Synthesis and Characterization of Langasite-type Materials

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Abstract

Possibilities of substitution was investigated in the Langasite ($La_3Ga_5SiO_{14}$) system. TiO_2 was substituted for SiO_2 followed by the substitution of Nd_2O_3 for La_2O_3. An effort to replace GeO_2, which is reported to have been substituted for SiO_2 in the Langasite system, for TiO_2 in $Nd_3Ga_5TiO_{14}$ was also undertaken. In another experiment, Y_2O_3 was substituted for La_2O_3. All of the substitution possibilities were investigated through solid state reactions and analyzed with an XRD. Further analysis was carried out with an SEM. Lastly, the dielectric constants of the sintered body were measured.

Introduction

The recent progress of the electronic technology requires new piezoelectric crystals with a higher thermal stability of the frequency and large electromechanical factors. Langasite single crystals, originally investigated for uses in LASERs by the Russians, was also found to have excellent piezoelectric properties meeting the above mentioned requirements.[1-2]

These Langasite single crystals have properties between that of Quartz and Lithium Niobate, which makes it an ideal candidate for uses in SAW filters, as well as resonators and oscillators. While Quartz has fair dependency on frequency, it has a narrow passbandwidth. On the other hand, Lithium Niobate has a wide passbandwidth but is unstable with changes in frequency. Characteristic analysis of Langasite crystals have shown that it not only is stable with changes in frequency, but also has a wide passband (3 times that of Quartz).[3-5]

In this study, we tried to substitute various compounds to synthesize other materials with a structure analogous to that of Langasite through solid state reactions.

Experimental Procedures

A stoichiometric batch was prepared by dry mixing high purity La_2O_3, Ga_2O_3, and TiO_2 powders in an agate mortar. This mixture was compacted in a uniaxial press at a pressure of 1 ton/㎠. XRD was then used to analyze the sequential changes of secondary and LGT phases at 1200℃, 1300℃, and 1400℃ for samples reacted for 3 hours. Since Langasite's melting temperature is 1470±20℃[6], we assumed $La_3Ga_4TiO_{14}$'s (hereafter phrased as LGT) melting temperture to be in the same general range. To observe LGT's phase changes in melt, the sample was treated for 10 hours at 1450℃.

In the second experiment, Nd_2O_3 was substituted for La_2O_3 in LGT. From a stoichimetric batch and a compact prepared in the same manner as LGT, phase changes from 5 hours of solid state reactions undergone at 1200℃, 1300℃, and 140 0℃ was observed.

Since GeO_2 was found to substitute SiO_2 in the Langasite system, GeO_2 was also substitued for TiO_2 in the $Nd_3Ga_5TiO_{14}$ compound. From a stoichiometric batch, XRD data was obtained from samples sintered at 1200℃, 1300℃ for 5 hours and at 1400 ℃ for 5 and 10 hours. To visually verify densification, SEM micrographs of sintered bodies were taken.

Lastly, an effort to replace the Y_2O_3 compound for La_2O in the Langasite compound was made. Unable to achieve synthesis by solid state reactions of a stoichiometric batch, $Y_3Ga_5O_{12}$ was first synthesized and an experiment with two end members ($Y_3Ga_5O_{12}$ and SiO2) was carried out. Further qualitive analysis was undertaken with an EDX.

From the XRD results, the lattice parameter was calculated, and a comparison of the lattice values were made. To determine the dielectric properties of these sintered bodies, their dielectric constants were measured using an impedence analyzer.

Results and Discussion

When samples with a TiO_2 substitution was sintered at high temperatures, secondary phases mainly consisting of perovskite structure $LaGaO_3$ were observed. But with an increase in temperatures, these secondary phases showed a gradual decrease with total elimination at 1400℃ leaving XRD peaks nearly analogous to the Langasite peaks with only a slight shift of the 2θ value. From the XRD results of the LGT sample sintered at 1450℃, volitalisation of Ga_2O_3 resulted in the dissociation of the stoichiometric LGT, and $LaGaO_3$ secondary phases were again visible in the XRD peaks. This data is consistent with reports on the Langasite compound.

