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# Crystal chemistry and growth of $La_3Ga_5SiO_{14}$ for the applications of filter and resonator

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# 필터와 레조네이터 응용을 위한 $La_3Ga_5SiO_{14}$의 결정화학 및 성장

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**Abstract** Langasite ($La_3Ga_5SiO_{14}$) is a new piezoelectric material which is similar to quartz, LN ($LiNbO_3$) and LT ($LiTaO_3$) in its acoustic behavior. In this study, pure Langasite and Langasite family groups were synthesized by the solid state reactions in air. The diffusion species for synthesis were investigated and the sintered body was studied on dielectric property to comparison of characteristics. Also, Langasite single crystals were grown by self-designed Czochralski system and characterized

**요 약** Langasite($La_3Ga_5SiO_{14}$)는 acoustic 특성에서 quartz, $LiTaO_3$와 $LiNbO_3$에 비교되는 새로운 압전재료이다. 본 연구에서는 새로운 Langasite 계열의 물질을 공기 중에서 고상반응법에 의해 합성하였고, 합성공정에서의 주요 확산종을 조사하였다. 이때 합성된 물질의 소결체를 제조하여 각각의 유전적 성질을 비교평가하였다. 또한, Langasite 단결정을 자체제작한 Czochralski 시스템을 사용하여 성장시키는데 성공하였고, 성장된 결정의 물성을 평가하였다.

## 1. Introduction

Rapid progress of electronic technologies require a development of new piezoelectric materials with smaller size, lower impedance and wide passband. For designing a filter devices, Langasite has new piezoelectric properties which show intermediate properties between those of quartz and lithium tantalate [1-3]. The phase transition of quartz at 573℃ limits the processing temperatures one can use in the fabrication of quartz resonator. While Langasite on the other hand has no phase transition up to its melting temperature 1470℃. 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 since the 1980s in Russia [6]. Its promise as a material for SAW, BAW and resonator devices was determined from it's acoustic characteristics [7]. It was a single oxide compound of the ternary system, and was grown by the Czochralski method. Langasite has a trigonal structure which belongs to point group 32, space group P321, and is isostructural to $Ca_3Ga_2Ge_4O_{14}$. There are four kind of cation sites in this structure

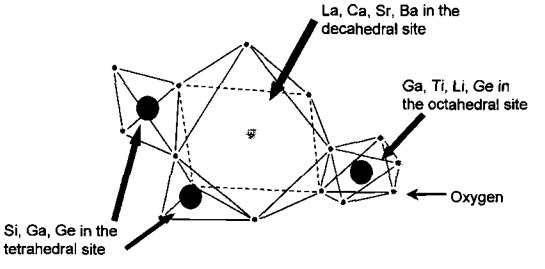

Fig. 1. Schematic diagram of Langasite structure.

and represent by the $A_3BC_3D_2O_{14}$. As shown in Fig. 1, A and B was located in a decahedral site and octahedral site, respectively. While C and D on the other hand was located in tetrahedral site. In case of Langasite, $La^{3+}$ occupies the A sites, $Ga^{3+}$ occupies the B, C and half of the D sites, and $Si^{4+}$ half of the D sites, respectively [4, 5]

In this present study, we will demonstrate the successful synthesis of Langasite and Langasite family group powders by solid state reactions in air. And then, characteristics of sintered body which made from synthesized powders will be discussed on dielectric and physical properties throughout structural characterization.

## 2. Experimental procedure

### *2.1. Synthesis and characterizations*

In order to compare with dielectric properties of sintered body and structural characterization of new composition, we needed completely synthesized powders. Starting materials for synthesis were 99.99 % oxide of $La_2O_3$, $Ga_2O_3$, $SiO_2$, $Ta_2O_5$ $SrCO_3$, $Al(OH)_3$ and $GeO_2$. The mixed materials were heated in alumina crucible at temperature range of 1000~1400℃ in air. And then, synthesized powders were identified using the powder X-ray diffractometer. In order to study diffusion process for synthesizing material such as $La_3Ga_5SiO_{14}$, $La_3Ta_{0.5}Ga_{5.5}O_{14}$, $La_3Ga_5GeO_{14}$ and so on, pellet of $La_2O_3$, $Ga_2O_3$ and $GeO_2$ which was pressed from powders, was stacked together and heated at various temperatures. The surfaces of sintered plates, which was in contact with each other during sintering, was analyzed by the energy dispersive X-ray spectroscopy (EDS) and wavelength dispersive X-ray spectroscopy (WDS).

