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Growth and Electric Properties of Al-substituted Langasite-type $La_3Ta_{0.5}Ga_{5.5}O_{14}$ Crystals at High Temperature

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ABSTRACT

We report an effective substitution of aluminum for gallium in langasite-type $La_3Ta_{0.5}Ga_{5.5}O_{14}$ (LTG) crystals for use in a pressure sensor at high temperature. Al-substituted LTG ($La_3Ta_{0.5}Ga_{5.5-x}Al_xO_{14}$; LTGA*x*) single crystals up to the solubility limit of x=0.5 have been grown by the conventional Czochralski technique. The electric properties of the LTGA*x* crystals were investigated and compared with those of LTG. By Al substitution, the piezoelectric constant d_{11} and the electromechanical coupling factors (k_{12}) became slightly larger. The LTGA*x* crystals showed a lower temperature dependence of d_{11} and a higher electric resistivity ρ than those of the LTG crystals.

INTRODUCTION

$La_3Ga_5SiO_{14}$ (langasite; LGS)-type single crystals are the most attractive piezoelectric materials for use at high temperature [1], because the LGS-type crystals show no phase transitions up to its melting temperature. Recently, combustion pressure sensors made of the LGS substrates have actually been developed on a laboratory scale. For practical use, the LGS crystal requires a low temperature dependence of the piezoelectric properties and a high electric resisitvity at high temperature. Until now, the LGS crystal grown in a conventional oxygen-containing atmosphere has a low ρ value (4.0E+8 Ωcm) at high temperature (400°C). The desired ρ value is higher than 1E+9 Ωcm at 400°C. Since there is limited information about the electric properties of other LGS-type crystals at high temperature, we can possibly improve the resisitvity ρ. Based on this situation, we have started to investigate the substitution effect of the component cations in LGS on the growth, structure and electric properties [2,3]. In ref.[3], we reported that the substitution of Al^{3+} for Ga^{3+} can effectively improve the electric resisitvity of the LGS. The Al-substituted LGS at 400 °C shows a ρ value one order of magnitude higher compared to LGS. However, the d_{11} values of the Al-substituted LGS crystals increases with the increasing temperature [4]. Therefore, we have paid attention to other LGS-type single crystals and chosen the $La_3Ta_{0.5}Ga_{5.5}O_{14}$ (LTG) single crystals, because it can easily be grown to a large size using the Czochralski (Cz) technique, as well as exhibiting high frequency stability and high electromechanical coupling factors [5,6]. This report will describe the synthesis, crystal growth and the electric properties at high temperature for the Al-substituted LTG with a comparison to those of LTG.

EXPERIMENTAL PROCEDURE

The determination of the solubility limit of Al in LTG was performed by the solid-state reaction. The starting materials were prepared by mixing 99.99 % pure La_2O_3, Ta_2O_5, Al_2O_3, and Ga_2O_3

powders at compositions corresponding to the chemical formula of $La_3Ta_{0.5}Ga_{5.5-x}Al_xO_{14}$ (LTGA*x*; x=0.0–5.0). The powders were fired for 2 h at 1400-1525 °C. The phase identification and lattice constant measurements for each sample were done by powder X-ray diffraction (XRD) method.
The LTGA*x* crystals with the Al-content(x) between 0.0 and 1.0 were grown by the conventional Czochralski technique using an Ir crucible with a 40-50 mm diameter and height. The growth atmosphere was Ar plus 1vol%O_2 gas mixture. The pulling direction was <001>. The pulling rate and the rotation rate were 1.5 mm/h and 15-20 rpm, respectively. The observation of bubbles and inclusions in the crystals was performed using an optical microscope. The grown crystals were pulverized and their phase was identified by powder XRD analysis.
The material constants were determined as reported in refs.[7,8]. The piezoelectric constant d_{11} was determined by the resonance method. The resonance and the antiresonance frequencies for the length-extensional vibration mode were measured using an impedance/gain phase analyzer (HP-4194A: Agilent). The dielectric constants ε_{11} were determined by measuring the capacitances of the resonators by taking the parasitic capacitance into account. The changes in d_{11} and the electric resistivity ρ in the temperature range from room temperature to 700 °C were investigated.