From XRD peaks of the NGT sample, secondary phases were again visible in the 1200℃ and 1300℃ sample. Unlike the LGT experiment, NGT showed mostly garnet structure $Nd_3Ga_5O_{12}$ as the dominant secondary phase. At 1400℃, secondary peaks

again dissipated leaving pure Langasite-type peaks.

In the Nd_2O_3-Ga_2O_3-GeO_2 system, pure Langasite-type peaks appeared at 1200℃, and no secondary peaks were observed at further elevated temperatures. SEM micrographs in figure shows the gradual densification of NGG with increasing temperatures.

In the last system with the Y_2O_3 substitute, no Langasite-type peaks were detected in temperatures ranging from 1200℃ to 1400℃. Further testing was carried out by trying to synthesize a $Y_3Ga_5SiO_{14}$ compound by mixing the garnet structrue $Y_3Ga_5O_{12}$ and SiO_2. In both cases, the stable garnet phase peaks were dominately detected in the XRD analysis. Using EDX, we were able to verify that indeed, SiO_2 does not participate in forming a Langasite-type material in this system. SiO_2 and the garnet phase were clearly isolated from each other.

The dielectric constants were measured for the LGT and NGG system, systems in which Langasite-type materials were successfully synthesized. Results show a gradual increase with frequency in ranges from 1KHz to 13MHz. This is thought to be due to the increase of the relaxation time between the electrode and the specimen surface.

References

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

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[4] G.D. Mansfield, *IEEE International Frequency Control Symposium*, 35-39 (1994)

[5] M. Takeuchi, K. Yamnouchi, *The 26th EM Symposium*, 69-72 (1994)

[6] G.G. Khodzhabagyan and B.V. Mill, *Russian Journal of Inorganic Chemistry*, **32** (2) 246-249 (1987)

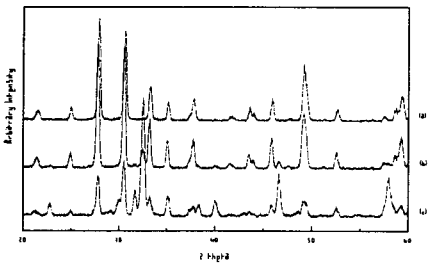

Figure XRD of LGT at various temperatures
(a) 1400℃ 3hrs. (b)1300℃ 3hrs. (c)1200℃ 3hrs.

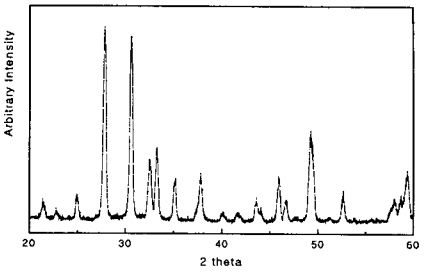

Figure XRD of LGT at 1450℃/10 hours
An increase in secondary phases observed

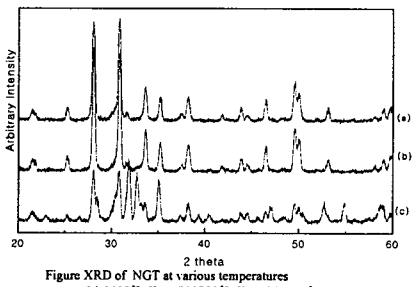

Figure XRD of NGT at various temperatures
(a) 1400℃ 5hrs. (b)1300℃ 5hrs. (c)1200℃ 5hrs.
Peaks show mostly a garnet phase with no Langasite characteristic peaks.

