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Effect of Gadolinium Substitution on the Linear Thermal Expansion of Barium Sodium Niobate

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$Ba_2NaNb_5O_{15}$ (B–S–N) exhibits a large thermal contraction in its *c*-axis between 350° and 750°C. This behaviour contributes to a serious cracking problem during its crystal growth. The substitutions of Gd for Ba and/or Na in B–S–N can be made with either anion or cation compensation. The former, namely, type *A*, compositions were found to eliminate the thermal contraction behaviors, and had small variations in their linear thermal expansion coefficients, α, between 50° and 650°C. With good ferroelectric and dielectric properties, they showed potentials to replace the B–S–N crystal in electro-optic devices.

I. Introduction

Orthorhombic barium sodium niobate $Ba_2NaNb_5O_{15}$ (B–S–N) is a ferroelectric material with excellent electro-optic properties. It is an outstanding nonlinear optic materials for the second harmonic generation of 0.53 μm radiation from 1.06-μm laser radiation (*1*). The thermal expansion behaviors of single-crystal B–S–N were measured and reported by Ballman and his co-workers (*2*). Their results are shown here in Fig. 1. They showed the following features: (a) a large linear length contraction in the *c*-axis of the crystal, (b) this *c*-axis contraction effect occurring over a wide temperature range, starting from 350°C, attaining a maximum slope at 570°C (ferroelectric curie temperature (*3*)), and ending at about 750°C, (c) Small thermal expansion anisotropy shown by the *a*- and *b*-axes of the crystal, and (d) Only the *a*- and *b*-axes showed abrupt thermal expansion changes at the tetragonal–orthrorhombic phase transition (275°C).

Such behaviors cause great difficulties in the Czoehralski growth of barium sodium niobate crystal. As the crystal is cooled through the ferroelectric transition temperatures, the *c*-axis

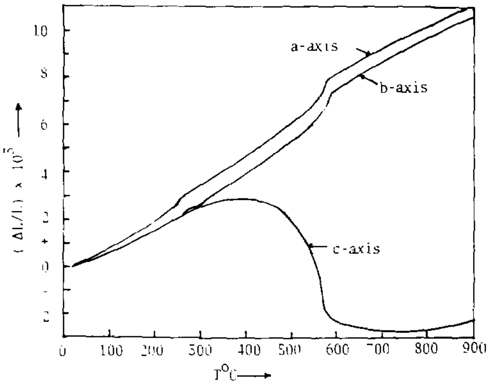

FIG. 1. Linear thermal expansion of single-crystal barium sodium niobate (after Ballman *et al.* (*2*)).

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contraction and the thermal expansion anisotropy can render the crystal susceptible to cracking. In order to alleviate this cracking problem during the crystal growth of B–S–N, careful slow cooling through the ferroelectric transition was successful. Mostly other efforts were directed to vary the melt compositions. Cracking and growth striations were reduced when nonstoichiometric compositions were used (*4*, *5*). They indicated significant changes in the thermal expansion behaviors due to the compositional variations (*5*).

In a study to be reported elsewhere (*6*), we made nonisoelectronic cation substitutions to the sintered polycrystalline (ceramic) B–S–N samples. Trivalent gadolinium (Gd) ions were used to substitute for divalent barium (Ba) and/or monovalent sodium (Na) ions. This type of substitution in amount of 0.1 mole produced linearly correlated changes in the three lattice parameters *a*, *b*, and *c* of the orthorhombic B–S–N. This paper reports on the effects on the linear thermal expansions of sintered B–S–N due to Gd substitutions.

II. Experimental Procedures

A. Sample Preparations

Conventional ceramic processing was used to prepare the niobate samples. An X-ray diffraction technique was employed to insure the completeness of the solid-state chemical reactions. Powder density, as determined by the pycnometer method, exceeded at least 98% of the theoretical (X-ray) density in every case. A second process was used to produce the ceramic pellets. Samples for dilatometric measurements were cut and ground from the pellets into sizes of about 0.4 in. long and 0.2 in. in diameter. Both ends of the sample were polished flat. The grain size for each sample was in the range between 10 and 15 μm.

