GROWTH AND CHARACTERIZATION OF $La_3Ga_5SiO_{14}$ SINGLE CRYSTALS BY THE FLOATING ZONE METHOD

Won Ki Yoon[a], Keun Ho Auh[b]
[a] Department of Inorganic Materials Engineering
[a, b] Ceramic Processing Research Center, Hanyang University, Seoul 133-791, Korea

ABSTRACT

The development of telecommunication and information technology requires to develop new piezoelectric materials with small size, low impedance, wide pass band width and high thermal stability of frequency. Langasite ($La_3Ga_5SiO_{14}$) single crystal has been researched substitute of quartz and $LiNbO_3$ for the applications of SAW filter, BAW filter and resonator. Its single crystal growth has been carried out by Czochralski Method. So, in order to get single crystal with higher quality, in this study, langasite ($La_3Ga_5SiO_{14}$) single crystal was grown by using Floating Zone (FZ) method and characterized. For the growth of langasite single crystals, the langasite powder was synthesized at 1350℃ for 5hrs and the feed rod was sintered at 1350℃ for 5hrs. The growing rate was 1.5mm/h and the rotation speed was 15 rpm for an upper rotation and 13 rpm for a lower rotation. In order to prevent the evaporation of gallium oxide, Ar and O_2 gas mixture was flowed. The growth direction was analyzed by Laue back-scattered analysis. The composition of grown crystal was analyzed using XRD and WDS. The electrical properties of grown crystal at various frequencies and temperature were discussed.

KEY WORDS

Langasite, $La_3Ga_5SiO_{14}$, Floating Zone, Piezoelectric

1. INTRODUCTION

The development of new digital telecommunication systems would require piezoelectric materials which can satisfy such requirements simultaneously as high electromechanical coupling constant over 30%, small frequency drift near ambient temperature, low acoustic loss (which means 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, the necessity has arisen to discover new piezoelectric crystals having intermediate properties between those of quartz and $LiNbO_3$[1-3]. Quartz and $LiNbO_3$ crystal are the current commercially available piezoelectric crystals. Quartz is stable at temperature change and has low acoustic cost. Low piezoelectric coupling constant makes it difficult to build compact broad band pass filters. $LiNbO_3$, on the contrary, has high piezoelectric coupling 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 number of applications especially in the mobile communication systems 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, A and B represent a decahedral (twisted Thomson cube) site coordinated by 8 oxygen anions, and an octahedral site coordinated by 6 oxygen anions, respectively. While both C and D represent tetrahedral sites coordinated by 4 oxygen anions, the size of the D site is slightly smaller than that of the C site. In the case of langasite single crystal, La^{3+} occupies the A sites, Ga^{3+} occupies the B, C and half of the D sites, and Si^{4+} occupies half of the D sites, respectively. (Fig. 1)[6,7]

The growth of langasite single crystal has been mainly carried out by Czochralski Method. In order to grow single crystal of higher quality, in this study, langasite ($La_3Ga_5SiO_{14}$) single crystal was grown by using Floating Zone (FZ) method and characterized.

2. EXPERAMENTAL PROCEDURE

2.1 Synthesis of powder and preparation of feed rods

Langasite powders were synthesized by using conventional solid state reaction. Stoichiometric amounts of high purity La_2O_3 (99.99%, Aldridch Chemical Co., Milwaukee, WI), Ga_2O_3 (99.99%, Aldridch Chemical Co., Milwaukee, WI), and SiO_2 (99.995%, Junsei Chemical Co., Tokyo, Japan) powders were weighted, 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 using a resistance furnace. The temperature used for the synthesis ranged from 1200 to 1400℃, and the holding time for solid state reaction was kept at 5 hours. After reaction, the reacted powder was pulverized. The pulverized powder was sealed in a rubber tube and pressed isostatically at 30,000psi for 1 minute by CIP (Cold Isostatic Press). The pressed rods were sintered at the temperature of 1300℃, 1350℃, 1400℃, for 5 hours. The dimensions of the sintered feed rods were 6-7mm in diameter and 60-70mm 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 5.4kW Xe-arc lamp. The sintered feed rod was suspended from the upper shaft and the seed crystal was fixed to the lower shaft. YAG ($Y_3Ga_5O_{12}$) single crystal and langasite single crystal were used as seed. The orientation of the seed crystal was parallel to the c-axis. In order to prevent the sublimation of the gallium oxide, Ar and O_2 gas mixture were used as atmosphere gas. The flow rates of the gases were 0.8L/min. for Ar gas and 0.4L/min. for O_2 gas. 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 5-20rpm for upper shaft and 5-15rpm for lower shaft.

