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X-ray Topography on Piezoelectric $La_3Ga_5SiO_{14}$ Single Crystal

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Piezoelectric $La_3Ga_5SiO_{14}$ (LGS) single crystal grown by Czochralski technique was characterized by high-resolution synchrotron X-ray measurements. Crystal quality of the LGS was evaluated by the rocking curve width of 16.75 arcsec. Due to the growth problem (homogeneity and faceting habit), the crystal quality of the LGS was worth than we expected. Diffraction topography revealed inhomogeneity of the LGS crystal. Super lattice structure indicating a Ga/Si ordering of *2d* (space group *P*321) site was observed. Weak broad peaks indicating a glassy behavior were also observed. These extra peaks are the first observation in LGS crystal and they are also the origin of degradation of the crystal quality.
Key words: langasite, synchrotron X-ray, topography, diffraction imaging, crystal characterization

1. INTRODUCTION

Fast development of a communication system, based on acoustoelectronic devices and operating with complex digital signals in a mode of real time (mobile phone, pagers, radio, TV, GPS, *etc.*), requires the application of piezoelectric materials [1]. Conventional piezoelectric crystals of quartz, $LiNbO_3$, and $LiTaO_3$ do not meet the requirements of communication standards. The appearance of piezoelectric langasite crystal, combining the best acoustic properties of lithium niobate (high value of electromechanical coupling coefficient) and quartz (temperature compensation of acoustic losses), permits us to design the miniature acoustoelectronic components with unique properties.

This work presents an experimental investigation of X-ray Bragg diffraction on a $La_3Ga_5SiO_{14}$ (langasite, LGS) crystal grown by the Czochralski (Cz) technique.

High sensitivity of X-rays to crystal lattice distortions allows X-ray diffraction and topography to be used for studying characterization of ingots. Synchrotron radiation sources coupled with high-resolution diffraction technique provide an interesting tool for the investigation of defects, homogeneity, and their configuration in single crystals.

As several reports have been indicated, the growth of an industrial-class crystal has been difficult due to unsolved problems caused by various defects such as cracks, twins, cores and subgrains [2]. This is because the langasite has a clear habit of faceting. The crystal characterization by the high-resolution synchrotron X-rays provide important information for the crystal growth. Moreover, the LGS single crystal with high-crystal quality can be applied to novel optical crystal for synchrotron X-ray measurements.

2. EXPERIMENTAL SETUP

X-ray diffraction from a LGS crystal was studied in a double axis X-ray diffractometer scheme at the optics beamline BL14B1 at the SPring-8 (see Fig. 1) [3].

X-ray energy was selected by a double Si (311) monochromator. Primary and secondary slits with vertical and horizontal gaps of 1 × 5 mm were used to collimate the X-ray beam. The double axis diffractometer can achieve an angular resolution of ~ 1 arcsec. An NaI scintillation counter was used to measure the diffracted intensity. When the X-ray diffraction topography performed, the reflected beam image was recorded by a 2D X-ray detector (Beam Monitor, BM) with the pixel size of 6.0 μm. The BM consisted of a fluorescent screen and a CCD (Hamamatsu Photonics Co.).

3. SAMPLE

LGS is a piezoelectric crystal of space group symmetry 32. The crystal lattice is similar to the one of quartz with the parameters a = 8.170 Å and c = 5.095 Å [4].

LGS single crystal was grown by the conventional RF-heating Cz technique using an iridium crucible (50 mm diameter and height) [5]. The starting materials were prepared by mixing 99.99 % pure La_2O_3, Ga_2O_3 and SiO_2 powders in a stoichiometric ratio. The LGS single crystal was pulled in the <001> direction. The grown LGS crystal had a 25 mm diameter and 110 mm length.

The LGS single crystal showed a smooth surface.

