PIEZOELECTRIC PROPERTIES OF $(Bi_{0.5}Na_{0.5})_{1-X}Ba_XTiO_3$ LEAD-FREE FERROELECTRIC CERAMICS

PROPIEDADES PIEZOELÉCTRICAS DE CERAMICAS LIBRES DE PLOMO DEL TIPO $(Bi_{0.5}Na_{0.5})_{1-X}Ba_XTiO_3$

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Lead-based piezoelectric compounds are used in a wide applications range spanning from sensors to transducers. However, these materials are environmentally-aggressive, so these must be replaced by using lead-free compounds. This paper presents the study on the electromechanical behavior and the main piezoelectric parameters of five piezoelectric ceramic compositions within the $(Bi_{0.5}Na_{0.5})_{1-x}Ba_xTiO_3$family, where $x = 8,\ 10,\ 12,\ 16,\ 18$ at %. The samples have been prepared by using the standard solid-state reaction method and then polarized under an electric field of 2 kV/mm for a temperature lower than that of the phase's transition temperature. Our results revealed d33 values higher than 120 pC/N for $x = 8,\ 10,\ 12$at %, better than those for lead-based compounds. There were also obtained d_{33}, d_{31} and g_{31} values higher than those reported in the literature for a large number of lead-free systems.

Los compuestos piezoeléctricos basados en plomo son muy utilizados en una gran gama de aplicaciones como sensores y actuadores. Sin embargo, son dañinos para el medio ambiente, por lo que es necesario reemplazarlos con materiales alternativos libres de plomo. En este trabajo se presenta el estudio del comportamiento electromecánico y de los principales parámetros piezoeléctricos para cinco composiciones de cerámicas piezoeléctricas libres de plomo, $(Bi_{0.5}Na_{0.5})_{1-x}Ba_xTiO_3$donde $x = 8,\ 10,\ 12,\ 16,\ 18$ at %. Las muestras fueron preparadas mediante el método cerámico tradicional, y polarizadas bajo un campo eléctrico de 2 kV/mm a una temperatura inferior a la temperatura de transición de fases. Los resultados arrojaron valores de $d_{33} > 120$ pC/N para $x = 8, 10, 12$ at %, superiores a compuestos basados en plomo. Se reportan, además, valores de d_{33}, d_{31} y g_{31} mejores que los reportados en la literatura para gran parte de los sistemas libres de plomo.

PACS: Piezoelectricity (piezoelectricidad), 77.65.-j; piezoelectric materials (materiales piezoeléctricos), 77.84.-s; piezoelectric constants (constants piezoeléctricas), 77.65. Bn

I. INTRODUCTION

Piezoelectric materials currently cover a large number of areas involving their use in electronic devices devoted to energy generation and storage [1], sensors for contaminating elements in food [2], multilayer capacitors [3], piezoelectric scalpels for piezo-surgery [4], and so on.

Several decades ago, there was a "boom" in piezoelectric research due to their interesting phenomenology and their impact on the industrial, military, medical and biotechnological fields [5–7].

However, most devices based in piezoelectricity involve lead-based, which have shown the best properties but are harmful for human´s health and hazardous to the environment. Therefore, it has been imperative for the scientific community to find alternative materials, which can replace the lead-based systems [3].

In this context, the $(Bi_{0.5}Na_{0.5})_{1-x}Ba_xTiO_3$family has emerged as a promising lead-free material, showing excellent piezoelectric properties [8, 9]. The aim of the present work is to study the piezoelectric properties of the $(Bi_{0.5}Na_{0.5})_{1-x}Ba_xTiO_3$($x = 8,\ 10,\ 12,\ 16,\ 18$ at %) ceramic system. In particular, the electromechanical behavior as well as the main piezoelectric figures of merit have been explored.

