



Crystal Growth and High Temperature Piezoelectricity of $\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.5-x}\text{Al}_x\text{O}_{14}$ Crystals

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Abstract. For the application of high temperature piezoelectric devices, Al^{3+} substituted $\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.5}\text{O}_{14}$ (LTG) crystals with chemical formula of $\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.5-x}\text{Al}_x\text{O}_{14}$ (LTGA) were synthesized and grown by μ -PD (Micro-pulling-down) and Czochralski technique. LTGA compound has been shown to exhibit congruent melting in a wide compositional range without destabilization of the melt during growth, while distribution coefficient of the substituted Al^{3+} ion was close to unity. LTGA crystals have shown preferable effects for temperature stability on piezoelectric properties in the range from R.T (room temperature) to 500°C.

Keywords: $\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.5-x}\text{Al}_x\text{O}_{14}$ (LTGA), crystal growth, micro-pulling-down, Czochralski, piezoelectric

Introduction

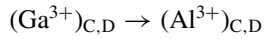
During the past decade, a number of research groups have sought to grow and characterize high-quality single crystals of $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ (CGG, $\text{A}_3\text{BC}_3\text{D}_2\text{O}_{14}$ structure) [1] type crystals such as $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ (LGS, langasite) $\text{La}_3\text{Nb}_{0.5}\text{Ga}_{5.5}\text{O}_{14}$ (LNG) and $\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.5}\text{O}_{14}$ (LTG), and their isomorphs for electronic-oscillator and filter applications [2–6]. The potential advantages of these materials over quartz include higher piezoelectric coupling, which enables devices to be made smaller with higher Q, which provides lower phase noise and enables operation at higher-frequencies. These crystals are congruently melting triple compounds grown by using the Czochralski (Cz) technique. They undergo no phase transitions up to the melting point, which allows devices to be operated at high temperatures and provides the capability of producing large crystals more easily and cheaply than with quartz. This last feature is important because the increasing use of large wafer processing techniques for surface acoustic wave (SAW) devices is pushing the limits of quartz crystal-growth technol-

ogy. They are not pyroelectric and thus possesses neither ferroelectric twins nor a Curie temperature T_C . The latter exhibit drawbacks like e.g. a phase transition at 573°C (quartz), a low Curie temperature of about 610°C (LiTaO_3) or a decomposition between about 300 and 900°C (LiNbO_3) [7, 8].

There are several reports on growth and piezoelectric properties of langasite family group crystals [3, 5, 6, 8, 9]. Up to now, LTG crystals have had the highest value in terms of piezoelectric properties. There are four kinds of cation sites in this structure, which is represented by the $\text{A}_3\text{BC}_3\text{D}_2\text{O}_{14}$. A and B are located on a decahedral site (twisted Thomson cube) coordinated by eight oxygens and an octahedral site coordinated by six oxygens, respectively, while C and D were located in tetrahedral sites coordinated by four oxygens. In the case of LTG crystals, La atom occupies the A sites, Ta atom fully occupies the B site, while Ga atom is located in the C and D site, respectively [10]. Thus, based on the information above, compounds with partial substitutions of Al^{3+} ($r^{\text{IV}} = 0.39\text{Å}$) for Ga^{3+} ($r^{\text{IV}} = 0.47\text{Å}$) in LTG [11] were synthesized and grown to investigate the effect of Al -substitution in tetrahedral (Ga site) site on their growth and piezoelectricity at room and high temperatures. In chemical formula, as Ga and Al ions are homologous

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elements, there was the possibility of easily substituting Ga by Al without any compensation like as following chemical formula.



where subscripts, C and D indicate two different tetrahedral sites. These substitutions produce crystals with the chemical formula, $\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.5-x}\text{Al}_x\text{O}_{14}$. Al_2O_3 crystals are well known as a strong insulator. It is expected that Al-substitution will lead to decrease electric conductivity at high temperature. So, this substituent could be assumed to be a reasonable method for investigating the intrinsic effect on piezoelectric properties. However, no report for the crystal growth and high temperature stability of LTGA crystals on piezoelectric properties has been reported. In this paper, we will make an attempt to grow LTGA crystals by μ -PD and Cz technique and piezoelectric properties of grown crystals will be compared with those of LTG crystals. We will also report the high temperature stability of piezoelectric properties of LTGA crystals for the first time.

