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Effect of iron and nickel substitution on the piezoelectric properties of PZT type ceramics

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Abstract

The effect of Fe and Ni doping on piezoelectric properties of a soft type piezoelectric material was investigated. The materials composition was as follows: $Pb_{0.95}Bi_{0.03}Nb_{0.02}Zr_{0.51}Ti_{0.49-x}M_xO_3$, where M stands for the transitional metals Fe or Ni and $x = 0$, 0.02, 0.04, 0.06, 0.08 and 0.10. The materials were prepared by the conventional ceramic technique. X-ray diffractograms showed that compounds were completely formed and they were situated in the nanometric range with an average crystallite size of about 95 nm. The optimum amounts of doping for both types of transitional elements were situated somewhere around $x = 0.06$ with better results for nickel doped samples. The maximum density for 0.06 nickel doped material was 7.87 and 7.80 g/cm^3 for iron doped one. The electromechanical coupling factor k_p for 0.06 nickel doped samples was 0.665 while for the correspondingly iron doped ones it was 0.638. The relative dielectric constant was about 4050 for nickel doped samples and 3400 for iron doped ones. The corresponding values for the charge constant d_{33} were 625 and 530 pm/V, respectively. These results were discussed in terms of the positions occupied by Ni and Fe into the lattice, the type of vacancies created by this and the shift of the morphotropic phase boundary.

Keywords: PZT; Perovskite; Piezoelectric properties; Dielectric properties; Sintering

1. Introduction

At present there is an increasing demand for high quality piezoelectric materials used for the fabrication of the piezoelectric transducers for various applications in the field of sensors and actuators for fine displacement systems, especially in microrobotics or microelectromechanical systems.

Actuators make use of the direct expansion of piezoelectric materials and therefore for such applications there is a need for piezomaterials with high displacement constant *d*.[1–7] Moreover, during the last years another striking application of the reverse piezoelectric effect was developed in the field of micromotors,[8–11] in large demand today as tiny motors for office equipment and microrobotics. Such piezoelectric micromotors are superior in the milimetric-size motor area to any other motors because their efficiency is completely insensitive to size. They can work with the same efficiency at low or high speed still retaining higher torque, have excellent controllability and fine position resolution, do not require gear mechanism, are very quiet in operation and are not affected by the external magnetic and radioactive fields. Therefore, piezoelectric materials with large charge constant *d* for such applications become imperative and the present investigation was conducted toward obtaining new PZT type materials with large *d* constant and still having high electromechanical coupling coefficient able to be used for actuators and micromotors sensors and transducers.

2. Experimental

The materials investigated in the present work were a soft type PZT material doped with nickel and iron and having the general chemical formula: $Pb_{0.95}Bi_{0.03}Nb_{0.02}Zr_{0.51}Ti_{0.49-x}M_xO_3$, where M stands for the transitional metal Ni or Fe and $0.00 \leq x \leq 0.10$. The raw materials used for the

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experiment were oxides of p.a. purity. The materials were processed by the conventional ceramic technique with the following detailed data: six charges of each dopant Ni and Fe were prepared, corresponding to $x = 0.00$, 0.02, 0.04, 0.06, 0.08 and 0.10, respectively. The stoichiometric amounts of oxides were wet mixed for 3 h by means of a planetary ball mill, in agate vials of 500 ml capacity, using agate balls of about 10 mm diameter in a weight ratio: ball/oxides/acetone of 100/100/250. The mixed slurries were dried with continuous agitation on electrical plates, manually crushed and sieved and then double calcined at 850 and 950 °C, respectively, for 2 h with an intermediate milling of 4 h and a final milling of 48 h. BET measurements of the final milled powders gave an average specific surface area between 10 and 12 m^2/g corresponding to an average particle diameter of about 90–100 nm. Disc shaped samples of 15 mm diameter and about 2 mm thick were next uniaxially pressed from these powders in a steel die at a pressure of about 50 MPa. The pressed samples were then sintered in dense alumina crucibles at temperatures between 1050 and 1300 °C for 4 h. The density of each sintered sample was determined by Archimede's method. Next, the sintered samples were processed by grinding on a mechanically grinding machine up to a final dimension of 10 mm diameter and 1 mm thick. After ultrasonically cleaning and thermally recovery at 700 °C for 1 h, the samples were silver electroded on both plan parallel surfaces and poled in a silicon oil bath at 220 °C under an electric field of 30 KV/cm and slowly cooled down to 80 °C under electric field after which the electric field was cut off and the samples taken out from the poling device. Piezoelectric properties were measured 24 h after poling by resonance spectroscopy using a HP 4194A Impedance gain/phase analyzer.