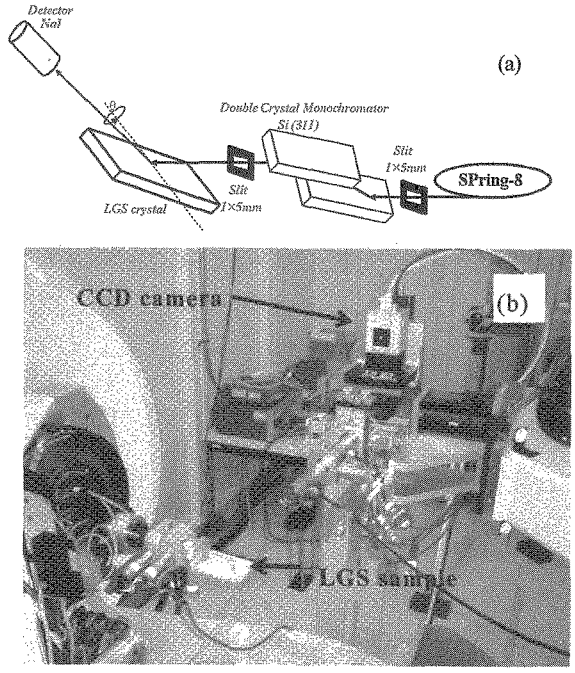

Fig. 1 (a) Schematic diagram of experimental setup. NaI detector was replaced with CCD camera when X-ray topography was performed. (b) Photograph of the experimental hutch around the LGS sample.

Since the X-ray penetration depth at 60 keV (λ = 0.2065 Å) of the LGS (about 5 μm) is much deeper than the surface roughness of the as-grown sample, we performed X-ray measurements without surface polishing.

4. EXPERIMENTAL RESULTS

4.1 Rocking curve measurement

A (110) growth plane of LGS was used for this experiment. Interplanar spacing for the (110) reflection in LGS is d = 4.087 Å. The X-ray energy was E = 60 keV. The crystal quality of the LGS single crystal was evaluate by the rocking curve width. Figure 2 shows the rocking curve profile of (25 25 0) reflection. The full width at half maximum (FWHM) was 16.75 arcsec and

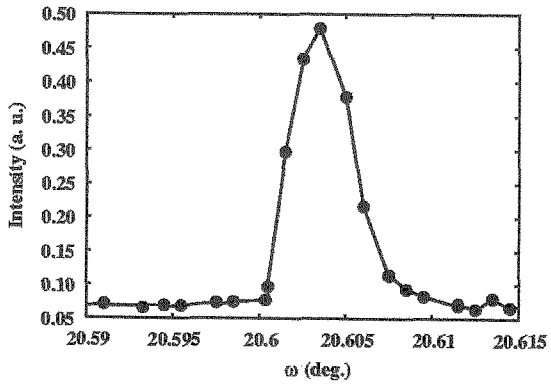

Fig. 2 Rocking curve profile of the LGS single crystal through (25 25 0) reflection

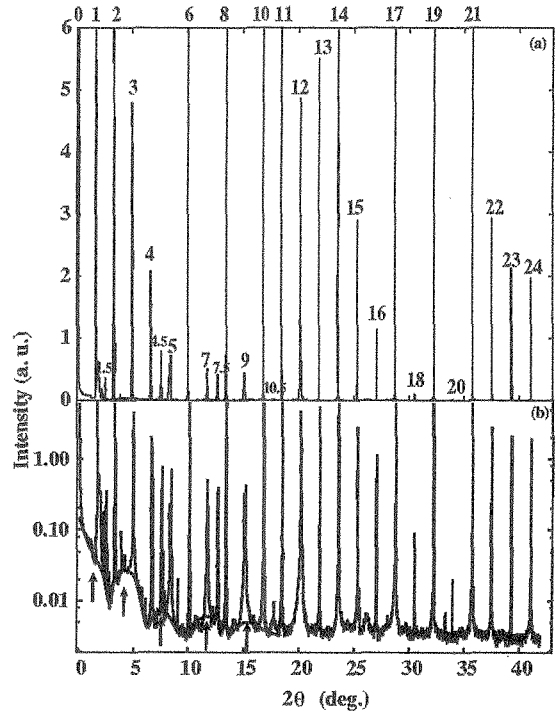

Fig. 3 (a) X-ray diffraction profile of the LGS single crystal along the (110) direction with 2θ/ω mode in linear scale. The numbers on the peak top positions show the index of (h h 0) reflections. The superlattice peaks of (h/2 h/2 0) are also visible. (b) The same data set in logarithmic scale. Arrows indicate weak broad peaks.