2.3 Characterization of crystals

In order to find the grown direction, Laue back-scattered analysis was performed. The composition of the grown langasite crystal was determined by the WDS analysis. The lattice parameters were determined by the X-ray power diffraction technique (XRD, D/Max-IIC, 40kV, 30mA, Rikagu Corporation, Tokyo, Japan) 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 200-800nm with a multichannel spectrophotometer. The relative dielectric constant of the as-cut crystals was measured at various temperatures with the change of the frequency. And the D.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($La_3Ga_5SiO_{14}$) phases were successfully synthesized over 1350℃ for 5 hours by solid state reaction. Langasite phase can be found over the temperature of 1100℃, but the secondary phases and unreacted phases, such as La_2O_3,

Ga_2O_3 and $LaGaO_3$ were main peaks. As the temperature went, higher the secondary phases decreased, and over the temperature of 1350℃ pure langasite single phase detected without other secondary or unreacted phases. There was some ignition loss, which was considered due to the evaporation of the gallium suboxide. By comparing the XRD result of 1350℃ and 1400℃, 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. However, calcination condition for synthesis of pure langasite single phases with no other secondary phases was found at 1350℃ for 5h for the preparation of feed rod.

With the powder synthesized at 1350℃ for 5 hours, langasite feed rods for the floating zone system were made. 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 30,000psi, the feed rod was severely crooked and it was too hard to drill the hole for Pt wire. So the feed rods were pressed at 30,000psi for 1 minute. After then, the pressed feed rods were sintered at 1300℃, 1350℃, and 1400℃ for 5 hours. By measuring the density of the feed rods and comparing the SEM micrographs(Fig. 3), the grain growth occurred over the temperature of 1350℃. There were dramatic density changes between 1300℃ and 1350℃, and over 1350℃ the density showed a little change. So the feed rods were sintered at 1350℃ for 5 hours, and the dimensions of the feed rod was 6-7mm in diameter and 60-70mm in length.

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. As there was some evaporation of gallium suboxide, in order to prevent the evaporation, Ar and O_2 gas mixture was flowed as mentioned. When the feed rod was melted in Ar atmosphere, some volatilization of Ga_2O was observed, but the increased oxygen content prevented the evaporation of gallium suboxide. The sintered feed rod was melted over the power of 30%. In 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. When the YAG crystal was used as a seed crystal, the melt of the feed rod flowed because of the bad contact between melt and seed crystal. By changing the seed crystal as langasite single crystal the stable melt on the seed crystal could be achieved.

Langasite single crystal could be grown with these conditions: the pulling rate was 1.5mm/h and the rotation rate was 15rpm for feed rod and 13rpm for seed crystal. The grown crystal was dark orange color and 12mm in length and 6mm in diameter (Fig. 4).

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. The grown direction of langasite crystal was [001] direction. The Laue back-scattered image (Fig. 5) shows that the crystal was grown along the [001] direction and the grown crystal belongs to the point group 32. The compositions of the grown crystal along the grown direction were analyzed by WDS analysis (Fig. 6). The result shows that the grown crystal is made up of langasite phase and the composition is same along the grown direction. There were no composition changes in grown crystal, which is connected to the congruent melting of the langasite. From the result of phase identification by the XRD patterns, grown crystals were consisted of langasite single phase without other secondary phases. The lattice parameters were determined by the X-ray power diffraction technique with silicon as internal standard (Fig. 7). The measured lattice parameters were almost same along the grown direction. The average of the lattice parameter of a-axis and c-axis ware 8.1993 Å and 5.0926 Å respectively.

