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Evaluation of material constants in $NdCa_4O(BO_3)_3$ piezoelectric single crystal

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Abstract A neodymium calcium oxoborate $NdCa_4O(BO_3)_3$ piezoelectric single crystal that belongs to the monoclinic system with point group *m* was grown by the Czochralski technique. A practical evaluation method was developed to determine the 27 independent material constants for acoustic wave device applications. A longitudinal effect face–shear vibration was analyzed and used in the resonance–antiresonance measurement. This method avoided measuring d_{11} and d_{33} directly by use of *X*-bar and *Z*-bar, in which leak of electric field would cause large errors because of the very small dielectric constants. At room temperature, dielectric constants were $\varepsilon_{11}^{\mathrm{T}}/\varepsilon_0 = 9.9$, $\varepsilon_{22}^{\mathrm{T}}/\varepsilon_0 = 15$, $\varepsilon_{33}^{\mathrm{T}}/\varepsilon_0 = 10$ and $\varepsilon_{13}^{\mathrm{T}}/\varepsilon_0 = -0.8$, respectively. All the independent dielectric and elastic constants were determined in this work. The simulation of surface acoustic wave velocity showed a good agreement with the measured value.

Keywords Piezoelectric single crystal · Material constants · Resonance–antiresonance measurement · SAW

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1 Introduction

In recent years, high-performance piezoelectric materials with smaller frequency–temperature coefficients, wider bandwidth response and lower propagation losses have been required for the rapid progress of digital technology in the mobile digital communications field. As new candidates, rare-earth calcium oxoborate $R\mathrm{Ca_4O(BO_3)_3}$ (*R*=rare-earth elements) single crystals have received considerable attention for surface acoustic wave (SAW) applications. Among them, neodymium calcium oxoborate $NdCa_4O(BO_3)_3$ (NdCOB) piezoelectric single crystal had been reported that its coupling factor of SAW (k^2) was 0.8% and the linear temperature coefficient of delay (TCD) was close to zero [1]. That was a very valuable result to indicate a great possibility for SAW applications with high temperature stability.

Those $R\mathrm{Ca_4O(BO_3)_3}$ single crystals belong to monoclinic symmetry system with point group *m*. There are 13 elastic, 10 piezoelectric and 4 dielectric independent material constants to be determined. However, evaluation method for those crystals is not established up to date. One of the problems is that the dielectric constants in the crystals are very small. This fact would cause large errors when *X*-bar and *Z*-bar are used for measuring d_{11} and d_{33} directly.

A few papers reported the material constants in $GdCa_4O(BO_3)_3$ and $LaCa_4O(BO_3)_3$ [2, 3]. However, thickness–shear vibration mode, *X*-bar and *Z*-bar length–extensional vibration modes were measured for calculating elastic compliances s^{E} and piezoelectric constants *d*. Strictly speaking, there are some basic problems to be solved.

In this paper, based on the relation equations expressed below,

$$e'_{nm} = \sum a_{ni} a_{mj} e_{ij} \tag{1}$$

$$d'_{nmp} = \sum a_{ni} a_{mj} a_{pk} d_{ijk} \tag{2}$$

$$s'_{nmpq} = \sum a_{ni} a_{mj} a_{pk} a_{ql} s_{ijkl} \tag{3}$$

all of the possible piezoelectric vibrations with rotated plates were calculated. After considering a matter in all its aspects, an improved evaluation method for those crystals was proposed. NdCOB single crystal was measured, and its SAW velocity was simulated using obtained elastic constants.

2 Crystal growth

To prepare compound powders for growing NdCOB single crystal, starting materials of 4N pure carbonate and oxides were weighed and mixed; then the mixture was synthesized at 1250 °C for 10 h. The crystal growth was carried on at 1470 °C from an Ir crucible in an Ar atmosphere by the Czochralski technique. The pulling rate with a growth direction of *b*-axis was 2 mm/h, and the seed rotation rate was 15 rpm. The crystal had a dark violet color, as shown in Fig. 1. Inclusion, crack or bubble free large-size crystals with 37 mm in diameter and 100 mm in length were successfully obtained. Composition analysis indicated that the crystal was grown from a congruent melt. The density was 3.59 g/cm^3. Lattice constants at room temperature were a=0.813, b=1.606, and c=0.359 nm, and β=101.4° [1]. Before evaluating the material constants, positive senses of the rectangular *X*-, *Y*- and *Z*-axis were determined by the static piezoelectric measurement of IEEE Standard on application of piezoelectricity [4].