II. EXPERIMENTAL PROCEDURE

$(Bi_{0.5}Na_{0.5})_{1-x}Ba_xTiO_3$ceramics for $x = 8,\ 10,\ 12,\ 16,\ 18$ at %, were prepared by using the standard solid-state reaction method. High purity oxides (Bi_2O_3: 99.999 %; $BaCO_3$: 99.36 %; TiO_2: 98 %; Na_2CO_3: 99.5 %) were mixed and milled for 2 hours (using alcohol). The powders were dried and uniaxilly pressed (1 ton/cm^2). The samples were calcined at 800°C for 1 hour in air atmosphere. The powders were milled again for 1 hour, dried and then uniaxilly pressed as thin discs by using 2 ton/cm^2. The samples were sintered at 115°C for 2 hours in air atmosphere using a covered alumina crucible.

Silver paint electrodes were applied on the opposite parallel surfaces of disk-shaped ceramic samples by a heat treatment at 590°C. The diameter and thickness of the disc samples were around 9 mm and 0.5 - 2 mm, respectively. The samples were hereafter labeled as BNBT–8, BNBT–10, BNBT–12, BNBT–16 and BNBT–18, for $x = 8, 10, 12, 16$, and 18 at% of Ba^{2+}, respectively.

The XRD data was collected on powdered ceramic samples using a Shimadzu XRD-6000. The patterns confirmed a pure perovskite structure for all compositions, without additional spurious phases. The polarization process was carried out at 120°C, applying an electric field of 2 kV/mm. For the analysis of the room temperature electromechanical response in the studied samples, a Hioki 3532-50 LCR meter was used, covering a wide frequency range (100 Hz–1 MHz). From the direct measurement of the frequency dependence of the capacitance (C), and the corresponding resonance (f_r) and antiresonance frequencies (f_a), the main piezoelectric parameters were calculated for the radial mode. The electromechanical coupling factors k_p and k_{31}, and the d_{31} and g_{31} piezoelectric coefficients were also obtained [10–14]. Direct measurements of the d_{33} piezoelectric coefficient were also carried out using an IACAS Z5-6A piezo d_{33} meter.

III. RESULTS AND DISCUSSION

Figure 1 shows the frequency dependence of the capacitance for the studied compositions. The main harmonic resonance mode is clear observed around 250–500 kHz, as expected based on the geometry and dimensions of the samples. Smaller peaks can be observed for higher frequencies, which can be associated to secondary harmonics for the radial mode and could also be the result of the shear effects due to defects in the samples.

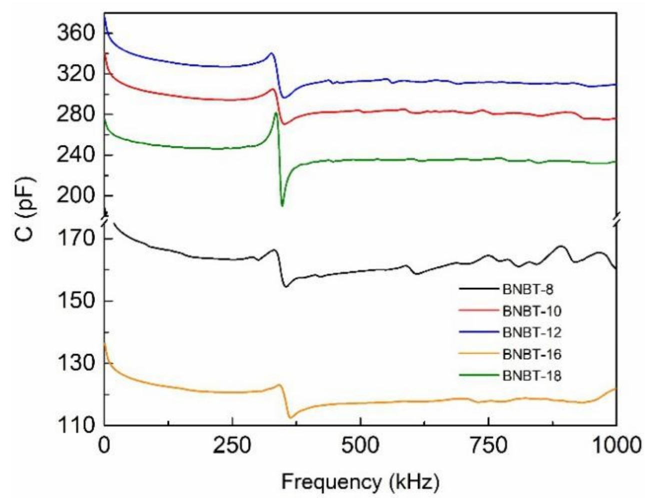

Figure 1. Frequency dependence of the capacitance for the studied samples at room temperature.

Table 1 summarises the obtained values for the eletromechanical and piezoelectric coefficients, with their corresponding uncertainties, for both radial and thickness modes. It can be observed that k_p and k_{31} values are similar for the BNBT–8, BNBT–10 and BNBT–16 samples, while the BNBT–12 composition shows values even higher than a 10 %. Therefore, it can be concluded that the BNBT–12 sample exhibits the best results for the radial mode.