The transmittance of the as-grown crystal was measured in the wavelength region of 200-800nm with a multichannel spectrophotometer. Fig. 8 is the figure of the transmittance versus frequency. The absorption peaks at about 360nm and 500 nm are considered to be connected to the orange color of the grown crystal, where the absorption edge is at 242nm. The dielectric properties of the as-cut crystals were measured at various temperatures with the change of the frequency. Fig. 9 is the figure of the dielectric constant of the grown crystal. As the temperature goes higher the dielectric constants increase a little. At low frequency, there is sharp rise in the apparent dielectric constant with the 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. Fig. 10 (a) shows the measured conductivity of grown crystal with the increase of frequency. In the range of 600℃-900℃, there was sudden increase of conductivity at about 2MHz and 4Mhz, and it seems to be connected with the resonant property of the grown crystal. The conductivity decreased with the temperature increase (Fig. 10(b)), which means the resistivity increased with the temperature like PTC resistor.

4. CONCLUSIONS

In present research, langasite powder was synthesized at 1350℃ for 5 hours by solid state reaction, and the feed rod was sintered at 1350℃ 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 growth rate was 1.5 mm/h and rotation speed was 15 rpm for feed rod and 13rpm for seed crystal.

The grown direction was [001] direction and the composition was analyzed. Also the optical and electrical properties were analyzed. The composition and lattice parameter showed almost same value along the grown direction, and the grown crystal to be langasite ($La_3Ga_5SiO_{14}$) single phase.

ACKNOWLEDGEMENTS

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

REFERENCES

[1] B.Chai, J.L.Lefaucheur, Y.Y. Ji and H.Qui, IEEE International Frequency Control Symposium, (1998) 748-752

[2] M.F.Dubovic, I.A.Andreyev, and Yu.S.Shmaly, IEEE International Frequency Control Symposium, (1994) 43-47.

[3] M.Sato, K. Moroishi and S.Ishigami, IEEE International Frequency Control Symposium, (1996) 379-383.

[4] S.Laffey, M.Hendrickson and John R.Vig, IEEE International Frequency Control Symposium, (1994) 245-250.

[5] H.Takeda, K. Shimamura, T.Kohno, and T.Fukuda, Journal of the Crystal Growth, (1996) 5284.

[6] H.J.Eichler, D.Ashkenasi, H.Jian and A.A.Kaminski, Physics State Solid, 146, (1994) 833-841.

[7] K.Shimamura, H.Takeda, and T.Fukuda, Journal of the Crystal Growth, 163 (1996) 388-92.

[8] I.M.Silvestrova, V.V.Bezdelkin, P.A.Senyusenkov and Yu.V.Pisarevski, IEEE International Frequency Control Symposium, (1993) 348-50.

FIGURE CAPTIONS

Fig. 1. Schematic diagram of langasite structure.

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

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

Fig. 4. Photograph of the grown langasite crystal

Fig. 5. Laue back scattered image of the grown langasite crystal

Fig. 6. WDS analysis result of the grown langasite crystal along the grown direction

Fig. 7 Lattice parameters of the grown langasite crystal

Fig. 8 Transmittance of the grown langasite crystal

Fig. 9 Relative dielectric constants of the grown langasite crystal with the change of the temperature at various frequencies

Fig. 10 Conductivity of the grown langasite crystal with the change of (a) frequency and (b) temperature