The compositions of the gadolinium substituted barium sodium niobate samples are listed in Table I. Two types of substituted compound were made. One is the type A, which is called the anion-compensated substitution. In the type A composition, Gd was used to substitute for either Ba, or Na, or Ba and Na, on an atom-for-atom basis. The electrical neutrality, upset by the nonisoelectronic substitutions, was maintained by the addition of oxygen anions beyond the stoichiometric barium sodium niobate formula amount. Additional oxygen was supplied to the sample during the sintering processes. The other is the type B, which is called the cation-compensated substitution. In the type B composition, the amount of Gd substitution for either Ba, or Na, or Ba and Na was such so

TABLE I

NOMINAL COMPOSITIONS FOR THE GADOLINIUM SUBSTITUTED BARIUM SODIUM NIOBATES

Sample no.	Type of substitution	Number of ions in each formula unit				
		Ba^{2+}	Na^{+}	Gd^{3+}	Nb^{5+}	O^{2-}
Single crystal (S.C.)	—	2.0	1.0	0	5.0	15.0
Gd-doped samples						
Gd–A1	*A*	1.9	1.0	0.1	5.0	15.05
Gd–A2	*A*	2.0	0.9	0.1	5.0	15.10
Gd–A3	*A*	1.95	0.95	0.1	5.0	15.075
Gd–B1	*B*	1.9	1.05	0.05	5.0	15.0
Gd–B2	*B*	2.0	0.9	0.03	5.0	15.0
Gd–B3	*B*	1.95	0.95	0.05	5.0	15.0
Gd–B4	*B*	1.85	1.0	0.1	5.0	15.0
Gd–B5	*B*	2.0	0.7	0.1	5.0	15.0
Gd–B6	*B*	1.9	0.9	0.1	5.0	15.0

that the electrical neutrality was maintained. This involved a decrease of the total number of cations and maintained the number of Nb and O ions to be constant. Because it was impossible to obtain sufficiently accurate chemical analyses of the samples, these nominal compositions are used as the actual compositions for our purposes.

B. Thermal Expansion Measurements

Measurements were made with the use of an automatic recording dilatometer. A linear variable differential transformer (LVDT) was employed to convert the linear dimensional change to electrical voltage signal. The sensitivity of the dilatometer was calibrated to be in the order of 1 × 10^{-6} cm/cm. Heating and cooling rates in the range of 3 to 4°C/min were used. Linear thermal expansion results were in the form of $(\Delta L)/L$, where L is the original sample length, and ΔL is the linear dimensional change from L. The measured $(\Delta L)/L$ results were used to fit a third-order polynomial in temperature T in degrees Celsius by the least-squares method. The correlation coefficient for the least-squares fit of the equation

$$\Delta L/L = C_1 + C_2T + C_3T^2 + C_4T^3 \qquad (1)$$

exceeded 0.96 in every case. The coefficient of linear thermal expansion, α in unit of centimeters per centimeters per degrees Celsius, was obtained by the first derivative of Eq. (1) with respect to T such as

$$\alpha = \frac{d(\Delta L/L)}{dT}. \qquad (2)$$

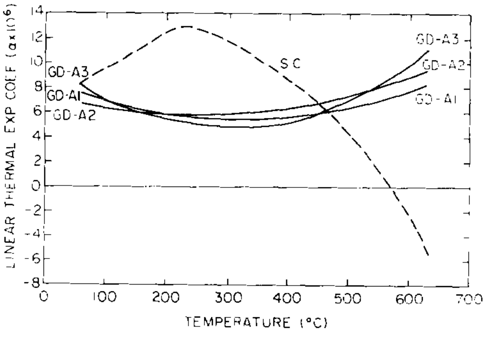

FIG. 2. Linear thermal expansion coefficient α as a function of temperature for samples GD-A1, -A2, and -A3. The SC curve was derived from the single-crystal data of Ballman and his co-workers (*2*).

The values of α plotted against temperature for the materials listed in Table I are shown in Figs. 2, 3, and 4. For comparison, a curve marked SC representing the polycrystalline undoped barium sodium niobate is included in each figure. This curve was derived from the single-crystal thermal expansion data of Ballman and his co-workers (*2*).

