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Dielectric and pyroelectric behavior of $(Pb_{0.8}Ba_{0.2})[(Zn_{1/3}Nb_{2/3})_{0.7}Ti_{0.3}]O_3$ ferroelectric ceramics

A. Peláiz-Barranco, I. González-Carmenate, F. Calderón-Piñar.

Facultad de Física-Instituto de Ciencia y Tecnología de Materiales, Universidad de La Habana.
San Lázaro y L, Vedado. La Habana 10400, Cuba; pelaiz@fisica.uh.cu†
†autor para la correspondencia

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Sumario. Cerámicas basadas en PZN han sido obtenidas por el método cerámico tradicional a partir de la composición nominal $(Pb_{0.8}Ba_{0.2})[(Zn_{1/3}Nb_{2/3})_{0.7}Ti_{0.3}]O_3$. Una estructura perovskita romboédrica fue obtenida a partir del estudio estructural y el análisis dieléctrico mostró un comportamiento relajador para la transición de fase ferroeléctrica-paraeléctrica con una temperatura de transición muy cercana a la temperatura ambiente. La histéresis ferroeléctrica mostró finos lazos de histéresis, característico de materiales con este tipo de comportamiento relajador. La figura de mérito piroeléctrica y la respuesta piroeléctrica dinámica mostró muy buenos resultados para aplicaciones de tipo piroeléctrica.

Abstract. Pyroelectric ceramics based on PZN have been obtained by standard ceramic technique. Samples of composition $(Pb_{0.8}Ba_{0.2})[(Zn_{1/3}Nb_{2/3})_{0.7}Ti_{0.3}]O_3$ were studied, showing a pure rombohedral related-perovskite phase. Dielectric measurements exhibit a relaxor ferroelectric behavior with a transition temperature closed to room temperature. Slim hysteresis loops with only small remanent polarizations were found. The figure of merit (R_V=9.7x10^{-10}C/cm^{2o}C) and the dynamical pyroelectric response show a suitable material to be used in pyroelectric applications. The room temperature value of the dielectric permittivity shows that the studied system could be considered for potential application in the manufacture of multilayer ceramic capacitor.

Keywords. Ferroelectric Materials 77.84.-s; Dielectric Function 77.22.Ch; Pyroelectric Effects 77.70.+a.

1 Introduction

Pyroelectric materials have been used since the early 60's in the detection of radiation and for laser power measurements as well as in solar energy technology, especially complex ferroelectric composites of perovskite structure[1-2]. In the last years the interest for the development of new ternary systems with the same structural characteristics and with best properties to be used as infrared sensors, especially for night vision equipment, has been grown[3]. One of the main properties for this application is a high value of the figure of merit at the operation temperature (usually room temperature), which it is possible when the ferroelectric transition temperature is closed to room temperature[2].

Modified lead titanate (PT) represents a typical sensor, whose modification with Zn and Nb (PZN-PT) has shown excellent piezoelectric properties[4]. However, the preparation of PZN system usually needs the addition of $BaTiO_3$ (BT) to obtain pure phases (without pyrochlore phase). Therefore, the ternary system PZN-PT-BT has received wider attention, showing high values of the dielectric permittivity and the pyroelectric coefficient[2]. This material shows lower diffuseness of the phase transition and weaker frequency dispersion of the dielectric response than that of the PZN-BT system[5]. It has been shown that it could be interesting try to decrease the transition temperature and to grow the value of the figure of merit[6] in order to obtain better materials for practical applications.

The aim of the present paper was to investigate the dielectric and pyroelectric properties of samples of the PZN-PT-BT ceramic system obtained by the ceramic method, showing better results than those previous reports[2].

2 Experimental procedure

Ceramic samples of nominal composition $(Pb_{0.8}Ba_{0.2})[(Zn_{1/3}Nb_{2/3})_{0.7}Ti_{0.3}]O_3$ were prepared by using the ceramic standard method. The reagent powders (PbO, $BaCO_3$, Nb_2O_5, TiO_2 and ZnO with Sr and Ca impurities in 0.5 % weight) were milled and calcined at 900°C during 2 hours in air. After that the powders were re-milled and pressed into cylindrical pellets with binder. The sintering process was carried out in suitable atmosphere at 1160°C during 1.5 hours. X-ray diffraction patterns on powder samples were made by using a Siemens D500 X-ray diffractometer and Cu-K radiation. By using a scanning electron microscope (SEM) (Cambridge-Leica Steroescan 440), microstructural evaluation was performed on fractured samples. Ceramic samples of high density (7.45g/cm^3) and lower average grain size (2.5 μm) than that of previous report[2] were obtained, showing a pure rombohedral phase in the x-ray pattern (Figure 1). The lower grain size has been associated to a lower sintering time in our study.