Experimental

To investigate solid solution range and congruency of the LTGA compounds, sintered samples were prepared with variations in composition of LTGA ($x = 0.1-0.9$). The oxide materials used were La_2O_3 , Ta_2O_5 , Ga_2O_3 and Al_2O_3 of 99.99% purity and were obtained from the Rare Earth Materials Co. The starting materials were prepared from mixture of the constituents together in ethanol. The prepared mixtures were then dried at 100°C for 24 h, and heated at 1400°C for 15–20 h to perform the XRD and TG/DTA analysis. To obtain a homogeneous phase, solid-state reaction of mixed powders was carried out several times. Table 1 details the solid solution and congruency behavior of the four oxide mixtures according composition. And the identification of synthesized phase was carried out by powder XRD analysis in the range of $20 \leq 2\theta \leq 60$. Congruency for each composition of LTGA was established by TG/DTA analysis at a heating rate of $10^\circ\text{C}/\text{min}$ from room temperature to 1550°C with Al_2O_3 ball as a standard sample.

Crystal growth experiments were carried with the micro-pulling-down system. The fibers were pull down from an of Ir crucible nozzle. The crystal growth was performed in an atmosphere of Ar and O_2 , with the

Table 1. The starting compositions of LTGA compounds with a function of x and the results of solid-state reaction and congruency.

Composition	Solid-state reaction	DTA result
$\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.5-x}\text{Al}_x\text{O}_{14}$		
$\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.4}\text{Al}_{0.1}\text{O}_{14}$ ($x = 0.1$)	O	Congruent
$\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.2}\text{Al}_{0.3}\text{O}_{14}$ ($x = 0.3$)	O	Congruent
$\text{La}_3\text{Ta}_{0.5}\text{Ga}_{4.9}\text{Al}_{0.6}\text{O}_{14}$ ($x = 0.6$)	O	Nearly congruent
$\text{La}_3\text{Ta}_{0.5}\text{Ga}_{4.6}\text{Al}_{0.9}\text{O}_{14}$ ($x = 0.9$)	X	Incongruent

pulling rate varying from 0.05 to 0.2 /min. On the basis of the solid solution and congruency results, three starting melt compositions, at $x = 0.1, 0.3, 0.6$ were selected for the micro PD growth of LTGA crystals. Single crystals of LTGA, where $x = 0.1, 0.3$ and 0.6 , were pulled down by the μ -PD technique in inductively heated iridium crucibles under argon ambient atmosphere with 1 volume % of oxygen.

Czochralski growth of LTGA compounds with single zone RF-heating furnace having a vertical temperature gradient of $10-25^\circ\text{C}/\text{cm}$ was used for growth runs. The RF generator had a maximum power of 30 kW, and an oscillation frequency of about 10 kHz. The purity of the oxide materials used was higher than four-nine La_2O_3 , Ga_2O_3 , Ta_2O_5 and Al_2O_3 and was obtained from Rare Earth Materials Co. After complete melting of charge, the melt was soaked for 5 hours for better homogenization, as solid solution growth involves complexity. By ensuring thermal symmetry, pulling commenced with a [001] crystallographic oriented LTG seed. All other conditions including the growth rate, the rotation speed, growth atmosphere and the seed used were identical. A cylindrical Iridium crucible, 50 mm in diameter, 50 mm in length, was used to contain the LTGA melt. Pure Ar and O_2 gases were flowed into the melt, Pt/13%Rh-Pt thermocouple was attached to the side part of the crucible. The growth parameters were a rotation of 10 rpm and a 1.0–2.0 mm/hr pulling rate.

