

Effect of ZnO Addition on the Structure, Microstructure and Dielectric and Piezoelectric Properties of $K_{0.5}Na_{0.5}NbO_3$ Ceramics

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Microstructure, structure and electrical and dielectric properties of ZnO-doped $K_{0.5}Na_{0.5}NbO_3$ (KNN) ceramics were investigated. Powders were obtained by the conventional solid-state method. Samples doped with 0 to 1 mol% of ZnO were sintered at 1125 °C for 2 h. Through XRD spectra, the perovskite structure was detected, in addition to small peaks corresponding to secondary phases. It was also observed that zinc changed the microstructure and grain size of KNN ceramics. The addition of 0.5 mol% of Zn^{2+} produced a softening effect in the ferroelectric properties of the material, and increased its final density. Conversely, the addition of 1 mol% of Zn^{2+} reduced the sample densification.

Keywords: A. Ferroelectrics, B. Solid-state reactions, C. Piezoelectricity

1. Introduction

From the view of the sustainable development, considerable attention for environment friendly lead-free piezoelectric ceramics has been paid to $K_xNa_{1-x}NbO_3$ -based ceramics (KNN) in recent years^{1,2}. Alkaline niobates have shown valuable piezoelectric and electric properties when the compositional ratio is near $x = 0.50$. This composition is reported to show a virtual morphotropic phase boundary where the total polarization is maximized by an increase in oriented domains. Moreover, the orthorhombic crystal structure at room temperature and a high T_C favor the use of this piezoelectric material for high temperature applications^{3,4}. Nevertheless, the dielectric and piezoelectric properties of pure KNN are relatively low ($d_{33} \sim 90$ pC/N) as compared to those achieved with PZT. This makes the replacement of conventional PZT with KNN very difficult⁵⁻⁷.

To solve this problem several options have been studied. Hot pressing could improve the final density of these ceramics. Although this technique is able to obtain high densities and better properties compared to conventional air-sintered samples, it needs careful investigation and optimization of sintering parameters to result in reproducible and high quality ceramics⁸. Additionally, it is a more expensive route compared to the conventional sintering process. Then, the study of different additives to obtain KNN with low porosity and good electrical properties by conventional methods is extremely important. In previous published papers we found⁹ that Ca^{2+} and Ba^{2+} ions substitute alkaline elements (Na^+ and K^+ ions) in “A” sites of the perovskite lattice producing cationic vacancies and consequently “softening” the properties of the ceramic. When dopant concentration is increased, Na^+ and K^+ are segregated. Sodium will tend to volatilize and to increase the porosity while the potassium will tend to form a glassy phase. Because of the increase in porosity and secondary

phases, properties get deteriorated with the incorporation of high dopant amounts.

Previous works have shown that the addition of zinc generates the formation of a liquid phase during sintering in air. This liquid phase would reduce sintering temperatures, preventing the volatilization of elements such as sodium during this process^{10,11}. However, it is also expected that Zn^{2+} ions (88pm) replaces niobium ions (Nb^{5+} , 78pm) of the lattice with the consequent oxygen vacancies generation producing a hardening effect on the ferroelectric properties of the material¹². Moreover, other authors suggest the possible A-site replacement of Zn^{2+} ions which provokes the cationic vacancies formation which produces a softening effect on the material properties¹³. Li et al. determined that with adding 0.6 mol% of ZnO, the Zn^{2+} first enters the A-site while higher amounts of Zn^{2+} substitutes B-site ions when the additive was incorporated in the initial mixture¹⁴.

Based on these studies, in this work the effect of the ZnO-doping on the structural and microstructural evolution and its influence on the final properties of $K_{0.5}Na_{0.5}NbO_3$ -based ceramics is presented. Different contents of Zn^{2+} were analyzed to provide an alternative approach for lead-free materials development.

2. Experimental

Lead-free potassium sodium niobate $K_{0.5}Na_{0.5}NbO_3$ (KNN) was produced by the conventional solid state reaction method from potassium carbonate (Biopack 99.5%, Argentina), sodium carbonate (BioPack 99.5%, Argentina), and niobium oxide (Aldrich 99.9%, USA). Powders with K:Na = 1:1 were mixed in 2-propanol and milled in a planetary laboratory ball-mill (Fritsch, Pulverisette 5), with zirconium oxide grinding jars and balls, for 6h at 1000 rpm. Afterwards, the resulting powders were calcined at 900°C for 5h in air. Then, powders were mixed with zinc oxide

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(Aldrich 99.5%, USA) using different Zn^{2+} concentrations ($x = 0, 0.5$ and 1 mol%) and remilled and dried.