The synthesized powders were isostatically pressed at 120 MPa into discs 10 mm in diameter and 1 mm in thickness. The microstructure after sintering was observed by scanning electron microscopy (SEM). And then, relative densities were measured by Archimedes method.

Physical and dielectric properties of sintered body with disc shape were investigated by the X-ray diffractometer (Rigaku Co.) and impedance analyzer (HP 4192A model).

### *2.2. Crystal growth and characterizations*

The starting materials were prepared from mixture of $La_2O_3$, $Ga_2O_3$, $SiO_2$.These materials were heated at 1300℃ in air for 3 h. After that, charge was melted in a gas mixture of argon and oxygen with 2 : 1 volume % which is continually passed through the chamber at a flow rate of about 1 *l*/min. When a melt has developed the c-axis seed crystal was dipped into the Langasite melt. And 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 optical transmittance by multichannel spectrophotometer. And also, 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 Co.).

## 3. Results and discussions

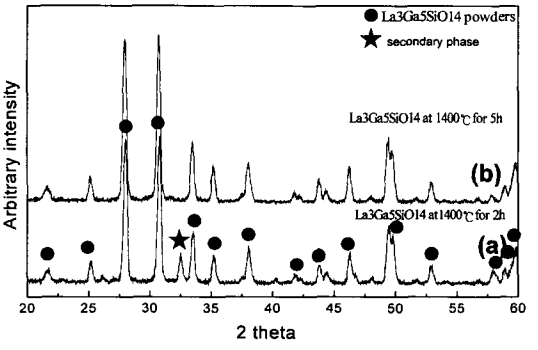


Fig. 2. Langasite phases were synthesized at 1400℃ for (a) 2 h, (b) 5 h, respectively; (b) pure Langasite phase.

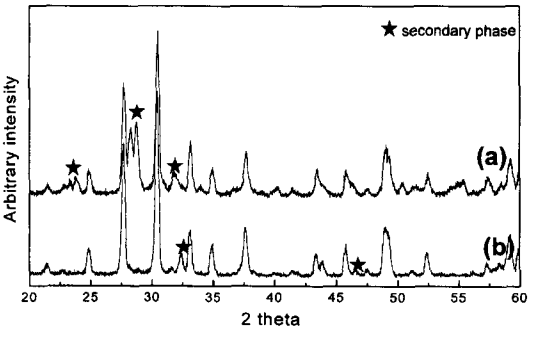


Fig. 3. $La_3Ta_{0.5}Ga_{5.5}O_{14}$ phase were synthesized at 1400℃ for (a) 5 h, (b) 10 h, respectively.

For development of new composition according to the crystal chemistry, the composition of $La_3Ga_5SiO_{14}$, $La_3Ta_{0.5}Ga_{5.5}O_{14}$, $La_3Ga_5GeO_{14}$ and $Sr_2Al_3LaGe_3O_{14}$ etc. were synthesized. Also, they have no phase transition up to the melting temperature 1350~1470℃.

As shown in Fig. 2., Fig. 3. and Fig. 4., XRD results needed to investigated the secondary phases and homogeneous single phase for calcination. In Fig. 2 where $La_3Ga_5SiO_{14}$ was calcined at 1400℃ for 5 h to synthesize powders through the solid state reactions, it was found that $La_3Ga_5SiO_{14}$ phase began forming at 1100℃ while a secondary phase and unreacted phase, $La_2O_3$, $Ga_2O_3$ and $LaGaO_3$ were mainly detected. These powders dissipating and then the quantity of secondary phase, $LaGaO_3$ was found to decrease with time and temperature. But main peak decreased with increasing temperature and time. It was considered that evaporation of gallium suboxide had an effect on synthesis of $La_3Ga_5SiO_{14}$ powders. In this experience, we were confirmed that quantity of evaporation of gallium oxide was 13 % in it's temperature and time. However, calcination condition for synthesis of pure $La_3Ga_5SiO_{14}$ single phases with no other secondary phases was found to be at 1400℃ for 5 h. As shown in Fig. 3., $La_3Ta_{0.5}Ga_{5.5}O_{14}$ single phases were synthesized in same conditions. In Fig. 4., while $La_3Ga_5GeO_{14}$ was synthesized at lower temperature. In case of synthesis such as Langasite and family group, synthesized powders were reacted the alumina crucible because synthesis temperature is around the melting temperature. But $La_3Ga_5GeO_{14}$ was not reacted the alumina crucible because $La_3Ga_5GeO_{14}$ phase was synthesized at lower temperature, 1300℃ compare with other Langasite and family group powders.