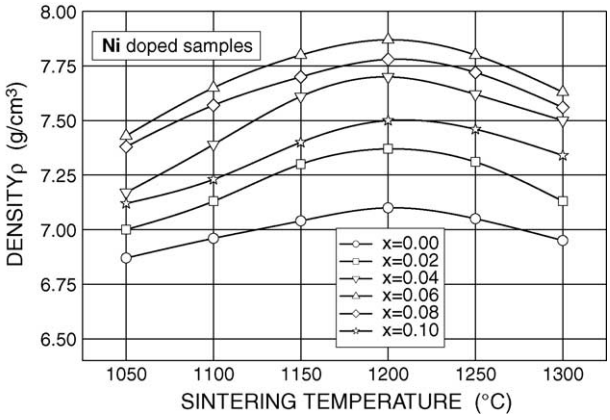

Fig. 1. The dependence of the density on the sintering temperature for Ni doped samples.

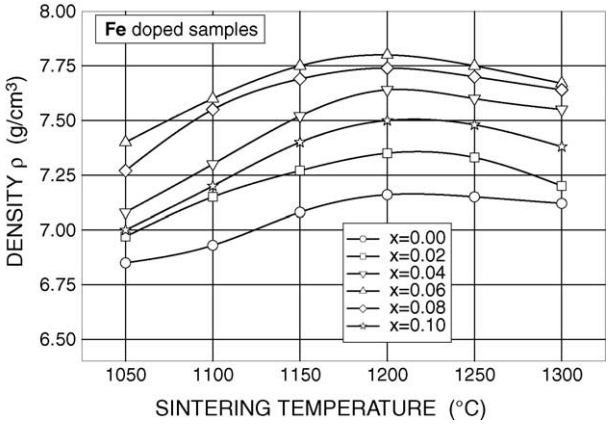

Fig. 2. The dependence of the density on the sintering temperature for Fe doped samples.

3. Results and discussion

The X-ray difractograms, both Ni and Fe doped powders, showed the well known phase with perovskite structure, indicating that the PZT material synthesis was completely achieved.

Figs. 1 and 2 illustrate the behavior of the densities of sintered samples as a function of the sintering temperature for all composition doped with Ni (Fig. 1) and Fe (Fig. 2), respectively.

One can see that for both types of composition there is an optimum sintering temperature centered on 1200 °C where the densities reach a maximum regardless the amount of dopant. With increasing the dopant amount x the densities increase, reaching the highest values for compositions with $x = 0.06$ and then decreasing again. This behavior is well illustrated in the graph from Fig. 3 where one can see the maximum densities of 7.87 and 7.80 g/cm^3 for the Ni and Fe doped samples, respectively, values which correspond to about 98.5 and 97.5%, respectively of the theoretical density (if 8 g/cm^3 is taken as the right figure for the theoretical density of a PZT material).[12] These values would be even slightly higher if the theoretical density should be considered as 7.95 g/cm^3,[13] or 7.98 g/cm^3.[14]

Such high values for the densities indicate that the sintered samples are fully densified with well-formed crystallites and rather poreless. This assertion is fully sustained by the

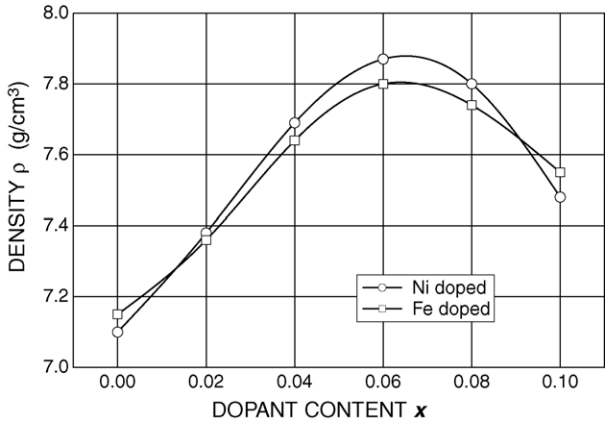

Fig. 3. The behavior of the maxim values of the density as a function of the dopant amount for Ni and Fe doped samples, sintered at 1200 °C.

