

High Quality of Piezoelectric Response of Nano Ni Doped $\text{Pb}_{1-x}\text{Ni}_x\text{TiO}_3$ Ceramic

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Abstract

A series of $\text{Pb}_{1-x}\text{Ni}_x\text{TiO}_3$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5) were prepared by the general ceramic and co-precipitation method. The grain size decreased with increasing Ni contents. The piezoelectric modulus d_{33} increased with increasing Ni contents. It was observed also the d_{33} of the nanocomposite $\text{Pb}_{1-x}\text{Ni}_x\text{TiO}_3$ prepared by co-precipitation method is higher than those of the prepared by general ceramic method. The coupling factor k_p increased by the more doping of Ni. The ultrasonic wave velocity decreased also with increasing Ni contents. The polarized nano-sample of composition $\text{Pb}_{0.5}\text{Ni}_{0.5}\text{TiO}_3$ is suitable for improving application of useful piezoelectric technology.

Keywords

Piezoelectric Ceramics, d_{33} Coefficient, Electromechanical Coupling Factor K_p

1. Introduction

Lead titanate PT ceramics modified by rare earth elements and alkaline earth elements have emerged as highly promising materials for several piezoelectric applications. This is due to existence of large electromechanical anisotropy in the coupling factors along and transfers direction of polarization [1]-[3].

Samarium modified PT ceramics are reported to exhibit best electric feature [4], [5]. In calcium, modified PT ceramics grain size and porosity is found to affect the behavior of permittivity and planar thickness frequency constant [6]. Additional of strontium in calcium modified PT ceramics increases piezoelectric anisotropy [7], [8]. By substitution of isovalent (Ca^{2+} , Ba^{2+} , Cd^{2+} ... etc.) ions into the Pb^{2+} sites, the lattice anisotropy is reduced [9], [10] and the samples become more dense result in a relatively large

thickness electromechanical coupling coefficient.

In the present work, a comparison between the piezoelectric modulus d_{33} and the electromechanical coupling factor k_p for polarized tablets of $Pb_{1-x}Ni_xTiO_3$ prepared by the usual ceramic method and those prepared by co-precipitation method. It is expected that the nano $Pb_{1-x}Ni_xTiO_3$ ceramics will have a pronounced characteristic of d_{33} and k_p than those of published data. This purpose can help in the improved technology.

2. Experimental

A series of $Pb_{1-x}Ni_xTiO_3$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5) were prepared by the usual ceramic method. The raw materials were presenter at $800^\circ C$ for 2 hours. The samples were in the form of tablets and then to be cooled gradually to room temperature.

A second series of $Pb_{1-x}Ni_xTiO_3$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5) were prepared using co-precipitation method. The chemical reagent were titanium chloride ($TiCl_3 \cdot 15 H_2O$) nickel (II) chloride, ($NiCl_2 \cdot 6 H_2O$), lead chloride ($PbCl_2$) and sodium hydroxide ($NaOH$). All the chemical reagents were dissolve in to 200 ml of distilled water. After mixing and stirring solutions for 6 hours, chemical precipitation was achieved at room temperature vigorous stirring by adding of $NaOH$ solution gradually the reaction system keep at $80^\circ C$ for 2 hours and PH solution ± 12 . After the system cooled to room temperature, the precipitates were washed with distilled water until PH-7. Finally the samples dried in oven at $200^\circ C$ for several hours and sintered at $1000^\circ C$ for 2 hours then left to be cooled gradually with the rate $50^\circ C/hr$.

The samples were examined by X-ray diffraction using a Philips model (PW-1729) diffractometer with $Cu-K\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$).

The microstructure of the sintered samples examined using SEM and TEM model Quanta 250 FEG (Field Emission Gun) attached with EDX unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 K.V., magnification 14x up tp 100,000 and resolution for Gun. 1n. FEI company, Netherlands EMITECH K550X sputter coate England and (JOEL-100SX) and HRTEM model (High Resolution Transmission Electron Microscope JOEL EM 2-100) respectively. The prepared tablets with silver electrodes were polarized by exposing to 2 KV per min at $150^\circ C$ for 1 Hour and then the tablets were left to be cooled under applying the dc field.

The piezoelectric modulus d_{33} was determined by taking the slope of the charge depended of the applied stress.

