RAMAN INVESTIGATION ON PZN-PT CRYSTALS

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ABSTRACT
Single crystal of (1-x) $PbZn_{1/3}Nb_{2/3}O_3$ – x $PbTiO_3$ (PZN-PT) is a relaxor ferroelectric material that has received much attention in the last years due to its high electromechanical coupling coefficients, longitudinal piezoelectric coefficients and electric induced strain. At room temperature, this system has a rombohedral structure at low Ti concentration. By increasing Ti concentration, PZN-PT shows a structural phase transition to a tetragonal structure. As in $PbTiO_3$-$PbZrO_3$ (PZT) solid solution, an almost vertical morphotropic phase boundary (MPB) was observed separating both structures. In this work, the structural phase transitions in PZN-PT poled crystals (x = 4.5 and 12 %) were studied using polarized Raman scattering between 10 and 700 K. Results are analyzed based on the PZN-PT phase diagram.

RESUMEN
Los monocristales de (1-x) $PbZn_{1/3}Nb_{2/3}O_3$ – x $PbTiO_3$ (PZN-PT) son materiales relajadores ferroeléctricos que han recibido mucha atención en los últimos años debido a su alto coeficiente de acoplamiento electromecánico, coeficiente piezoeléctrico longitudinal y deformación eléctricamente inducida. A temperatura ambiente este sistema tiene una estructura romboédrica a bajas concentraciones de titanio. Aumentado el contenido de Ti, el PZN-PT presenta una transición de fase a una estructura tetragonal. Como en la solución sólida $PbTiO_3$-$PbZrO_3$ (PZT) un contorno de fases morfotrópico (MPB) casi vertical separa las dos fases. En este trabajo, las transiciones de fase estructurales en cristales polarizados de PZN-PT (x = 4.5 y 12 %) fueron estudiadas usando espectroscopia Raman polarizada entre 10 y 700 K. Los resultados fueron analizados de acuerdo al diagrama de fases del PZN-PT.

INTRODUCTION

Relaxor ferroelectrics have received very much attention during the last decades due their exceptional piezoelectric and dielectric properties [1]. Among the different kinds of relaxors, the family formed by mixed perovskites oxides is widely used in technological applications as actuators, high power ultrasonic transducers, underwater acoustic and so on. The temperature vs. concentration phase diagram of most of these compounds is characterized by the existence of a morphotropic phase boundary (MPB), which separate two ferroelectrics phases with different orientations of the polarization. Recently, different low symmetry phases have been observed in the MPB region of several relaxor ferroelectrics [2-4]. These phases connect both adjacent ferroelectric phases providing a new perspective for understanding the outstanding properties of these materials. According to theoretical considerations [5,6], the low symmetry phases allow the possible paths of polarization rotation between the ferroelectric phases locate at both sides of the MPB.

Recently, La-Orauttapong **et al**. [2] have been studied the (1-x) $PbZn_{1/3}Nb_{2/3}O_3$ – x $PbTiO_3$ (PZN-xPT) system using high resolution synchrotron x-ray powder diffraction. They show the existence of an orthorhombic phase at low temperatures between 9 and 11 % of titanium concentration, as shown in Figure 1. In this work we study crystals of PZN-xPT with concentrations corresponding to the rhombohedral (x = 0.045) and tetragonal (x = 0.12) phases, using impedance spectroscopy and Raman scattering between 10 and 600 K. Our results are in good agreement with the phase diagram proposed by La-Orauttapong **et al**., and allow us to show the temperature dependence of the phonon spectra of this system.

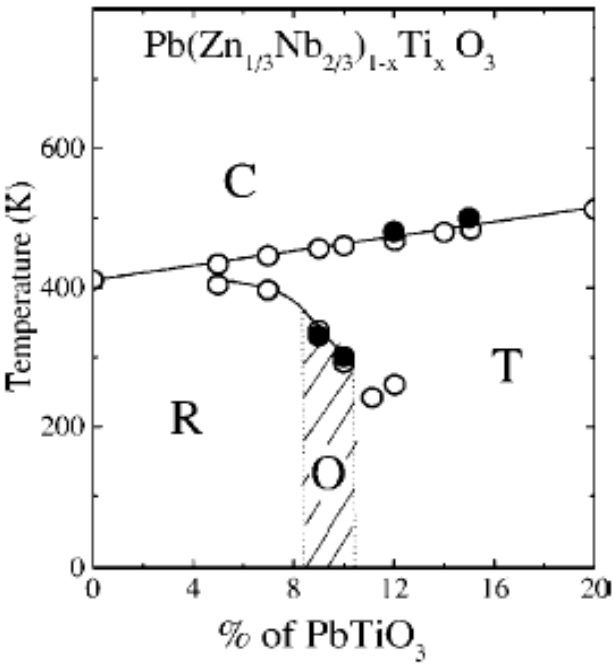

Figure 1. Phase diagram of PZN-xPT relaxor ferroelectric around the MPB according Reference [2].