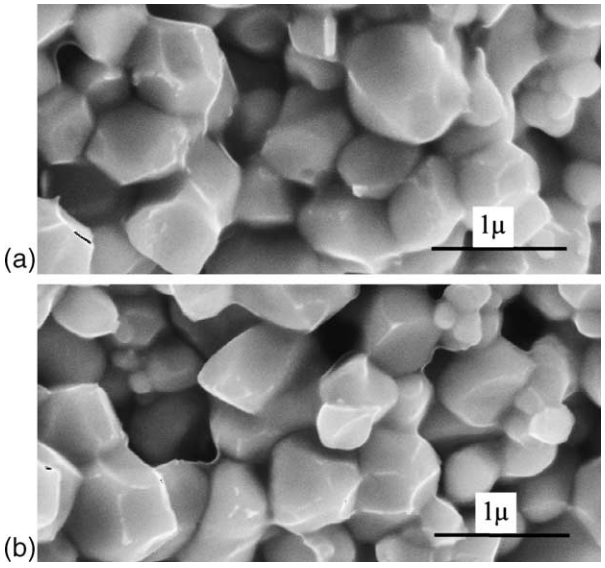

Fig. 4. Fracture SEM images of the sintered samples doped with 0.06 Ni (a) and 0.06 Fe (b), respectively.

fracture SEM images from Fig. 4 made on 0.06 Ni and 0.06 Fe doped samples with the highest densities.

One can see the lack of pores, and the well formed submicronic crystallites. One may expect the best piezoelectric properties for these samples as will be confirmed further.

The decrease of the densities for samples with $x > 0.06$ could possibly be explained by a slight inhibiting effect of the dopants for higher concentrations. Fig. 5 shows a micrograph of a Fe doped sintered sample with $x = 0.10$ where the crystallites are smaller and some pores are present. The piezoelectric properties were determined only on samples with maximum densities, i.e. the samples sintered at 1200 °C.

Fig. 6 shows the dependence of the planar coupling coefficient k_p on the dopant concentration. One can see that k_p reaches maximum values of 0.665 and 0.638 for the compositions with $x = 0.06$ both for Ni and Fe doped samples, respectively. The same trends and behaviors were recorded for charge constant d_{33} and dielectric permittivity ε_r either as shown in Figs. 7 and 8.

A remarkable thing about these graphs is the high values of the constants mentioned before. Thus, for Ni doped samples, a maxim value of about 625 pm/V for d_{33} was measured and 530 pm/V for Fe doped samples, respectively. Such values

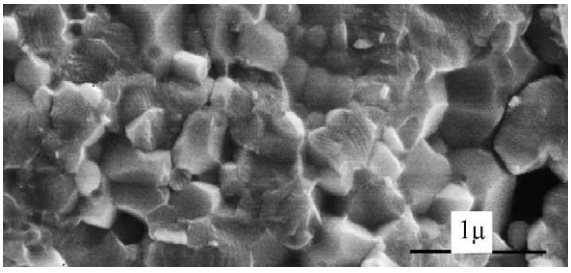

Fig. 5. Fracture SEM image of a sample doped with 0.10 Fe.

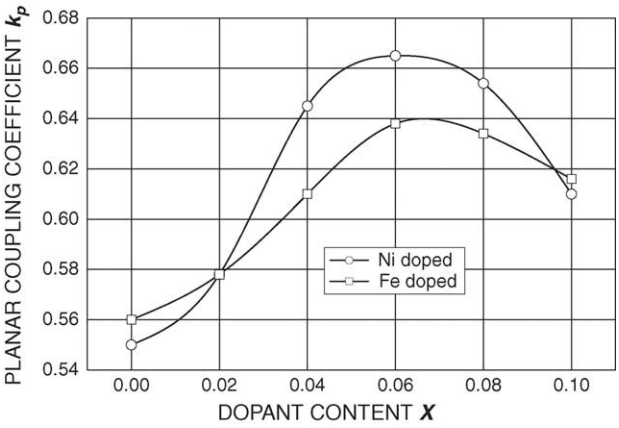

Fig. 6. The dependence of the planar coupling factors of Ni and Fe doped samples on the dopant concentration.

