Journal of Korean Association of Crystal Growth
Vol. 9, No. 6 (1999) 547-552

Growth of $La_3Ga_5SiO_{14}$ single crystals by the floating zone method

Won Ki Yoon*, Jong Cheol Kim** and Keun Ho Auh***

*Department of Inorganic Materials Engineering, Hanyang University, Seoul 133-791, Korea
**Ceramic Materials Research Institute, Hanyang University, Seoul 133-791, Korea
***Ceramic Processing Research Center, Hanyang University, Seoul 133-791, Korea

(Received June 9, 1999)

Abstract Langasite ($La_3Ga_5SiO_{14}$) single crystal was successfully grown by Floating Zone (FZ) method and characterized. The growth rate was 1.5 mm/h and the rotation speed was 15 rpm for an upper rotation and 13 rpm for a lower rotation. The grown crystal was 12 mm in length and 6 mm in diameter. The grown crystal was dark orange color and it was grown along [001] direction. The composition of grown crystal and the structure were analyzed using XRD and WDS. The electrical properties of grown crystal at various frequencies and temperatures were discussed.

1. Introduction

The development of new digital telecommunication systems require piezoelectric materials which can satisfy such requirements as high electromechanical coupling constant over 30 %, small frequency drift near ambient temperature, low acoustic loss (high Q value), and slow acoustic velocity (which can make device small). For designing devices such as filters with wide pass band, high stability and small insertion attenuation, it is necessary to discover new piezoelectric crystals having intermediate properties between those of quartz and $LiNbO_3$ [1-3]. Quartz and $LiNbO_3$ crystals are current commercially available piezoelectric crystals. Quartz is stable at temperature change and has low acoustic loss. Low piezoelectric coupling constant makes it difficult to build compact broad band pass filters. $LiNbO_3$, on the contrary, has high piezoelectric coupling constant but the temperature drift is very large which is undesirable for band pass filters for mobile communication systems. Among all the desired properties, temperature compensation is the most difficult one to find, since it requires special crystal structure which has either negative thermal expansion or increasing elastic stiffness to compensate the slow down of the elastic wave propagation with increasing temperature [1-3].

Langasite ($La_3Ga_5SiO_{14}$) is a promising piezoelectric material that satisfies such properties as mentioned above. Langasite crystal has temperature compensation at near room temperature and also adequate electromechanical coupling constant. Moreover, it has very low acoustic friction, which is an indication of high Q factors.[6] Combination of all these properties makes langasite crystal very useful for a number of applications especially in the mobile communication systems such as SAW filter, BAW filter, and resonator devices.

Langasite has the $Ca_3Ga_2Ge_4O_{14}$ type structure with the space group P321. There are four kinds of cation sites in this structure and this structure can be represented by the chemical formula, $A_3BC_3D_2O_{14}$. In this chemical formula, and represent a decahedral (twisted Thomson cube) site coordinated by 8 oxygen anions, and an octahedral site coordinated by 6 oxygen anions, respectively. While both and represent tetrahedral sites coordinated by 4 oxygen anions, the size of site is slightly smaller than that of site. In the case of langasite single crystal, La^{3+} occupies the sites, Ga^{3+} occupies , and half of sites, and Si^{4+} occupies half of sites, respectively (Fig. 1) [6, 7].

The growth of langasite single crystal has been mainly carried out by the Czochralski Method but the

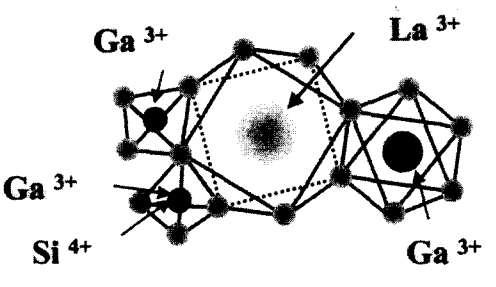

Fig. 1. Schematic diagram of langasite structure.

crystal growth of this crystal by the floating zone method was not reported [1, 5]. In general the floating zone method was used to grow high quality crystal because of the zone refining effect in the absence of the crucible. The crystal growth without crucible can reduce the contamination from the crucible material in the grown crystal. Langasite ($La_3Ga_5SiO_{14}$) single crystal was grown by floating zone (FZ) method and characteri- zed, in order to grow single crystal of good quality.

