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# Nickel doped PZT ceramics by a spray dried-PVA assisted method

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**Ferroelectric thin material of PZT modified with $Ni^{2+}$, with a Zr/Ti molar ratio 54/46 was prepared by spray drying the nitrate solution of lead, zirconium ,titanium and nickel in a stoichiometric ratio followed by stirring at 80 °C for 36 hours in 3% v/v PVA. The gel prepared by the PVA method was then calcined at 550 °C. Tetragonal perovskite type phases were identified as being present in the calcined powder. The remanent polarization (Pr) and the coercive field (Ec) were found to be 5.1 $\mu Ccm^{-2}$ and 46.2 KV/cm, respectively. The d33 value in PZT was found to be $192 \times 10^{-12}$ C/N at 33 KV/cm at 1.5 atomic percent dopant concentration. SEM micrographs showed the grain size in the range of 0.5 μm. In conclusion, $Ni^{2+}$ incorporation in a PZT material contributes to the polarizibility and the spray dried PVA method slightly lowers the Pr and increases the Ec when compared to the sol.gel technique or magnetron sputtering technique.**

**Key words: PZT material, piezoelectric characterization, hysteresis loop, XRD characterization, scanning electron microscopy, spray dried -PVA method.**

## Introduction

Lead zirconate titanate Pb $(Zr_xTi_{1-x})$ $O_3$ is an important member of the $ABO_3$ family. PZT solid solution ceramics are well known for their excellent piezoelectric, dielectric and pyroelectric properties [1]. The composition with Zr/Ti - 54/46 lies at the morphotropic phase boundary, which corresponds to a transition from the rhombohedral to tetragonal structure [2]. At this phase boundary, the piezoelectric coefficient shows an optimum value [3], hence incorporation of $Ni^{2+}$ has been done at Zr/Ti -54/46. A considerable amount of work has been done on modified PZT but the effect of ferromagnetic dopants such as $Ni^{2+}$ has not been studied properly. Therefore, we have incorporated nickel at varying concentrations in PZT (54/46) and a detailed piezoelectric study has been carried out for a better understanding of the material for applications.

$Ni^{2+}$ having ionic radius 0.64 Å occupies the B - site of the perovskite structure. Lead zirconate titanate modified with Ni has been made with the following formula- $Pb[(Zr_xTi_{1-x})_{1-Y}(Ni)_Y]O_3$, where x = 0.54 and Y = 0.5,1.0 &1.5 atomic percentage of $Ni^{2+}$.

## Experimental

Unmodified PZT material as well as modified with nickel have been prepared by taking a starting solution of lead nitrate prepared from lead nitrate (Loba Chemi make, purity 99.55%), zirconium nitrate prepared from zirconium oxychloride ($ZrOCl_2{\cdot}8H2O$) (Loba Chemi make), titanium nitrate prepared from titanium tetrachloride ($TiCl_4$ Emerch, Germany make) and nickel nitrate solution prepared from nickel nitrate nanohydrate. Nitrate solutions were mixed in stoichiometric proportions for Y = 0, 0.5, 1.0 & 1.5 atomic percent and spray dried with the help of a spray dryer (Eyela, Japan make). Spray dried powder was then stirred for 36 hours at 80 °C with a PVA solution (3% v/v). The PZT gel was then calcined at 550 °C for one hour. XRD tests of calcined powders were carried out to analyze the phases. Small cylindrical pellets (diameter 10 mm) were made from calcined powders by cold pressing applying a pressure of 200 MPa. Pellets were sintered at 1100 °C with a soaking time of one hour. Ferroelectrics hysteresis analyses of sintered samples were done by measuring the polarization at varying applied electric fields at 500 Hz. The piezoelectric strain coefficients (d33) of the samples were measured using a Berlin Court piezo-d33 meter model CPDT-3000 of M/S Channel product, USA, at varying poling fields.

## Result and Discussion

A XRD pattern of calcined powder of PZT (54/46) modified with nickel is shown in Fig. 1. The diffraction lines are found to be very sharp indicating good homogeneity in the powder. Reflections were indexed and lattice parameters were determined using a computer program. X-ray analysis indicates that the specimen was of a tetragonal perovskite type. Ferroelectrics hysteresis analysis of a sintered sample is given in Fig. 2. The remanent polarization (Pr) and the coercive field (Ec) were found to be 5.1 $\mu C\ cm^{-2}$ and 46.2 KV $cm^{-1}$ , respectively. Fig. 3 shows a SEM

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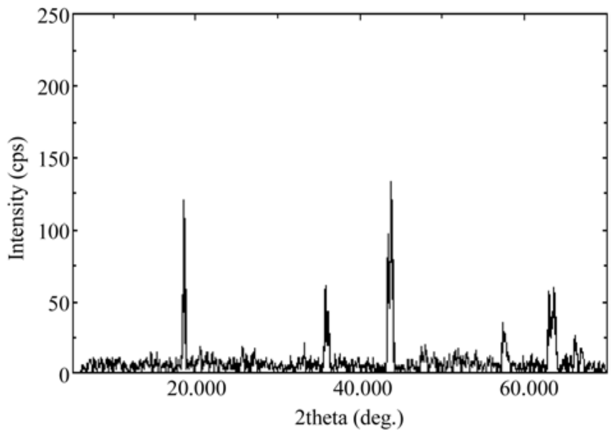

Fig. 1. XRD pattern of 1.5% nickel modified PZT(54/46) ceramic.