The coupling factor k_p was estimated from the resonance frequency f_r and antiresonance frequency f_a for the radial mode of vibration [4], [5]:

$$k_p = \sqrt{\frac{2.55 * (f_a - f_r)}{f_r}}$$

The ultrasonic wave velocity C was determined from the relation:

$$f_r = \frac{C}{2\pi a}$$

where a is radius of polarized tablets.

3. Results and Discussion

Room temperature XRD patterns of the sintered tablets of $\text{Pb}_{1-x}\text{Ni}_x\text{TiO}_3$ for the two methods of preparation are shown in **Figure 1**. These have sharp and single diffraction peaks, indicating better homogeneity and crystallization of the samples. All the reflection peaks were indexed and correlated with JCPDS card file number 70 - 4057 showing the perovskite structure for all composites. The average particle size D was determined from the half width of the stronger reflections of X-ray using Scherer's equation:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where λ is the wavelength of the X-ray for Cu-K α radiation ($\lambda = 1.541 \text{ \AA}$) and β is the full width at half maximum of the peak.

The particle size determined from X-ray diffraction for all samples using Scherer's equation are found to be close nearly to be found from TEM micrographs as shown in **Table 1**, **Figure 1** and **Figure 2**.

Figure 3 shows the scanning electron micrographs (SEM) of sintered and co-precipitation method of $\text{Pb}_{1-x}\text{Ni}_x\text{TiO}_3$ indicate homogenous distribution of grain brought out the surface of material. The average grain size calculated from micrograph of PbTiO_3 is $0.25 \mu\text{m}$. As Ni^{2+} concentration increases the grain size decreases as given in **Table 1**. **Figure 2** shows the transmission electron micrographs (TEM) of the usual

