Crystal growth and piezoelectric properties of langasite \(\text{La}_3\text{Ga}_5\text{SiO}_{14}\) crystals

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Abstract

Langasite \(\text{La}_3\text{Ga}_5\text{SiO}_{14}\) is a new piezoelectric material which is similar to quartz, LN \((\text{LiNbO}_3)\) and LT \((\text{LiTaO}_3)\) in its acoustic behavior. In this study, langasite single crystals were grown by the self-designed Czochralski system. We also investigated optical transmittance and coloring of grown crystals in accordance with growth atmosphere and piezoelectric properties. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The rapid progress of electronic technologies requires a development of new piezoelectric materials with smaller size, lower impedance and wide passband. For designing filter devices, langasite has novel piezoelectric properties which show intermediate properties between those of quartz and lithium tantalate [1–3]. The phase transition of quartz at 573°C limits the processing temperatures one can use in the fabrication of quartz resonators. While langasite, on the other hand, has no phase transition up to its melting temperature 1470°C. This may allow higher temperature stability through high temperature processing [4,5].

Langasite is a crystal which has been grown and investigated for laser devices in Russia since the 1980s [6]. Its promise as a material for SAW, BAW and resonator devices was determined from its acoustic characteristics [7]. It is a single oxide compound of the ternary system, grown by the Czochralski method. Langasite has a trigonal structure which belongs to point group 32, space group P\(3\overline{2}1\), and is isostructural to \(\text{Ca}_3\text{Ga}_5\text{Ge}_2\text{O}_{14}\). There are four kinds of cation sites in this structure, which is represented by \(\text{A}_3\text{B}_1\text{C}_1\text{D}_2\text{O}_{14}\). As shown in Fig. 1, A and B are located on the decahedral site and octahedral site, respectively. While C and D, on the other hand, are located in tetrahedral site. In langasite, \(\text{La}^{3+}\) occupies the A sites, \(\text{Ga}^{3+}\) occupies the B, C and half of the D sites, and \(\text{Si}^{4+}\) half of the D sites [4,5].

In this present study, we will demonstrate the successful growth of langasite single crystals and characteristics of grown crystals according to growth...
conditions will be discussed. Then, piezoelectric properties will be analyzed.

2. Experimental

The starting materials were prepared from a mixture of $\text{La}_2\text{O}_3$, $\text{Ga}_2\text{O}_3$, $\text{SiO}_2$. These materials were heated at 1300$^\circ$C in Ar for 3 h. After that, charge was melted in a gas mixture of argon and over 30% oxygen, under 30% oxygen which is continually passed through the chamber at a flow rate of about 1 l/min. Then, langasite single crystals were grown in oxygen-less atmosphere in order to compare with coloring of grown crystals in oxygen-containing atmosphere. When a melt has developed, the $c$-axis seed crystal was dipped into the langasite melt. Then, crystal was pulled at a rate of 1.8–3.6 mm/h with a rotation speed of 5–12 rpm.

Grown langasite single crystal was cut and polished so that cross sections perpendicular to the growth direction could be observed by optical transmittance using a multichannel spectrophotometer. Also, the electromechanical coupling coefficient ($K\%$) of grown langasite single crystal ($z$-cut) in the transverse mode ($K_{31}$) was obtained by measurement of resonance–antiresonance frequencies in the admittance–frequency characteristics using the network analyzer (HP).

3. Results and discussion

XRD results are needed to investigate the secondary phases and homogeneous single phase for calcination. However, when $\text{La}_4\text{Ga}_5\text{SiO}_{14}$ was calcined at 1400$^\circ$C for 5 h to synthesize powders through the solid state reactions, it was found that the $\text{La}_4\text{Ga}_5\text{SiO}_{14}$ phase began forming at 1100$^\circ$C while a secondary phase and unreacted phases, $\text{La}_2\text{O}_3$, $\text{Ga}_2\text{O}_3$ and $\text{LaGaO}_3$ were mainly detected. These powders dissipated and then the quantity of the secondary phase, $\text{LaGaO}_3$ was found to decrease with time and temperature. But the main peak decreased with increasing temperature and time. It was considered that evaporation of gallium suboxide had an effect on synthesis of $\text{La}_4\text{Ga}_5\text{SiO}_{14}$ powders. In this experiment, we confirmed that the quantity of evaporation of gallium oxide was 13% at this temperature and time. However, calcination condition for synthesis of pure $\text{La}_4\text{Ga}_5\text{SiO}_{14}$ single phases with no other secondary phases was found to be at 1400$^\circ$C for 5 h.