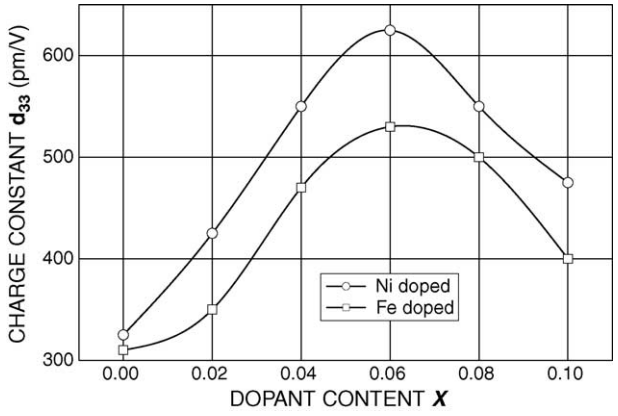

Fig. 7. The dependence of the charge constant d_{33} of Ni and Fe doped samples on the dopant concentration.

can be considered very high for an ordinary doped PZT material [see for instance Refs. [16–19]] and this fact makes such materials excellent candidates for actuators or micromotors.

At the same time the dielectric permittivities at room temperature reach also high values of nearly 4050 and 3400 for Ni and Fe doped samples, respectively. This might be the

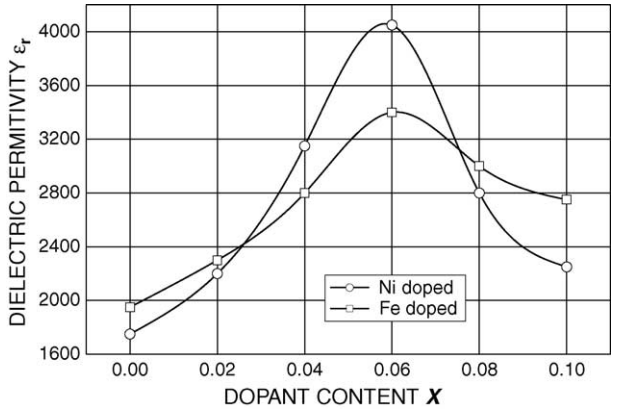

Fig. 8. The dependence of the relative dielectric permittivity of Ni and Fe doped samples on the dopant concentration.

result of a slight decrease of the Curie temperature. In fact, all these experimental results can be explained by the assumption that the presence of the dopants gives rise to a vacancies into the PZT lattice with the direct consequence of rising the dielectric constant, the piezoelectric coupling factor and the charge constant.[15] This is consistent with the ionic radius rule. Thus, Ni^{2+} has an ionic radius of 0.69 Å and enters the Ti^{4+} position, which has a radius of 0.68 Å. On the other hand Fe^{2+} with its 0.75 Å ionic radius, most probably enters Zr^{4+} position with 0.80 Å ionic radius. Thus, the tetragonal and the rhombohedral phases are equally affected by the presence of Ni and Fe and forms a new morphotropic phase boundary probably at $x = 0.06$,[20] where the piezoelectric properties are subsequently enhanced because of the increased easy of reorientation during poling.[21] A shift of R and T phases is also possible by the new distribution of Ni and Fe ions into the lattice.

Such a shift forms stronger piezoelectric effects by the easiness of domain reorientation. Within the R side the number of 180° domains is greater and they are more easily aligned along the poling field direction than the 90° domains, which switch harder. In this way, it seems easy to assume a higher degree of alignment of dipoles after removal of the field and consequently higher piezoelectric parameters for the Ni doped compositions.