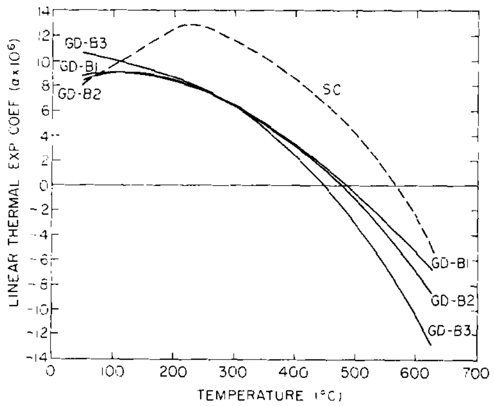

FIG. 3. Linear thermal expansion coefficient α as a function of temperature for samples Gd-B1, -B2, and -B3. The SC curve was derived from the single-crystal data of Ballman and his co-workers (*2*).

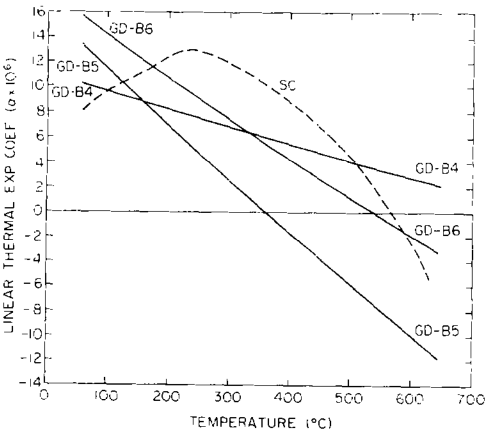

FIG. 4. Linear thermal expansion coefficient α as a function of temperature for samples GD-B4, -B5, and -B6. The SC curve was derived from the single-crystal data of Ballman and his co-workers (*2*).

III. Discussion

B–S–N has a tungsten bronze structure (*7*). In this structure, NbO_6 octahedra are connected by corner oxygen ions with each oxygen shared by two niobium ions. The Nb to O ratio is therefore 1:3. In the (001) plane, the NbO_6 octahedra link together into rings of 3, 4, and 5 octahedra. The sites enclosed by rings of 3, 4, and 5 octahedra are given by the site symbols γ, α, and β, respectively. Each unit cell contains ten formula units of $Ba_2NaNb_5O_{15}$. In the unit cell of stoichimetric B–S–N, all the α and β sites are completely occupied by cations. Two α sites are occupied by Na and four β sites are occupied by Ba; all four γ sites are vacant. In this structure, ten NbO_6 octahedra in each unit cell require ten positive ionic charges to maintain the electrical neutrality.

The number of cation sites and the number of positive ionic charges provide excellent monitors about the cation substitutions into B–S–N.

In the type *B* compositions, i.e., the cation-compensated substitutions, the Nb to O ratio remains at 1:3. This confirms the network of NbO_6 octahedra in them as in the stoichiometric B–S–N. Only some of the α or β sites became vacant. Because of the network of NbO_6 octahedra remaining intact, these type B compositions are essentially unchanged from B–S–N structurally. It is reasonable to expect that their thermal expansion behaviors should show the same behavior as the stoichiometric (SC) B–S–N. This is shown to be the case by Figs. 3 and 4.

The maximum in the α values of the undoped B–S–N (SC) is due to the orthorhombic to tetragonal transition of B–S–N around 275°C (*2*). This phase transition produced abrupt changes in the thermal expansion data of single-crystal B–S–N. In polycrystalline samples, their thermal expansion data did not reveal this transition. Consequently, no maximum was found in the α values for the type B compositions.

The overall α values for the undoped as well as type B substituted B–S–N samples decreased as temperature was increased to 650°C. This was due to the length contraction in the *c*-axis for the case of undoped B–S–N (SC). The agreement of this feature by the type B composition can be readily explained by the fact that they also have the net work of NbO_6 octahedra, as does the undoped B–S–N (SC). Generally, the α values for SC are larger than the values for the type B compositions. This is due to the lower densities (about 89% of the theoretical density) of the ceramic samples. During the sintering process, vapor transport was found to be a mechanism of mass transport in B–S–N (*8*). Lower density would cause a decrease in the α values.

At lower temperatures (below 200°C), the type B compositions showed higher α values than those of the SC sample. They are apparently dependent on the defects on the cation sites. The number of vacant α- and β-sites per unit cell is 0, 0.6, 0.1, 0.1, 0.2, and 0.4 for samples Gd-B1, -B2, -B3, -B4, -B6, and -B5, respectively. The amount of increase in α values over that of the SC sample is in the increasing order of sample Gd-B2, -B1, -B1, -B4, -B3, -B5, and -B6. Similarity in these two sequences indicates that the greater the number of vacant α- and β-sites, the larger is the increase in α over the SC sample. As the site selection of the substituted Gd cations is not known, it is impossible to differentiate the effect of vacant α- from that of vacant β-site.