The resulting powders were uniaxially pressed into discs of 6 mm diameter and 0.5 mm thick. In order to analyze the influence of zinc addition on KNN-ceramics, all samples were sintered using the same sintering cycle ($1,125^\circ\text{C}$ for 2 hours in a conventional furnace using $5^\circ\text{C}/\text{min}$ heating and cooling rates).

The apparent density was measured by the Archimedes method and the porosity was determined using the theoretical density⁵. The crystalline phases were assessed by X-ray diffraction, using a Philips PW1830 diffractometer running with $\text{CuK}\alpha$ radiation, at 40kV and 30mA. Raman spectra were acquired at room temperature with a Renishaw in Via Raman spectrometer by means of the 514 nm Ar-ion laser line (10 mW nominal power). The microstructure of the samples was examined by Scanning Electron Microscopy (SEM), using a JEOL JSM-6460LV microscope. Image Pro-Plus Analyzer was used to measure the grain size distribution. The shape of each grain was copied onto a transparent sheet, and then digitized and processed before to be analyzed by the software.

For the electrical measurements, silver electrodes were painted on both faces of the sintered samples. Dielectric properties were measured using a frequency range of 0.10 Hz to 10 MHz, employing both Hioki 3535 and 3522-50 LCR meters. Polarization versus electric field hysteresis loops were obtained in a silicone oil bath at room temperature by applying an electric field of sinusoidal waveform at a frequency of 50 Hz by means of a modified Sawyer-Tower bridge. For the measurement of the piezoelectric constant, samples were first polarized inside a silicone bath using 2.5 kV/mm for 30 min at 150°C , and finally, the piezoelectric coefficients d_{33} were recorded using a quasi-static piezoelectric d_{33} meter (Piezo d_{33} Test System Model: YE2730-Sinocera Inc.).

3. Results and Discussion

Figure 1 shows XRD patterns corresponding to KNN-based ceramics doped with different ZnO amounts (0 to 1 mol%). The presence of a predominant phase related to KNN with a main orthorhombic perovskite structure has been detected. Moreover, small peaks associated to the presence of a secondary phase can be assigned to $K_4Nb_6O_{17}$ (JCPDS76-0977) resulting from slight changes in stoichiometric ratio due to highly volatile alkaline elements during sintering process. Rubio-Marcos et al. studied the effects of ZnO addition on the structure of a more complex system $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_3$ (KNL-NTS)¹³. They found that the perovskite structure with tetragonal symmetry predominated in all samples. Moreover, samples showed slight evolution of the tetragonal (0 0 2) and (2 0 0) diffraction peaks with increasing ZnO content. They attributed this structural evolution to three factors: (i) the incorporation of Zn^{2+} cations into the perovskite structure, (ii) the existence of a phase polymorphism on KNN-based materials composed of a main tetragonal phase and traces of a residual, low temperature orthorhombic phase and (iii) the presence of a secondary phase. However, in our samples the lattice parameters of KNN ceramics do not

change significantly with the addition of ZnO content, indicating that few Zn^{2+} ions enter the matrix of the KNN ceramics. This behavior could be associated with the additive incorporation after the formation of the KNN-phase.

In order to obtain additional information about the structural evolution, Raman spectroscopy analysis were carried out on sintered samples (Figure 2). This technique is a very sensitive tool to study the structural deformations of the ceramic unit cell at a local scale. In the KNN structures, the main vibrations are associated with the NbO_6^- octahedron (BO_6^-)¹⁵. Therefore, the deformations are induced by the tilting of octahedral and the cationic displacements¹⁶. These modifications induce large changes in internal modes associated with NbO_6^- octahedron resulting in a modification of the Raman spectra¹⁷. Therefore it can be seen that the Raman spectrum peaks

