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Growth and SAW properties of rare-earth calcium oxoborate crystals

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Abstract

Rare-earth calcium oxoborate $RCa_4O(BO_3)_3$ (R, rare-earth elements; RCOB) (R = Pr, Nd, Sm, Eu, Dy, Ho, Er) bulk single crystals were grown by the Czochralski technique. Their melting temperature increased with a decrement of a rare-earth ion radius in RCOB. Surface acoustic wave (SAW) and pseudo-SAW (PSAW) properties of the RCOB crystal were investigated. The electro mechanical coupling factors k^2 values of NdCOB were the highest of all RCOB crystals. For SAW, k^2 of 0.80% and velocity of 3400 m/s at *X*-axis propagation were obtained on the *Y*-cut substrate. For PSAW, 1.95% and 3900 m/s at *Y*-axis propagation were obtained on the *Z*-cut substrate. Moreover, the thermal stability of the SAW of NdCOB (TCD = 3 ppm/°C) is equivalent to a quartz crystal (TCD = 0 ppm/°C).

Keywords: Crystal growth; Thermal analysis; Acoustic properties

1. Introduction

Due to the recent progress of electric and communication technology, there is a demand for new piezoelectric crystals, which show a high thermal stability of frequency and a large electromechanical coupling factor (k^2). These crystals can improve existing piezoelectric devices such as filters, delay lines, resonators and oscillators. As new candidates, we have paid attention to rare-earth calcium oxoborate $RCa_4O(BO_3)_3$ (R, rare-earth elements; RCOB) crystals, which can be grown by the Czochralski (Cz) technique at a low cost. So far, a RCOB crystal, which belongs to monoclinic system, point group *m*, space group *Cm*, was developed as a non-linear optical crystal for frequency conversion. Hence, many studies have been done about its optical properties [1–5]. In contrast, insufficient piezoelectric research has been conducted to date. Up to now, surface acoustic wave (SAW) properties of YCOB, GdCOB, LaCOB, $Gd_xY_{1-x}COB$ ($0 \leq x \leq 1$) have been reported [6–9]. In this study, we grew single crystals by Cz technique and investigated SAW properties of the RCOB (R = Pr, Nd, Sm, Eu, Dy, Ho, Er) crystals.

2. Experimental procedure

The starting material was prepared by a solid-state reaction of 4N R_2O_3 (R = Pr, Nd, Sm, Eu, Dy, Ho, Er), $CaCO_3$ and B_2O_3. The mixture was calcined at 1000 °C for 10 h, cooled and ground, and then fired again at 1250 °C for 10 h. The sintered material was identified by X-ray powder diffraction (XRD) with Cu Kα_1 radiation (λ = 0.15405 nm) by a graphite monochromator. A scanning speed of 4°/min was applied to record the pattern in the 2θ range of 10°–70°.

The starting material was melted in Ir crucibles (50 or 100 mm in diameter and height). Crystals were grown at 2.0–3.0 mm/h pulling rate and 10–30 rpm rotation rates in an Ar atmosphere. When the crystal growth finished, the temperature was cooled down to room temperature at a rate of 15–75 °C/h. The melting temperature of the crystals was determined by thermogravity differential thermal analysis (TG-DTA) with the heating rate 10 °C/min in air. The

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chemical composition was determined by inductively coupled plasma emission spectrometry (ICP-ES).

To characterize the SAW properties, *X*-, *Y*- and *Z*-cut substrates, which were polished optically flat on one face, were prepared from the grown crystals. Then, inter-digital transducers (IDTs), which were made of aluminum (Al), were fabricated on the polished surface of the substrates by a photolithography process. The *S*-parameters of the IDTs were measured by a network analyzer (HP 8510C), and the frequency response and filter characteristics were obtained. From these results, the SAW velocity (v) and the coupling factor (k^2) were determined. The temperature coefficient of delay (TCD) was evaluated based on the temperature dependence of the frequency from 5 to 45 °C.