2. Experamental procedure

2.1. Synthesis of powder and preparation of feed rods

Langasite powders were synthesized by solid state reaction. Stoichiometric amounts of high purity La_2O_3 (99.99 %, Aldridch Chemical Co., Milwaukee, WI, USA), Ga_2O_3 (99.99 %, Aldridch Chemical Co., Milwaukee, WI, USA), and SiO_2 (99.995 %, Junsei Chemical Co., Tokyo, Japan) powders were batched, and then ball-milled in alcohol for 6 hours. After mixing, alcohol was evaporated by heating, while stirring to prevent any preferential settling. With the resulting powder mixture, the langasite powders were synthesized in a resistance furnace. The temperature used for the synthesis ranged from 1200 to 1400°C, and the retention time for solid state reaction was kept for 5 hours to find the optimum conditions for the synthesis of homogeneous langasite powder. After the reaction, the synthesized powder was pulverized, sealed in a rubber tube and pressed isostatically at 30,000 psi for 1 minute by Cold Isostatic Press. The feed rods were sintered at the temperature of 1300°C, 1350°C, 1400°C, for 5 hours to find the optimum conditions for feed rods. The dimensions of the sintered feed rods were designed to be 6~7 mm in diameter and 60~70 mm in length.

2.2. Growth of single crystal

The growth apparatus used in this study was a self-made single ellipsoid image furnace. The infrared radiation source used for crystal growth was a 5.4 kW Xe-arc lamp. The sintered feed rod was suspended from the upper shaft and the seed crystal was fixed to the lower shaft. <111> oriented YAG ($Y_3Ga_5O_{12}$) single crystal and langasite single crystal were used as seed. The orientation of the langasite seed crystal was parallel to the c-axis. In order to prevent the sublimation of gallium oxide, Ar and O_2 gas were used as atmosphere gas. The flow rates of the gases were 0.8 *l*/min. for Ar gas and 0.4 *l*/min. for O_2 gas, respectively. The growth rate was changed in the range of 1.5~3.6 mm/h, and the rotation rate was changed in the range of 5~20 rpm for upper shaft and 5~15 rpm for lower shaft to find the optimum conditions for the growth of single crystal.

2.3. Characterization of crystals

In order to find the grown direction, XRD(XRD, D/Max-IIC, 40 kV, 30 mA, Rikagu Corporation, Tokyo, Japan) and Laue back-scattered analysis was performed. The phase identification of the grown crystals was performed by X-ray diffractometer. The chemical compositions of the grown langasite crystal were determined by the WDS analysis. The lattice parameters were determined by the X-ray power diffraction technique with silicon as internal standard. The grown crystals were cut parallel to the (001) plane and both sides of the specimen were then polished to be a mirror surface. The transmittance of the as-grown crystal was measured in the wavelength region of 200~800 nm with a multichannel spectrophotometer. The relative dielectric constant of the as-cut crystals was measured at various temperatures with the frequency change, and the A.C. conductivity of the grown crystal was measured.