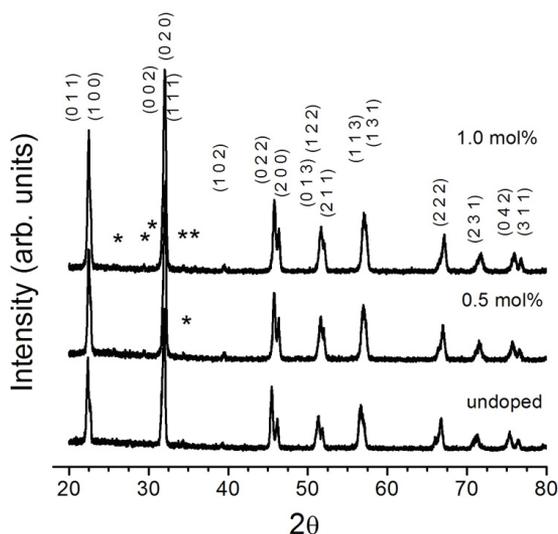


Figure 1. XRD patterns of pure and zinc-doped KNN ceramic. (*) Signals corresponding to $K_4Nb_6O_{17}$ (JCPDS 76-0977).

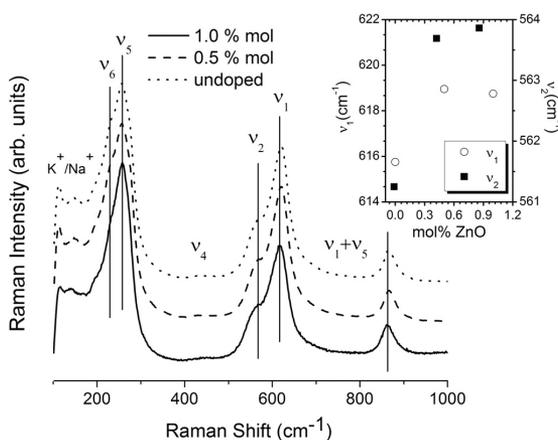


Figure 2. Raman spectra corresponding to pure KNN and KNN doped with several zinc amounts (0.5 to 1 mol%). *Insert:* v_1 and v_2 Raman modes obtained after fit Raman spectra as a function of zinc concentration.

related to the vibrations of the NbO_6^- octahedron consist of $A_{1g}(\nu_1) + E_g(\nu_2) + F_{1u}(\nu_3, \nu_4) + F_{2g}(\nu_5) + F_{2u}(\nu_6)$. Vibrations modes $A_{1g}(\nu_1) + E_g(\nu_2) + F_{1u}(\nu_3)$ are stretching modes, and the rest of them are bending modes. In particular, $A_{1g}(\nu_1)$ and $F_{2g}(\nu_5)$ have been detected as being relatively strong scatterings in similar systems to the one studied in this work due to a near-perfect equilateral octahedral symmetry. Finally, the peaks in the region between 100 and 160 cm^{-1} can be associated with translational models of alkaline niobates K^+/Na^+ and rotational modes of the NbO_6^- octahedron^{18,19}.

The insert of Figure 2 shows the deconvolution of vibration modes ν_1 and ν_2 , performed using two Lorentzian functions. It is observed that ν_1 and ν_2 wave numbers move to higher values when ZnO concentration increases at to 0.5 mol%. However, when the doping level is increased, ν_1 moves toward low frequency. This change can be related to a decrease in binding strength caused by an increase in the Nb-O distance associated with the oxygen vacancies formation²⁰. On the other hand, the increasing in ν_2 by the Zn concentration can be related to modifications in the stabilized perovskite structure.

The increasing in ν_1 suggests that the stiffness of the bond between cations in B-positions and the coordinated oxygen become stronger. This behavior can be related to an enlargement in the tetragonality degree and to the substitution of Na^+ or K^+ in A-positions by Zn^{2+} ions. Comparing with other additives previously studied, such as calcium or barium⁹, Zn^{2+} ions replace alkaline elements or niobium ions depending on the doping level.

In Table 1, the values of density and porosity values of KNN ceramics with different percentages of ZnO are presented. From this table, the addition of the smallest Zn^{2+} amount (0.5 mol%) increases the density value, although the highest concentration increases the porosity. This behavior could be attributed to the sintering aid effect of this additive, and the formation of the secondary phase which possesses a lower theoretical density than the perovskite phase²¹.