it was broader than we had expected. For example, the FWHM of LGS crystal grown at "FOMOS Materials Co." was 5 arcsec [6]. We speculated that the degradation of the crystal quality should originate from inhomogeneity and faceting habit in the growth process and it should be clarified by further investigation.

4.2 Superlattice peak

Figure 3(a) shows 2θ/ω scan spectra of (110)-growth plane of the LGS crystal. Sharp Bragg peaks were

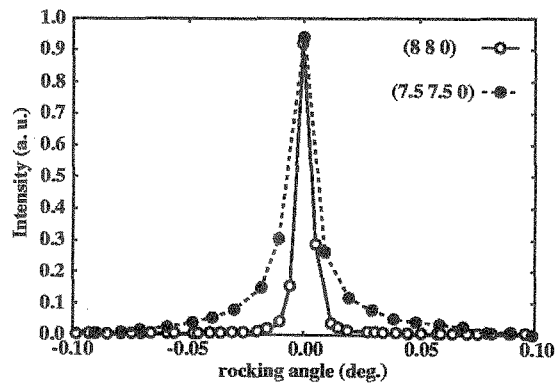

Fig. 4 Rocking curve profiles of the LGS single crystal through (8 8 0) fundamental peak and (7.5 7.5 0) superlattice peak.

observed through large 2θ region, confirming that the LGS is single crystal. In addition to the strong (*hh*0) Bragg peaks, (3/2 3/2 0), (9/2 9/2 0), (15/2, 15/2 0) and (21/2 21/2 0) peaks are visible in this profile. Although the (3/2 3/2 0), (9/2 9/2 0) and (15/2 15/2 0) peaks were also visible in laboratory X-ray measurement (RU-300, Rigaku Co., 50 kV 200mA), it is difficult to distinguish that the double periodic peaks are originate from the essential superlattice structure or higher harmonics of the laboratory X-ray source. The detailed measurements by the synchrotron X-ray revealed that the 3*H*/2 (only *H* = 1, 3, 5, 7) superlattice peaks existed. The FWHM of the superlattice peaks are broader than those of the (*hh*0) fundamental peaks, as shown in Fig. 4. Especially, the superlattice peaks showed large amount of diffuse scattering around off-Braggs, which imply that the coherence length of superlattice peaks is shorter than that of fundamental peaks. We have no idea to explain the origin of the superlattice structure, but it seems that somewhat self-correlation should exist. For example, one of a possibility of the superlattice reflections is a chemical ordering of Ga and Si in the *2d* site. Note that