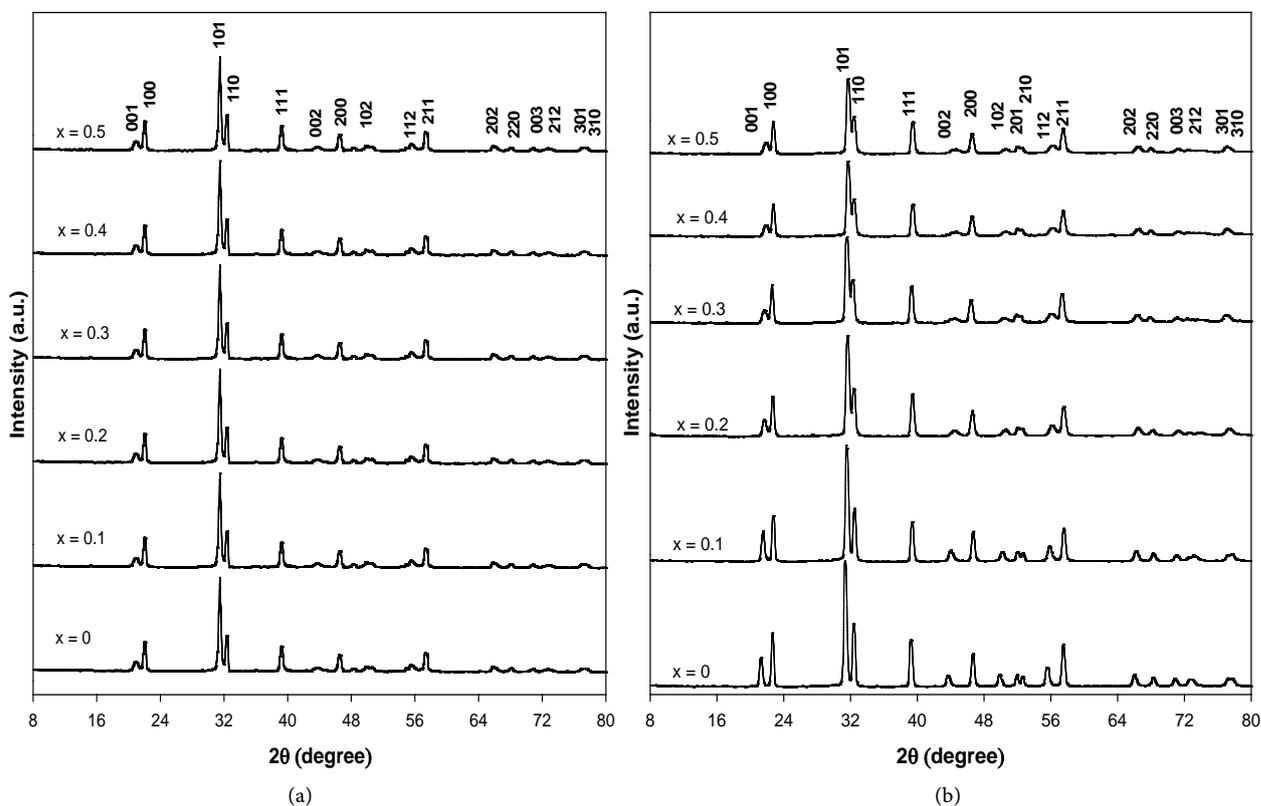


Figure 1. XRD pattern of " $\text{Pb}_{1-x}\text{Ni}_x\text{TiO}_3$ " system for different ratios of Ni content x , for (a) Ceramic method; (b) co-precipitation method.

Table 1. Indicates the value of particle size of $Pb_{1-x}Ni_xTiO_3$ for 1) usual method and 2) co-precipitation method.

x	Particle size (nm)	
	P.S1	P.S2
0.0	60.359	28.417
0.1	55.337	27.044
0.2	44.274	20.478
0.3	42.17	20.435
0.4	37.959	18.605
0.5	35.92	18.949