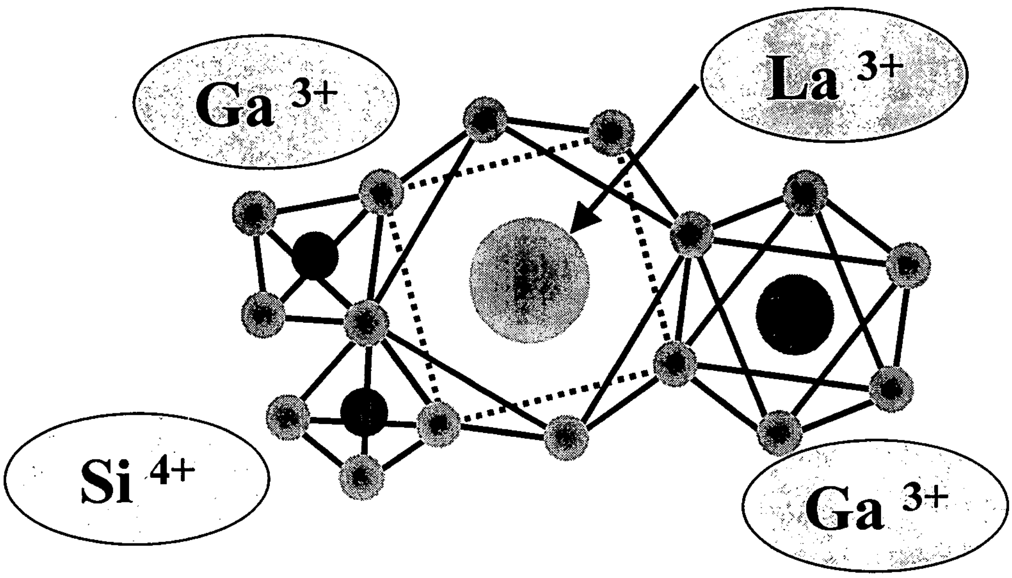


Fig. 1 Schematic diagram of the structure of langasite[6,7]

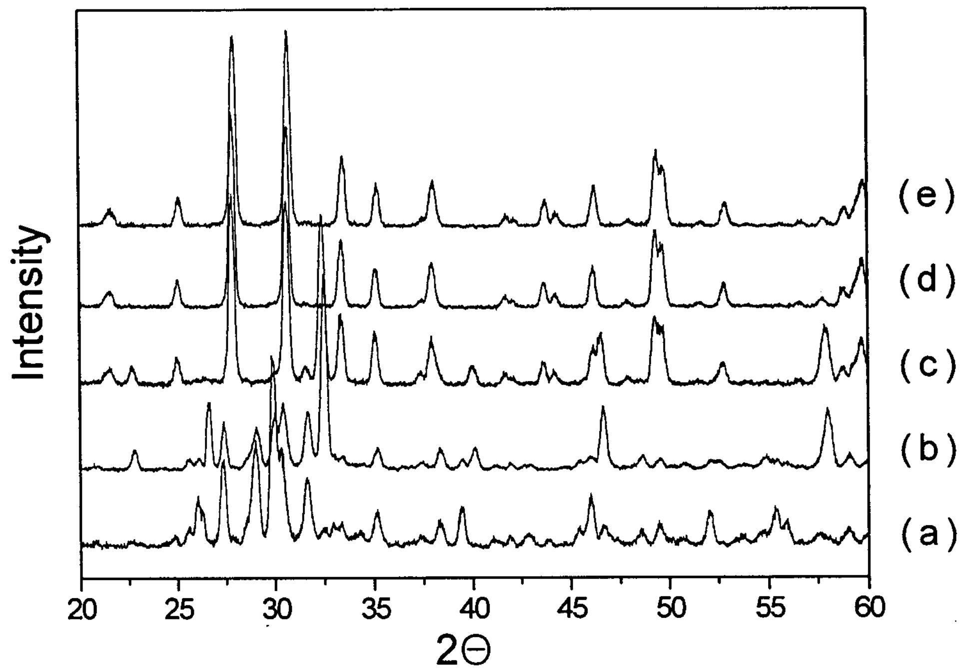
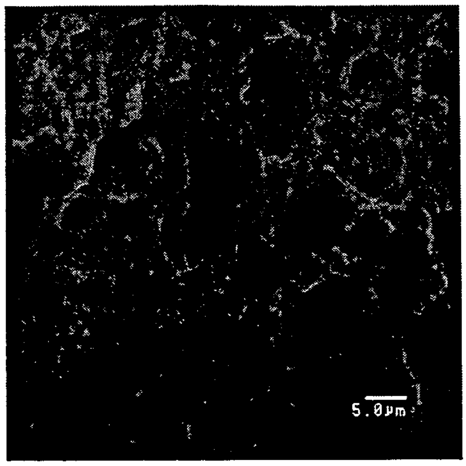
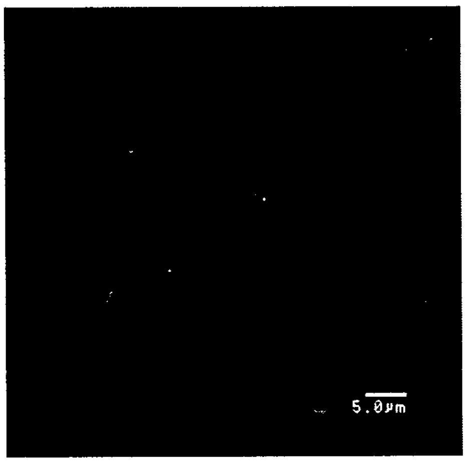