4. Summary

A soft type PZT material was doped with nickel and iron within a narrow compositional range. The materials were prepared by the conventional ceramic technique and were sintered at temperatures up to 1300 °C. The optimum sintering temperature proved to be 1200 °C for both types of doped samples. The samples sintered at this temperature and having a doping level of 6% atomic, gave the highest parameters values: densities of 7.87 and 7.8 g/cm^3, electromechanical coupling factors of 0.665 and 0.638, dielectric permittivities of 4050 and 3400 and charge constants of 625 and 530 pm/V for Ni and Fe samples, respectively. The Ni doped samples were better than Fe doped ones.

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References

1. Newnham, R. E. and Ruschan, G. R., Smart electroceramics. *J. Am. Ceram. Soc.*, 1991, **74**, 463–480.
2. Sporn, D., Watzka, W., Schonecker, A. and Pannkoke, K., Smart structures by integrated piezoelectric thin fibers. *NATO Sci. Ser. High Techn.*, 2000, **76**, 87–97.
3. Ukino, K., *Piezoelectric Actuators and Ultrasonic Motors*. Kluwer Academic Publishers, 1996.
4. Fujita, H., Future of actuators and microsystems. *Sens. Actuators A*, 1996, **56**, 105–111.
5. Hauden, D., MEMS Application of piezoelectric materials. *NATO Sci. Ser. High Tech.*, 2000, **76**, 335–346.
6. Sakai, T., Terai, Y. and Ishikiriyama, M., Improvement in durability of piezoelectric ceramics for actuators. *Jpn. J. Appl. Phys.*, 1995, **34**, 5276–5278.
7. Schuh, C., Lubitz, K., Steinkopff, T. and Wolf, A., Piezoelectric components for technical applications. *NATO Sci. Ser. High Tech.*, 2000, **76**, 391–399.
8. Uchino, K., Piezoelectric ultrasonic motors: overview. *Smart Mat. Struct.*, 1998, **7**, 273.
9. Kasuga, M. T., Satoh, N., Tsukada, T., Yamazaki, F., Ogawa, M., Suzuki, I. *et al.*, Compact ultrasonic motors. *J. Soc. Precision Eng.*, 1991, **57**, 63–68.
10. Uchino, K. and Koc, B., Compact piezoelectric ultrasonic motors. *NATO Sci. Ser. High Tech.*, 2000, **76**, 309–320.
11. Ueha, S. and Tomikawa, Y., *Ultrasonic Motors*. Oxford Science Publishers, 1993.
12. Wittmer, D. E. and Buchanan, R. C., Low temperature densification of lead zirconate titanate. *J. Am. Cer. Soc.*, 1981, **64**, 485–490.
13. Hankey, D. L. and Biggers, J. V., Solid state reactions in the system PbO-TiO_2-ZrO_2. *J. Am. Cer. Soc.*, 1981, **64**, 172–173.
14. Nielsen, E. R., Ringgaard, E. and Kosek, M., Liquid phase sintering of PZT. *J. Eur. Cer. Soc.*, 2002, **22**, 1847–1855.
15. Jaffe, B., Cook, W. R. and Jaffe, H., *Piezoelectric Ceramics*. Academic Press, London New York, 1971, pp. 7 and 10.
16. Setter, N., ABC of piezoelectricity and piezoelectric materials. In *Proceeding of International Conference on Piezoelectric Materials for End Users*, 2002.
17. Wolny, W. W., Applications of piezoceramics. In *Proceeding of International Conference on Piezoelectric Materials for End Users*, 2002.
18. Gonnard, P., Piezoelectric materials for power applications. In *Proceeding International Conference on Piezoelectric Materials for End Users*, 2002.
19. Shrout, T. R., Eitel, R. and Randal, C., High performance piezoelectric ceramics. In *Proceeding of International Conference on Piezoelectric Materials for End Users*, 2002.
20. Yamamoto, T., Ferroelectric properties of the $PbZrO_3$-$PbTiO_3$ system. *Jpn. J. Appl. Phys.*, 1996, **35**, 5104–5108.
21. Cao, W. and Cross, L. E., Theoretical model for the morphotropic phase boundary in lead zirconate-lead titanate solid solution. *J. Am. Phys. Soc. Phys. Rev.*, 1993, **47**, 4825–4830.