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Single crystal growth of $LiTaO_3$ by FZ

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1. Introduction

$LiTaO_3$(LT) has been used in SAW device in early days(1,2), and the other applications are also attractive in the fields of optical waveguides, electromodulators, infrared image sensors and infrared detectors by utilizing exellent piezoelectric, pyroelectric and electrooptic properties(3-9). Because of a high nonlinear refractive index and a high optical damage resistance, LT is highlighted in a solid state laser and SHG(second harmonic generation) devices in these days(10-14).

To the present studies, LT single crystals with a large diameter were grown by the conventional CZ method using Ir or Pt-Rh crucible(15,16). But the persistant problems was a fluctuation of the compositon in the growth due to Li_2O vaporization and a diffusion of the crucible material. In contrast to the CZ method, the floating zone method has many advantages in crystal growing. The diffusion of crucible materials could be avoided. The fluctuation of the Li_2O composition is smaller than that of the CZ method. High purity crystals could be obtained in various atmospheres.

In this study, we studied the growth characteristics of LT single crystals using the halogen floating zone method and characterizations of the grown crystals. Calcination and sintering parameters were established. Optimum crystal growth conditions were investigated by a controlling of growth rates, rotation speeds and atmospheres.

2. Experimental procecure

LT polycrystalline powders of a congruent melting composition were synthesized using Li_2CO_3, Ta_2O_5 powders with a purity of 99.99 %. Raw powders were ball-milled for 20 h and dried with a halogen lamp. Dried powders were calcined at 850℃ for 10 h. The LT feedrod with a circular column form was prepared in a silicon rubber mold using CIP with a 1800

Kg/cm^2, and sintered for at 1450℃ for 10 h. LT single crystals were grown using a FZ SS-10W system using the feedrod with a diameter of 7mm. During the crystal growth, the optimum growth conditions were established by a controlling the powers, growth rates, rotation speeds, atmospheres. After crystal growth, annealings were conducted at 1200℃ for 10 h in order to decrease a thermal stress and defects. Curie temperatures of the annealed crystals were measured in the section of the part of top, body and tail. Refractive index distributions of the grown crystals were measured in 25 points on a wafer with a interval of 0.7 mm and a length of 0.6 mm from the center of the wafer using a PLASMOS SD-1000 ellipsometer. Transmittance of the grown crystals was measured using a spectrophotometer.

3. Results

In Fig. 1, a weight loss of CO_2 in calcining Li_2CO_3 and Ta_2O_5 was observed between 720℃ and 800℃, so that the complete reaction is formed at 800℃. The peaks of unreacted Li_2CO_3 and Ta_2O_5 are observed at $2\theta =$ 28.32°, 28.9°, 36.7° on the X-ray diffraction pattern of the calcined powders at 750℃. At 850℃, unreacted peaks were disappered and the peaks of $LiTaO_3$ was identified to the XRD pattern(Fig. 2). For a preparation of feedrods, it was appropriate to be sintered at 1450℃ for 10 h.

Melting aspects of the LT feedrods in FZ system were very abnormal, because of a low thermal conductivity and a low infrared absorption coefficient of LT. Especially, a low surface tension of LT made melt flow to seed crystal easily. In the case of $LiNbO_3$, the stability of the molten zone could be increased using Pt suspender[17]. However in the case of LT, it is impossible because of a high melting temperature.

During the crystal growth of LT, we manipulated to stabilize the molten zone by controlling the growing powers, growing rates, rotation speeds and atmospheres. In a growth of LT crystals in air or N_2 atmosphere, the stable conditions could not be found. Because the feedrod was melted far above normal melting point of LT, the melting aspect was irregular and the shape of molten zone was convex to the feedrod. However in Ar atmosphere, the feedrod was molten of a normal melting temperature of LT. The melting aspect in Ar was regular and more stable than in air or N_2 atmosphere. The shape of the molten zone was almost flat. The grown crystal was about 20 mm in length and light brown. Fig. 3 shows a photograph of the grown LT single crystal. The crystal color was vanished after annealing at 1200℃ for 10 h in an air atmosphere. The established optimum conditions for crystal growth in this study are as follows.