RESULTS AND DISCUSSION

Fig. 1 shows the LTGA*x* phases synthesized by a solid-state reaction at 1470-1525 °C. We observed the LTGA*x* single phase at x values up to 2.0. As secondary phases, $La(Ga,Al)O_3$ and Ta_2O_5 appeared over x>2.5. Moreover, at x>3.5, the powders were only composed of the secondary phases. When the melting point was visually determined, the temperature increased with the change in the Al content. This observation suggested that Al^{3+} ions are easily incorporated into the crystals during the growth process, and the segregation coefficient of Al is greater than unity. This result agreed with the melting behavior of the Al-substituted LGS single crystal [9].
Fig. 2 shows the change in the lattice constants of LTGA*x* versus the Al-content. The powder samples synthesized at 1470°C and without any secondary phases were used for the measurement. Both lattice constants, a and c, decreased with an increase in x. This indicated that Al^{3+} with a smaller ionic radius than Ga^{3+} [10] was smoothly incorporated into the LTG crystal lattice. Based on these observations, we found that the solubility limit of Al in LTG as a polycrystal was determined to be 2.0. Kumatoriya *et al.*[9] reported that the solubility limit value (x=0.9) of Al in the Al-substituted LGS single crystal was smaller than those (x=1.5) in the polycrystal state.

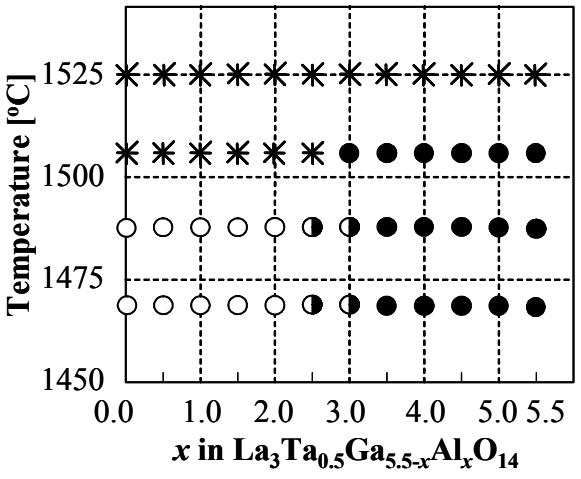

Fig. 1 Results of the solid-state reaction of LTGA*x* polycrystals. ○:LTG single phase, ●:$La(Ga,Al)O_3$+Ta_2O_5, ◑: Mixture, ✳: melted.

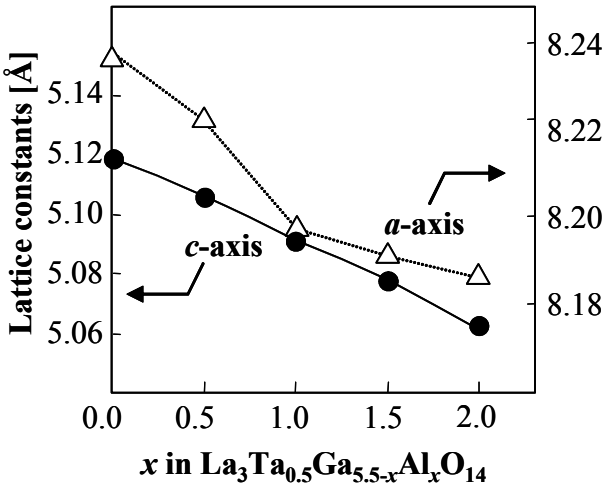

Fig. 2 Dependence of lattice constants on Al-content (x) in the LTGA*x* polycrystals.

Therefore, in this study, we tried to grow LTGAx crystals with 0.0(LTG)≤x≤1.0.

An as-grown LTGA1.0 crystal is shown in Fig. 3(a). The crystal had a smooth surface but was opaque with a light orange color. Many inclusions were observed inside the crystal. Therefore, we have grown LTGAx crystals from the starting material with incremental changes in the Al-content of 0.1. Fig. 3(b) shows an as-grown LTGA0.1 crystal. Since no growth instability appeared during the growth, the uniform diameter of the grown crystals was easily controlled. The crystals showed a smooth surface and were transparent with a orange color. No cracks or inclusions were found inside the grown crystals. All peaks of the powder XRD patterns of the boule were identified to be those of the LTG-type structure. Inclusions started to appear again in the LTGAx with x=0.6. Finally, we obtained LTGAx (0<x≤0.5) single crystals with no secondary phases. These LTGAx crystals were easily grown in the same way as the LTG one. The measured densities (D_m = 6.067 g/cm^3) of the LTGA0.5 crystals were slightly lower than that (6.111 g/cm^3) of the pure LTG ones. This result is supported by the atomic weight (W_{Al}(26.98)<W_{Ga}(69.72)). Therefore, we confirmed the Al substitution into the LTG. Three crystal (LTG, LTGA0.3 and LTGA0.5) samples were chosen for the investigation of the Al substitution effect on the physical properties. The evaluated material constants of the LGS, LTGA0.3 and LTGA0.5 single crystals are also shown in Table I. With an increase in the Al content, the piezoelectric constant d_{11} increases by about 0.8% for LTGAx.