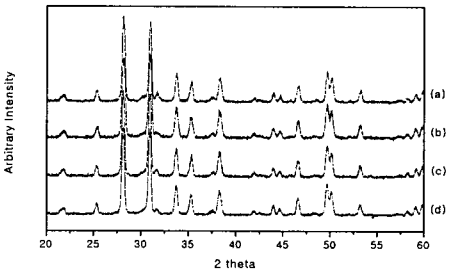

Figure XRD of NGG at Various Temperatures
(a) 1400℃ 10hrs. (b) 1400℃ 5 hrs.
(c) 1300℃ 5hrs. (d) 1200℃ 5hrs.

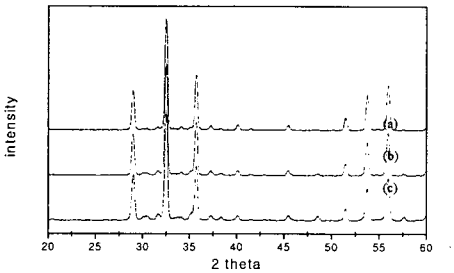

Figure XRD of YGS at 1300℃ for 5hrs.
(a) A stoichiometric batch of Y_2O_3-Ga_2O_3-SiO_2
(b) Two end members ($Y_3Ga_5O_{12}$-SiO_2)
(c) Ga_2O_3-3(Y_2O_3)2(SiO_2)

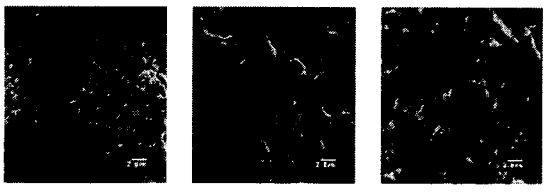

Figure SEM Micrographs of sintered $Nd_3Ga_5GeO_{14}$
(a) 1200℃, 5h, (b)1300℃, 5h, (c) 1400℃, 5h,

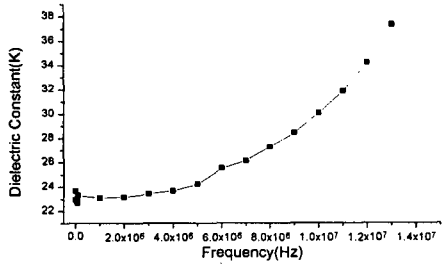

Figure Changes in dielectric constants of LGT with changes in frequency

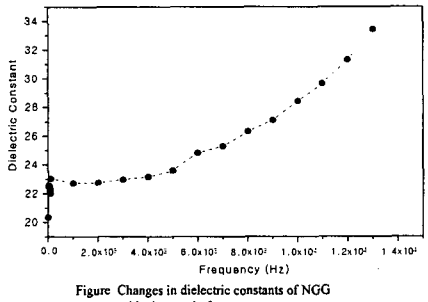

Figure Changes in dielectric constants of NGG with changes in frequency

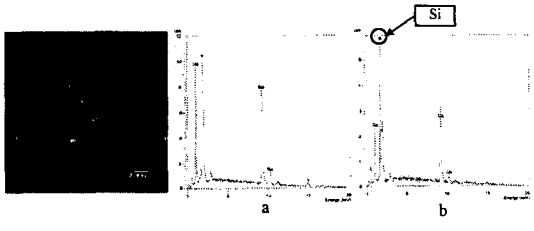

Figure SEM Micrographs and EDX of a Y_2O_3-Ga_2O_3-SiO_2 compound treated at 1500℃ for 5 hours. This shows that SiO_2 does not participate in the synthesis of a $Y_3Ga_5SiO_{14}$ compound

Compound	Lattice parameters (Å)	
	a	c
$La_3Ga_5SiO_{14}$	8.1620	5.0870
$La_3Ga_5TiO_{14}$	8.2241	5.1020
$Nd_3Ga_5TiO_{14}$	8.0392	5.0949
$Nd_3Ga_5GeO_{14}$	8.0784	5.0848

Table. Lattice parameters of new Langasite -type materials in comparison with $La_3Ga_5SiO_{14}$