Fig. 1 As-grown NbCOB single crystal

3 Theoretical analyses of evaluation method

The dielectric constants ε_{11}, ε_{22} and ε_{33} can be directly obtained from the capacitances of *X*-, *Y*- and *Z*-cut plates. According to Eq. 1, ε_{13} could be calculated from the capacitance of an (*XZw*)45° plate using the relation equation

$$\varepsilon'_{11} = (\varepsilon_{11} + \varepsilon_{33} - 2\varepsilon_{13})/2.$$

The piezoelectric and elastic constants d and s^{E} can be obtained by using the resonance–antiresonance method. d_{12}, d_{13}, d_{31} and d_{32}, and s^{E}_{11}, s^{E}_{22} and s^{E}_{33}could directly be measured through transverse effect length–extensional (LE) vibrations in *XY*-, *XZ*-, *ZX*- and *ZY*-plates.

The piezoelectric constants d_{11} and d_{26} always appear in pairs as well as d_{33} and d_{24}. Because of the small dielectric constants, $\varepsilon^{\mathrm{T}}_{11}/\varepsilon_0 = 9.9$ and $\varepsilon^{\mathrm{T}}_{33}/\varepsilon_0 = 10$, *X*-bar or *Z*-bar has a very small capacitance of 0.1 pF. In this case, antiresonance frequency could not be measured correctly. Therefore, we should avoid using longitudinal effect LE vibration for determination of d_{11} and d_{33}.

The piezoelectric constants d_{24} and d_{26} correspond to longitudinal effect face–shear (FS) vibration. Since other $d_{2\mathrm{j}}$ constants are zero, a pure shear motion excited by d_{24} or d_{26} could be separated out without mode coupling. A sample with size of 1×3×20 mm and electrode on *Y*-side is conceivably suitable for measurement. In this case, capacitance of the sample becomes 0.9 pF. The relations between resonance and antiresonance frequencies and material constants are given as

$$\begin{aligned} {k'_{24}}^2 &= \frac{\pi}{2}\frac{f_{\mathrm{r}}}{f_{\mathrm{a}}}\tan\left(\frac{\pi}{2}\frac{f_{\mathrm{a}}-f_{\mathrm{r}}}{f_{\mathrm{a}}}\right) \\ s^E_{44} &= \frac{1}{4b^2 f_{\mathrm{a}}^2 \rho\left(1-{k'_{24}}^2\right)} \\ {d_{24}}^2 &= {k'_{24}}^2 s^{\mathrm{E}}_{44} \varepsilon^{\mathrm{T}}_{22} \end{aligned} \tag{4}$$

where f_r and f_a are resonance and antiresonance frequencies, b is width, and ρ is density of the sample. For the case of d_{26}, relation expressions can be similarly written as above.

Derived from Eq. 2, d_{11} and d_{33} can be then obtained by measuring transverse effect LE motions in (*XYw*)45° and (*ZYw*)45° plates based on the relation equations

$$d_{12}' = \sqrt{2}(\mathrm{d}_{12} + d_{11} - d_{26})\Big/4$$

and

$$d_{32}' = \sqrt{2}(\mathrm{d}_{32} + d_{33} - d_{24})/4,$$

respectively.

The piezoelectric constants d_{15} and d_{35} can also be obtained by measuring transverse effect LE vibrations in (*XZw*)±45° plates based on the relation equation

$$d_{13}' = \sqrt{2}(d_{11} + d_{13} - d_{35} \pm d_{15} \mp d_{33} \mp_{31})/4.$$

All the d constants could be determined by the above resonance–antiresonance measurement.

The elastic compliances s_{44}^{E} and s_{66}^{E} can be obtained simultaneously with d_{24} and d_{26} according to Eq. 4. Moreover, s_{12}^{E} can be obtained simultaneously with d_{11} according to the relation equations

$$s_{22}'\mathrm{E} = \frac{1}{4l^2 f_r^2 \rho}$$

$$s_{22}' = (s_{22} + 2s_{12} + s_{66} + s_{11})/4,$$

where l is sample length. s_{23}^{E} can also be obtained simultaneously with d_{33} according to the relation equation