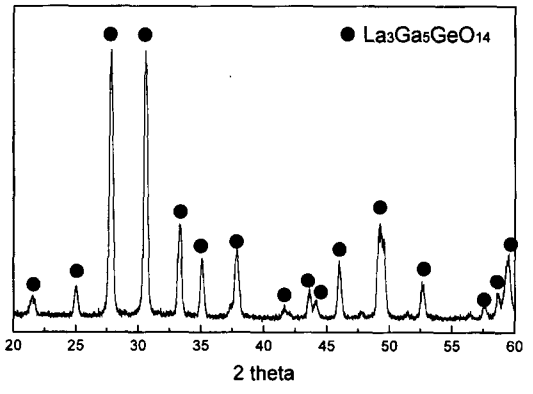


Fig. 4. XRD pattern of $La_3Ga_5GeO_{14}$; this material was synthesized at 1300℃ for 5 h.

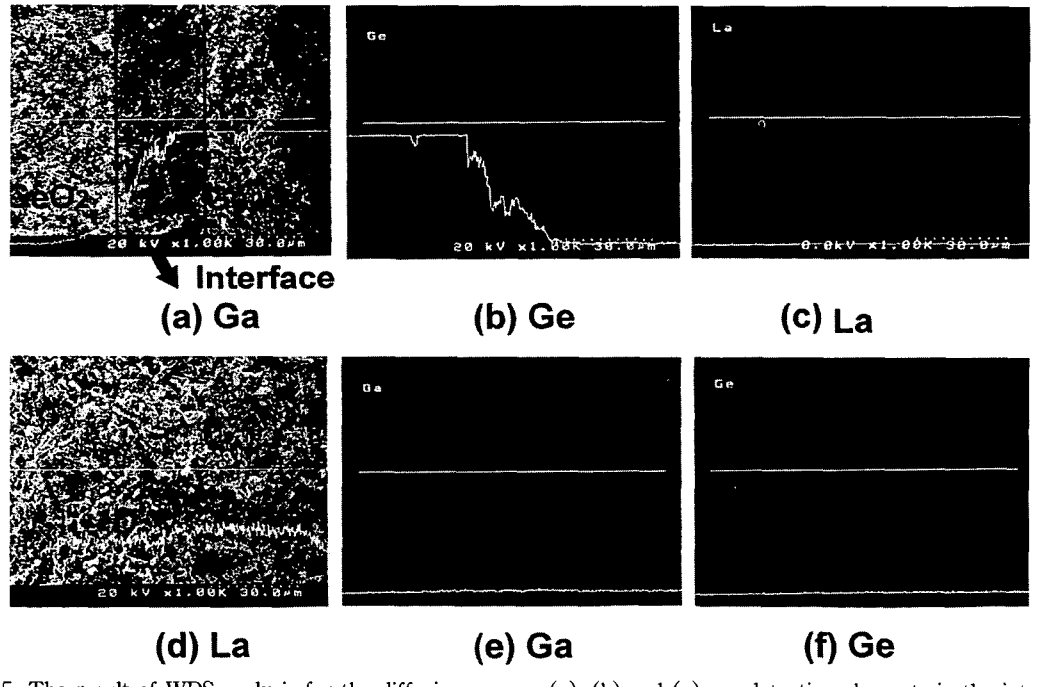


Fig. 5. The result of WDS analysis for the diffusion process (a), (b) and (c) are detecting elements in the interface of $GeO_2$ and $Ga_2O_3$. (d), (e) and (f) are detecting elements in the interface of $La_2O_3$ and $Ga_2O_3$.

Also, new chemical compound of $Sr_2Al_3LaGe_3O_{14}$, which was not contained $Ga_2O_3$, was completely synthesized at 1300℃ for 10 h. And this material was confirmed that melting temperature was at lower, 1330~1350℃, than that of other materials.

In Fig. 5., diffusion process for synthesizing material such as $La_3Ga_5SiO_{14}$, $La_3Ta_{0.5}Ga_{5.5}O_{14}$, $La_3Ga_5GeO_{14}$ and so on, pellet of $La_2O_3$, $Ga_2O_3$ and $GeO_2$ which was pressed from powders, was stacked together and sintered at various temperatures. The surfaces of sintered plates, which was in contact with each other during sintering, was analyzed by the energy dispersive X-ray spectroscopy (EDS) and wavelength dispersive X-ray spectroscopy (WDS). As the above results, diffusion reaction occurs on the interface of $Ga_2O_3$ and $GeO_2$ while it was not observed on that of $La_2O_3$ and $Ga_2O_3$. So, Ga and Ge ions were main diffusion species and thus when $La_3Ga_5GeO_{14}$ is synthesized, $Ga_2O_3$ and $GeO_2$ is thought to react with one another previous to the full synthesis of $La_3Ga_5GeO_{14}$.