EXPERIMENTAL

Single crystals of PZN-xPT with x = 0.045 and 0.12 were poled under a field of 1 kV/mm along the [001] direction of the cubic phase. Raman measurements were performed using a T64000 Jobin Yvon Spectrometer equipped with an Olympus microscope and a N_2- cooled CCD to detect the scattered light. The spectra were excited with an Argon ion Laser (λ = 514.5 nm, power 50 mW). The spectrometer slits were set to give a spectral resolution always better than 2 cm^{-1}. A Nikon 20x objective with focal distance 20 mm and numeric aperture N.A. = 0.35 was used to focus the laser beam on the polished sample surface. Low temperature measurements were performed using an Air Products closed-cycle refrigerator, which provides temperatures ranging from 7 to 300 K. A Lakeshore controller was used to control the temperature with precision of the order of ± 0.1 K. To perform the dielectric measurements gold electrodes were sputtered on the sample faces. These measurements were done employing an Impedance Analyzer HP 4194A in a frequency range from 1 kHz to 1 MHz in a cooling and heating cycle (from 550 K to 20 K and from 20 K to 550 K) using a cryogenic refrigeration system (APD Cryogenics Inc.) with a rate of 2 K/min.

RESULTS AND DISCUSSION

In order to identify possible phase transitions, we firstly investigated the PZN-xPT crystals by impedance spectroscopy. As can be observed in Figure 2, both samples show anomalies in the dielectric permittivity above room temperature, whose characteristic temperatures agree with those of the phase transition into the cubic for two different Ti concentrations. Due to this fact, these anomalies can be associated to phase transitions. Furthermore, the frequency dispersion of the dielectric permittivity maximum characterizes the relaxor behavior of the PZN-xPT system. In the inset of the Figure 2b, we show the low temperature dependence of the dielectric permittivity in the sample with x = 0.12, where another anomaly with frequency dispersion can be observed. Following the high temperature observations, we should associate it to the tetragonal to orthorhombic phase transition. The transition temperature is in accordance with the observations of Kuwata et al. [8], but differs from the D. La-Orauttapong et al. results because these authors claimed that crystals with x = 0.12 are tetragonal at 15 K while for x = 0.11, PZN-xPT transforms into the orthorhombic phase at approximately 250 K. However, horizontal shifts of the concentration vs. temperature phase diagram of about 1 % are expected on this system and should be originated from differences in the growth conditions.

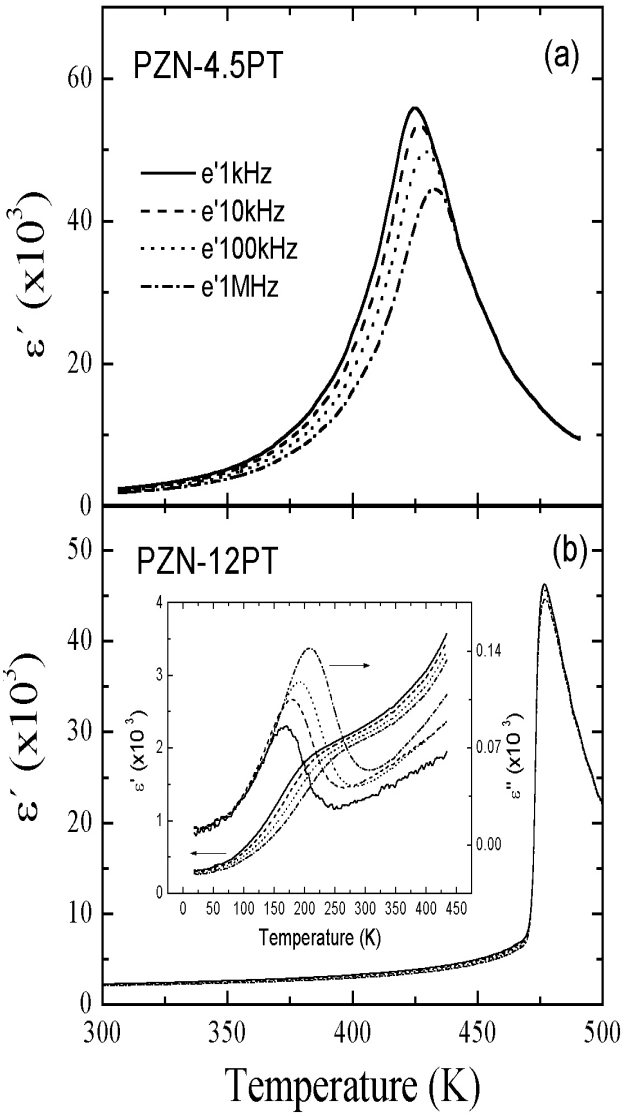

Figura 2. Temperature dependence of the dielectric permittivity in PZN-xPT crystals along the cubic [001] direction.