Figure 3 shows Scanning Electron Microscopy (SEM) images of the sintered samples. The SEM-micrographs show the typical KNN morphology consisting of faceted grains with a bimodal grain size distribution. Undoped samples present cubic grains with an average grain size of $1.61 \pm 1.02 \mu\text{m}$. On the other hand, samples with 0.5 mol% of ZnO present similar grain size, distribution and morphology, although a small increase in the average grain size ($1.65 \pm 0.95 \mu\text{m}$) and the apparition of some glassy phase are observed. Samples with highest ZnO amount (1 mol%), also present a bimodal grain distribution in which large grains (~ 6 to $8 \mu\text{m}$) and the small ones (~ 0.5 to $2 \mu\text{m}$) with an average grain size of $\sim 1.68 \pm 1.10 \mu\text{m}$. For this

reason, it can be observed in the histogram a heterogeneous distribution with a few big grains joint a large amount of small grains, generating an average size similar to undoped ceramics.

According to the phase diagram the niobium excess forms a liquid at 1,058°C that could promote sintering with grain coarsening^{16,20}. Also, the appearance of the secondary phase is associated with the transitory liquid phase that assisted sintering process. From SEM images, the formation of a liquid phase during the sintering process is responsible for the existence of big grains conformed by other small grains, and of small bonded grains.

Moreover, as the amount of zinc increases, niobium is replaced from the perovskite lattice and, consequently, the transient liquid phase and niobium-rich secondary phases are promoted. From these results, this additive could improve the grain growth due to the liquid phase formation during the sintering process favoring the use of lower sintering temperatures.

Figure 4 shows real permittivity and loss tangent values as a function of frequency for samples with different additive amounts. In all cases, it can be observed that at low frequency, permittivity decreases with frequency due to a space charge relaxation process characteristic of the polycrystalline material. Additionally, a relaxation process at high frequency ($\sim 6\text{MHz}$) which is associated with a dipolar relaxation phenomenon can be detected. In these samples, the addition of zinc oxide reduces the effect of frequency and increases the real permittivity values at low frequencies, probably due to a better densification of doped ceramics.

Table 1, also shows values of real permittivity (ϵ'), loss tangent ($\tan\delta$) and piezoelectric constant (d_{33}) corresponding to KNN with different zinc amounts (0 to 1 mol%). From these values, it can be observed that the incorporation of this additive improves the dielectric properties of the device, increasing the real permittivity and decreasing the loss tangent. Moreover, an improvement in the piezoelectric constant value with the lowest percentage of zinc was found. These enhanced properties are associated with the high density values obtained with the ZnO addition, using the same sintering cycle.

Figure 5 presents the hysteresis loops at room temperature of sintered samples. Pure KNN sample shows a remnant polarization (P_r) $13.8 \mu\text{C}/\text{cm}^2$, which is greater than the Zn-doped samples with 8.5 and $5.4 \mu\text{C}/\text{cm}^2$ for samples with 0.5 mol% and 1 mol%, respectively. The coercive electric field (E_c), and the saturation polarization values (P_s), for the doped samples with 0 to 1 mol% of Zn^{2+} , are 17.3, 19.0 and $14\text{kV}/\text{cm}$ and 18.3, 13.3 and $10.8 \mu\text{C}/\text{cm}^2$, respectively.

Table 1. Density and porosity values, and dielectric and piezoelectric properties of the studied samples. Theoretical density $4.51 \text{ g}/\text{cm}^{3[5]}$.

Sample	Density (g/cm^3)	Porosity (%)	ϵ' (10kHz)	$\tan\delta$ (10kHz)	d_{33}
KNN pure	4.3 ± 0.9	5.8 ± 2.5	352	0.13	86
KNN 0.5%mol ZnO	4.4 ± 0.1	3.3 ± 1.0	359	0.13	95
KNN1.0%mol ZnO	4.3 ± 0.1	5.8 ± 0.7	408	0.10	90