Electrodes were fabricated on the parallel faces by using Au strips and an organogold paste. The dielectric properties were measured as a function of frequency by using an impedance analyzer HP 4192A, applying 1V to the samples. The measurements were made from 18 to 175°C and from 5 to 13 MHz for the frequency range. A Sawyer-Tower circuit was used at 1 Hz and several temperatures[7]. For pyroelectric measurements the samples were poled by cooling from 60 to 25°C under a dc bias field of 2kV/mm. The pyroelectric current was measured by using a Takeda TR 8651 as the sample temperature was changed at a constant rate (3°C/min). Then, the pyroelectric coefficient (p_i) and the figure of merit ($R_v=p_i/\varepsilon$) were calculated. For the dynamical pyroelectric study, the samples were subjected to light radiation, illuminating perpendicularly the facing layers of each sample from the same distance. The samples response (voltage output), at room temperature, were measured by using the Takeda TR 8651.

2 Results and discussion

The temperature dependence of the dielectric permittivity (ε) at several frequencies is shown in Figure 2. One of salient features is the enhanced frequency-dependence of dielectric permittivity, which might be related to the widening of size distribution of polar microregions.

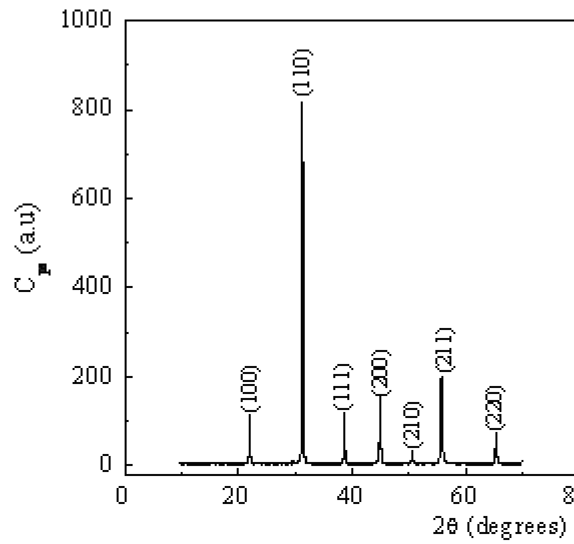

Figure 1. X-ray diffraction pattern at room temperature for the PZN-PT-BT ceramic system.

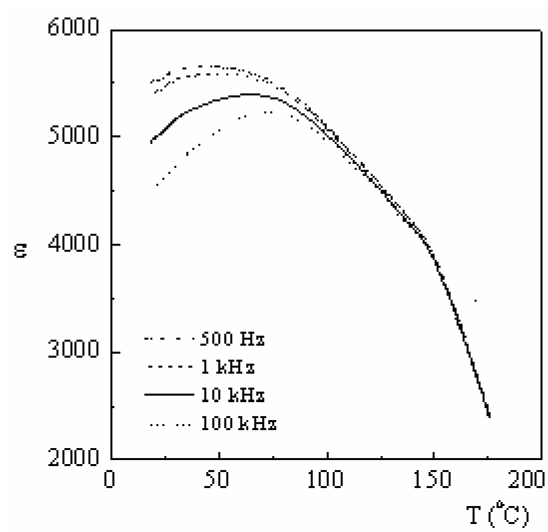

Figure 2. Temperature dependence of the dielectric permittivity at several frequencies for the PZN-PT-BT ceramic system.

Table I
Dielectric properties of the studied ceramics and results previously reported.

Ceramic system	ε_{max} (1 kHz)	ε (25°C)	T_m (°C)
PZN-PT-BT[a]	9969	4600	74
PZN-PT-BT	5620	5400	51

a) Reference [2]

The studied system exhibits typical ferroelectric relaxor behavior, i.e. the paraelectric-ferroelectric phase transition extends over a broad temperature region[8-12] in contrast with the sharp phase transition frequently observed in normal ferroelectrics; the temperature of the dielectric permittivity maximum (T_m) shifts toward higher temperature while its value decreases as the measuring frequency is increased over several order of magnitude; the temperature dependence of the dielectric losses shows its maximum below T_m (also studied but not shown here). For relaxors, smearing-out of paraelectric to ferroelectric phase transition has been attributed to the presence of local compositional fluctuation on a microscopic scale, giving rise to a distribution of phase transition temperatures. Some microstructural studies reveal that the compositional inhomogeneity in $Pb(B'_{1/3}B''_{2/3})O_3$-type perovskites, in particular, originates from the existence of B-site 1:1 short-range ordered nanodomains[13]. These nonstoichiometric domains are rich in B' cations and embedded in B"-rich matrix. Moreover, strong charge imbalance develops where the ordered domains carry a net negative charge as opposed to the disordered matrix.

Table I shows some dielectric properties for the studied ceramics and previous report without Ca and Sr impurities[2]. The presence of the Sr and Ca impurities provides a decrement of $\varepsilon(T_m)$ and T_m. The higher ε value at room temperature is associated to the lower T_m value, which is much closed to room temperature. The advantage of this better result at room temperature is, when this relaxor ferroelectric is considered for potential application in the manufacture of multilayer ceramic capacitor (MLCC), which is one of the dominant application areas for relaxors, the value of room temperature capacitance is improved in conjunction with its reduced temperature coefficient. The room temperature value of the dielectric permittivity is larger than that of the previous report[2]; hence, this composition is suitable for MLCC application given its phase transition behavior.