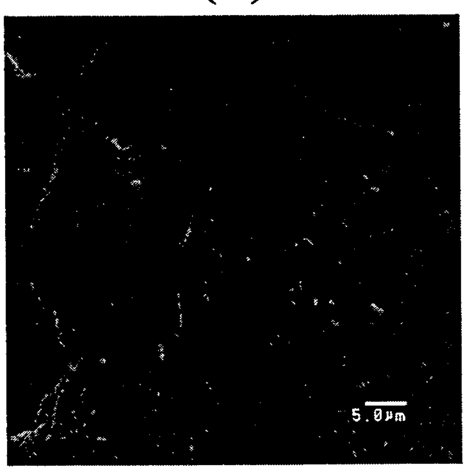
Fig. 2 XRD result of langasite powder synthesized at (a) 1200℃, (b) 1250 ℃, (c) 1300 ℃, (d) 1350 ℃, and (e)1400 ℃



(a)



(b)



(c)

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

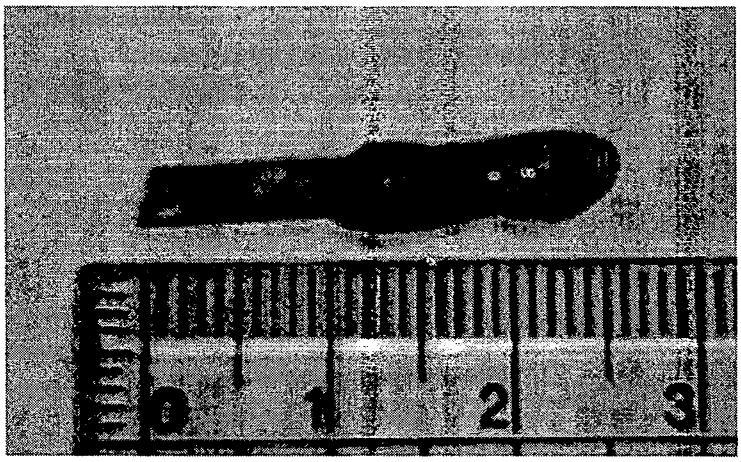


Fig. 4 Photograph of the grown langasite crystal

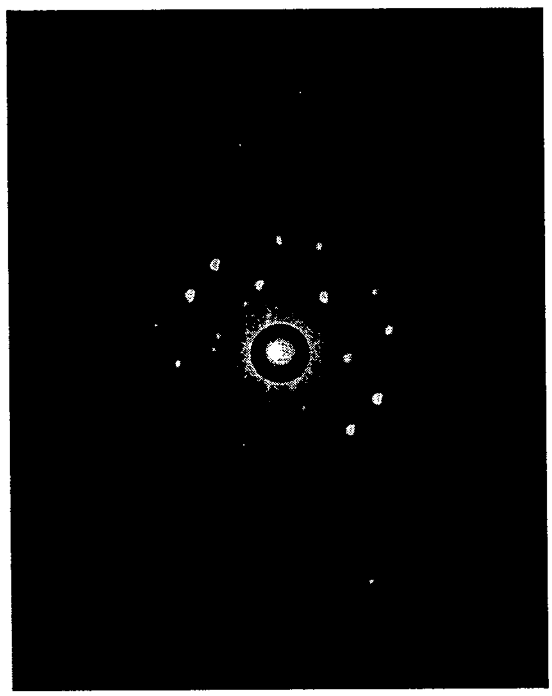


Fig. 5 Laue back scattered image of the grown langasite crystal

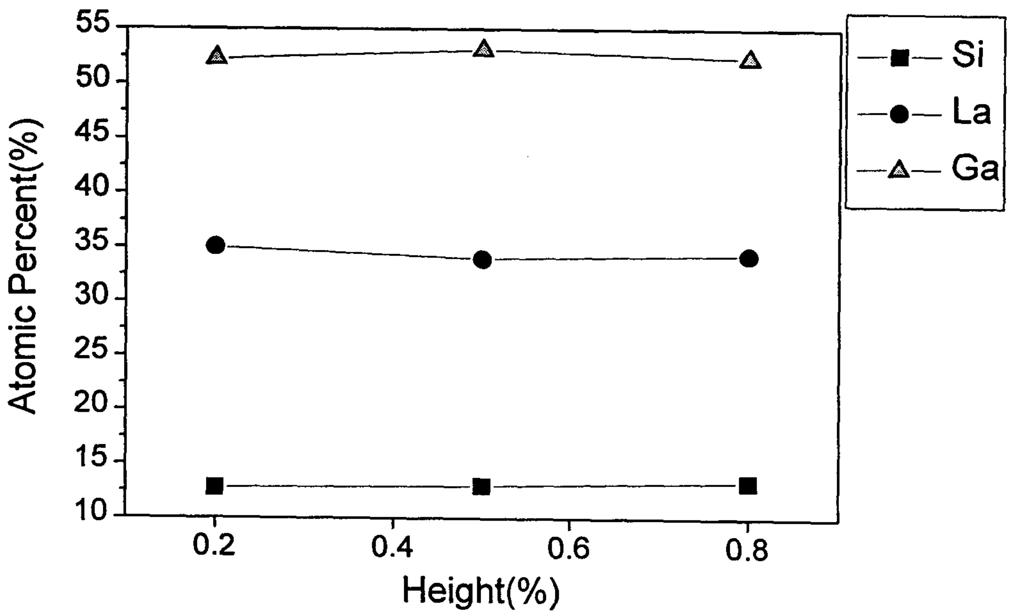


Fig. 6 WDS analysis result of the grown langasite crystal along the grown direction