The grown crystals were cut into (001) oriented wafers, and their chemical composition was determined by electron probe microanalysis (EPMA). The phase identification was performed by powder x-ray diffraction pattern ($\text{Cu } K_\alpha$, $\lambda = 1.5406 \text{ \AA}$) and lattice constants were calculated by least square method. Y-cut resonators were cut and polished in the form of $10 \text{ mm} \times 4 \text{ mm} \times 0.5 \text{ mm}$ for the measurement of

piezoelectric properties and high temperature stability with elevated temperature. The electromechanical coupling factor and piezoelectric modulus were evaluated by measuring the resonance and anti-resonance frequencies of these resonators in the thickness-longitudinal mode. The resonance behavior of crystal samples was examined using a network analyzer (HP 4194A) by the real and imaginary part of impedance curve.

Results and Discussion

The results of solid-state reaction are presented in Table 1. From the XRD pattern, it shows the existence of single phase belonging to LTGA for $0 \leq x \leq 0.6$, whereas for $0.6 < x \leq 0.9$ a mixture of phases was detected. These results imply that Al^{3+} substituted for Ga^{3+} up to $x = 0.6$ in LTG. The thermal analysis data was collected at the temperature near melting and crystallization peaks. In the DTA curve, one endothermic peak during the heating period and an exothermic peak during cooling was observed for all four samples, starting at around 1505°C . The overlapping of two endothermic peaks for all compositions confirmed the incongruent melting behavior of LTGA compound having x values of 0.6 and 0.9, not evident at $x = 0.1, 0.3$. The above results based on solid solution and congruency indicates the possibility of μ -PD growth for the three compositions ($x = 0.1, 0.3, 0.6$).

The μ -PD growth for the compound of LTGA was undertaken in the same manner as that of langasite family group crystal growth [12–14] previously reported. As-grown LTGA fiber crystals and growth results are shown in Fig. 1 and Table 2, respectively. The cell parameters of grown LTGA crystals, a (\AA) and c (\AA) of crystals with molar concentration, x , were determined. The variations of lattice constants are shown in Fig. 2. Comparing the lattice constants of LTG crystal

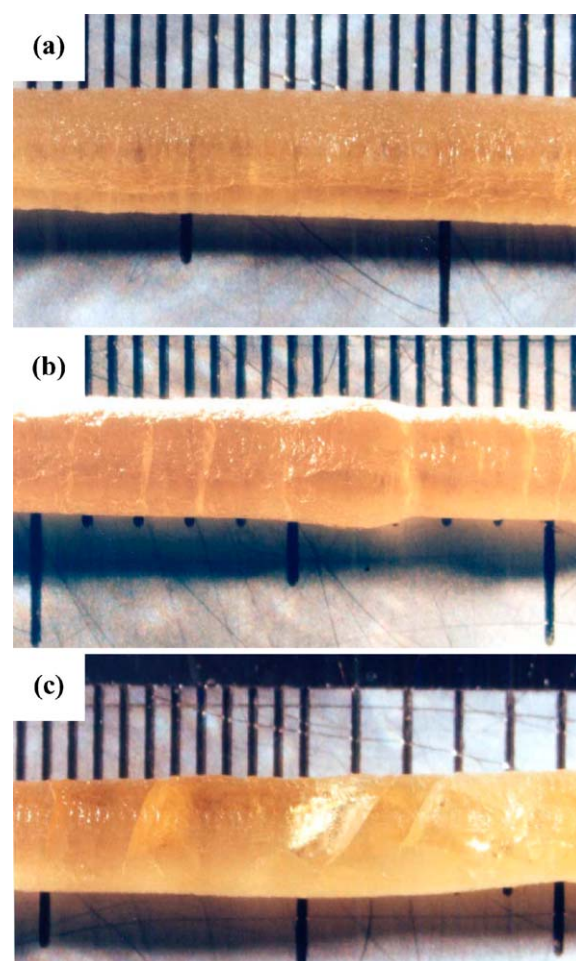


Fig. 1. As-grown LTGA fiber crystals; (a) $x = 0.1$, (b) $x = 0.3$ and (c) $x = 0.6$.