3. Results and discussion

3.1. Synthesis of powder and preparation of feed rods

The XRD results (Fig. 2) showed that langasite phases were successfully synthesized over 1350°C for 5 hours by solid state reaction. Langasite phase was found over the temperature of 1100°C, but the strong peaks of the secondary phases and unreacted phases, such as La_2O_3, Ga_2O_3 and $LaGaO_3$ peaks remained. As the temperature increased the secondary phases decreased, and over the temperature of 1350°C pure langasite single phase detected without any other secondary or unreacted phases. In the floating zone system, it is necessary to use homogeneously synthesized powder for the feed rod to grow. When there remains any secondary powder or unreacted powder, they would affect stability of the melt between feed rod and

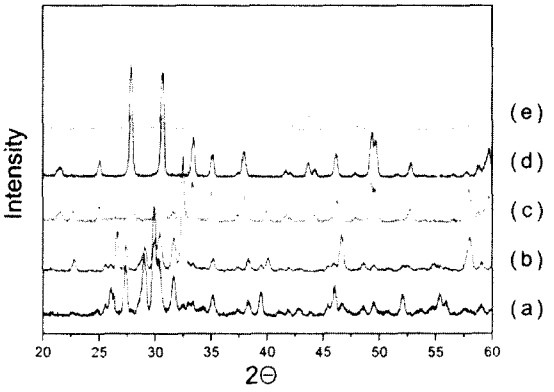

Fig. 2. XRD result of langasite powder synthesized at (a) 1200°C, (b) 1250°C, (c) 1300°C, (d) 1350°C, and (e)1400°C.

seed crystal. There was some ignition loss, which was considered due to the evaporation of the gallium suboxide. By comparing the XRD result of 1350°C and 1400°C, the main peak intensity decreased a little with the temperature increase, which means that evaporation of gallium suboxide had an effect on synthesis of langasite powders. So, in this experiment, Ar and O_2 gas were flowed to prevent the evaporation during the growing. In floating zone system, it is necessary to use fine particles for making the feed rod. By analysis of the SEM, it was shown that the particle size increased with the increase of the reaction temperature and time. So the langasite powder for the feed rods was synthesized at 1350°C for 5 h.

The feed rods for the floating zone system were made with the powder synthesized at 1350°C for 5 hours. In order to find the optimum conditions for feed rod, feed rods were pressed at various pressures with the change of time. Over the pressure of 30,000 psi, the feed rod was severely deformed. So the feed rods were pressed at 30,000 psi for 1 minute because the feed rod must be straight in order to get stable melt. After that the pressed feed rods were sintered at 1300°C, 1350°C, and 1400°C for 5 hours, respectively. By measuring the density of the feed rods and comparing the SEM micrographs (Fig. 3), the grain growth occurred over the temperature of 1350°C. There were dramatic density changes between 1300°C and 1350°C, and over 1350°C the density showed almost constant value. So the feed rods were sintered at 1350°C for 5 hours to prevent the abnormal grain growth in the feed rod so as to it to be melted regularly. The dimensions of the feed rod were 6~7 mm in diameter and 60~70 mm in length.

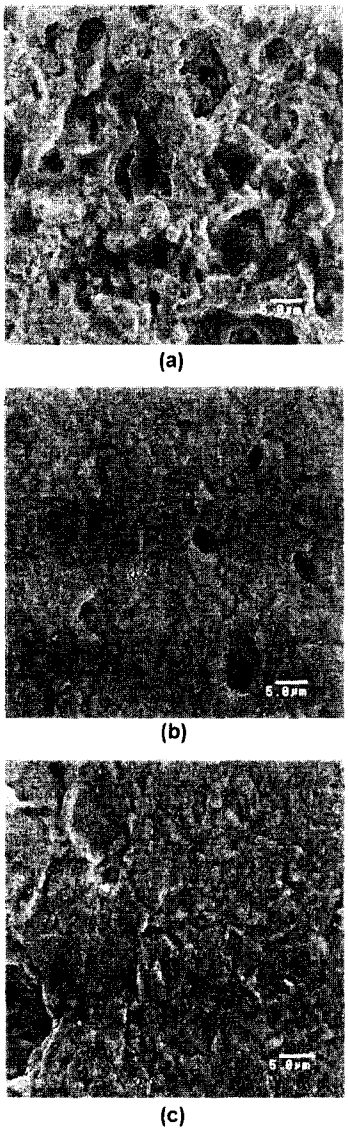

Fig. 3. SEM micrograph of the feed rod sintered at (a) 1300°C, (b) 1350°C, and (c) 1400°C.