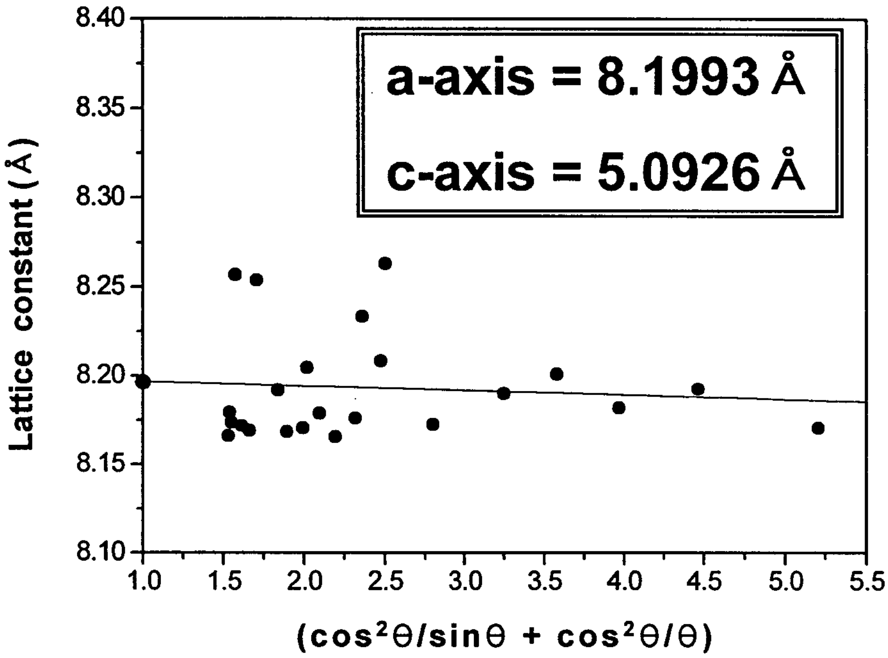


Fig. 7 Lattice parameters of the grown langasite crystal

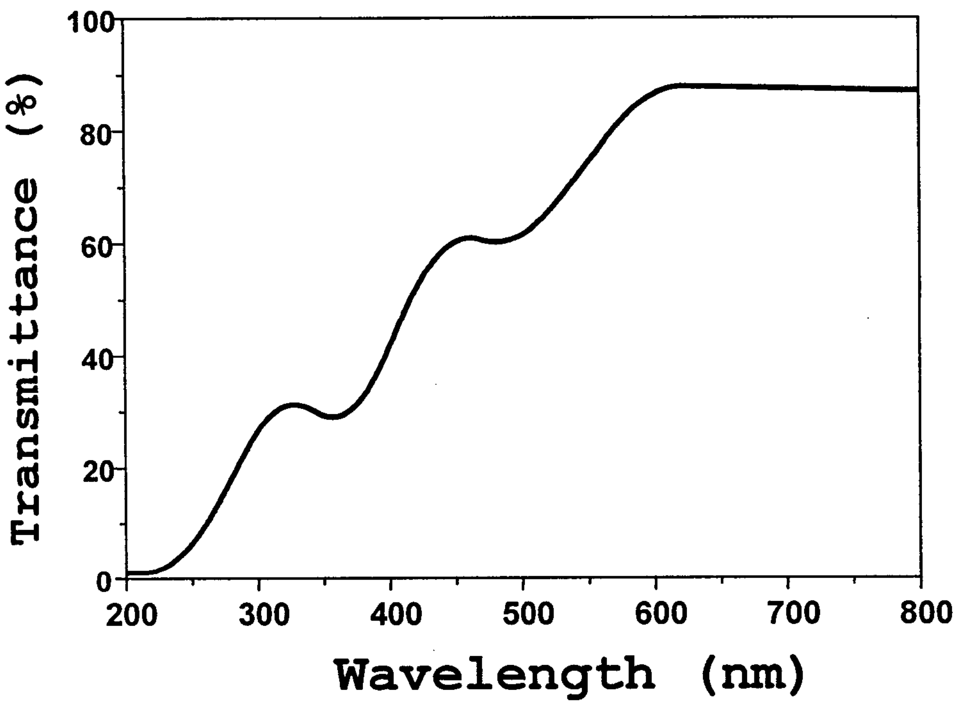


Fig. 8 transmittance of the grown langasite crystal