From the above results, starting material for the crystal growth was prepared by a mixture of high purity oxides to prevent composition change of grown crystal due to the volatilization of $\text{Ga}_2\text{O}_3$. The pre-melting of crucible with starting materials was carried out in Ar atmosphere. When melting in Ar atmosphere, volatilization of $\text{Ga}_2\text{O}_3$ was observed.
The increased oxygen content was thus prevented. With the method we mentioned above, the compositional change of grown crystal could be removed. Fig. 2 shows the grown langasite single crystal with [001] direction. The grown crystal in oxygen-less atmosphere was colored light orange. In comparison with previous results, grown crystals in oxygen-containing were dark orange. It was considered that this phenomenon is related to cation and oxygen vacancy in order to maintain the electronic neutralization. Further study is necessary to understand this. For three kinds of growth atmosphere, langasite single crystals with 47, 40, 23 mm in diameter and 25, 35, 34 mm in length, were successfully grown by the Czochralski method. This crystal was pulled at a rate of 1.8–2.6 mm/h with a rotation speed of 10 rpm using a platinum crucible. No crack and inclusions were observed. Langasite single crystal would be stably grown even when the crystal diameter was rapidly extended by realizing a lower temperature gradient over the melt using the heat reservoir system. Grown crystal in oxygen-containing atmosphere was dark orange and transparent. Table 1 shows the stoichiometric composition of grown crystals. From the result of phase identification by the XRD patterns, grown crystals consisted of langasite single phase without other secondary phases.

Fig. 3 shows a optical transmittance of grown crystal according to different growth conditions. In both cases, samples have an absorption edge 242 nm and some absorption peaks below 590 nm. The transmittance of two samples was about a constant

<table>
<thead>
<tr>
<th>Table 1</th>
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<tbody>
<tr>
<td>Lattice constant was obtained using the least-square method. Sample a: grown crystal in oxygen-containing (under 30 vol.% oxygen); b: grown crystal in oxygen-containing (over 30 vol.% oxygen); c: grown crystal in oxygen-less atmosphere</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Position</th>
<th>Top sample</th>
<th>Body</th>
<th>Tail</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (a, Å)</td>
<td>a</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td>Lattice constant (c, Å)</td>
<td>5.088</td>
<td>5.088</td>
<td>5.088</td>
</tr>
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</table>
Fig. 3. Optical transmittance of grown langasite crystals were measured by the multichannel spectrophotometer in the ultraviolet to infrared range.

value in the wavelength region over 590 nm. But crystals grown in an atmosphere of over 30% oxygen and under 30% oxygen had a transmittance of 82% and 88%, respectively. These results indicate that the growth atmosphere with less than 30% oxygen is better for the growth of higher transmitting langasite crystal. For grown crystal in oxygen-less atmosphere, defect and transmittance studies are now in progress, which will be published elsewhere.

The electromechanical coupling factor $K$ is one of the fundamental characteristics that indicate the quality of piezoelectrics. The electromechanical coupling factor of grown langasite crystals was obtained by measurements of resonance and antiresonance frequencies in the admittance–frequency characteristics. In these transverse mode ($K_{31}$) calculations, the ratios of length to width and the width to thickness were changed. Table 2 shows the admittance–frequency characteristics of grown langasite crystal in $z$-cut plate. The electromechanical coupling coefficient of $z$-cut plate in the transverse mode ($K_{31}$) was obtained as follows:

$$
\frac{K_{31}^2}{1-K_{31}^2} = \frac{\pi f_p}{f_r} \tan \left( \frac{\pi f_p}{2f_r} \right)
$$

where $f_r$ = resonance frequency and $f_p$ = antiresonance frequency.

Figs. 4–6 show the admittance–frequency characteristics with changing the ratio of length to width and width to thickness.

In the former case, length was held constant and the width was changed since changes in the length in the direction of vibration have influence. With an

<table>
<thead>
<tr>
<th>Factor</th>
<th>Resonance frequency (Hz)</th>
<th>Antiresonance frequency (Hz)</th>
<th>Quality factor ($Q$)</th>
<th>Static capacitance ($C_s$, pF)</th>
<th>Electromechanical coupling coefficient ($K_{31}$%, $%$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>1667.613</td>
<td>1697.416</td>
<td>3.2 $\times 10^4$</td>
<td>6.45</td>
<td>21–25</td>
</tr>
</tbody>
</table>
increase in the ratio, the difference between the mountain and valley of the admittance–frequency curve increased, and the resonance and antiresonance frequencies moved to the higher frequency region. This means that the electromechanical coupling factor $K$ increases as the ratio increases. In the latter case, the peaks became sharper with increase in ratio and resonance, and the antiresonance frequency was constant regardless of the change in the ratio. From the above results, it is clear that a larger ratio of...
width to thickness is desirable for the application of piezoelectric devices.

Finally, the appropriate ratio of langasite crystal for obtaining large and accurate electromechanical coupling factor was more than 5 for length to width and large ratio of width to thickness. The value of electromechanical coupling coefficient ($K_{31}\%$) and quality factor ($Q$) at room temperature were measured to be 21–25 and 32 000, respectively.

4. Conclusions

(1) In the present research, langasite single crystals were successfully grown by the Czochralski method. Grown crystals with [001] direction were observed without crack and inclusions inside the crystal and the rotation speed was 10 rpm.

(2) Coloring and optical transmittance were changed with amount of oxygen-containing. In case of grown crystal in oxygen-less atmosphere, crystal was lighter orange than that of oxygen-containing crystal. These results indicated that the growth atmosphere with less than 30% oxygen is better for the growth of higher transmitting langasite crystals.

(3) The appropriate ratio of langasite crystal for obtaining large and accurate electromechanical coupling factor and piezoelectric applications was more than 5 for length to width and large ratio of width to thickness.

(4) The values of the electromechanical coupling coefficient ($K_{31}\%$) and the quality factor ($Q$) at room temperature were measured to be 21–25 and 32 000, respectively.

Acknowledgements

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References