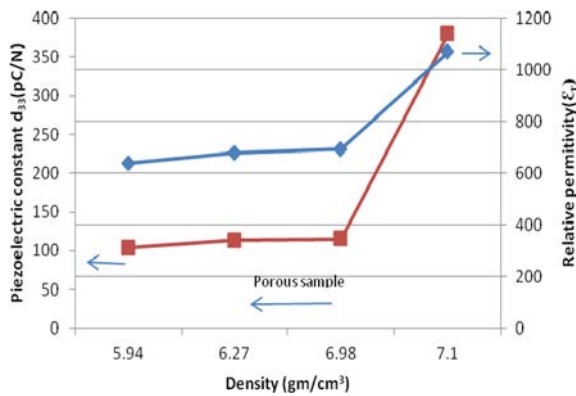


Fig. 13. Variation of d_{33} and ϵ_r as a function of density of porous PZTPCN ceramics with PVC as PFA.

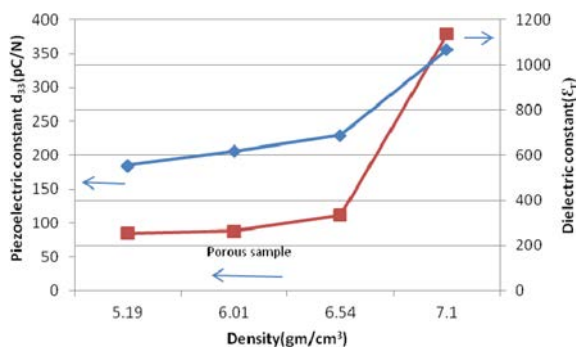


Fig. 14. Variation of d_{33} and ϵ_r as a function of density of porous PZTPCN ceramics with SA as PFA.

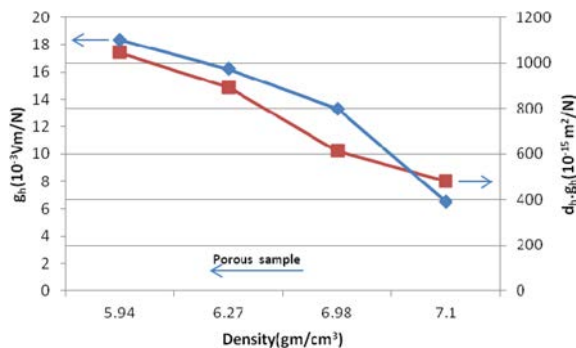


Fig. 15. Variation of g_h and $d_h g_h$ as a function of density of porous PZTPCN ceramics with PVC as PFA.

ceramics.

The results obtained for all samples are summarized in Table 1.

Longitudinal piezoelectric coefficient (d_{33}) and dielectric constant (ϵ_r) of porous PZT-PCN ceramics as a function of density are shown in figures 13 and 14, respectively. Both d_{33} and ϵ_r of PZTPCN ceramics decreased with the decreasing density, as would be expected. The (d_{33}) of PZTPCN ceramics decreased with decreased density as for the observation from Carroll and Holt [18], the enhanced stress near the pores leads to an increase in microscopic stress and strain, which can not only inhibit the movement of domain walls but also prevent grain growth and

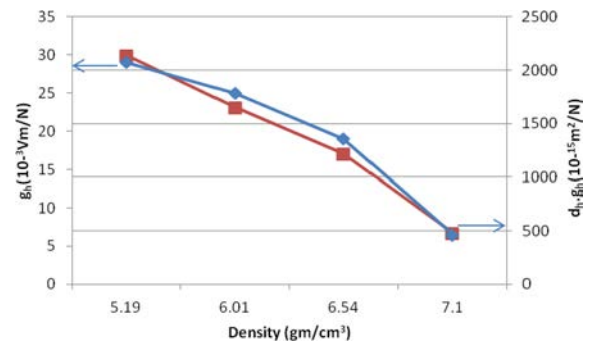


Fig. 16. Variation of g_h and $d_h g_h$ as a function of density of porous PZTPCN ceramics with SA as PFA.

decrease grain size. According to the space-charge theory from Okazaki and Nagata [19], there is a specific amount of space-charge sites such as lattice vacancies or impurity atoms bounding inside grain boundaries as well as domain walls and forming the space-charge fields which inhibit the movement of domain walls. As the grain size decreases, the surface area of the space-charge layer will decrease, so the space-charge field will decrease simultaneously [20–22], thus the piezoelectric coefficient decreases.

The decrease in the ϵ_r values with decreasing density and/or increasing porosity which is due to the dominating effect of passive phase (porous) over the active phase (PZTPCN) of the material. These results agree with earlier reports [23, 24]

Hydrostatic piezoelectric voltage coefficient (g_h) and hydrostatic figure of merit ($d_h g_h$) of porous PZTPCN ceramics as a function of density are shown in figures 15 and 16, respectively. Both g_h and $d_h g_h$ of porous PZT-PCN ceramics were increased sharply with decreasing density. But d_h and g_h values are relatively low in the case of the porous specimen made from PVC where is high in the case of SA. This clearly shows that, order of porosity in case of PVC specimens was lower than SA. The hydrostatic figure of merit ($d_h g_h$) of porous PZTPCN ceramics made from 15 wt% SA and with porosity of about 36% reached $2138 \times 10^{-15} \text{ m}^2/\text{N}$ approximately four times more than that of dense ceramic.

Conclusions

Porous PZTPCN piezoelectric ceramics was synthesized by adding different pore formers (PVC and SA) and sintered at 1200 °C for 2 h.

The results indicated that the density was decreased with an increase in the content of pore formers, the decreased density and /or increased porosity led to a decrease in d_{33} and ϵ_r for all the porous PZTPCN ceramics which can be explained by the space-charge theory from Okazaki.

A decrease in density caused an increase in hydrostatic figure of merit ($d_h g_h$) and porous PZTPCN

ceramics made with porosity of about 36% reached $2138 \times 10^{-15} \text{ m}^2/\text{N}$ approximately four times more than that of dense PZTPCN ceramic.

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