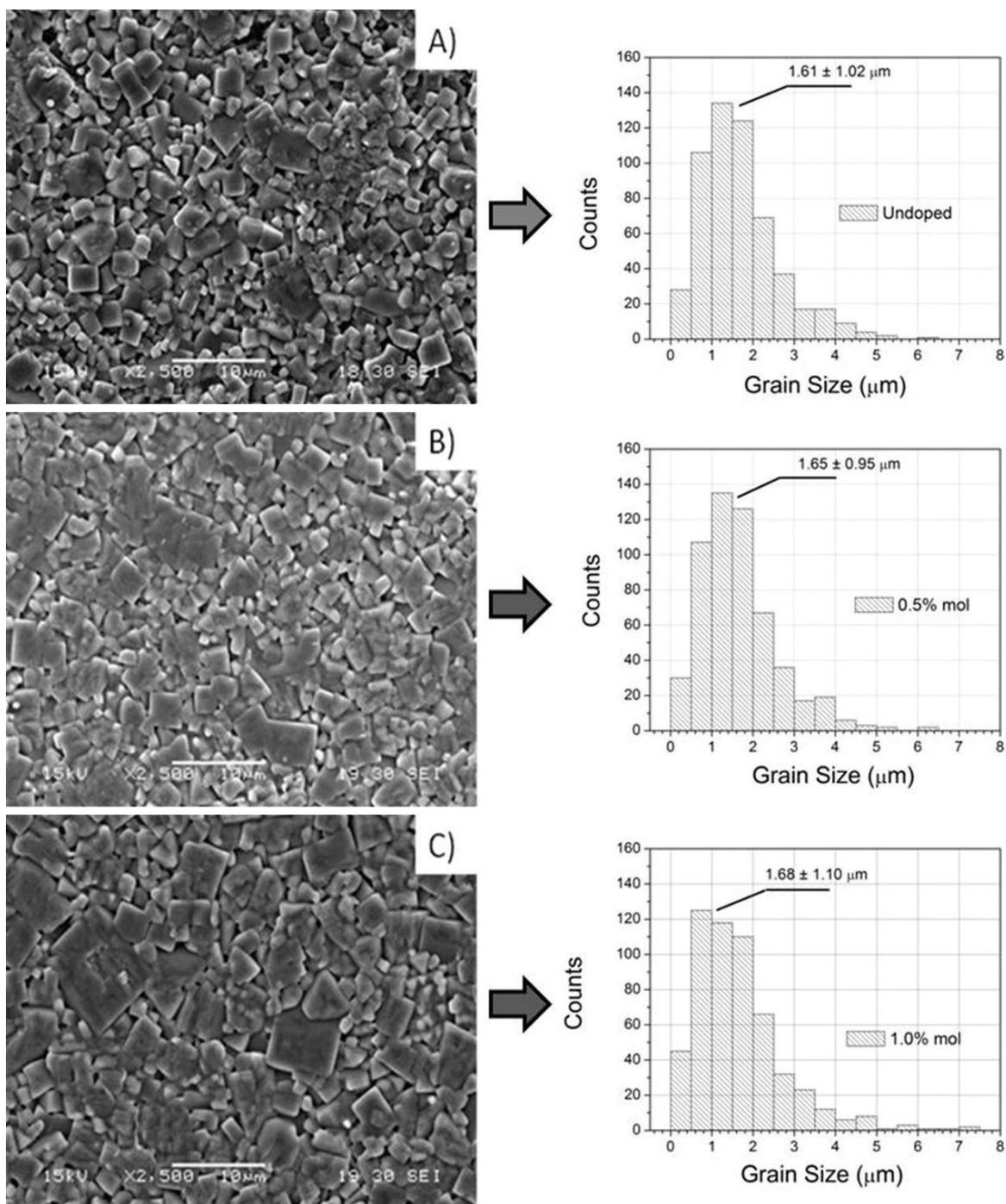


Figure 3. SEM images of pure KNN (A) and KNN doped with several zinc amounts 0.5 mol% (B), and 1 mol% (C).

From the decrease in the coercive electric field value, a softening effect on the ferroelectric properties of KNN with zinc addition is detected. This result cannot be related to the possible Zn^{2+} substitution in Nb^{5+} positions of the lattice with the consequent oxygen vacancy generation, which produces a hardening effect on the ferroelectric properties of the material. Then, the small decrease of E_c can be attributed to a decrease of the oxygen vacancies amount due to Zn^{2+}

donor ions (A-site replacement) that pinned the domain wall motion. Moreover, the increasing in the grain size reduces the anchoring effect of grain boundaries which limit the material polarization and decrease the coercive field of the samples and the energy involved to change the polarization of the material. Hayati et al. found that nano-ZnO additive increased the grain size of the KNN ceramics considerably and, larger grains lead to lower coercive fields¹². The larger