3. Results and discussion

3.1. The XRD and the thermal analysis

The XRD analysis of sintering materials suggests the some unreacted raw materials were observed after the first calcined process of 1000 °C for 10 h. However, RCOB single phase was obtained at 1250 °C for 10 h. The thermal behavior of RCOB crystals was measured by TG-DTA. Fig. 1 shows the TG-DTA curve of the NdCOB crystal as a typical example of RCOB crystals. Until the crystal was melt at 1470 °C, there were no endothermic and exothermic peaks related to any phase changes. Moreover, single NdCOB is not ferroelectric, it does not need monodomainization compared with $LiTaO_3$. We also confirmed the other RCOB crystals show non-ferroelectricity and found the relationship between the melting temperature and a rare-earth ionic radius of RCOB as shown Fig. 2. It indicates that the melting temperature of RCOB rises with the decrement of a rare-earth ion radius. The melting point of LaCOB is 1420 °C and the lowest in all rare-earth calcium oxoborares. This means that a platinum crucible could be used to grow the LaCOB crystal. The use of platinum crucible is very important for mass-production.

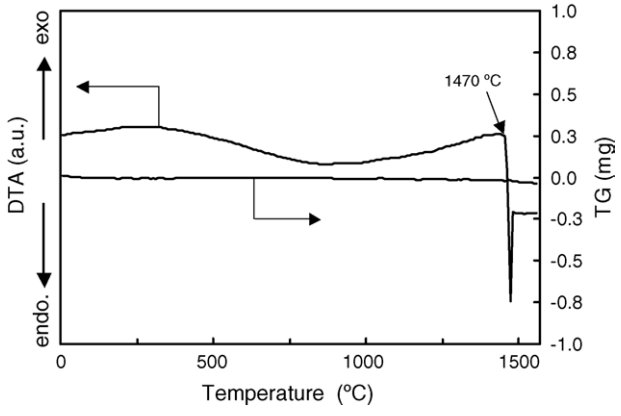

Fig. 1. A TG-DTA curve of $NdCa_4O(BO_3)_3$ crystal.

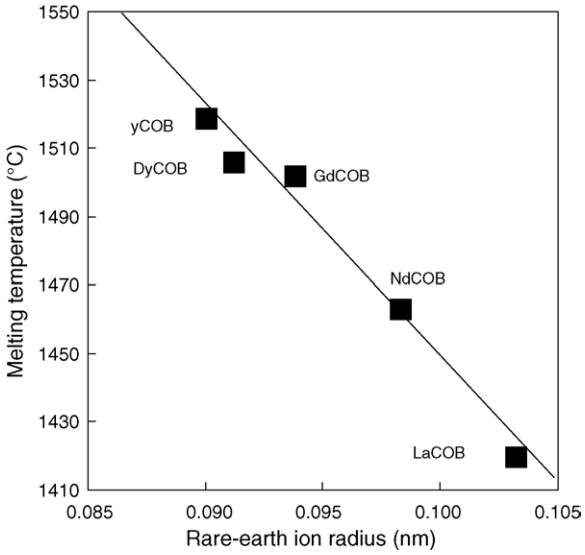

Fig. 2. The relationship between the melting temperature and a rare-earth ionic radius of RCOB.

3.2. Single crystal growth and optical characterization

Fig. 3 shows the as-grown NdCOB crystal with a 2.0 mm/h pulling rate at a seed rotation of 15 rpm. The pulling direction was along the *b*-axis, which is perpendicular to the mirror plane in the crystal. The crystal was 100 mm in length and 37 mm in diameter and without inclusions, cracks or bubbles. As can be seen the ingot diameter is of high constancy over the whole length. The $\{1\,0\,1\}$ and $\{2\,0\,\bar{1}\}$ facets always appear on the NdCOB crystal. Therefore, the cross-sectional crystal shape, which is normal to the pulling direction, is a parallelogram. Two growth ridges assigned as $\{1\,0\,0\}$ facets are observed on a major diagonal axis of the parallelogram. Furthermore, $\{0\,1\,0\}$ facets were observed on the solid–liquid interface at the bottom of the crystal. The facet on the solid–liquid interface led to a core structure during the previ-