Table 1. Piezoelectric parameters for the studied ceramics

Parameters	BBNT-8	BBNT-10	BBNT-12	BBNT-16	BBNT-18
k_p	0.372 ± 0.002	0.375 ± 0.003	0.418 ± 0.002	0.369 ± 0.002	0.269 ± 0.002
k_{31}	0.219 ± 0.001	0.220 ± 0.002	0.245 ± 0.001	0.217 ± 0.001	0.158 ± 0.001
d_{31} (10^{-12} CN^{-1})	54.3 ± 0.4	54.0 ± 0.4	63.9 ± 0.5	41.1 ± 0.8	31.5 ± 0.8
g_{31} (10^{-3} m^2 C^{-1})	8.71 ± 0.06	8.77 ± 0.07	9.42 ± 0.08	10.5 ± 0.2	7.43 ± 0.21
d_{33} (10^{-12} CN^{-1})	8.71 ± 121 ± 1	8.77 ± 142 ± 1	9.42 ± 125 ± 1	10.5 ± 98 ± 1	7.43 ± 92 ± 1

The k_p and d_{31} values are similar (or even higher) than those reported for other piezoelectric materials, such as $(Ba_{0.85}Ca_{0.15})(Ti_{0.95}Zr_{0.05})O_3$, with d_{31} = 43 pC/N [15]; $[(K_{0.5}Na_{0.5})_{0.94}Li_{0.06}]_{0.97}La_{0.01}(Nb_{0.9}Ta_{0.1})O_3$ with d_{31} = 17 pC/N and k_p = 0.34 [16]; $(1-x)Bi_{0.5}Na_{0.5}TiO_3$–$xK_{0.5}Na_{0.5}NbO_3$ + 1 wt. % Gd_2O_3, with k_p values ranging from 0.364 to 0.533 depending of the KNN concentration [17]; and other ceramics based on $Bi_{0.5}Na_{0.5}TiO_3$ [18].

The g_{31} values, except for the BNBT–8 composition, reveal to be higher than those reported for other piezoelectric materials; $[(K_{0.5}Na_{0.5})_{0.94}Li_{0.06}]_{0.97}La_{0.01}(Nb_{0.9}Ta_{0.1})O_3$, with $g_{31} = 2.41 \times 10^{-3}$ m^2C^{-1} [16] and $(K_Na)NbO_3$–$KTiNbO_3$, $g_{31} = 8.3 \times 10^{-3}$ m^2C^{-1} [19], both lower than those obtained for the studied lead-free ceramics. Several $PbTiO_3$-based ceramics, such as $(Pb_{0.82}Eu_{0.08})TiO_3$, $(Pb_{0.82}Sm_{0.08})TiO_3$ and $(Pb_{0.82}Gd_{0.08})TiO_3$, have also shown g_{31} values two orders of magnitude lower than the obtained in the present work [13].

For the thickness mode, there have been obtained d_{33} values higher than those reported for some lead-free compounds such as $Bi_{0.5}Na_{0.5}TiO_3$ [3] and $BiFeO_3$ [20]. In particular, the BNBT–8, BNBT–10 and BNBT–12 samples exhibit higher d_{33} values (d_{33} > 120 pC/N) than those for $0\cdot65\,BiFeO_3{-}_0\cdot35\,BaTiO_3$ [20], $0\cdot1\,Ba(Zr_{0.2}Ti_{0.8})O_3{-}_0\cdot9\,(Ba_{0.7}Ca_{0.3})TiO_3$ [21], $(1-x)Bi_{0.5}Na_{0.5}TiO_3$-$xK_{0.5}Na_{0.5}NbO_3$+1 wt. % Gd_2O_3 (x = 0–0.02) [17] and several materials based on $Bi_{0.5}Na_{0.5}TiO_3$ [22].

On the other hand, the BNBT–18 composition displays the lowest parameters, which could be associated to the highest barium concentration, which could provide an important influence of the semiconductor character for the $BaTiO_3$ system on the piezoelectric properties.