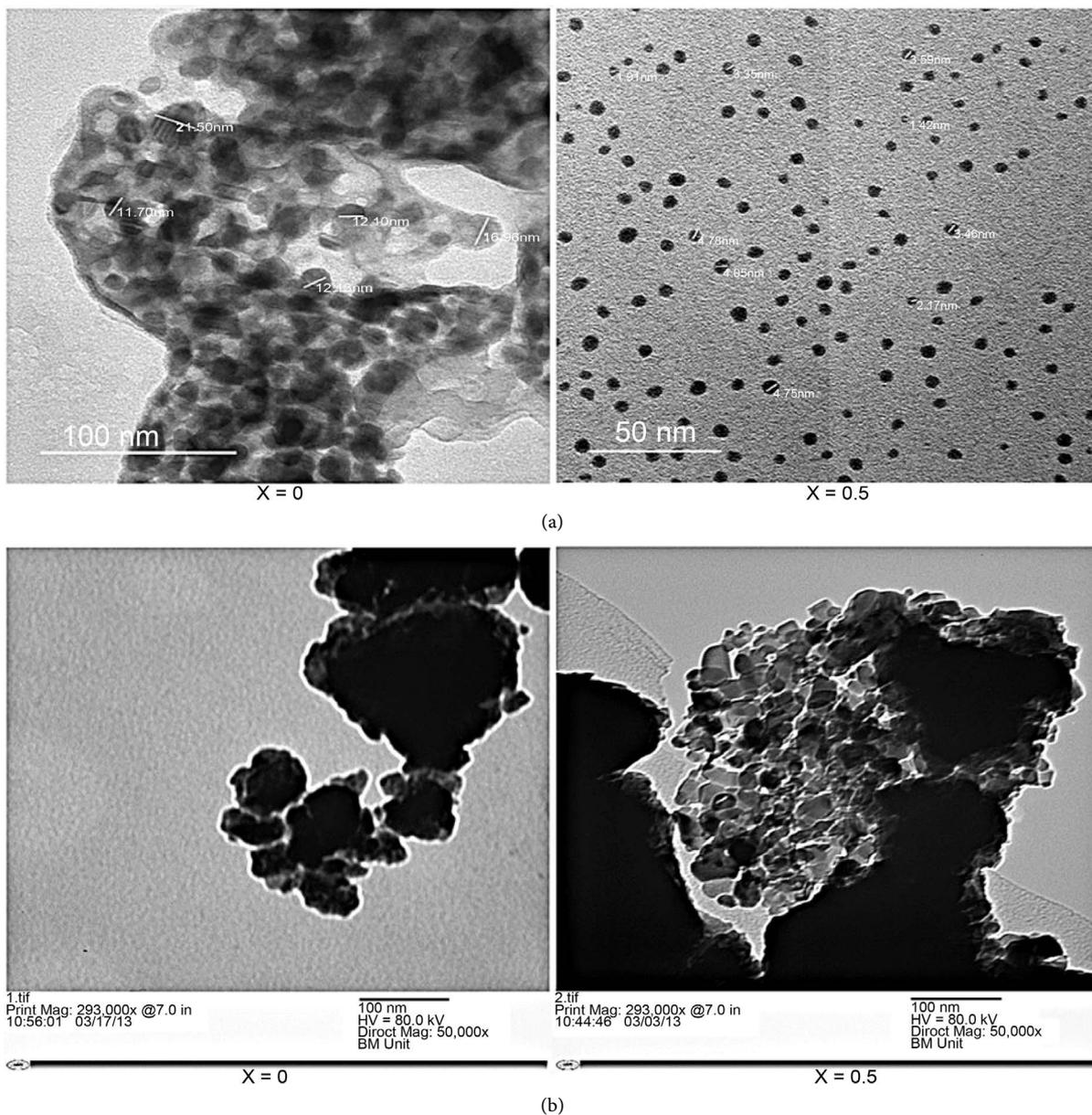


Figure 2. (a) TEM of co-precipitation $Pb_{1-x}Ni_xTiO_3$ samples; (b) TEM of ceramic $Pb_{1-x}Ni_xTiO_3$ samples.