It is important to note that the rombohedral phase shows a relaxor behavior and the transition temperature is closed to room temperature[14] as we have seem from the dielectric studies. Therefore, the polar clusters are more independent and disordered and it is difficult to induce a long-range ferroelectric order even by using a high electric field.

On the other hand, the hysteresis loops of the studied system at several temperatures were obtained. Figure 3 shows the results at 0°C and 30°C, as examples of the general behavior when the temperature increases. Slim P-E loops with only small remanent polarizations were found. The values of remanent polarization and coercive field decreased with increasing temperature.

The slim-loop nature of the P-E curves suggests that most of the aligned dipole moments switch back to a randomly oriented state upon removal of the field. This behavior has previously been observed in ferroelectric relaxors, being interpreted in terms of correlated polar nanodomains embedded in a paraelectric matrix[15]. A detailed study of the relaxor behavior has been previously published[16].

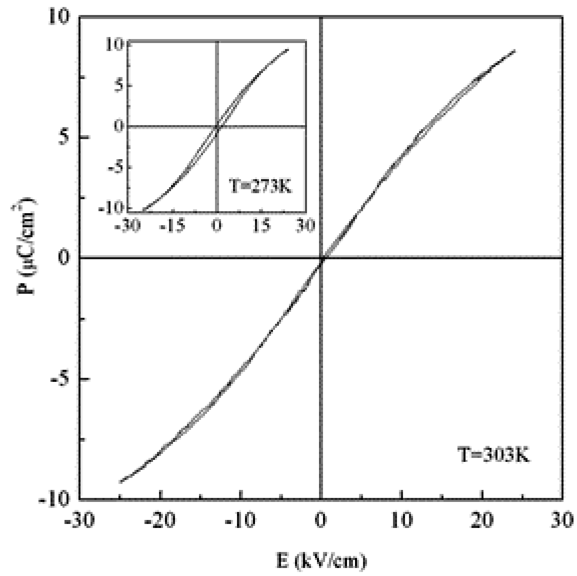

Figure 3.- Hysteresis loops at 0°C and 30°C for the PZN-PT-BT ceramic system.

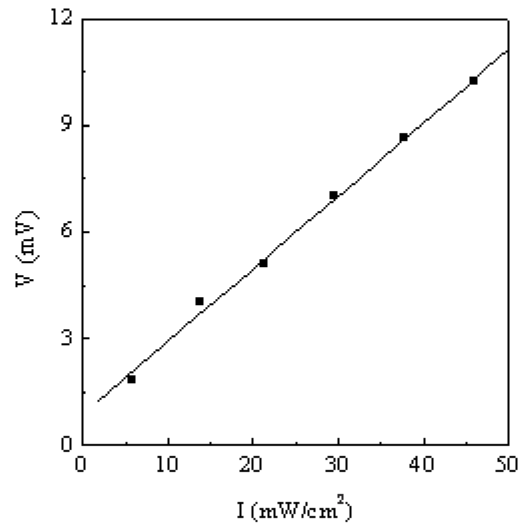

Figure 4. Voltage output (V) versus intensity of the light radiation (I) for PZN-PT-BT system, measured at room temperature.

Table II

Pyroelectric coefficient and figure of merit at room temperature (RT), for the studied PZN-PT-BT ceramic and other materials, which have been reported for pyroelectric applications.

Compounds	p_i ($\mu C/cm^{2o}C$)	R_V ($x10^{-10}$) ($C/cm^{2o}C$)
PZN-PT-BT[a]	0.82 (peak of p_i)	1.34 (peak of p_i)
PZN-PT-BT	5.31 (RT)	9.70 (RT)
Modified $PbTiO_3$	0.04 (RT)	1.73 (RT)
PLZT 6/65/35	0.07 (RT)	0.62 (RT)
PLZT 12/40/60	0.05 (RT)	0.44 (RT)

a) Reference [2]

Finally, from pyroelectric measurements the pyroelectric coefficient (p_i) and the figure of merit ($R_v=p_i/\varepsilon$) were calculated at room temperature (RT) and collected in Table II. There is included other materials, which have been reported for pyroelectric applications[2,17-18]. The value of R_v for the studied ceramics is specially higher, showing their suitability as pyroelectric detector materials. Note that previous report for this material[2] has showed a maximum figure of merit (at the peak of the pyroelectric coefficient) lower than that of the studied ceramics at room temperature.

For the dynamical pyroelectric study, as we have commented in the Experimental Procedure, the samples were subjected to light radiation, illuminating perpendicularly the facing layers of each sample from the same distance. The samples response (voltage output), at room temperature, exhibits a linear behavior with the intensity of the light radiation (Figure 4), showing a suitable material for pyroelectric applications.

3 Conclusions

As summary, pure rombohedral related-perovskite of PZN-PT-BT was obtained, showing excellent properties to be used in dielectric and pyroelectric applications. The presence of Sr and Ca decreases the transition temperature towards room temperature, remaining the relaxor characteristics. Slim P-E loops with only small remanent polarizations were found, which has been previously observed in ferroelectric relaxors. The pyroelectric properties show a suitable material to be used in pyroelectric applications.

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