GROWTH AND CHARACTERIZATIONS OF $La_3Ga_5SiO_{14}$ SINGLE CRYSTALS AND SINTERED BODY FOR THE APPLICATIONS OF FILTER AND RESONATOR

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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. For the synthesis process, diffusion species were investigated and sintered body of synthesized powders were studied on dielectric property according to surface microstructures.

I. Introduction

Rapid progress of electronic technologies required the development of new piezoelectric materials with smaller size, lower impedance and wide passband. For designing a filter devices, Langasite is a new piezoelectric properties intermediate 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 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 the solid state reactions in air. And then, characteristics of sintered body which made from synthesized powders will be discussed by dielectric and physical properties.

II. Experimental Procedure

The starting materials for the synthesis were used 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 by dry mixing 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 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).

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.

A 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).

III. Results and Discussions

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. As far as piezoelectric coefficient and insertion attenuations are concerned, $La_3Ta_{0.5}Ga_{5.5}O_{14}$, $La_3Ga_5GeO_{14}$ will be expected to surpass the quartz and $La_3Ga_5SiO_{14}$. Also, they have no phase transition up to the melting temperature 1470 ~ 1500 ℃.

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 5h 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 5h. 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. Also, new chemical compound of $Sr_2Al_3LaGe_3O_{14}$, which was not contained Ga_2O_3, was completely synthesized at 1300 ℃ for

10h.

In Fig. 5. and Fig. 6., 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 $La_3Ga_5GeO_{14}$.

$$3La_2O_3 + 3Ga_2O_3 = 6LaGaO_3 \text{ ---------- (1)}$$

$$2\ Ga_2O_3 + GeO_2 = Ga_4GeO_8 \text{ ---------- (2)}$$

$$6LaGaO_3 + Ga_4GeO_8 + 2Ga_2O_3 = 2La_3Ga_5GeO_{14} \text{ --- (3)}$$

The reaction is thought to occur in the order of equation (1), (2) and (3).

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 3h was analyzed. Fig. 7. and Fig. 8. show the relative density of the compact bodies sintered from 1300 to 1400 ℃ for 3h under air condition and surface microstructures. The relative density of the sample (a) sintered at 1300 ℃ was 92.7% and those of other sample (b) and (c) sintered at 1350, 1400 ℃ reached almost theoretical values. Fig. 8(a) and Fig. 8(b) show the surface morphology sintered at 1400 ℃ for 3h 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.

In Fig. 9., 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 new composition materials can be used microwave frequencies from the dielectric characteristics.

In Fig. 10., surface morphology of Langasite was indicated to [001] direction. So it was confirmed that preferred growth orientation was [001] direction.

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 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.

Acknowledgements

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<Figure and Table>

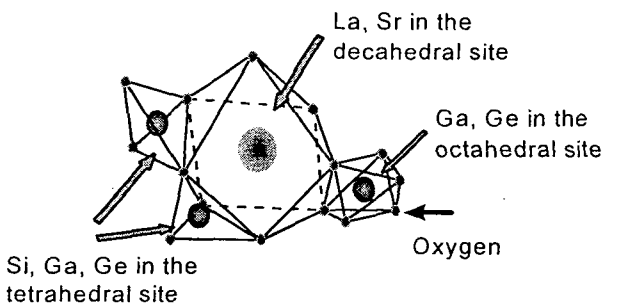


Fig. 1. configuration of Langasite structure

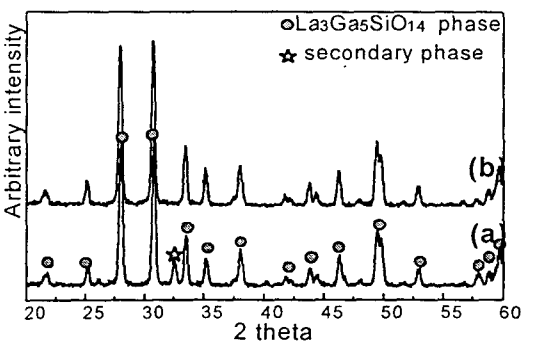


Fig. 2. Langasite phases were synthesized at 1400℃ for(a) 2h and (b) 5h , respectively ; (b) pure Langasite phases .

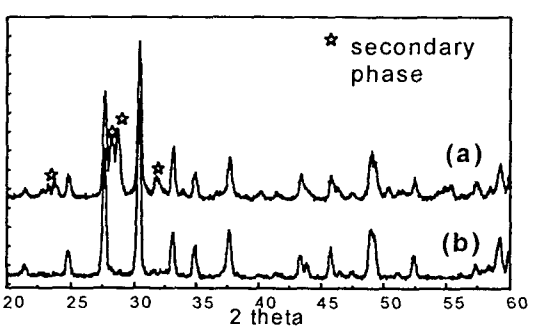


Fig.3. $La_3Ta_{0.5}Ga_{5.5}O_{14}$ phases were synthesized at 1400 ℃ for (a)5h and (b) 10 h, respectively.

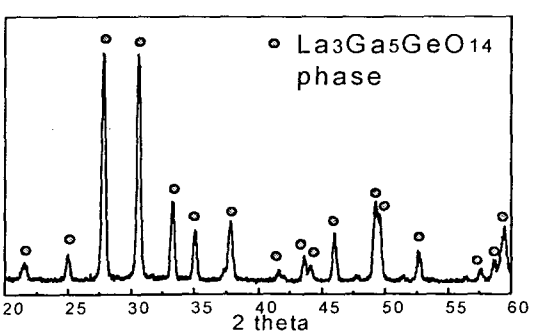


Fig.4. $La_3Ga_5GeO_{14}$ phases were synthesiz -ed at 1300℃ for 5h.