3.2. *Growth of single crystal*

With the sintered feed rod, langasite single crystals were successfully grown along <001> direction by the floating zone method above. In order to prevent the evaporation in growing, Ar and O_2 gas mixture was flowed as mentioned. When the feed rod was melted in Ar atmosphere, some volatilization was observed, but the increase in oxygen content prevented the evaporation of gallium suboxide. The sintered feed rod was melted over the power of 30 %. In

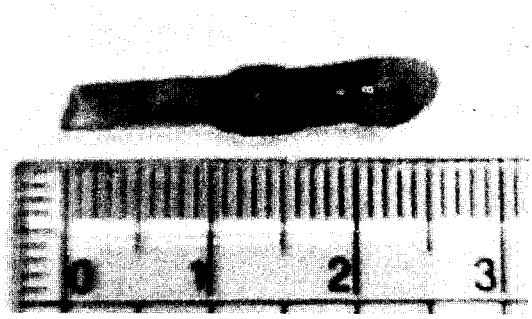

Fig. 4. Photograph of the grown langasite crystal.

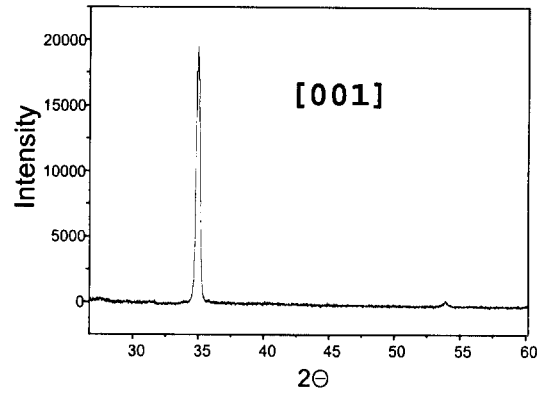

Fig. 5. XRD relust of the grown langasite crystal.

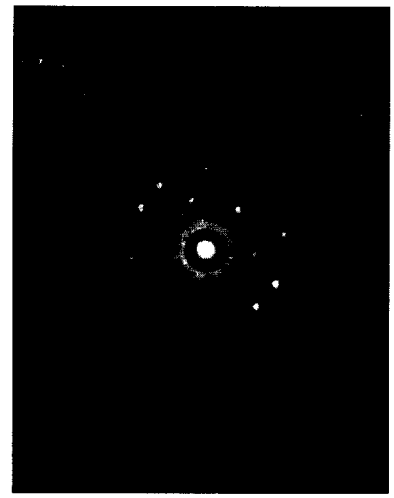

Fig. 6. Laue back scattered image of the grown langasite crystal.

order to find out the optimum conditions for growing, various kinds of conditions such as power, seed crystal, pulling rate, and rotation rates were changed. At first the <111>YAG crystal was used as a seed crystal as it was done in Russia for the first growth of langasite. The melt of the feed rod overflowed because of the bad contact between melt and seed crystal. This is thought to be the difference in the lattice parameters of two crystals. By changing the seed crystal with [001] langasite single crystal the stable melt on the seed crystal was achieved. In order to reduce the influence of the defect in the seed crystal, it was polished and etched with hydrogen fluoride solution. In order to maintain the stable melt between feed rod and seed crystal, the power, the rotating rate, and the pulling speed were adjusted slightly. In order to reduce the influence of the defect in the seed crystal, it was polished and etched with hydrogen fluoride solution.

Langasite single crystal was grown at the pulling rate of 1.5 mm/h and the rotation rate was 15 rpm for feed rod and 13 rpm for seed crystal. The grown crystal was dark orange color and 16 mm in length and 6 mm in diameter (Fig. 4). There were some melt overflowed at the end of grown the crystal, so the single crystal region is 12 mm in length.