Figures 2, 3 and 4 show the results for the studied samples and some commercial lead-based (BM901, BM921, BM941) and $PbTiO_3$-based (BM300) materials [23]. Both electromechanical coupling factors (k_p and k_{31}) are higher for the lead-free studied samples (figure 2). These parameters are as much as twice higher than those observed for the commercial lead-based materials.

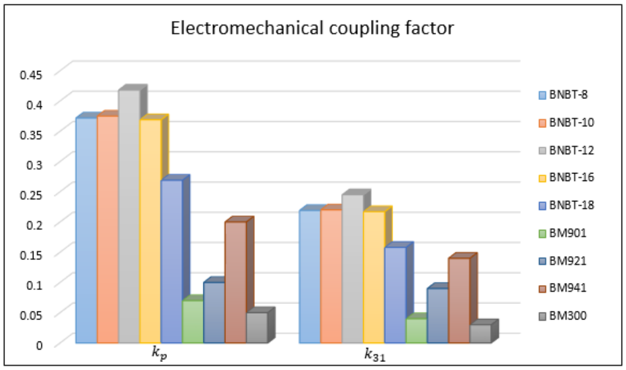

Figure 2. Electromechanical coupling factors for the radial mode (k_p and k_{31}), for the studied samples and some commercial piezoelectric materials (BM901, BM921, BM941 and BM300) [23].

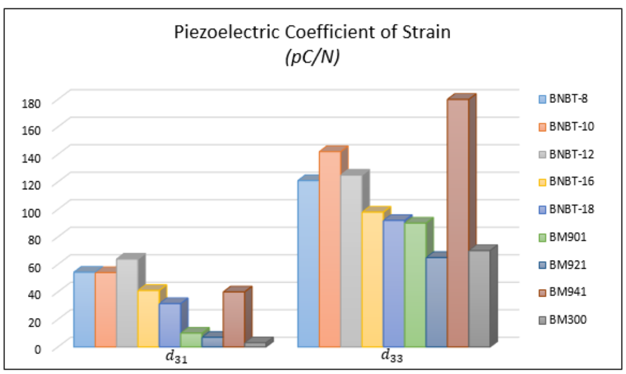

Figure 3. Piezoelectric coefficients of strain for the radial and thickness modes (d_{31} and d_{33}), for the studied samples and some commercial piezoelectric materials (BM901, BM921, BM941 and BM300) [23].

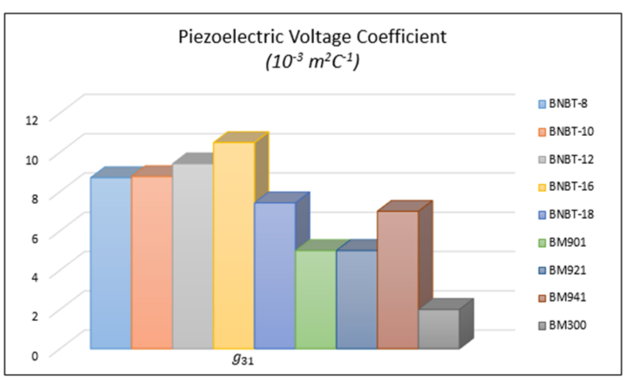

Figure 4. Piezoelectric coefficients of voltage for the radial mode (g_{31}), for the studied samples and some commercial piezoelectric materials (BM901, BM921, BM941 and BM300) [23].

For g_{31} (figure 4), it can be seen that the lead-free ceramics under study have better values than those for lead-based commercial materials BM901, BM921, BM941 and BM300.

For the d_{31} piezoelectric parameter (figure 3), only the BM941 shows better results, higher than BNBT–18. However, for d_{33}, it shows better results than all the studied samples.

Finally, it must be noted that the studied samples have shown better properties for a lower polarization field than those reported for other piezoelectric ceramics (even in the case of commercial ones). It could be suggested that a higher polarization field could promotes even higher piezoelectric parameters.