($x = 0$), we found that lattice constant (a) of LTGA just decreased within the range of $0 \leq x \leq 0.1$ and lattice constant (c) of LTGA crystals decreased linearly with increase of Al-content. This is in good agreement with the assumption that Al would be substituted for Ga in the tetrahedral site. In case of lattice constant (a), above $x = 0.1$, the cell parameter does not change as shown in Fig. 2. The decrease of lattice constant (a) in the range of $0 \leq x \leq 0.1$ might contribute to edge sharing between decahedral and two tetrahedrals. As in the LTGA solid solution, a keep almost constant in a and decrease in c parameter is observed, which can easily be understood as due to the small ionic size of Al^{3+} in comparison to Ga^{3+} . On the crystal grown from Al content of 0.6, foreign phase was detected as perovskite $\text{La}(\text{Ga},\text{Al})\text{O}_3$.

Table 2. The μ -PD growth results of LTGA crystals.

Composition $\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.5-x}\text{Al}_x\text{O}_{14}$	Lattice constants		Phase result
	a (\AA)	c (\AA)	
$\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.4}\text{Al}_{0.1}\text{O}_{14}$ ($x = 0.1$)	8.2009	5.1049	LTGA
$\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.2}\text{Al}_{0.3}\text{O}_{14}$ ($x = 0.3$)	8.1982	5.0943	LTGA
$\text{La}_3\text{Ta}_{0.5}\text{Ga}_{4.9}\text{Al}_{0.6}\text{O}_{14}$ ($x = 0.6$)	8.1980	5.0844	LTGA + $\text{La}(\text{Ga},\text{Al})\text{O}_3$

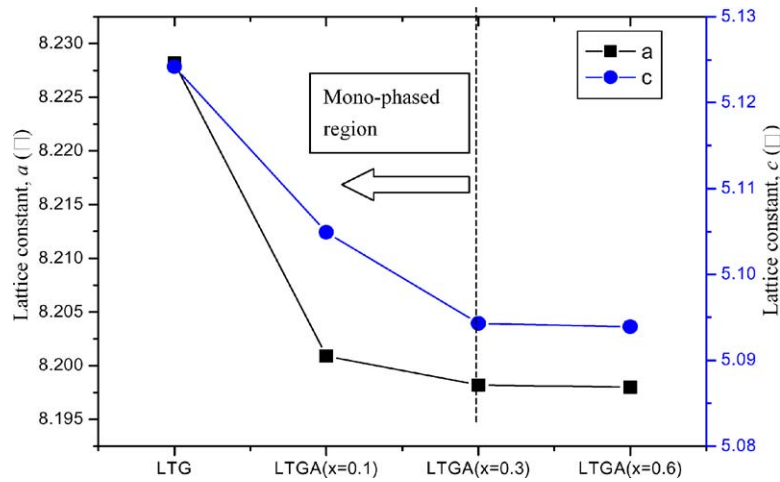


Fig. 2. The variation of lattice constants, a and c on the LTGA crystals, as a function of molar ratio, x .

For the Cz growth, the Al content in LTG was set at $x = 0.1$ and 0.3 , based on the solid solution and μ -PD growth results. On applying a rotation rate of 10 rpm and a pulling rate of 2–1.5 mm/h, growth was found to have difficulties such as sudden increase in the diameter of the crystal, which causes crystal cracking. Hence, the growth was preceded with an increase in rotation rate of 20 rpm and a reduction in the pulling rate of 1–1.5 mm/h. Growth process was found to be smooth during seeding and shouldering process. Although the growth temperature was slightly decreased with the increase of Al content, no difference was observed in the substitution of Al for Ga in terms of growth characteristics. After seeding, most stable crystal growth could be realized compared with LTG growth even if crystal diameter rapidly increased. As-grown LGTA crystals are shown in Fig. 3. Both crystals are crack and inclusion free and shown high optical transparency.