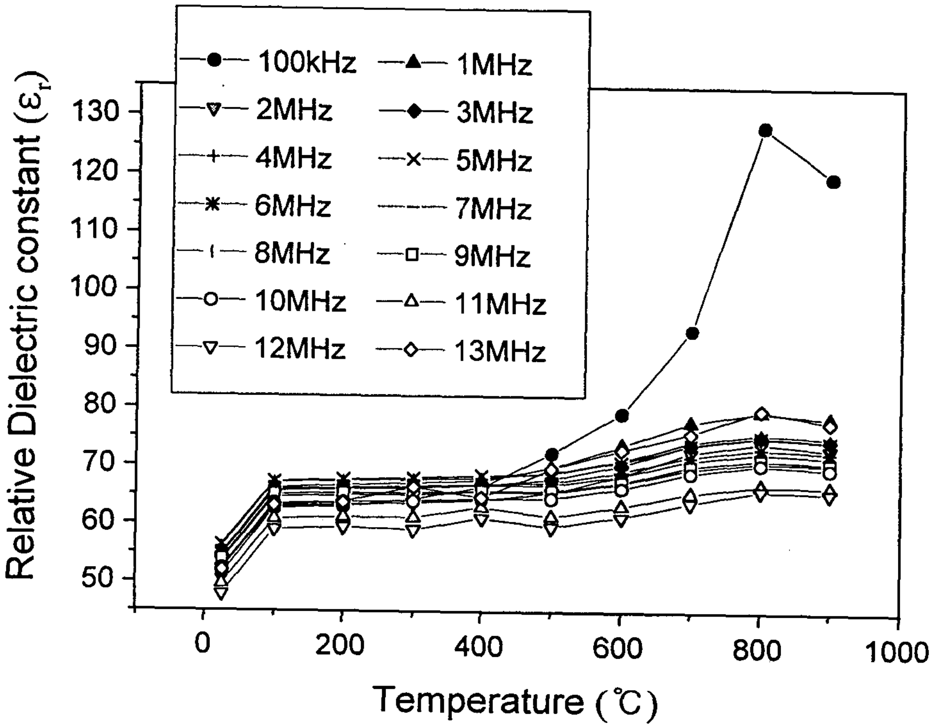


Fig. 9 Relative dielectric constants of the grown langasite crystal with the change of the temperature at various frequencies