IV. CONCLUSIONS

The electromechanical behavior of the BNBT–x ceramic system ($x = 8, 10, 12, 16, 18$ at %) was studied through direct and indirect measurements. The best piezoelectric parameters were obtained for the BNBT–12 composition. The results revealed that the studied lead-free ceramics have better properties for the thickness mode than those reported for other ceramics and also for some commercial piezoelectrics, showing potentiality for pulse/echo applications. These ceramic compositions could be considered as an alternative to lead-based piezoelectrics for some applications.

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REFERENCES

[1] N. Castellano, Inventum **15**, 35 (2013).
[2] C. de Sousa, L. Manganiello, Rev. Ing. UC **25**, 433 (2018).
[3] P. Kumari, M. Lal, S. Prakash, R. Rai, Smart Materials for Smart Living, (Nova Sci. Publ. Inc., 2017), pp. 205-255.
[4] J. González, J. Molina, J. Marque, Rev. Esp. Cir. Oral y Maxilofac. **31**, 26 (2009).
[5] S. Shkuratov, E. Talantsev, J. Baird, Piezoelectric Ceramics, (Intech, 2010), pp. 269-294.
[6] S. Grondel, C. Delebarre, Piezoelectric Materials and Devices: Practice and Applications, (Intech, 2013), pp. 69-91.
[7] E. Gómez Suaste, J. J. González Morán, A. Flores Cuautle, Piezoelectric Ceramic, (InTech, 2010), pp. 209-228.
[8] P. K. Panda, J. Mat. Sci. **44**, 5049 (2009).

[9] T. Takenaka, K. Maruyama, K. Sakata, Jap. J. Appl. Phys. **30**, 2236 (1991).
[10] ANSI/IEEE Standard on Piezoelectricity **43**, 28 (1996).
[11] B. A. Auld, Piezoelectric Materials and Devices: Acoustics fields and waves in solids (John Wiley & Sons, 1973), pp. 35-52.
[12] E. Misael, P. D. Mininni, Estudio del comportamiento de un material piezoeléctrico en un campo eléctrico alterno, (Dep. Fis., Fac. Cienc. Exactas Nat., Buenos Aires, 1996).
[13] Y. García Puente, "Sistema para la detección de pulsos mecánicos mediante un sensor piezoeléctrico", Tesis de Ingeniería Física, Facultad de Física, Universidad de La Habana, Cuba, 2012.
[14] A. J. Moulson, J. M. Herbert, Electroceramics, (John Wiley & Sons, 2003).
[15] H. Maiwa, W: Sakamoto, Ferroelectrics **446**, 67 (2013).
[16] H. H'Mork, A. Duarte, J. Portelles, J. Fuentes, M. D. Durruthy-Rodriguez, O. Raymond, J. Heiras, M. P. Cruz, J. M. Siqueiros, Rev. Cub. Fis. **29**, 28 (2012).
[17] S. Pattipaka, A. R. James, P. Dobbidi, J. Alloys Compd. **765**, 1195 (2018).
[18] I. Coondoo, N. Panwar, A. Kholkin, J. Adv. Dielect. **3**, (2013).
[19] A. Tsuji, T. Kasashima, M. Yamazaki, Y. Okimura, J. Ceram. Society of Japan **128**, 464 (2020).
[20] S. Kim, G. Prasad, S. Ueno, C. Moriyoshi, Y. Kuroiwa, S. Wada, J. Appl. Phys. **122**, (2017).
[21] Y. Bai, A. Matousek, P. Tofe, V. Bijalwan, B. Nan, H. Hughes, T. W. Button, J. Eur. Ceram. Soc. **35**, 3445 (2015).
[22] T. Zheng, J. Wu, D. Xiao, J. Zhu, Prog. Mater. Sci. **98**, 552 (2018).
[23] Ltd., Sensor Technology., (2014) (www.sensortech.ca, https://sensortechcanada.com/wp-content/uploads/2014/03/Piezoelectric-Ceramic-Materials.pdf