The sintering of Langasite is solid state reaction accompanying thermal energy, the change in density using the Archimedes method from 1300 to 1400℃ at 50℃ intervals with time fixed for 3 h was analyzed. The relative density of the sample sintered at 1300℃ was 92.7 % and those of other samples sintered at 1350, 1400℃ reached almost theoretical values. Figure 6(a) and Fig. 6(b) show the surface morphology sintered at 1400℃ for 3 h and the etched surface by HF : $H_2O$ in 1 : 2 volume ratio for 40 min at room temperature. The decrease in porosity and the concurrent densification resulted in a higher relative density.

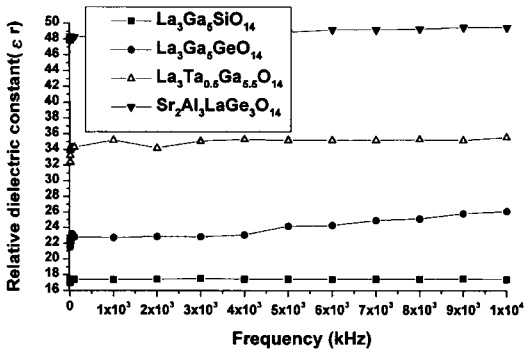


Fig. 7. Dielectric constant of polycrystalline Langasite and family groups were measured by impedance analyzer (HP4192A) at room temperature; Samples were sintered at 1400℃ for 5 h.

In Fig. 7., dielectric constant of polycrystalline Langasite was measured to be 17~18 and $La_3Ga_5GeO_{14}$ had a 22~27 in the range of 1 kHz to 13 MHz. In specially, $Sr_2Al_3LaGe_3O_{14}$ was measured to be 48~50. This value is higher than that of other materials. Also, in these materials, phase transition was not observed up to around the melting temperature. So, these materials can be produced high temperature processing. And also, it will be expected that materials having a new composition can be used microwave frequencies from the dielectric characteristics.

As shown in Table 1, the lattice constants of $La_3Ga_5SiO_{14}$, $La_3Ta_{0.5}Ga_{5.5}O_{14}$ and $La_3Ga_5GeO_{14}$, $Sr_2Al_3LaGe_3O_{14}$ were measured to be a = 8.1455, 8.228, 8.2009, 8.192 Å and c = 5.102, 5.124, 5.1142, 4.975 Å, respectively. Crystal structure and lattice anisotropy of Langasite family group were similar to those of

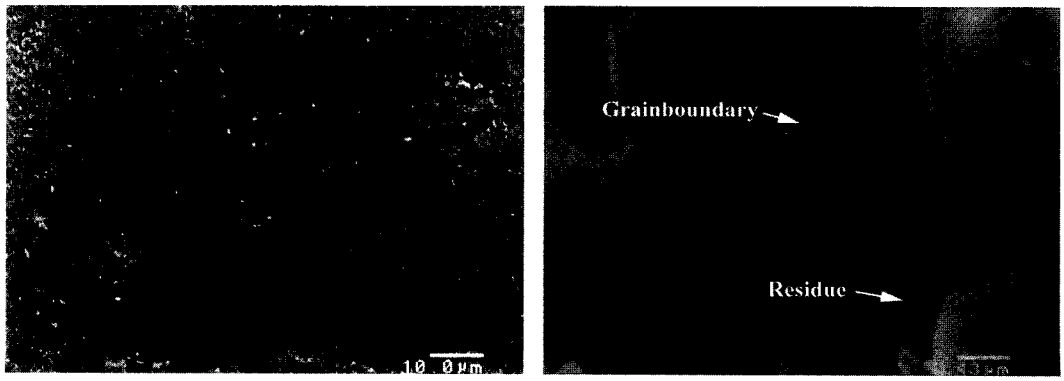


Fig. 6. SEM micrographs of sintered body; Sample (a) was sintered at 1400℃ for 3 h and sample (b) was etched with HF : $H_2$ = 1 : 2.