From the EPMA results along the growth direction (see Table 3), The values of the distribution coefficient

(k) were calculated from following equation.

$$C_s/C_0 = k(1 - g)^{k-1}$$

where C_0 and C_s represent the concentration of Al ion in the starting melts and in the grown crystal at the solidified fraction, g , respectively. The k values were obtained by taking the logarithm of above equation. The distribution coefficients, k , of LTGA ($x = 0.1, 0.3$) was determined to have a value of 0.9889 and 0.9656, respectively. This indicates that Al ion is easily incorporated into the LTG crystals and the Al concentration of the liquid is diluted in the vicinity of the crystal-melt interface.

The variations of lattice constants in LTGA with Al content, as a function of solidified fraction, g , are represented in Fig. 4. With increasing Al content, the decrease of both lattice constants was observed. This result was thought to be due to the incorporation of Al in the LTG crystal as shown in Table 3. As a result, an Al substitution had a great effect on the lattice, c , whereas it had a little effect on the lattice, a . In other words, the decrease of lattice parameters in LTGA crystals results from the smaller size of Al compared with Ga ions, indicating that Al ions are effectively incorporated into the complex lattice of LTG crystals. These results supported the assumption that Al ions mainly substituted for Ga ions in the two tetrahedral sites.

For investigating piezoelectric properties of LTGA crystals, Y-cut resonators were cut and polished in

Table 3. The Cz growth results of LTGA crystals.

Composition	k	Phase result
$\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.5-x}\text{Al}_x\text{O}_{14}$	(Al distribution coefficient)	
$\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.4}\text{Al}_{0.1}\text{O}_{14}$ ($x = 0.1$)	0.9889	LTGA
$\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.2}\text{Al}_{0.3}\text{O}_{14}$ ($x = 0.3$)	0.9656	LTGA

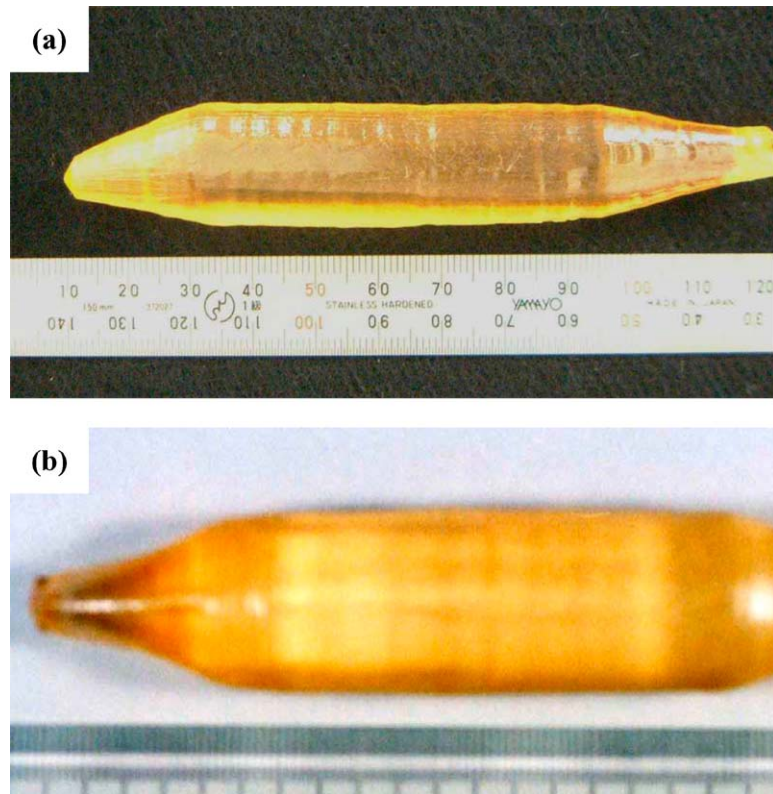


Fig. 3. As-grown Cz crystals of LTGA compounds; (a) $x = 0.1$ and (b) $x = 0.3$.

