The elastic and piezoelectric properties of tungsten bronze ferroelectric crystals $(Sr_{0.7}Ba_{0.3})_2NaNb_5O_{15}$ and $(Sr_{0.3}Ba_{0.7})_2NaNb_5O_{15}$

Wenhua Jiang
The City University of Hong Kong, Kowloon, Hong Kong, China

Wenwu Cao[a)]
The City University of Hong Kong, Kowloon, Hong Kong, China
and Department of Mathematics and Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802-4800

Xiujie Yi and Huanchu Chen
Crystal Institute, Shandong University, Jinan, Shandong, China

(Received 12 October 2004; accepted 3 February 2005; published online 21 April 2005)

The elastic and piezoelectric constants of tungsten bronze ferroelectric crystals $(Sr_{0.7}Ba_{0.3})_2NaNb_5O_{15}$ (SBNN70) and $(Sr_{0.3}Ba_{0.7})_2NaNb_5O_{15}$ (SBNN30) are determined by using the ultrasonic and resonance methods. The measured results show that these single crystals have larger dielectric constant and good piezoelectric property compared to other known lead-free perovskite ferroelectric crystals. The measurements show that the SBNN70 has larger dielectric and piezoelectric constants than SBNN30 since the former is near the morphotropic phase boundary composition. Our results confirmed that the SBNN single-crystal system is another good candidate as lead-free piezoelectric and dielectric materials. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1881777]

I. INTRODUCTION

Ferroelectric crystals with tungsten bronze structure are another attractive family beside perovskite structure ferroelectrics due to their superior dielectric, piezoelectric, pyroelectric, and nonlinear optical properties.[1–6] The chemical formulas of the tungsten bronze ferroelectric crystals can be either $(A_1)_4(A_2)_2C_4B_{10}O_{30}$ or $(A_1)_4(A_2)_2B_{10}O_{30}$, where A, B, and C are the pentagonal, tetragonal, and triangular sits formed by tetragonal B (Nb or Ta)–O octahedral, respectively, and will be occupied by some cations. For compounds with the former formula, all lattice sits are filled, while compounds with the latter formula could be either filled or unfilled, depending on whether or not all the A_1 and A_2 sits are occupied. For example, $Sr_{1-x}Ba_xNb_2O_6$ (SBN) is unfilled with one of A_2 sits unoccupied. On the other hand, $Sr_2NaNb_5O_{15}$ (SNN) and $Ba_2NaNb_5O_{15}$ (BNN) are filled cases. There are many kinds of compounds in tungsten bronze family, which differ by the filling status. Among them systems that could have potential morphotropic phase boundary (MPB) are the most attractive ones for practical applications since the piezoelectric and dielectric properties peak at the MPB.

It is known that crystals with tungsten bronze structure have the point group symmetry $4/mmm$ at their high-temperature phase. Therefore, the lower temperature ferroelectric phase could be either tetragonal ($4mm$) or orthorhombic ($mm2$). The MPB potentially exists in some binary or ternary systems. For compounds having the MPB, the dielectric, piezoelectric, and electro-optic properties can be greatly enhanced for the composition in the vicinity of the MPB. Oliver *et al.*[2] have extensively discussed the systems with MPB and their advantages and disadvantages in the applications of the dielectric, piezoelectric, and pyroelectric devices. In general, most of the functional properties will be enhanced near the MPB.

For the piezoelectric applications, such as making ultrasonic transducers and piezoelectric actuators, it is desirable to have high electromechanical coupling coefficients and relatively large dielectric constants in addition to a large piezoelectric coefficient. Large electromechanical coupling coefficient makes the transducer to have a broader bandwidth and the larger dielectric constant can make the electric impedance matching between the transducer and its driving power supply easier for small size transducers, such as medical imaging arrays. For this reason, $Pb(Zr,Ti)O_3$ (PZT) ceramics become the dominant material in the ultrasonic transducer industry in the past 40 years. But Pb compounds have been recognized as an environmentally nonfriendly material; hence, researchers have been searching for a lead-free piezoelectric material which may be used as an alternative to the PZT ceramics. Unfortunately, among the existing lead-free ferroelectric crystals, the piezoelectricity of $LiNbO_3$ and $LiTaO_3$ is weak, while $BaTiO_3$ has low phase-transition temperature and also very expensive to fabricate. Although $KNbO_3$ has a relatively larger piezoelectric coefficient, its domain configuration is not so stable and it is difficult to fully pole the crystal.[7]