$$s_{22}' = (s_{22} + 2s_{23} + s_{44} + s_{33})/4.$$

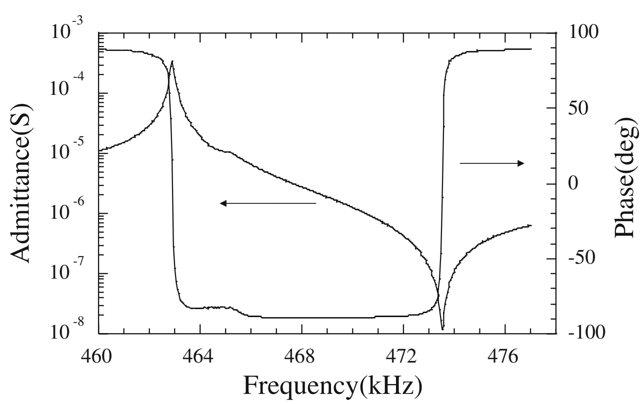

Fig. 2 Frequency characteristics of admittance and phase for longitudinal effect FS motion

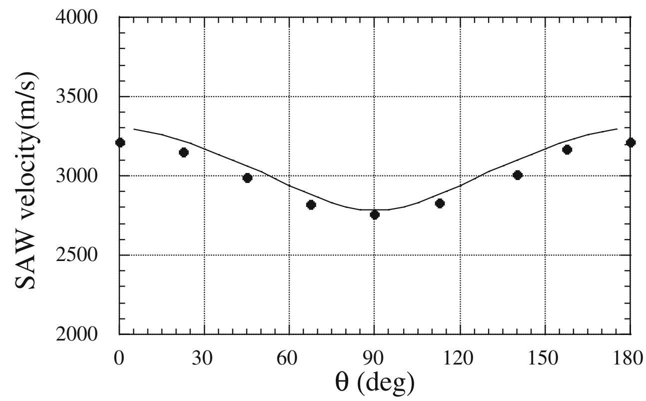

Fig. 3 Angular dependence of SAW velocity for *Z*-cut substrate. *Solid line* is simulated curve; *filled circle* is measured values

After calculating all the possible piezoelectric vibrations in *Y*-axis-rotated cuts, we can obtain some useful motions for determination of the constants. In this case, the piezoelectric d matrix remains as the former state. Except d_{24}' and d_{26}', other d_{2j}' are zero. As discussed before, a pure longitudinal effect FS vibration could be separated out. Using a (*XZw*)45°-cut with size of 1×3×20 mm and electrode on *Y*'-side, s'^{E}_{44} could calculated from its resonance and antiresonance frequencies, as given in Eq. 4. The elastic s_{46}^{E} is then obtainable from the next relation equation

$$s_{44}' = (s_{44} + 2s_{46} + s_{66})/2.$$

Transverse effect LE vibrations are also valuable in *Y*-axis-rotated plates. Relation equation

$$s_{33}' = \cos^4\theta s_{33} + \sin^2\theta\cos^2\theta(2s_{13} + s_{55}) + 2 \times \sin^3\theta\cos\theta s_{15} + 2\sin\theta\cos^3\theta s_{35} + \sin^4\theta s_{11}$$

is obtained from Eq. 3. This is a simultaneous equations in three unknowns, if we chose θ=22.5, 45 and 67.5°. Therefore, s_{15}^{E}, s_{35}^{E} and $\left(2s_{13}^{\mathrm{E}} + s_{55}^{\mathrm{E}}\right)$ can be determined by using (*XZw*)22.5°, (*XZw*)45° and (*XZw*)67.5° plates.

The elastic s_{25}^{E} is obtainable from a transverse effect LE vibration in a double-rotated (*YZtw*)45°/45° cut according to the following equation

$$s_{33}' = (s_{11} + s_{33} + 2s_{13} + s_{55})/16 + (s_{15} + s_{35} + s_{44} + s_{66})/8 + (s_{12} + s_{22} + s_{23} + s_{25} + s_{46})/4.$$

For all possible uncoupled vibration, $\left(2s_{13}^{\mathrm{E}} + s_{55}^{\mathrm{E}}\right)$ is always present together in related equations. To separate $\left(2s_{13}^{\mathrm{E}} + s_{55}^{\mathrm{E}}\right)$, we use a mode-coupled transverse effect FS motion. After rotating 45° around *X*-axis, all d_{3j}' constants appear. d_{36}' could excite a FS motion which mode-couples with a width vibration caused by d'_{31}. In this case, the two coupled resonance frequencies are given as [5]

$$f_1 = \frac{1}{2b}\sqrt{\frac{(c_{11}+c_{66}) - \sqrt{(c_{11}-c_{66})^2 + 4c_{16}^2}}{2\rho}}$$

$$f_2 = \frac{1}{2b}\sqrt{\frac{(c_{11}+c_{66}) + \sqrt{(c_{11}-c_{66})^2 + 4c_{16}^2}}{2\rho}}.$$