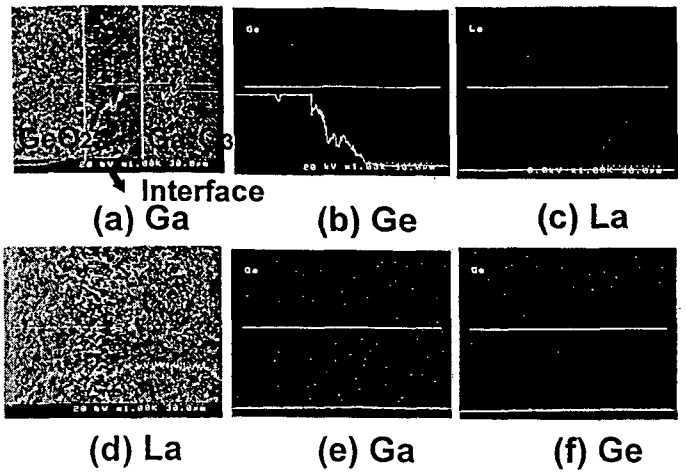
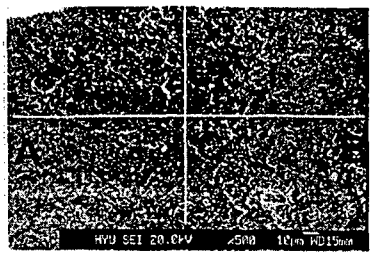


Fig.5. The result of WDS analysis for the diffusion process (a), (b) and (c) are detecting elements in the interface of GeO_2 and Ga_2O_3. (d), (e) and (f) are detecting elements in the interface of La_2O_3 and Ga_2O_3.



A ----------> C

Element	at%
La	27.97
Ga	35.57
Ge	36.46

B ----------> C

Element	at%
La	25.49
Ga	42.12
Ge	32.39

Fig. 6. The result of EDS analysis.

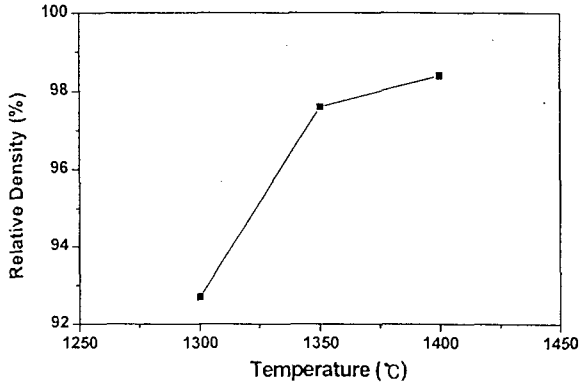


Fig.7. Relative density on air sintering temperature.

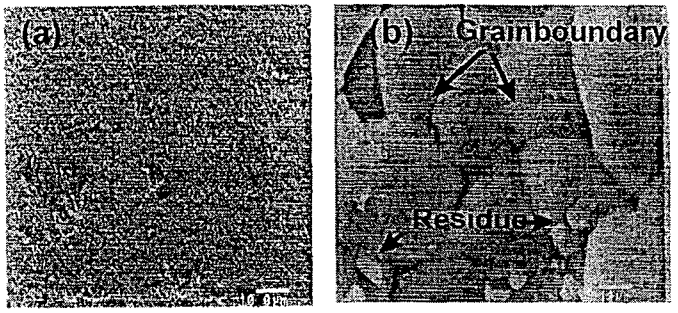


Fig.8. SEM micrographs of sintered body; Sample (a) was sintered at 1400℃ for 3 h and sample (b) was etched with HF : H_2O=1:2.

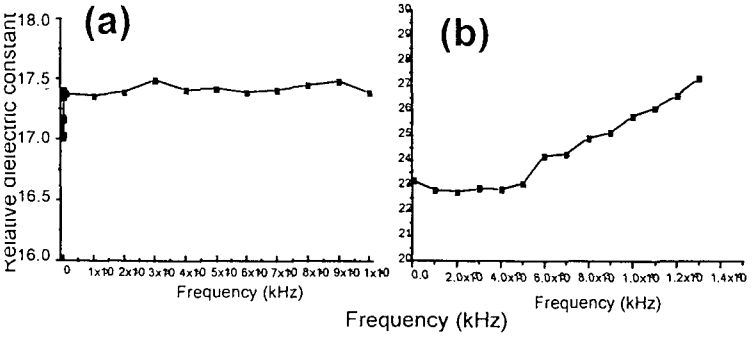


Fig. 9. Dielectric constant of polycrystalline Langasite and $La_3Ga_5GeO_{14}$ were measured by impedance analyzer(HP4192A) at room temperature ; Samples were sintered at 1400℃ for 5h and prepared disc shape of (a) 9 mm in diameter and 0.7mm in thickness and (b) 10 mm in diameter and 0.47 mm in thickness.

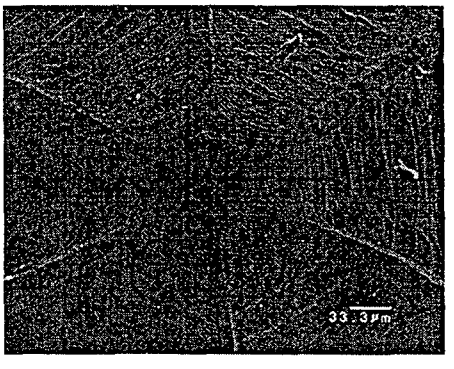


Fig. 10. Growth characteristic of Langasite. Surface morphology was indicated to [001] direction.