- Crytal growing rate : 3-5 mm/h
- Rotation speed : upper 16-20 rpm, lower 18-20rpm
- Atmosphere gas : Ar
- Flow rate of atmophere gas : 1 L/min

To investigate the growth direction of LT crystals, we analyzed Laue back reflection pattern. Fig. 4 shows that the growth orientation of LT single crystal was identified to be a Y-axis. The LT crystals have a nonstoichiometric composition, and the curie temperature increases depending on the [Li]/[Ta] ratio[18]. The fluctuation of the Li_2O composition could be investigated by measuring a curie temperature in the section of the part of top, body and tail. The curie temperature fluctuation of grown crystal parts was 1℃. Table 1 shows the reflective index fluctuation on a grown LT single crystal wafer. Average reflective index was 2.089 and standard deviation of reflective index fluctuation was 0.004. In Fig. 5 the transmittance of the grown crystal was ranged between 75-80 % in visible and infrared wavelengths.

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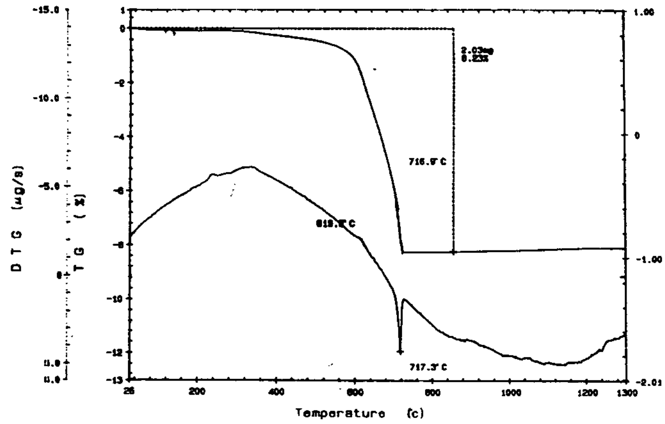

Fig 1. DT-TGA graph of LT powder

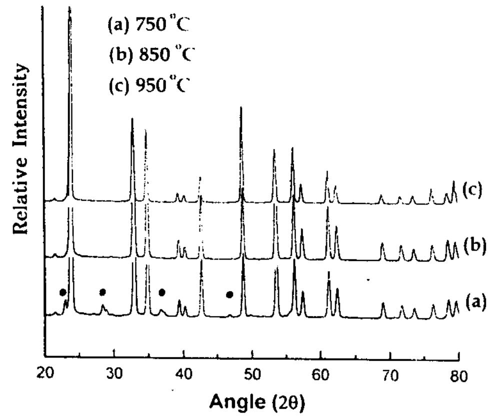

Fig 2. XRD patterns of the LT powders synthesized at temperature of (a)750℃, (b)850℃, (c)950℃.

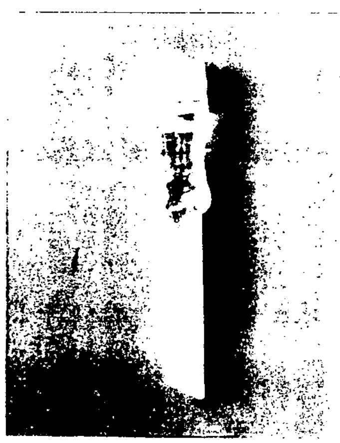

Fig 3. A typical LT single crystal grown by FZ method

Fig 4. Laue back-reflection photograph of LT crystal grown in the Y-axis orientation

Table 1. Refractive index fluctuation of the grown LT wafer

Position(mm)	-1.2	-0.6	0	0.6	1.2
1.4	2.091	2.093	2.090	2.088	2.087
0.7	2.088	2.087	2.091	2.086	2.092
0	2.093	2.091	2.090	2.089	2.093
-0.7	2.087	2.089	2.089	2.090	2.089
-1.4	2.093	2.092	2.086	2.093	2.090

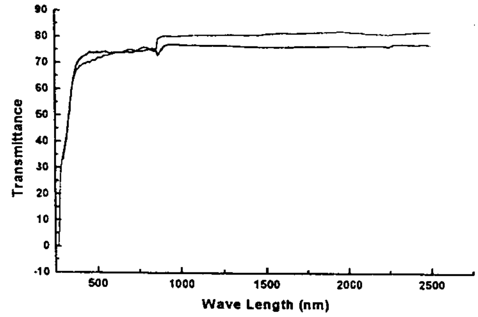

Fig 5. Transmittance of the grown LT wafer