3.3. Characterization of crystals

The grown crystals were cut parallel to the (001) plane and then both sides of the specimen were polished to be a mirror surface. From the result of phase identification by the X-ray powder diffraction patterns of the grown crystal, the grown crystals were consisted of langasite single phase without other secondary phases. The grown direction of langasite crystal was [001] direction. The XRD result (Fig. 5) and Laue back-scattered image (Fig. 6) shows that the crystal was grown along the [001] direction and the grown crystal belongs to the point group 32. The chemical compositions of the grown crystal along the growth direction were analyzed by WDS analysis (Fig. 7). The result shows that the grown crystal is made up of langasite phase and the composition is same along to the growth direction. There were no composition changes in single crystal region of the grown crystal, and this is related to the congruent melting of the langasite. The lattice parameters were determined by the X-ray power diffraction technique with silicon as an internal standard (Fig. 8). The measured lattice parameters were almost same along the growth direction. The lattice parameters of a-axis and c-axis were 8.1993 Å and 5.0926 Å respectively. These values are almost same as those reported earlier.

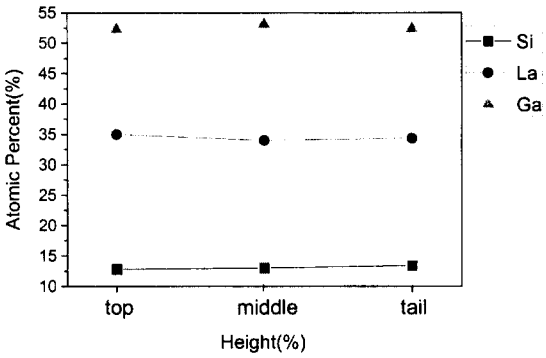

Fig. 7. WDS analysis result of the grown langasite crystal along the grown direction.

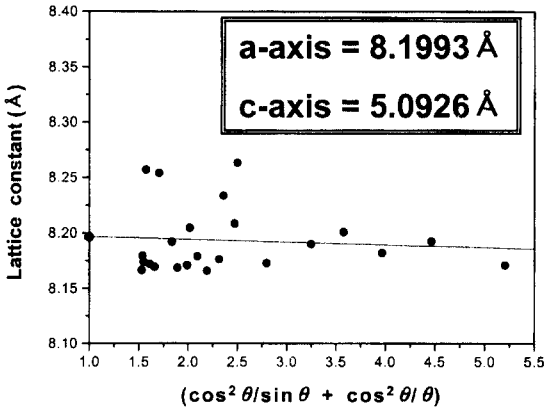

Fig. 8. Lattice parameters of the grown langasite crystal.

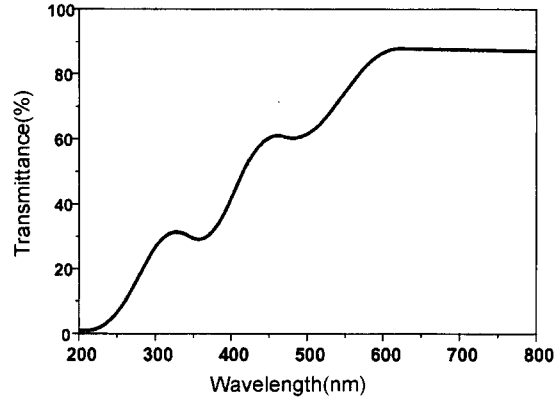

Fig. 9. Transmittance of the grown langasite crystal.