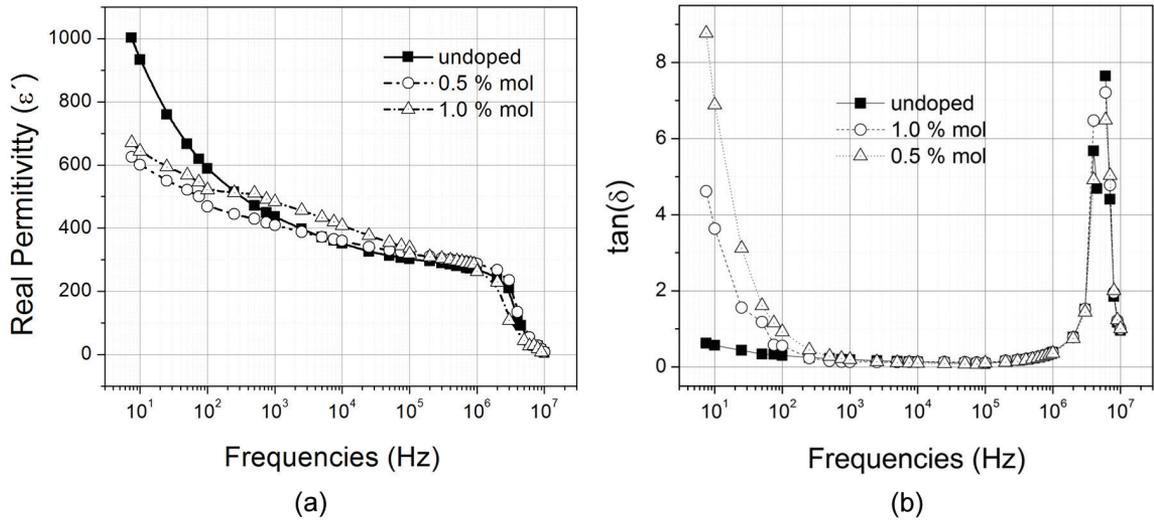


Figure 4. Curves of real permittivity (a) and loss tangent (b) as a function of frequency at room temperature.

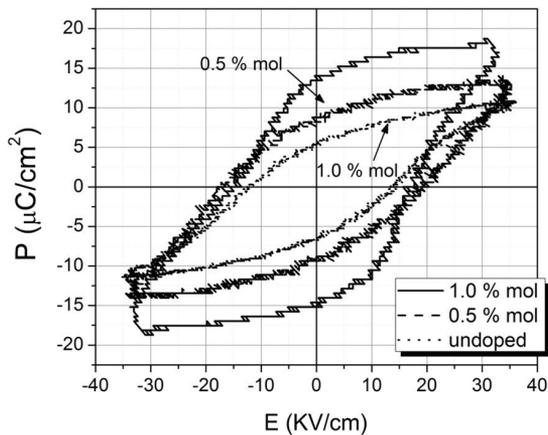


Figure 5. Hysteresis loops of sintered samples. Measuring conditions: room temperature, *ac* field, electric field of 35 kV/cm and frequency of 50Hz.

the grains gives the larger the domain size and smaller the domain wall width. Decreasing the domain wall width facilitates the domain wall switching which results to lower coercive fields. Furthermore, with the highest doping level Zn^{2+} ions enter in B-positions. It is known, that when Zn^{2+} ions substitute in B positions (Nb^{5+} ion sites) in perovskite structure, which results in the formation of oxygen vacancies that makes the ceramic hard, a higher coercive field than pure KNN is expected¹⁴. According to these results, coercive electric field and saturation polarization values were strongly dependent on structural and microstructural modifications produced by this additive.

4. Conclusions

In this study, the microstructure, crystalline phases, and electrical properties of ZnO-doped KNN ceramics were investigated. For ZnO-doped samples, a secondary phase was observed by XRD, accompanied by an increase in the grain size. At the lowest doping level used in this work (0.5 mol%), density and piezoelectric properties were improved. A shift in the A_{1g} vibration mode (ν_1) to higher wave numbers related to the Zn^{2+} substitution in A-positions of the perovskite structure was observed. This variation was associated with an increasing in the tetragonal phase. This result produced an electric softening of the material properties, which was evidenced by an increase in the piezoelectric properties. The diminution in the density value with the highest doping level was attributed to the alkali elements volatilization. Furthermore, from Raman spectroscopy the substitution of niobium ions by zinc ions was observed.

Finally, considering that Zn^{2+} ions replace alkaline elements in A-positions of the perovskite lattice, the incorporation of this additive at the initial stage of the $K_{0.5}Na_{0.5}NbO_3$ synthesis would increase the A-site replacement and hence the loss of the alkali elements (mainly sodium).

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