The most interesting results are, however, those of the type A compositions, i.e., the anion-compensated substitutions, as shown in Fig. 2. They exhibited a minimum in their α values. All their α-values were positive. They increased as the temperature was increased to 650°C.

It is obvious that the type A compositions eliminated the *c*-axis contraction. As the Nb to O ratios in the type A compositions are smaller than $\frac{1}{3}$, their structures must have some breakages in the Nb–O linkage between the NbO_6 octahedra. Such a decoupling allows greater degrees of freedom for some of the

NbO_6 octahedra to move during heating. It also changes the geometrical packings about some of the α- and β-sites. They should have direct bearing on the thermal expansion behavior as well.

In the type A compositions, all the α- and β-sites are occupied. They showed very small changes in their α values from 50 to 650°C. In sample Gd-A3, its α values ranged between $(4.6 \text{ and } 11.1) \times 10^{-6}$. In sample Gd-A1, they ranged between $(5.2 \text{ and } 8.2) \times 10^{-6}$. In these cases, the site selection of Gd is known. In sample Gd-A3, half of the Gd ions were on the α-sites, the other half on the β-sites. In sample Gd-A2, Gd ions occupied the α-sites. In sample Gd-A1, Gd ions occupied the B-sites. This may be the reason for the smaller differences in α values in the Gd-A1 sample. Or, since the same amount of Gd ions was used for either samples Gd-A1 and -A2, it also means that a smaller amount of defect β-sites (0.2/4) occurred in the sample Gd-Al as against the case of sample Gd-A2 when the amount of defect α-sites was 0.2/2.

From a practical viewpoint, the type A compositions provide another means to alleviate the cracking problem of B–S–N– crystals during their growths. The ferroelectric curie temperatures were found to be 560°, 538°, 539°, 506°, 533°, and 544°C for samples Gd-A1, -A2, -A3, -B1, -B2, and -B3, respectively. They were lower than that of single-crystal B–S–N, i.e., 570°C. At room temperature, the relative dielectric constants, measured at 1 KHz, for single-crystal B–S–N were found to be 222 for K_{11}, 227 for K_{22}, and 32 for K_{33}. For ceramic samples, the relative dielectric constants were found to be 96.7, 98.1, 91.8, 62.5, 59.6, and 57.3 for samples Gd-A1, -A2, -A3, -B1, -B2, and -B3, respectively. From these results, the type A compositions, especially those of the Gd-substitutions as in Gd-A1, Gd-A2, and Gd-A3, showed good ferroelectric and dielectric properties. They warrant further investigations so as to ascertain that, first, these type A compositions do alleviate the cracking problem during crystal growth; and second, some of these type A compositions have sufficiently good ferroelectric and dielectric properties to replace the use of B–S–N crystals.

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References

1. J. E. Gensic, H. J. Levinstein, S. Singh, R. G. Smith, and L. G. Van Uitert, *Appl. Phys. Lett.* **12**, 306 (1968).
2. A. A. Ballman, J. R. Carruthers, and H. M. O'Bryan, Jr., *J. Cryst. Growth* **6**, 184 (1970).
3. L. G. Van Uitert, H. J. Levinstein, J. J. Rubin, C. D. Capio, E. F. Dearborn, and W. A. Bonner, *Mater. Res. Bull.* **3**, 47 (1968).
4. K. G. Barraclough, I. R. Harris, B. Cockayne, J. G. Plant, and A. W. Vere, *J. Mater. Sci.* **5**, 389 (1970).
5. W. A. Bonner, J. R. Carruthers, and H. M. O'Bryan, Jr., *Mater. Res. Bull.* **5**, 243 (1970).
6. J. L. Mukherjee, C. P. Khattak, K. P. Gupta, and F. F. Y. Wang, Effect of nonisoelectronic cation substitution on lattice parameters of barium sodium niobate, *J. Mater. Sci.*, to appear (1977).
7. P. B. Jamieson, S. C. Abrahams, and J. L. Bernstein, *J. Chem. Phys.* **50**, 4352 (1969).
8. K. P. Gupta, R. W. Siegel, and F. F. Y. Wang, *J. Mater. Sci.* **9**, 867 (1974).