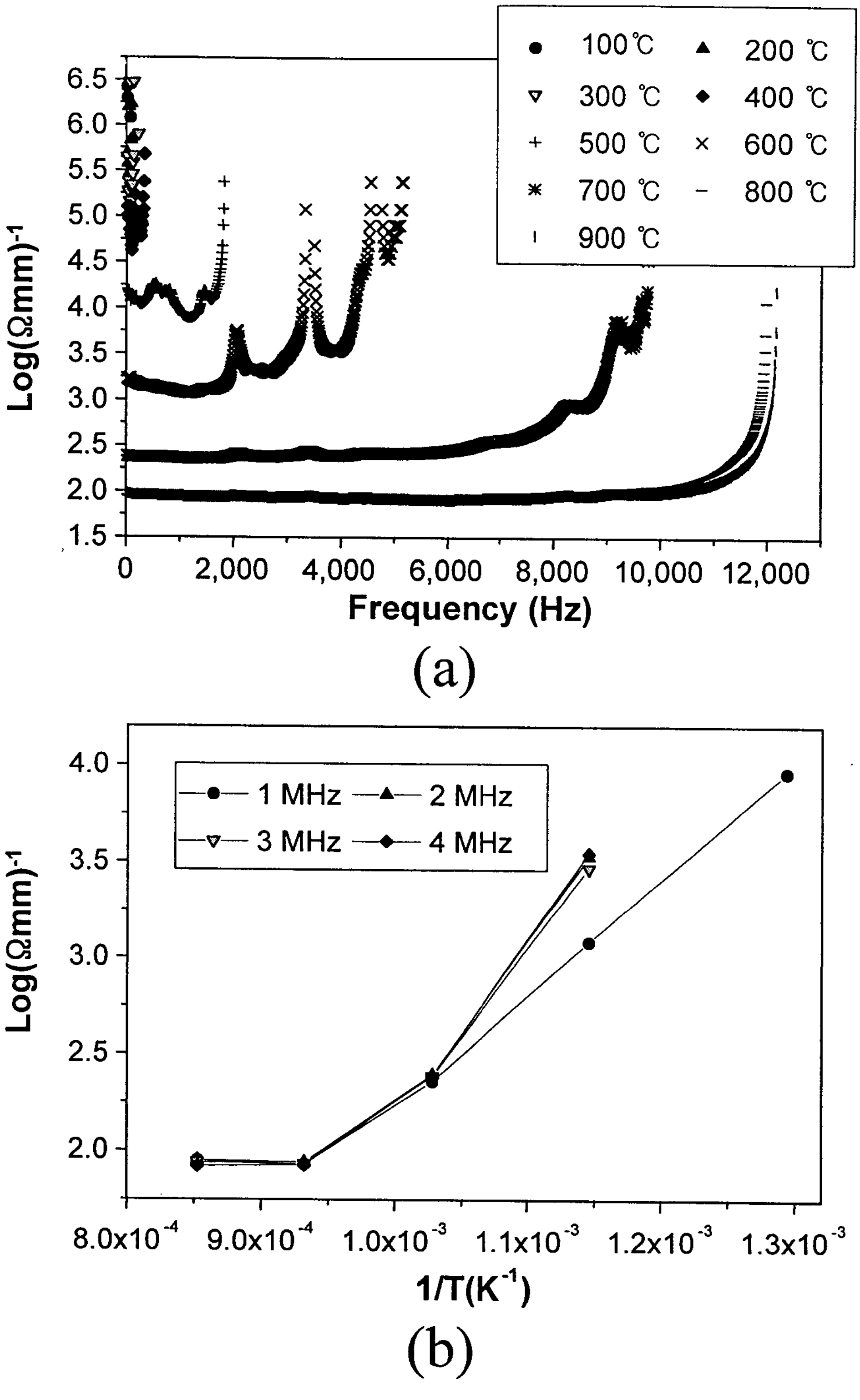


Fig. 10 Conductivity of the grown langasite crystal with the change of (a) frequency and (b) temperature