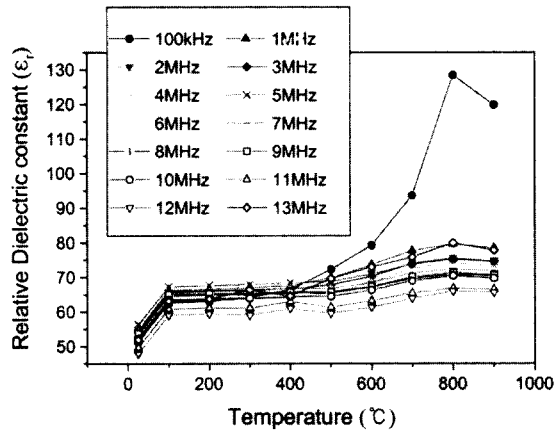

Fig. 10. Relative dielectric constants of the grown langasite crystal with the change of the temperature at various frequencies.

The grown crystal was dark orange, and this darkness is related to the growing atmosphere. It is reported that the oxygen content of the atmosphere is related to the color of the grown langaiste crystal. As the oxygen content increases, the color of the grown crystal gets darker. The transmittance of the as-grown crystal was measured in the wavelength region of 200~800 nm with a multichannel spectrophotometer. Figure 9 is the figure of the transmittance versus frequency. The absorption peaks at about 360 nm and 500 nm are related to be connected to the orange color of the grown crystal, where the absorption edge is at 242 nm. The dielectric properties of the as-cut crystals were measured at various temperatures with frequency change. Figure 10 is the figure of the dielectric constant of the grown crystal. As the measuring temperature increases, the dielectric constants increase slightly. At low frequency, there is sharp rise in the apparent dielectric constant with increasing temperature, corresponding to both ion jump orientation effects and space charge effects resulting from the increased concentration of charge carriers. The conductivity was measured with the increase of frequency at various temperatures. Figure 11(a) shows the measured conductivity of grown crystal frequency increase. In the range of 600°C~900°C, there was sudden increase in conductivity at about 2 MHz and 4 Mhz, and it seems to be related to the resonance property of the grown crystal. The conductivity decreased with the measuring temperature increase (Fig. 11(b)), which means the resistivity increased with temperature increase like PTC resistor.

4. Conclusions

The starting material was synthesized from the

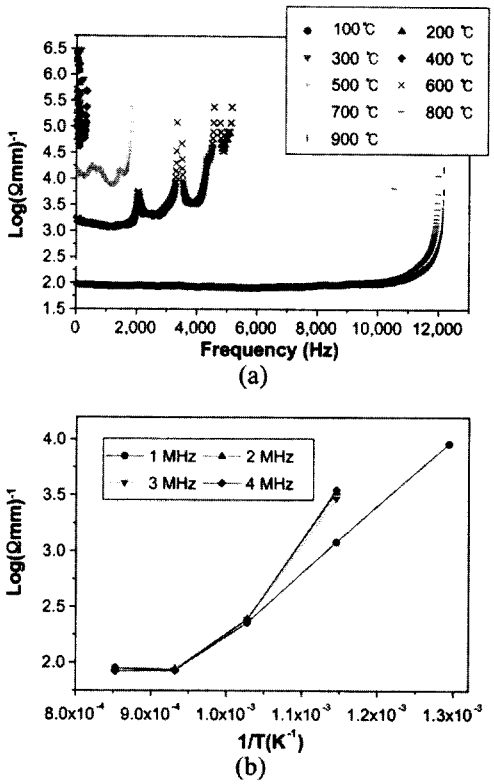

Fig. 11. Conductivity of the grown langasite crystal with the change of (a) frequency and (b) temperature.

binary compounds at 1350°C for 5 hours by solid state reaction, and sintered at 1350°C for 5 hours. Langasite single crystals were successfully grown by the floating zone method. It was grown along the [001] direction with dark orange color. The chemical composition, optical, and electrical properties of the grown crystal were analyzed. The composition and lattice parameter show almost same value along the growth direction, and the grown crystal was confirmed to be langasite single phase.

Acknowledgements

This study was financially supported by the Korean Science and Engineering Foundation (KOSEF) Research Funds.

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