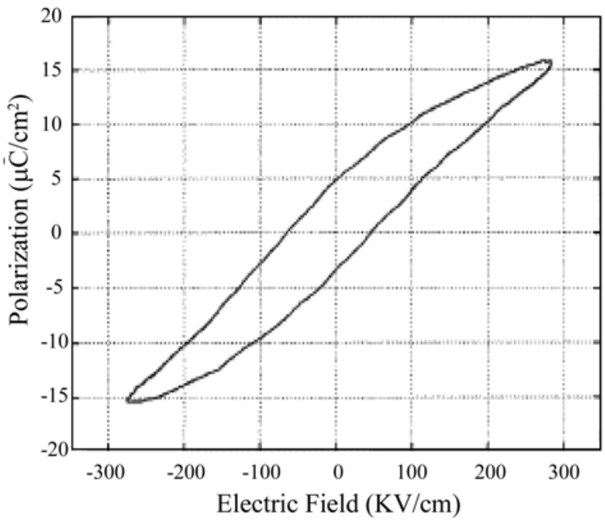

Fig. 2. Hysteresis loop of nickel (1.5%) doped PZT (54/46) ceramic.

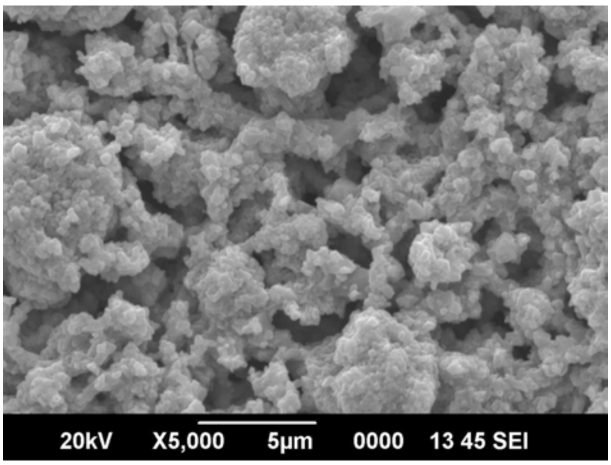


Fig. 3. SEM micrograph of sintered PZT(54/46) + 1.5% Ni.

micrograph of PZT (54/46) modified with nickel (1.5 atomic percent). The spherical grain size can be observed clearly. It has been found that grain size in PZT (54/46) pellets with 1.5% nickel sintered at 1100 °C varies from 0.5 μm to 1.5 μm. A moderate decrease in the grain size

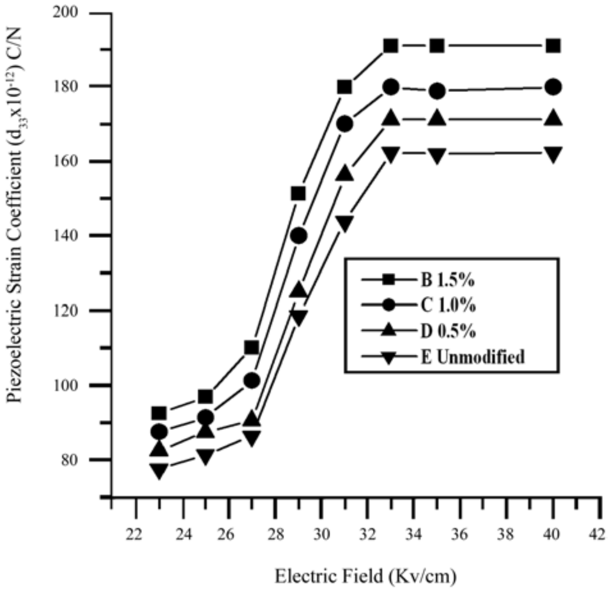


Fig. 4. Variation of d33 with poling field.

after incorporation of the $Ni^{2+}$ additive is due to the smaller ionic radius of the dopant in comparison with the ionic radius of $Zr^{+4}$ and $Ti^{+4}$ [4].

The variation in piezoelectric strain coefficient with poling field in PZT (54/46) doped with $Ni^{2+}$ at different concentrations is shown in Fig. 4. It is observed that the d33 value increases with an increase of the applied DC field and it shows maximum value at 35 KV/cm. It also shows that the d33 value increases with an increase of dopant concentration upto 1.5 atomic % of $Ni^{2+}$ . The increase in the d33 value with an increase of the applied DC field is due to an increase in the mobility in the ferroelectric domain walls with an increase of the DC field [5]. Polarizibility comes to a saturation point at 35 KV/cm.

## Conclusions

PZT doped with $Ni^{2+}$ has been successfully prepared by a spray dried PVA method. Tetragonal perovskite type phases were identified as being present in the calcined powder. The remanent polarization (Pr) and the coercive field (Ec) in PZT(54/46) +1.5 atomic % $Ni^{2+}$ were found to be 5.1 $\mu Ccm^{-2}$ and 46.2 kv $cm^{-1}$ , respectively. SEM micrographs show the grain size in the range of 0.5 μm. The d33 value increases with an increase of the applied DC field and it shows a maximum value at 35 KV/cm. It also shows that the d33 value increases with an increase of dopant concentration upto 1.5 atomic % of $Ni^{2+}$. The increase in the d33 value with an increase of the applied DC field is due to an increase in the mobility in the ferroelectric domain walls with an increase of The DC field. In conclusion, $Ni^{2+}$ incorporation in PZT material contributes to the polarizibility and the spray dried PVA method slightly lowers the Pr and increases the Ec compared to the sol.gel technique or magnetron sputtering technique [6-9].

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