dimensions of $10 \times 4 \times 0.5$ mm. The electromechanical coupling factor was evaluated by measuring the resonance and anti-resonance frequencies of these resonators in the thickness-longitudinal mode. The resonance behavior of crystal samples was examined using a network analyzer by the real and imaginary part of the measured impedance curve. The peak frequency of the impedance curve was chosen as the sort resonator frequency and determined by fitting the center frequency of a Gaussian function to the selected data. The piezoelectric coefficient, d_{12} , was determined on small rectangular parallelepipeds using the direct piezoelectric effect in the range from 25 to 500°. The crystal samples were carefully ground to achieve parallel end faces and flat surfaces. Measuring with a compensation technique resulted in accurate measurements. The piezoelectric properties may be described by their piezoelectric coefficients, d_{ij} (Voigt notation). In case of class 32 to which the langasite structure belongs, only two components are independent due to the symmetry factors,

usually denoted as d_{11} and d_{14} . The force, F , was applied on certain faces and the resulting charge, Q , was collected on the metallized faces and measured with a charge amplifier. Typical relationships for this coefficient (d_{12}) are expressed as follows;

$$d_{12} = \frac{Q}{F} \times \frac{A_2}{A_1} = (d_{14} - d_{11})/2$$

where Q is resulting charge, F the applied force, A_2 the area of applied surface, and A_1 the area of electrode surface. Detailed sample shape for measurement is described in Fig. 5.

The results of the measurements of piezoelectric properties are represented in Table 4. It can be seen that LTGA crystals are showing lower value than LTG in terms of d_{11} and K_{12} . But, d_{14} value of LTGA crystal has slightly larger value than that of LTG crystals. The largest difference lies in cationic distribution between these crystals on the tetrahedral sites. Since Ga and Al

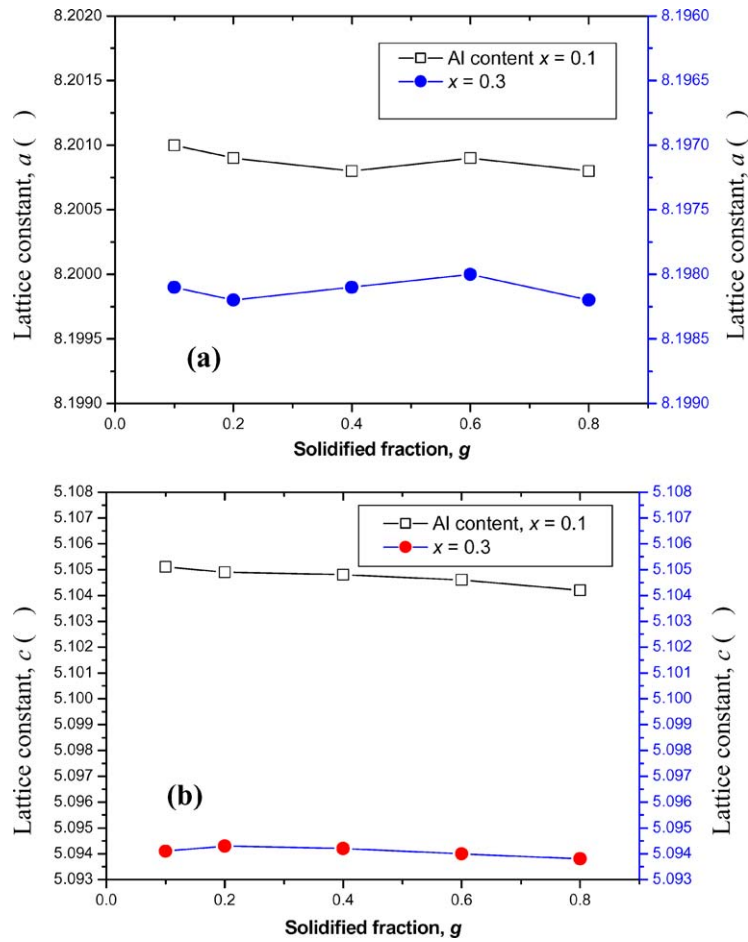


Fig. 4. Comparison of lattice constant with Al-contents.

atoms coexisting at the tetrahedral sites have difference ionic radius even if they have the same valence, it seems that a mixing of two atoms with different ionic radius lead to degradation of piezoelectric properties. This suggests that an additional influence, such as a

Table 4. Comparative data of piezoelectric constants between LTG and LTGA ($x = 0.1, 0.3$) crystals.