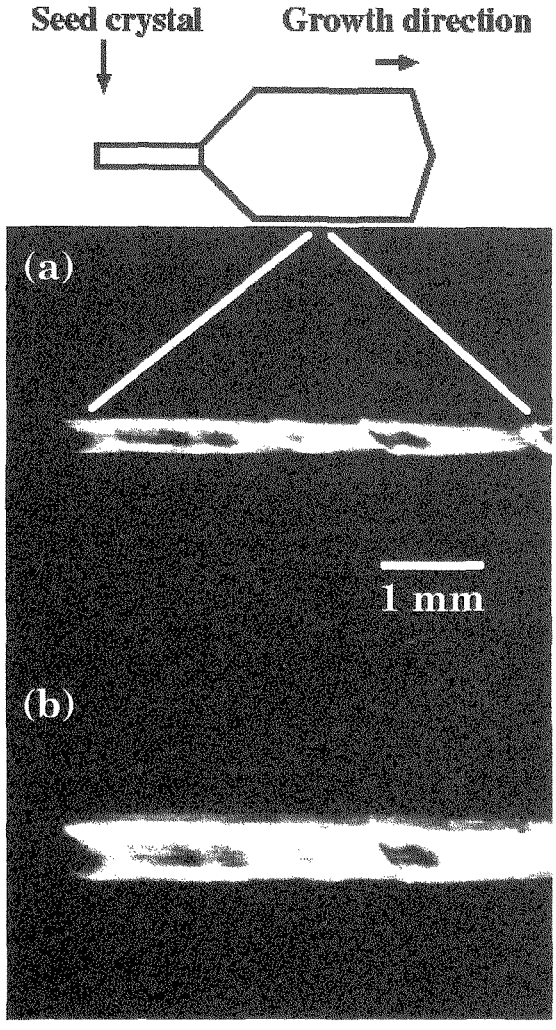

Fig. 5 X-ray diffraction topography image of the LGS single crystal with (a) (5 5 0) and (b) (7 7 0) reflections, respectively.

the structure analysis of this LGS single crystal has already performed by Takeda *et al.* and they refined the structure of the LGS single crystal [5].

4.3 Glassy behavior

Figure 3(b) shows $2\theta/\omega$ scan spectra of (110)-growth plane of the LGS crystal in the logarithmic scale. Broad peaks were observed around $2\theta = 4°$, 7° and 12°. These broad oscillations looks like that of amorphous samples. We speculated that these broad peaks are originated from the LGS of amorphous state. There have been some reports on the amorphous ferroelectric materials those were prepared by rapid quenching [7-9]. In the case of crystallization from amorphous state, it is often observed that the atomic position of the crystallized sample was disordered from the ideal position toward that of the amorphous state [10,11]. The LGS crystal was grown by the Cz technique and it was crystallized from LGS melt. Therefore, the LGS crystal should be grown in the matrix of the liquid and the amorphous LGS. The local network of the liquid and the amorphous LGS may be the cause of the fluctuation of the grown single crystal and it may affect the crystal quality. Although there is no long-range order structure, a rigid local network exists in the liquid and the amorphous LGS. Such local structure introduced a fluctuation into the grown single crystal and degraded the crystal quality [12].

4.4 X-ray topography

According to the preliminary experiments, the superlattice structure and the glassy behavior exist in the LGS single crystal grown by the Cz technique. These additional structures have a possibility for degradation of the crystal quality. Therefore, more detail experiment is needed to evaluate the LGS single crystal. One of the novel techniques is X-ray topography. X-ray diffraction imaging, historically called X-ray topography, is a classical technique used for the visualization of defects (dislocations, twins, domain walls, inclusions, impurity distribution, *etc.*) and macroscopic deformations (curvature, acoustic waves, *etc.*) present within the single-crystal sample [13-15]. The modern third-generation radiation sources offer enhanced possibilities thanks to the high energy and the low emittance of the electron beam, compared to that of previous synchrotron diffraction imaging [16, 17]. Thus, diffraction topographic investigations of heavy and bulky samples are feasible. These advantages can also be exploited for experiments with the LGS single crystal [18-20].

Figures 5(a) and 5(b) show the X-ray diffraction topography images of (550) and (770) reflections with the 60-keV high-resolution synchrotron X-ray. Since similar topographic images were obtained by using the different reflections, the topographic images exactly show the strain field of the LGS crystal. It has been indicated that the disproportion of the in-plane direction along the growth axis, but this is in the growth direction. This is the first time to observe such a strain field in our knowledge. The origin of the strain field should be the

Ga/Si ordering domain and the amorphous LGS phase, as mentioned before. It is necessary to control the Ga/Si ordering and to remove the lattice strain from the amorphous structure. We are planning to use the LGS single crystal for an X-ray optical crystal. The Bragg reflection from the LGS surface modulated by the surface acoustic wave (SAW) will separate depending on the input voltage without degrading the crystal quality. Since the X-ray intensity reduces without changing optical properties, the SAW-modified LGS crystal can be use for a novel attenuator.