Table 1
Comparison data with lattice constants of Langasite crystal

| Materials | Lattice constant | | Lattice anisotropy (a/c) |
|---|---|---|---|
| | a | c | |
| $La_3Ga_5SiO_{14}$ | 8.1455 | 5.1020 | 1.597 |
| $La_3Ga_5GeO_{14}$ | 8.2009 | 5.1142 | 1.604 |
| $La_3Ta_{0.5}Ga_{5.5}O_{14}$ | 8.2280 | 5.1240 | 1.606 |
| $Sr_2Al_3LaGe_3O_{14}$ | 8.1920 | 4.9750 | 1.647 |

Langasite. But, in case of $Sr_2Al_3LaGe_3O_{14}$, it has higher lattice anisotropy than that of other materials. As far as piezoelectric properties are concerned, $Sr_2Al_3LaGe_3O_{14}$ will be expected to superior to other materials.

In this study, starting material for the growth was prepared by mixture of high purity oxides to prevent composition change of grown crystal due to the volatilization of $Ga_2O$. The premelting of crucible with starting materials was carried out in Ar atmosphere. When melting in Ar atmosphere volatilization of $Ga_2O$ was observed, the increased oxygen content was prevented from this phenomena. With the method I mentioned above, the compositional change of grown crystal could be removed. Langasite single crystals with 47 mm in diameter and 25 mm in length were successfully grown by the Czochralski method. This crystal was pulled at a rate of 1.8 mm/h with a rotation speed of 10 rpm by using Platinum crucible. And then, no crack and inclusion was observed. Langasite single crystal would be stable 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 was shown in color of dark orange and transparent. From the result of phase identification by the XRD patterns, grown crystal consisted of Langasite single phase without other secondary phases.

Table 2 shows the stoichiometric composition of grown Langasite crystal. The change of lattice constant was not observed in shoulder, body and tail part. From this result, we considered that grown crystals had a stoichiometric composition.

Table 2
Stoichiometric composition of grown crystal according

| Position | Lattice constants (Å) | |
|---|---|---|
| | a | c |
| Top | 8.1458±0.0001 | 5.1020±0.0001 |
| Body | 8.1459±0.0001 | 5.1020±0.0001 |
| Tail | 8.1455±0.0001 | 5.1018±0.0001 |

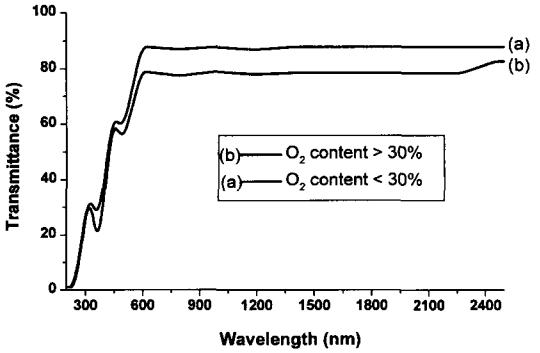


Fig. 8. Optical transmittances of grown crystal according to growth conditions.

Figure 8 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 constant value in the wavelength region over 590 nm. But crystals grown in an atmosphere of over 30 % oxygen and under 30 % oxygen were shown in transmittance of 82 %, 88 %, respectively. These results indicate that the growth atmosphere with less than 30 % oxygen is better for the growth of higher transmitting Langasite crystal.

Table 3 shows the admittance-frequency characteristics of grown Langasite crystal in z-cut plate. The resonance-antiresonance method is used to obtain the electromechanical coupling coefficient of piezoelectric materials. In this study, resonance and antiresonance frequency were obtained from calculated admittance-frequency characteristics. Electro mechanical coupling coefficient of z-cut plate in the transverse mode ($K_{31}$) was obtained as follows;

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

Table 3
Piezoelectric characteristics of Langasite crystal

| | Z-cut Langasite crystal |
|---|---|
| Resonance frequency | 1667613 Hz |
| Antiresonance frequency | 1697416 Hz |
| Quality factor | 32000 |
| Static capacitance | 6.45 pF |
| Electromechanical coupling factor ($K_{31}$%) | 25 |

*Measurement temperature: 298 °K.

Where fs = resonance frequency, fp = antiresonance frequency

The value of electromechanical coupling coefficient ($K_{31}$ %) and quality factor (Q) at room temperature were measured to be 25 and 32000, respectively.

However, as far as piezoelectric characteristics are concerned from the structural characterization of Langasite family group , $La_3Ta_{0.5}Ga_{5.5}O_{14}$, $La_3Ga_5GeO_{14}$ and $Sr_2Al_3LaGe_3O_{14}$ will be expected to surpass the quartz and $La_3Ga_5SiO_{14}$. The growth and characterization of Langasite family group crystals are now in progress and will be published elsewhere.

## Acknowledgements

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