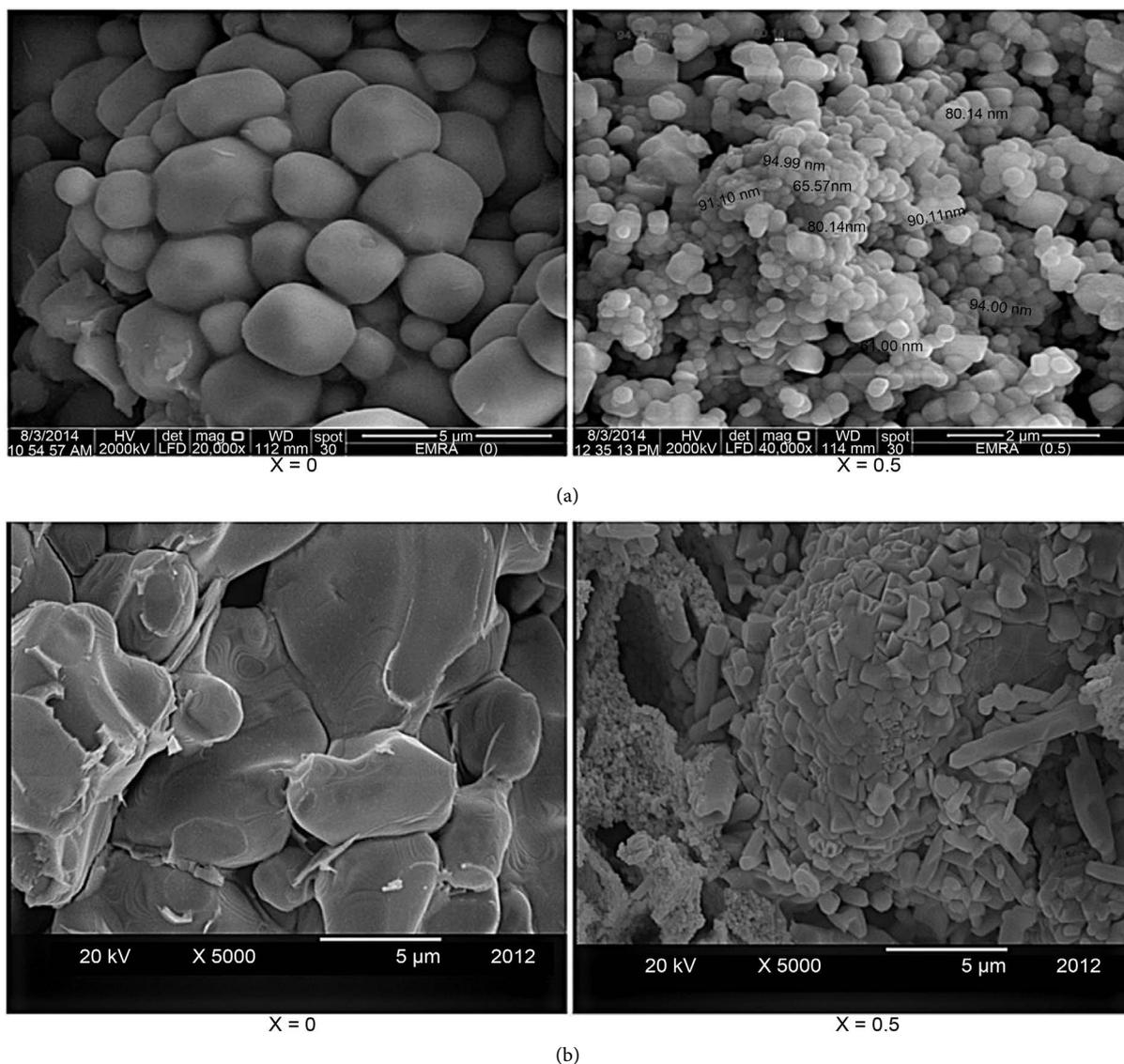


Figure 3. (a) SEM of co-precipitation $\text{Pb}_{1-x}\text{Ni}_x\text{TiO}_3$ samples; (b) SEM of ceramic $\text{Pb}_{1-x}\text{Ni}_x\text{TiO}_3$ samples.

ceramic samples and nano polycrystalline samples prepared by co-precipitation method. It is obvious that the increase of Ni content decrease the particle and grain size. This is due to the following: Ni^{2+} ions enter the lattice and replace some lead ions (Pb^{2+}). These doped ions precipitate at grain boundaries and retard its motions. The increase of Ni^{2+} ions inhabit the grain growth keeping the grain size small. Our explanation in similar to previous work [10], [11].

3.1. Effect of Ni Content on the Piezoelectric Modulus d_{33}

The effect of Ni content on the piezoelectric modulus d_{33} is shown in **Figure 4**. It is observed that d_{33} of the polarized samples prepared by co-precipitation method are higher than those prepared by ceramic method. Doping ions concentrate near the domain boundaries in which some dislocations might act as precipitating centers for migration

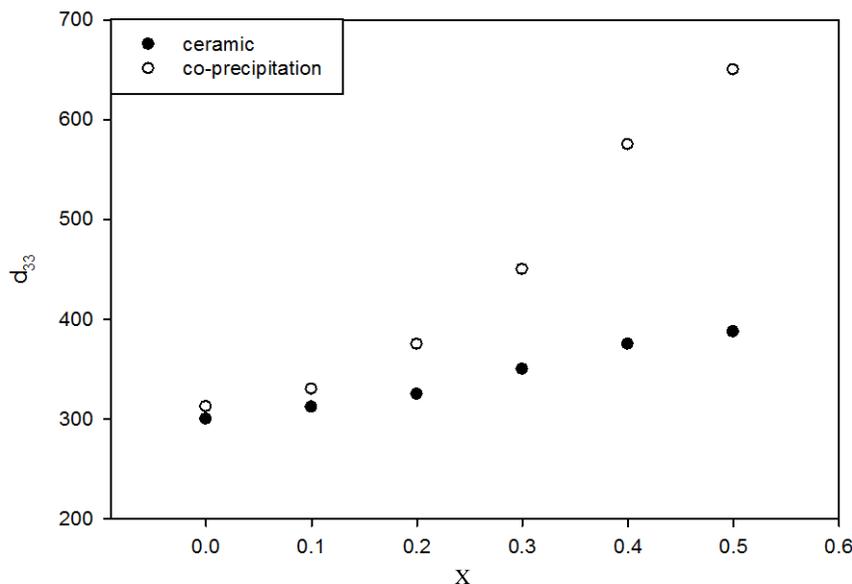


Figure 4. The piezoelectric coefficient d_{33} of “ $Pb_{1-x}Ni_xTiO_3$ ” for ceramic and co-precipitation methods.

of these ions, which in turn act as pinning points causing further dislocations. Also the coulomb attraction between the doping ions and the induced vacancies leads to continuous formation of more lattice vacancies since many of them might act as sinks for these point defects.

Thus, the domain walls are expected to be quite free in smaller particle size and grain size considering that grain boundaries will give additional pinning points to the moving walls. The beneficial result of the reduction in grain boundary is the decrease in coupling effect between boundaries and the domain walls leading to increase in domain wall mobility.