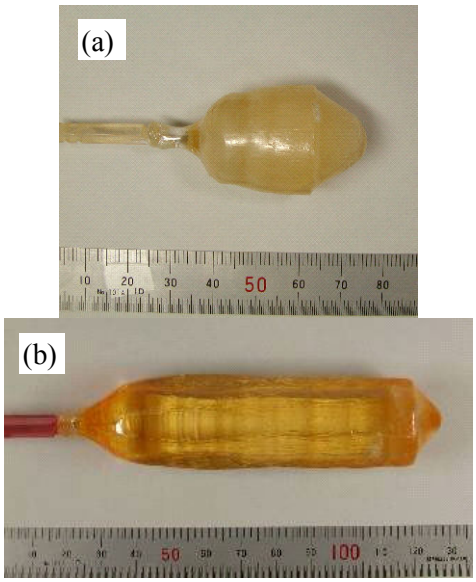

Fig. 3 As-grown (a) LTGA1.0 and (b) LTGA0.1 as-grown crystals.

Table 1. Properties of LTGAx crystals

LTGAx crystals	LTG	LTGA0.3	LTGA0.5
Relative dielectric coefficient ε_{11} / -	20.1	20.2	20.4
Electromechanical coupling factor k_{12} / %	16.4	16.4	16.6
Piezoelectric constant d_{11} / pC/N	6.59	6.62	6.64
Elastic compliance s_{11} / 10^{-12} m^2/N	9.07	9.07	9.09

Using the LTG and LTGA0.5 single crystals with the maximum Al content, their electric properties at high temperature were investigated. Fig.4 shows the temperature dependence of the piezoelectric constant d_{11} of the LTG and LTGA0.5 crystals. In this figure, the relative piezoelectric constant d_{11}^* represents the ratio of the d_{11} value at the measurement temperature and that at room temperature (25 °C). The d_{11}^* increased with temperature for all the crystals. Small differences in the thermal behaviors were observed between the LTG and LTGA x=0.5 crystals. The LTGA0.5 crystals show a small change (1.5%) compared to the LTG crystal, and this is an advantage for

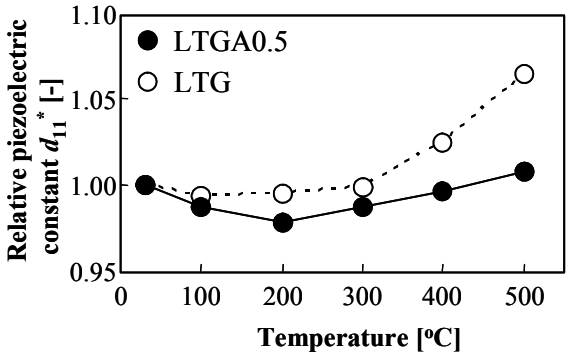

Fig. 4 Temperature dependences of the piezoelectric constant d_{11} of the LTG and LTGA0.5 crystals.

actual applications.
Fig.5 shows the temperature dependences of the electric resistivity ρ of the LTG and LTGA0.5 as-grown crystals. The ρ values decrease with the increasing temperature. However, the LTGA0.5 crystals have ρ values one order of magnitude higher compared to the LTG crystals at high temperature. The ρ values almost met for the required values at 400 ^{o}C. Therefore, we found that the Al substitution can effectively improve the electric resistivity.

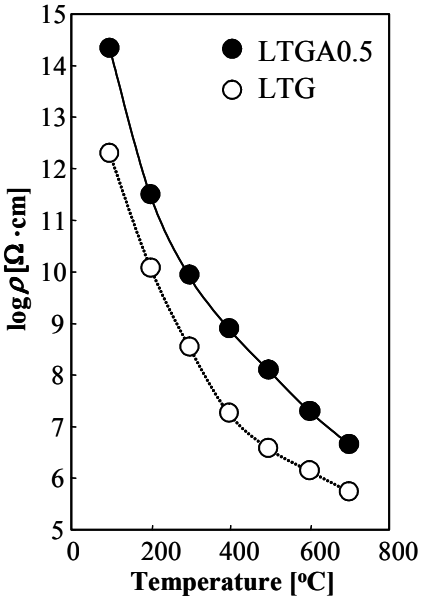

Fig. 5 Temperature dependences of electric resistivity ρ of the Y-cut LTG and LTGA0.5 crystals.

CONCLUSIONS

We grew Al-substituted LTG crystals by the conventional Cz technique and investigated their characteristics at high temperature. By Al-substitution, the LTG crystals acquired a low temperature dependence of its piezoelectric properties and a higher electric resistivity. Furthermore, the Al substitution enables the use of a lower amount of expensive gallium oxide as the raw material. At present, the LTGA0.5 crystal is a leading candidate for combustion pressure sensor materials.

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