5. SUMMARY

LGS single crystal grown by the Cz technique was investigated by X-ray topography with synchrotron sources. Clear strain field was observed even in the LGS single crystal, which showed a sharp rocking curve width. We also observe the superlattice structure which originate from the Ga/Si ordering and the hollow peak due to the short-range network of the amorphous LGS. These extra peaks should cause the strain field, which is observed by the X-ray topography.

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REFERENCES

[1] H. Fritze and H. L. Tuller, *Appl. Phys. Lett.*, **78**, 976-77 (2001).
[2] S. Uda, A. Bungo and C. Jian, *Jpn. J. Appl. Phys.*, **38**, 5516-19 (1999).
[3] Y. Yoneda, N. Matsumoto, Y. Furukawa and T. Ishikawa, *Physica Scripta*, **T115**, 995-97 (2005).
[4] E. Chilla, C. M. Flannery, H.-J. Fröhlich and U. Straube, *J. Appl. Phys.*, **90**, 6084-91 (2001)
[5] H. Takeda, S. Izukawa, H. Shimizu, T. Nishida, S. Okamura and T. Shiosaki, *Trans. of the Materials Research Soc. of Jpn.*, **30**, 63-66 (2005).
[6] D. V. Roshchupkin, D. V. Irzhak, R. Tucoulou, O. A. Buzanov, *J. Appl. Phys.*, **94**, 6692-96 (2003).
[7] A. M. Glass, M. E. Lines, K. Nassau and J. W. Schiever, *Appl. Phys. Lett.*, **31**, 249-51 (1977).
[8] A. A. Bahgat and T. M. Kamel, *Phys. Rev.*, B **63**, 012101 (2000).
[9] M. Takashige, S. Hamazaki, Y. Takahashi, F. Shimizu, T. Yamaguchi, M.-S. Jang and S. Kojima, *Jpn. J. Appl. Phys.*, **39**, 5716-18 (2000).
[10] Y. Yoneda, J. Mizuki, R. Katayama, K. Yagi, H. Terauchi, S. Hamazaki and M. Takashige, *Appl. Phys. Lett.*, **83**, 275-77 (2003).
[11] Y. Yoneda, S. Kohara, S. Hamazaki, M. Takashige and J. Mizuki, *Nucl. Inst. and Methods*, B **238**, 150-53 (2005).
[12] K. Suzuya, S. Kohara, Y. Yoneda and N. Umesaki, *Phys. Chem. Glasses*, **41**, 282-85 (2000).
[13] Y. Yoneda, Y. Kohmura, Y. Suzuki, S. Hamazaki and M. Takashige, *J. Phys. Soc. Jpn.*, **73**, 1050-53 (2004).
[14] Y. Yoneda, J. Mizuki, Y. Kohmura, Y. Suzuki, S. Hamazaki and M. Takashige, *Jpn. J. Appl. Phys.*, **43**, 6821-24 (2004).
[15] Y. Yoneda, Y. Kohmura, Y. Suzuki, S. Hamazaki, M. Takashige and J. Mizuki, *Trans. of the Materials Research Soc. of Jpn.*, **30**, 51-54 (2005).
[16] J. Baruchel, P. C. de Camargo, H. Klein, I. Mazzaro, J. Nogues and A de Oliveira, *J. Phys. D: Appl. Phys.*, **34**, A114-16 (2001).
[17] J. Baruchel, J. Hartwig and P. Pernot-Rejmankova, *J. Synchrotron Rad*, **9**, 107-12 (2002).
[18] Z. H. Hu, P. A. Thomas, A. Snigirev, I. Snigireva, A. Souvorov, P. G. R. Smith, G. W. Ross and S. Teat, *Nature*, **392**, 690-93 (1998).
[19] M. Drakopoulos, Z. W. Hu, S. Kuznetsov, A. Snigrev, I. Snigreva and P. A. Thomas, *J. Phys. D: Appl. Phys.*, **32**, A160-65 (1999).
[20] J.Brauchel, P. Cloetems, J. Hartwig, W. Ludwig, L. Mancini, P. Pernot and M. Sclenker, *J. Synchrotron Rad.*, **7**, 196-201 (2000).

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