	LTG	LTGA $x = 0.1$	0.3
e_{11} (C/m ²)	-0.449	-0.038	-0.036
e_{14} (C/m ²)	0.084	0.097	0.099
d_{11} (pC/N)	-7.02	-6.58	-6.43
d_{14} (pC/N)	4.49	5.14	5.23
k_{12}	0.169	0.163	0.165

*Measurement was done at R.T (25°C).

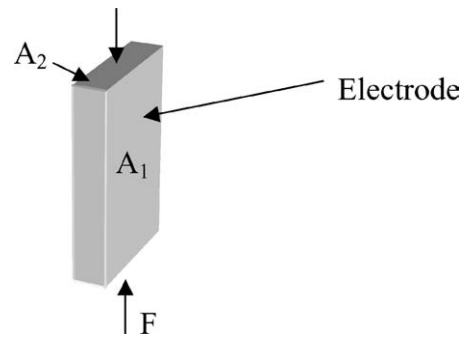


Fig. 5. Sample preparation for the measurement of d_{11} value.

structural distortion of some kind, may contribute to the observed degradation. Any information does not have on what microscopic change might be occurring within the substitution with that would result in such

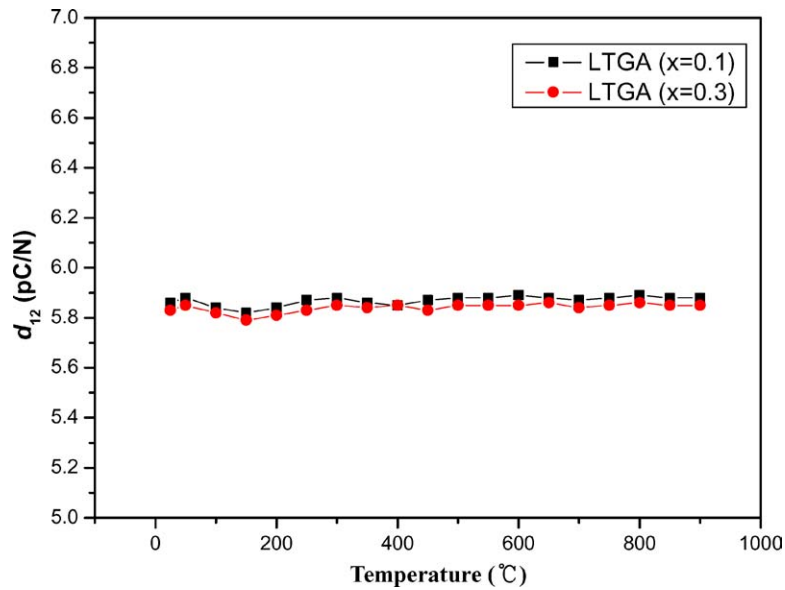


Fig. 6. Piezo-value (d_{12}) measurement with elevated temperature of LTGA crystals.

decreases in terms of piezoelectricity. One intriguing possibility could be that some part of its complex structure is nearly unstable to the kinds of structural distortions that give rise to piezoelectricity. However, d_{12} slightly increased with increasing of Al-content as can be seen in Fig. 6. This difference should lie within estimated error due to discrepancy such as precise crystal size, polished surface and so on. But, the crystals show stability with elevated temperature. Thus, Al substitution in LTG crystals has been shown to have positive potential for the high temperature piezoelectric applications.

Conclusions

Al-substituted LTG crystals have been successfully grown by μ -PD and Cz technique. In Cz grown crystals, crystals have no crack and inclusions and show high optical transparency. LTGA crystals show lower value than LTG in terms of d_{11} and K_{12} . But, d_{14} value of LTGA crystal has a slightly larger value than that of LTG crystals. The crystals also show temperature independence with elevated temperature. These results bring light to possibilities for the development and applications for high temperature devices. More detailed

piezoelectric properties will be reported in the near future.

Acknowledgments

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