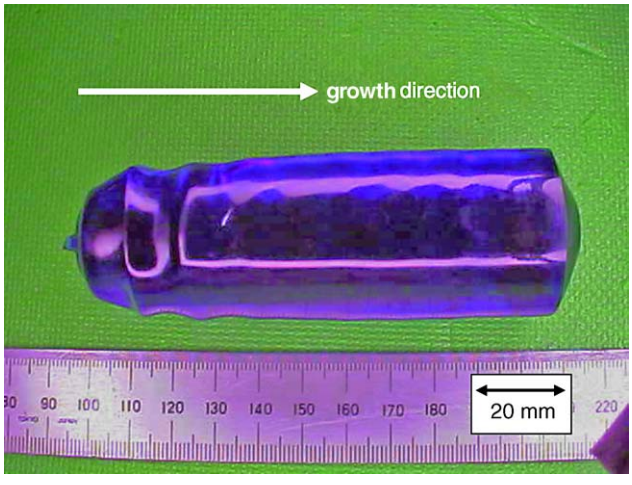

Fig. 3. As-grown $NdCa_4O(BO_3)_3$ crystal.

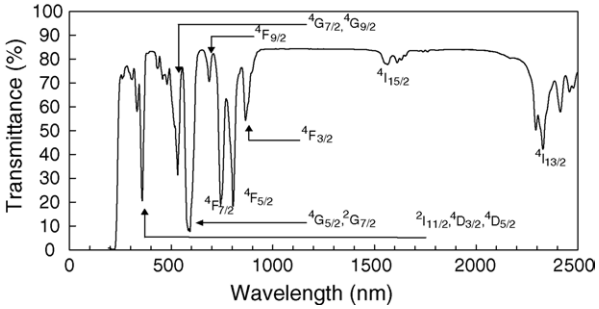

Fig. 4. Transmission spectrum of $NdCa_4O(BO_3)_3$ single crystal.

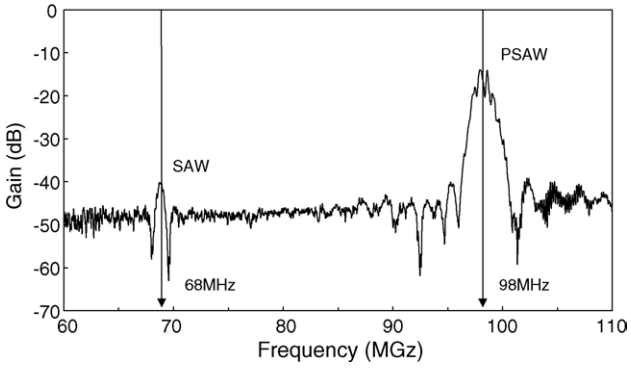

Fig. 5. Frequency response of a *Y*-axis propagation SAW filter fabricated on the *Z*-cut NdCOB substrate.

ous RCOB crystal growth [10]. In our study, the core was also observed in the center of crystal along the pulling direction. Though it is undesirable for the uniformity of the wafer, we could eliminate the core by the rotation rate control during the crystal growth.

The chemical composition of grown RCOB crystals was determined by ICP-ES. The composition was almost uniform from the top to the bottom of the crystal, and the same as that of the starting material. Therefore, we consider that RCOB crystals congruently melt.

We characterized the optical property of RCOB crystals. Fig. 4 shows the transmittance spectrum (0–2500 nm) of NdCOB crystal (0 1 0) plane as a typical example of RCOB crystals. The crystal is of good transparency and shows a violet color. The cutoff wavelength is approximately 220 nm and that there are some kinds of complicated absorptions, which are attributed to the neodymium ion. The corresponding transitions of the main peaks are denoted in Fig. 4. In other RCOB crystals, all absorption peaks are also assigned to transitions of the constituting rare-earth ion in the crystal.

3.3. Piezoelectric characterization

After crystal growth, we characterized the piezoelectric properties. The IDTs were fabricated with various propagation directions on the RCOB substrate. These were placed at 22.5° intervals of azimuthal angle on the substrate. Each of the input and output IDTs has 20 finger pairs with 9.4 μm line period (λ = 37.4 μm) and an aperture of 2.0 mm. The distance between a pair of IDTs was 0.5 mm.