In Figure 3 we show the Raman spectra of PZN-12PT recorded in the y(zz)y and y(xz)y scattering geometries. One dominant feature is the band at approximately 780 cm-1, which is assigned to the Nb-O-Zn stretching mode on the analogy to the Nb-O-Mg stretching mode in PMN [9]. As it can be observed there are small differences between both polarizations. Furthermore, although the band wavenumbers show no appreciable temperature dependence between 10 and 300 K, evident changes are observed in their relative intensities. In this way, as it is usual in this kind of compounds [10], in Figure 4 we plot the depolarization ratio (I_{zz}/I_{xz}) as a function of the temperature for the band around 780 cm^{-1}. The anomaly present in this figure at approximately 170 K is similar to those reported previously and characterizes the existence of a transition into a low symmetry phase [10,11].

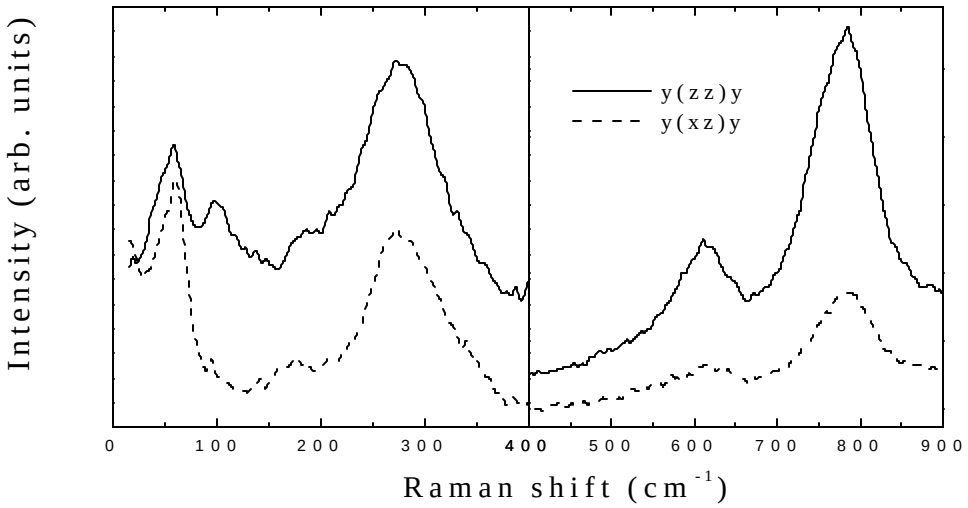

Figure 3. Raman spectra of PZN-12PT at room temperature in the y(zz)y and y(xz)y scattering geometries.

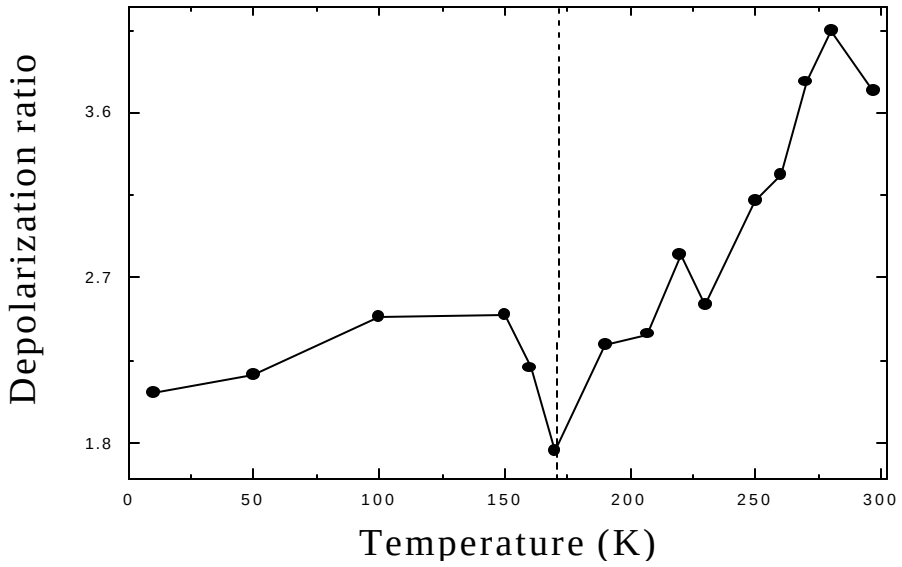

Figure 4. Depolarization ratio of the 780 cm^{-1} band of PZN-12PT as a funtion of the temperature.

CONCLUSIONS

Dielectric permittivity and Raman spectra of PZN-xPT crystals were measured as a function of the temperature. From the analysis of this data, we verify the existence of several high temperature phase transitions, which are in accordance with the previously determined phase diagram. Contrary to the La-Orauttapong **et al**. [2] results, crystals with x = 0.12 present a structural phase transition at approximately 170 K. This transition has a relaxor-like behavior and the new phase can be associated to the orthorhombic phase observed by high resolution synchrotron x-ray powder diffraction.

ACKNOWLEDGMENTS

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