The single crystals $(Sr_{1-x}Ba_x)_2Nb_5O_{15}$ studied here attract our attention due to two factors: (1) this is a lead-free material and has reasonable piezoelectric coefficient (Ref. 1). (2) It is a binary compound with a MPB. The compound of $(Sr_{1-x}Ba_x)_2Nb_5O_{15}$ can be considered as a binary system of SNN and BNN. Although both have weak orthorhombic

[a)]Electronic mail: cao@math.psu.edu

point group $mm2$ symmetry at room temperature with the symmetry of BNN almost tetragonal $4mm$, they have different space-group symmetry, $Bbm2$ for SNN and $Ccm2_1$ for BNN. Thus, a potential MPB of $Ccm2_1-Bbm2$ will occur for the xSNN-$(1-x)$BNN (SBNN) system at certain composition.[2]

The properties of SBNN system with the form of sintering ceramics have been investigated before.[2–4] It was found that the working frequency of such ceramic transducers is limited to relatively low frequencies because the loss is large at high frequencies from the scattering of ultrasound at grain boundaries. Recently, SBNN single crystals with different ratio of Sr/Ba have been successfully grown by us. The structure, dielectric, and optical properties for one composition of SBNN single crystal have been reported.[1] However, the complete elastic-piezoelectric-dielectric constant matrix for the SBNN system is not available. In this paper, we report a complete set of elastic and piezoelectric constants of two SBNN crystals with compositions $(Sr_{0.7}Ba_{0.3})_2NaNb_5O_{15}$ (SBNN 70) and $(Sr_{0.3}Ba_{0.7})_2NaNb_5O_{15}$ (SBNN30). It is known that the MPB occurs at the composition of $(Sr_{0.6}Ba_{04})_2NaNb_5O_{15}$ (SBNN60).[4] Thus, SBNN 70 is nearer to the MPB and the SBNN30 is away from the MPB.

II. THE METHODS USED TO DETERMINE THE ELASTIC AND PIEZOELECTRIC CONSTANTS OF SBNN SINGLE CRYSTALS

At room temperature, SBNN crystals are orthorhombic with point group symmetry $mm2$. Therefore, there are 17 independent materials constants: nine elastic, five piezoelectric, and three dielectric constants. To determine all those independent constants, both ultrasonic and resonance methods are used since it would need less number of samples to isolate all the constants.[8] For the ultrasonic measurements, two samples are used. One is a cube or a rectangular parallelepiped with the face orientations of (100), (010), and (001), respectively. Another is a thick plate with the major face to be (110). By using those two samples, 12 independent velocities (V) can be measured. The elastic constants associated with those velocities are as follows:

(a) Along [100]
 Longitudinal wave $\rho V^2=c_{11}^E$
 Shear wave with polarization along [010] $\rho V^2=c_{66}^E$
 Shear wave with polarization along [001] $\rho V^2=c_{55}^D$

(b) Along [010]
 Longitudinal wave $\rho V^2=c_{22}^E$
 Shear wave with polarization along [100] $\rho V^2=c_{66}^E$
 Shear wave with polarization along [001] $\rho V^2=c_{44}^D$

(c) Along [001]
 Longitudinal wave $\rho V^2=c_{33}^D$
 Shear wave with polarization along [100] $\rho V^2=c_{55}^E$
 Shear wave with polarization along [010] $\rho V^2=c_{44}^E$

(d) Along [110]
 Quasilongitudinal wave $4\rho V^2=G+H+\sqrt{(G-H)^2+4I^2}$
 Quasishear wave $4\rho V^2=G+H-\sqrt{(G-H)^2+4I^2}$
 Shear wave with polarization along [001]
 $2\rho V^2=c_{55}^E+c_{44}^E+(e_{15}+e_{24})^2/\varepsilon'$

Where ρ is the mass density,
$G=c_{11}^E+c_{66}^E$; $H=c_{22}^E+c_{66}^E$, $I=c_{12}^E+c_{66}^E$,
and $\varepsilon'=(\varepsilon_{11}^S+\varepsilon_{22}^S)/2$.