This mechanism may affect domain wall motion towards the increase of polarization and hence the observed increase of d_{33} and generated piezoelectric charges under applied stress. Moreover, the d_{33} of nanoparticles of co-precipitation method is higher due to smaller area of grain boundaries compared to those in the samples prepared by ceramic method. This small area helps the domain wall mobility to be increased giving rise to polarization under applied stresses. The behavior of our results is similar to those in previous work on lead titanate zirconate ceramics [12], [13].

3.2. Electromechanical Coupling Factor k_p

The planer-coupling factor k_p , as a function of Ni dopant is shown in **Figure 5**, for the prepared polarized tablets by usual ceramic and co-precipitation method. As Ni additions increase, k_p increases. This can be explained as follows:

Ni^{3+} substituted Pb^{2+} sites of the perovskite tetragonal structure. For each Pb^{2+} cation replaced with Ni^{3+} that a vacancy is created to maintain the charge neutrality of the system. It is in the tetragonal polarized ferroelectric materials, two types of domains are

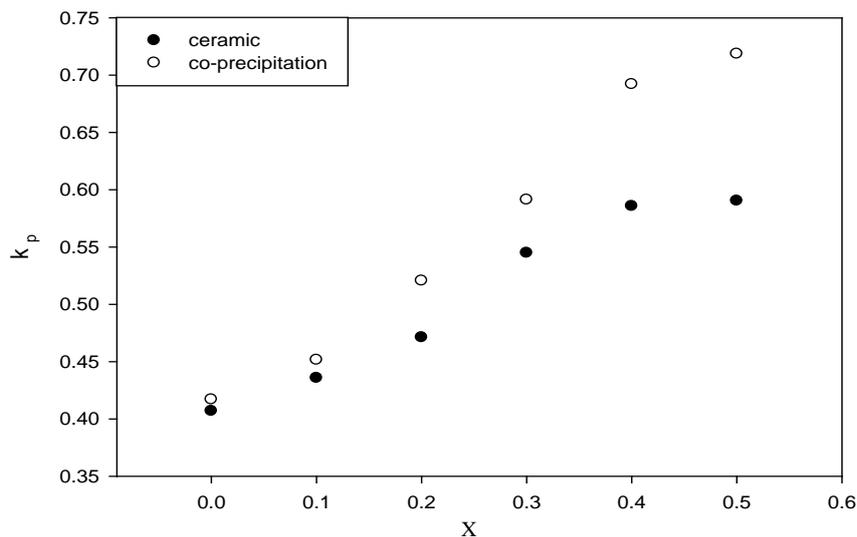


Figure 5. Effect of “ $\text{Pb}_{1-x}\text{Ni}_x\text{TiO}_3$ ” on the coupling factor k_p for ceramic and co-precipitation methods.

existed, 90° and 180° domains. The 180° domains remain entirely after poling process, and small percentage of 90° domains oriented in its position after poling. When ac field applied to the resonator (disc). The existence of lattice vacancies facilitates to these domains to be vibrated at lower frequency [12]. This led to decrease the resonance frequency of the polarized tablets. The increase of Ni content increases the lattice vacancies caused the decrease of resonance frequency giving rise to k_p .

The increase of k_p in the nano $\text{Pb}_{1-x}\text{Ni}_x\text{TiO}_3$ polarized discs than those prepared by usual ceramic method is due to the lower grain boundary area which facilitates the domain wall motion under applied ac field. This led to increase k_p of the nano disc of $\text{Pb}_{1-x}\text{Ni}_x\text{TiO}_3$. From **Table 2** it is noticed that the particle size of the co-precipitation method is smaller for the usual ceramic in all Ni contents. Ni^{3+} ions enter the lattice instead of pb^{2+} ions. The small area of grain boundary of the nanoparticle of the co-precipitation method helped the domains wall mobility to be increased. This led to increase the piezoelectric characteristic properties in the nano crystallite of the co-precipitation method than those prepared by usual ceramic method.

3.3. Effect of Ni Contents on the Ultrasonic Velocity

Figure 6 illustrates the effect of Ni content on the velocity of ultrasonic wave for the radial mode of vibrating polarized tablets. It is obvious that the velocity decreases with increasing x. This could be explained as following:

The velocity of sound wave for poled $\text{Pb}_{1-x}\text{Ni}_x\text{TiO}_3$ of the two method of preparation can be evaluated in the radial mode may be due to the following:

The decrease in sound wave velocity with doping may be due to the creation of lead vacancies. These vacancies help the domain wall to vibrate early leading to decrease the ultrasonic wave velocity. Our explain is in close to previous work on PZT [11].