Fig. 5 shows the frequency response of a *Y*-axis propagation SAW filter fabricated on the *Z*-cut NdCOB substrate. As can be seen, two frequency responses corresponding to SAW and pseudo-SAW (PSAW) exist at 68 and 98MHz, respectively. Then, we evaluated the v of the SAW was 2700 m/s and the k^2 was 0.04% and that the v of the PSAW was 3900 m/s and the k^2 was 1.90%. The angular dependence of k^2 of NdCOB demonstrated that the SAW at *X*-axis propagation on *Y*-cut shows the highest k^2 in SAW-mode waves. For PSAW-mode waves, the maximum k^2 was observed at *Y*-axis propagation on *Z*-cut substrate. In order to investigate the effect of the rare-earth atom, we examined k^2 of SAW-mode at *X*-axis propagation on *Y*-cut of RCOB (R = La, Pr, Nd, Sm, Eu, Dy, Ho, Er) crystals as shown in Fig. 6. As a result, the k^2 value (0.80%) of NdCOB is the highest in all RCOB crystals and its velocity is 3400 m/s. Moreover, we found that the thermal stability of the SAW of NdCOB (TCD = 3 ppm/°C) was equivalent to a quartz crystal (TCD = 0 ppm/°C) and the k^2 value is nearly seven times larger than that of a quartz one. For PSAW-mode, NdCOB also showed the highest k^2 of 1.95% and velocity of 3900 m/s at *Y*-axis propagation on the *Z*-cut substrate and its thermal stability (TCD = 31 ppm/°C) was comparable with $LiTaO_3$ (TCD = 18 ppm/°C). In addition, a computer simulation using the full set of the elastic, piezoelectric and dielectric constants and their temperature coefficients are indispensable for understanding the piezoelectric behavior. We have been measuring those of constants and simulate the piezoelectric behavior. The results can be reported in the near future.

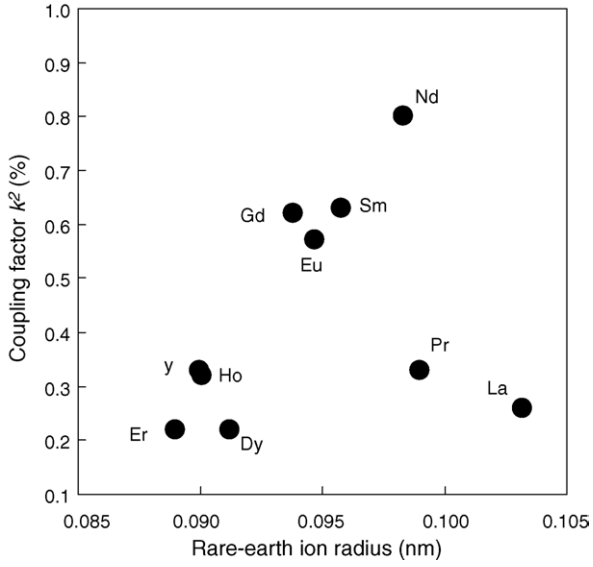

Fig. 6. The k^2 of SAW-mode at *X*-axis propagation on *Y*-cut of RCOB crystals vs. rare-earth ion radius.

4. Conclusions

We grew rare-earth calcium oxoborate bulk single crystals (RCOB: R = Pr, Nd, Sm, Eu, Dy, Ho, Er) by the Czochralski technique. The thermal analysis of these crystals revealed that the melting temperature increase with the decrement of a rare-earth ion radius of RCOB. We studied the piezoelectric properties such as the surface acoustic wave and pseudo-SAW parameters of the RCOB crystal. The k^2 values of NdCOB are the highest of all RCOB crystals. For SAW, k^2 of 0.80% and velocity of 3400 m/s at *X*-axis propagation were obtained on the *Y*-cut substrate. For PSAW, 1.95% and 3900 m/s at *Y*-axis propagation were obtained on the *Z*-cut substrate. Moreover, it turned out that the thermal stability of the SAW (TCD = 3 ppm/°C) is equivalent to a quartz crystal (TCD = 0 ppm/°C). We expect that the NdCOB crystal becomes application-competitive with the quartz, which is widely used in existing devices.

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