Thus, from the ultrasonic measurements the elastic constants $c_{11}^E, c_{22}^E, c_{33}^D, c_{44}^E, c_{55}^E, c_{66}^E, c_{12}^E, c_{44}^D$, and c_{55}^D are determined.

For the resonance measurements, four samples are required: a plate with the normal along [001] (k_t plate), a bar with the length along [001] (k_{33} bar), two bars with length along [100] (k_{31} bar) and [010] (k_{32} bar), and thickness along [001]. From the measured resonance and antiresonance frequencies of these resonators, the elastic compliances s_{11}^E, s_{22}^E, s_{33}^E, and s_{33}^D, elastic stiffness constants c_{33}^E, as well as the electromechanical coupling coefficients k_t, k_{33}, k_{31}, and k_{32} are obtained.

For materials with $mm2$ (also $4mm$) symmetry, s_{44}^E, s_{55}^E, and s_{66}^E are simply equal to $1/c_{44}^E$, $1/c_{55}^E$, and $1/c_{66}^E$, respectively. So they can be singled out from the nine independent elastic constants. Among the remaining six elastic stiffness and six compliance constants, $c_{11}^E, c_{22}^E, c_{33}^E, c_{12}^E$, as well as s_{11}^E, s_{22}^E, and s_{33}^E have been experimentally determined. The others, i.e., c_{13}^E, c_{23}^E, s_{12}^E, s_{13}^E, and s_{23}^E can be deduced from the corresponding conversion formulas. In principle, if any six among the total 12 elastic stiffness and compliance constants are known, the rest six unknowns can be calculated from the conversion formulas. But since the formulas are nonlinear, the results are not unique. In order to have self-consistent solutions, among c_{12}^E, c_{13}^E, and s_{23}^E, at least one should be measured directly. In our experiment, c_{12}^E is selected to be determined by ultrasonic measurement along [110].

The free dielectric permittivity is simply determined by capacitance measurements at low frequency (1 kHz). With the known permittivity, the piezoelectric strain constants d_{33}, d_{31}, d_{32}, and d_{15} and d_{24} can be calculated from the experimentally determined electromechanical coupling coefficients k_{33}, k_{31}, k_{32}, k_{15}, and k_{24}. The piezoelectric stress constants e_{33}, e_{31}, e_{32} and e_{15} and e_{24} can be obtained by using the conversion formulas. From such a procedure, all independent material constants, i.e., nine elastic, five piezoelectric, and three dielectric constants are obtained.

III. RESULTS AND DISCUSSIONS

The SBNN crystals used in the experiments are grown by the Czochralski technique using high-purity $SrCO_3$, $BaCO_3$, Nb_2O_5, and $NaCO_3$. The x-ray diffraction analysis shows that the as-grown crystals have the stoichiometric composition nearly identical to the starting materials.[1]

The samples are cut from the crystal boules to have desired dimensions and aspect ratios. The poling process is conducted under an electric field of 800–1000 V/mm at room temperature.

The ultrasonic velocities are measured by using a conventional pulse-echo method. The measurement system consists of a pulser/receiver (Panametrics 5900 PR) and a digital oscilloscope (Tek TDS 460A). The transducers with a center frequency of 10 MHz are used for both longitudinal (Pana-

TABLE I. The elastic, piezoelectric, and dielectric constants of $(Sr_{0.7}Ba_{0.3})_2NaNb_5O_{15}$ (SBNN 70) and $(Sr_{0.3}Ba_{0.7})_2NaNb_5O_{15}$ (SBNN 30) single crystals.