Table 2. k_p and d_{33} of the published data and our present data.

composition	k_p	d_{33} (PC/N)	
PbTiO ₃	0.3	56	[14], [15]
BaTiO ₃	0.35	191	[16]
PZT:Nb	0.54	—	[17]
PZT:(La + Nb)	0.57	—	[17]
PZT	0.32	220	[18]
Pure PZT (52/48)	0.47	—	[18]
Pb(Zr _{0.52} , Ti _{0.48})O ₃	0.53	223	[16]
Pb _{0.9725} (Zr _{0.52} Ti _{0.48}) _{0.945} Nb _{0.055} O ₃	0.59	386	[19]
PZT:Sr	0.52	—	[20]
BZT-50BCT	0.5	546	[21]
PZT5A	0.6	374	[21]
PZT:Mg	0.381	—	[22]
PZT:Zr	0.446	—	[22]
Pb _{0.9} Ni _{0.1} (Zr _{0.52} , Ti _{0.48})O ₃	—	121	[10]
Pb(Mn _{1/3} Nb _{2/3})O ₃	0.45	—	[23]
0.5(0.1BiYbO ₃ -0.9PbTiO ₃)-0.5Pb(Zn _{1/3} Nb _{2/3} O ₃)(BYPT-PZN)	0.23	85	[24]
Pb _{1-3x/2} Fe _x (Zr _{0.52} Ti _{0.48}) _{1-5y/4} Nb _y O ₃ (PFZTN)	—	300	[25]
Pb _{0.95} Bi _{0.03} Nb _{0.02} Zr _{0.51} Ti _{0.49-x} M _x O ₃	0.665	625(pm/V)	[26]
Nano Pb _{0.5} Ni _{0.5} TiO ₃ crystallite	0.73	650	Present work

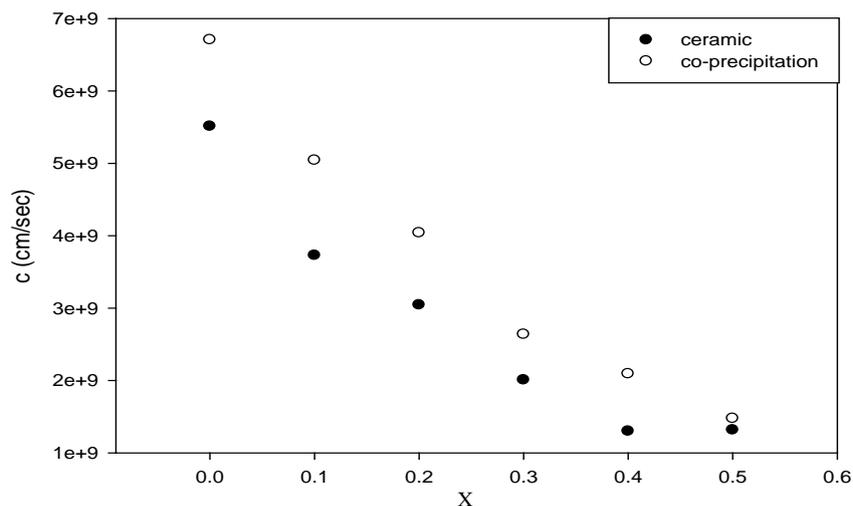


Figure 6. Effect of x on ultrasonic velocity for ceramic and co-precipitation methods.

4. Conclusions

In this paper, the piezoelectric d_{33} for the Pb_{1-x}Ni_xTiO₃ ceramics prepared by co-pre-

precipitation method were found to be higher than those prepared by ceramic method. This caused by inhibition of grain wall volume.

The increase of k_p for samples prepared by co-precipitation method was due to entering Ni ions the lattice and substitute Pb^{2+} ions. This caused creation of vacancies. These vacancies helped the dipoles to vibrate at lower frequency.

The decrease of ultrasonic waves with enhancing Ni contents was due to creation of vacancies, which scattered the propagation of the waves.

It is clearer the present sample $Pb_{0.5}Ni_{0.5}TiO_3$ possessed higher d_{33} and k_p than those in previous work [12] which is useful in technology.

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