In the equation, c_{ij} constants are given in terms of the elastic compliances by the formula

$$c_{ij} = (-1)^{k+l}\Delta^{kl}/\Delta; \quad k,l = 1,2,3$$

where Δ is the determinant

$$\Delta = \begin{vmatrix} s'_{11} & s'_{12} & s'_{16} \\ s'_{12} & s'_{22} & s'_{26} \\ s'_{16} & s'_{26} & s'_{66} \end{vmatrix}$$

and Δ^{kl} is the minor obtained by suppressing the kth row and lth column. For a $ZYw(45°)$ cut, s'_{ij} constants are expressed as

$$s'_{11} = s_{11}$$
$$s'_{12} = [s_{12} + (2s_{13} + s_{55})/2 - s_{55}/2]/2$$
$$s'_{16} = s'_{15}\Big/\sqrt{2}$$
$$s'_{22} = (s_{22} + 2s_{23} + s_{44} + s_{33})/4$$
$$s'_{26} = \sqrt{2}(s_{35} + s_{25} + s_{46})/4$$
$$s'_{66} = (s_{66} + s_{55})/2.$$

f_1 and f_2 are corresponding to the mode-coupled FS and width vibrations, respectively. Using the numerical simulation for a given s^E_{55}, f_1 and f_2 can be fitted, thereby obtaining s^E_{55} as well as s^E_{13}.

4 Experimental

All the necessary samples were cut out according to the analyses in the last section. An impedance/gain phase analyzer (HP 4194A) was employed for measurements at room temperature. Electromechanical coupling factors k_{12}, k_{13}, k_{31} and k_{32} were determined as 15.4%, 16.8%, 4.7% and 9.4%, respectively. Figure 2 shows the resonance and antiresonance frequency characteristics of admittance and phase for longitudinal effect FS vibration in ZX-cut. The phase changed to –88° with a much better shape comparing with the longitudinal effect LE vibration in X- or Z-bar. All the 27 material constants were determined in this work. The dielectric and elastic constants, and part of piezoelectric constants are shown below

$$\varepsilon^{\mathrm{T}}/\varepsilon_0 = \begin{bmatrix} 9.9 & 0 & -0.8 \\ & 15 & 0 \\ & & 10 \end{bmatrix},$$

$$s^{\mathrm{E}} = \begin{bmatrix} 8.3 & -2.0 & -3.5 & 0 & -0.9 & 0 \\ & 7.5 & -1.6 & 0 & 0.5 & 0 \\ & & 9.4 & 0 & 0.9 & 0 \\ & & & 34 & 0 & 1 \\ & & & & 22 & 0 \\ & & & & & 20 \end{bmatrix} \left(\mathrm{pm}^2/\mathrm{N}\right),$$

$$d = \begin{bmatrix} 1.7 & 3.9 & -4.9 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & d_{26} \\ -1.4 & -2.5 & 1.5 & 0 & d_{35} & 0 \end{bmatrix} (\mathrm{pC/N}).$$

Using the above data, the Rayleigh SAW velocity for X-, Y- and Z-cut plates were theoretically simulated using the Campbell and Jones method [6]. All the calculated SAW velocities were close to those measured values. Figure 3 shows the typical results for the Z-cut substrate.

5 Conclusion

A neodymium calcium oxoborate $NdCa_4O(BO_3)_3$ piezoelectric single crystal was grown by the Czochralski technique. After considering all the possible piezoelectric vibrations in all rotated cuts, a practical evaluation method was developed for determining the dielectric, piezoelectric and elastic constants in the NdCOB crystal. Instead of measuring d_{11} and d_{33} directly by use of X- and Z-bar, d_{24} and d_{26} were firstly determined using the longitudinal effect FS vibration. To separate $\left(2s^E_{13} + s^E_{55}\right)$, a mode-coupled transverse effect FS motion was used. According to the material constants obtained in this work, the Rayleigh SAW velocity for X-, Y- and Z-cut substrates were theoretically simulated, which showed a good agreement with the measured values.

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