Elastic Properties					
$c^E(10^{11}N/m^2)$	SBNN70	SBNN30		SBNN70	SBNN30
c_{11}^E	2.268	2.44	s_{11}^E	34.46	5.33
c_{22}^E	2.267	2.44	s_{22}^E	34.46	5.33
c_{33}^E	1.86	1.56	s_{33}^E	8.301	8.04
c_{12}^E	2.12	1.02	s_{12}^E	−30.94	−1.71
c_{13}^E	1.198(9)	0.74	s_{13}^E	−2.28	−1.72
c_{23}^E	1.198(4)	0.74	s_{23}^E	−2.26	−1.72
c_{44}^E	0.607	0.65	s_{44}^E	16.46	15.44
c_{55}^E	0.607	0.65	s_{55}^E	16.46	15.44
c_{66}^E	0.71	0.73	s_{66}^E	14.08	13.70

Piezoelectric and dielectric properties					
$d(10^{-12}C/N)$	SBNN70	SBNN30	$e(C/m^2)$	SBNN70	SBNN30
d_{15}	91.36	67.30	e_{15}	5.50	4.36
d_{24}	90.55	67.30	e_{24}	5.55	4.36
d_{31}	−32.35	−12.40	e_{31}	−7.12	−0.38
d_{32}	−37.36	−12.40	e_{32}	−7.2	−0.38
d_{33}	68	53	e_{33}	4.23	6.43
$\varepsilon_{ij}^T(\varepsilon_0)$			$\varepsilon_{ij}^S(\varepsilon_0)$		
ε_{11}^T	590	380	ε_{11}^S	533	347
ε_{22}^T	567	380	ε_{22}^S	511	347
ε_{33}^T	240	121	ε_{33}^S	151	82.3

Coupling coefficients							
	k_{33}	k_{31}	k_{32}	k_{15}	k_{24}	k_t	$\rho(g/cm^2)$
SBNN70	0.51	0.12	0.14	0.31	0.31	0.26	5.1
SBNN30	0.57	0.17	0.17	0.30	0.30	0.52	5.3

metrics V202) and shear (Panametrics V221) waves. The resonance and capacitance measurements are conducted on the Agilent 4294A impedance analyzer.

The measured elastic, piezoelectric, and dielectric constants are listed in Table I. From the table it is seen that the differences between c_{11}^E and c_{22}^E, c_{44}^E and c_{55}^E, as well as c_{44}^D and c_{55}^D are not detectable using the ultrasonic technique because of the limited number of effective digits in the velocity measurements. This is consistent with the fact that the crystals are very weak orthorhombic and they are often called pseudotetragonal.[2]

The measured results indicate that ε_{11}, ε_{22}, and d_{15} of both SBNN70 and SBNN30 are larger than, respectively, their ε_{33} and d_{33}. Also, the ε_{33} and d_{33} of SBNN70 system are larger than those of SBNN30. This shows that the dielectric and piezoelectric properties have been enhanced as the composition of the crystals approaches the MPB. For comparison, we also listed some piezoelectric, dielectric constants, and electromechanical coupling coefficients of some lead-free perovskite ferroelectric materials in Table II. One can see that the piezoelectric and dielectric properties of the tungsten bronze ferroelectric crystals are superior to most of

TABLE II. The piezoelectric, dielectric constants, and electromechanical coefficients of some tungsten bronze and perovskite ferroelectric crystals.

	Tungsten bronze family			Perovskite family			
Constant	SBNN70	SBNN30	SBN[a]	$LiNbO_3$[b]	$KNbO_3$[c]	$LiTaO_3$[b]	$BaTiO_3$[d]
$d_{33}(10^{-12}m^2/N)$	68	53	130	6	29.3	8	85.6
$\varepsilon_{33}^T/\varepsilon_0$	240	121	880	30	44	45	169
k_{33}(%)	51	57	47.5	16	57	19	56
$e_{33}(C/m^2)$	4.14	6.43	12	1.3	4.4	1.9	3.66
$\varepsilon_{33}^S/\varepsilon_0$	151.5	82	633	29	24	43	114
$k_{t(\%)}$	26	52	44	16	43	18	27

[a]Ceramic, after Shrout *et al.* (Ref. 6)
[b]After Warner *et al.* (Ref. 9)
[c]After Zgonik *et al.* (Ref. 10)
[d]Crystal (Ref. 11)

the perovskite ferroelectric single crystals except $BaTiO_3$. Although $BaTiO_3$ has a reasonable larger piezoelectric coefficient, its ferroelectric phase-transition temperature is lower than that of the SBNN crystals. Hence, the properties of SBNN are less temperature sensitive compared to those of $BaTiO_3$. It is expected that the dielectric and piezoelectric properties of SBNN system can be further improved if the composition is closer to the MPB, which makes the SBNN family a good lead-free piezoelectric material.

We found that the poling process has strong influence to the dielectric property of the measured crystals. For example, the dielectric constants $\varepsilon_{33}=595$ and $\varepsilon_{33}=176$, respectively, are found for unpoled SBNN70 and SBNN30. After poling, the corresponding dielectric constants become $\varepsilon_{33}=240$ (SBNN70) and $\varepsilon_{33}=128$ (SBNN30). For the measured materials the dielectric constant in (001) direction is smaller than in (100) or (010). The reduction of ε_{33} due to the poling process shows that the poling process used in our measurement mainly eliminated 90° domains while these 90° domain walls have substantial contribution in the unpoled state. We found that the poling of those crystals is not an easy task and the poling process has large effect on the final property.

IV. SUMMARY

By using the ultrasonic and resonance methods, the complete set of elastic-piezoelectric-dielectric constant matrices are determined for two SBNN single crystals, i.e., $(Sr_{0.7}Ba_{0.3})_2NaNb_5O_{15}$ and $(Sr_{0.3}Ba_{0.7})_2NaNb_5O_{15}$. The measured results show that the piezoelectric and dielectric properties of the measured tungsten bronze ferroelectric crystals are better and/or more temperature stable than those of other known lead-free perovskite ferroelectrics. Also, strong enhancement of piezoelectric and dielectric properties is observed for SBNN system closer to the MPB composition. With some improvement using doping and making composition closer to the MPB, it is expected that the SBNN system can be a very good lead-free candidate for piezoelectric applications, such as ultrasonic transducers and piezoelectric actuators.

ACKNOWLEDGMENTS

This work was supported by the Research Grants Council of Hong Kong Joint Research Scheme (Project No. N_CityU 014/01) and the National Natural Science Foundation of China Grant No. 50131160737.

[1] B. Yang, F. Li, J. P. Han, X. J. Yi, H. L. W. Chan, H. C. Chen, and W. Cao, J. Phys. D **37**, 921 (2004).
[2] J. R. Oliver, R. R. Neurgaonkar, and L. E. Cross, J. Am. Ceram. Soc. **72**, 202 (1989).
[3] M. Kimura, T. Minamikawa, A. Ando, and Y. Sakabe, Jpn. J. Appl. Phys., Part 1 **36**, 6051 (1997).
[4] K. S. Rao, T. N.V.K.V. Prasad, A. S. V. Jabrahmanyam, J-H Lee, J-J Kim, and S-H Cho, Mater. Sci. Eng., B **98**, 279 (2003).
[5] S. Singh, D. A. Draegert, and J. E. Geusic, Phys. Rev. B **2**, 2709 (1970).
[6] T. R. Shrout, L. E. Cross, P. Moses, H. A. McKinstry, and R. Neurgaonkar, Proceedings of 1980 IEEE Ultrasonics Symposium, 1980, p. 414.
[7] S. Wada, A. Seike and T. Tsurumi, Jpn. J. Appl. Phys., Part 1 **40**, 5690 (2001).
[8] J. H. Yin, B. Jiang, and W. Cao, IEEE Trans. Ultrason. Ferroelectr. Freq. Control **47**, 285 (2000).
[9] A. W. Warnar, M. Onoe, and G. A. Coquin, J. Acoust. Soc. Am. **42**, 1223 (1967)
[10] M. Zgonik, R. Schlesser, I. Biaggio, E. Voit, J. Tscherry and P. Gunter, J. Appl. Phys. **74**, 1287 (1993)
[11] K. H. Hellwege, *Landolt-Bornstein: Numerical Data and Functional Relationship in Science and Technology, Group III* Vol. No. 1 (Springer, New York, 1987).