Temperature Dependence of Second-Harmonic Intensity and Raman Shift in Langasite-Type Phases

Yoshihiro TAKAHASHI, Kenji KITAMURA,* Satoru INOUE,* Rie IHARA,** Yasuhiko BENINO,**
Takumi FUJIWARA** and Takayuki KOMATSU**

International Center for Young Scientists, National Institute for Materials Science, 1–1, Namiki, Tsukuba-shi, Ibaraki 305–0044
*Advanced Materials Laboratory, National Institute for Materials Science, 1–1, Namiki, Tsukuba-shi, Ibaraki 305–0044
**Department of Chemistry, Nagaoka University of Technology, 1603–1, Kamitomioka-cho, Nagaoka-shi, Niigata 940–2188

ランガサイト相における第二高調波強度及びラマンシフトの温度依存性

高橋儀宏・北村健二*・井上　悟*・井原梨恵**・紅野安彦**・藤原　巧**・小松高行**

物質・材料研究機構若手国際研究拠点，305-0044 茨城県つくば市並木 1-1
*物質・材料研究機構物質研究所，305-0044 茨城県つくば市並木 1-1
**長岡技術科学大学化学系，940-2188 新潟県長岡市上富岡町 1603-1

In this study, we examined the temperature dependence of the second-harmonic (SH) intensity and Raman shift in the langasite-type $Ba_3Ga_2Ge_4O_{14}$ (BGG) and $Na_2CaGe_6O_{14}$ (NCG) crystalline phases. The SH intensity curves revealed an anomalous temperature behavior around 370°C and 270°C in the BGG and NCG phases, respectively. Furthermore, as a result from the Raman spectral measurement, it was suggested that the anomaly observed in the lagasite-type phases originated in the *A*-site. 〔Received July 15, 2005; Accepted August 19, 2005〕

Key-words : Langasite-type phase, Second-harmonic generation, Raman spectroscopy, Temperature dependence

1. Introduction

Langasite $(La_3Ga_5SiO_{14})$-type crystals (space group *P*321) are expected to be promising materials for surface acoustic wave devices for mobile communications. To date, a number of langasite-type single crystals have been grown and extensively investigated from the standpoint of their piezoelectric property.[1)-5)] It is reported that the langasite crystal has no phase transition up to the melting temperature, meaning that the langasite crystal should not show any structural changes. However, from research on the langasite-type single crystals, an anomalous temperature behavior could be noticed.[6)-9)] Lakin et al. reported that the $La_{2.7}Nd_{0.3}Ga_5SiO_{14}$ crystal had anomalies of thermal expansion of the unit cell.[6)] In addition, the observation of an abnormal thermal expansion above 230°C was also reported for the $Sr_3TaGa_3Si_2O_{14}$ crystal by Wang et al.[9)] Nevertheless, the origin of the anomaly is still unclear.

The optical property is a result from the interaction between the incident light, and the atom, ion and lattice in the material. That is to say, a variation in the optical properties corresponds to the change in the bonding state in the crystal. Therefore, it is expected that the second-order optical nonlinearity and Raman spectroscopy are quite sensitive to the change in the distance between the oxygen and cation in the crystal[10)] and the phase transition.[11),12)] In this study, we measured the second-harmonic (SH) intensity and Raman shift in the langasite-type $Ba_3Ga_2Ge_4O_{14}$ and $Na_2CaGe_6O_{14}$ phases as a function of the temperature for the first time in order to check the anomalous temperature behavior in the langasite-type phases and to clarify which site acts as the key role in the anomaly.

2. Experimental

2.1 Sample preparation

The langasite-type phases examined in the present study were $Ba_3Ga_2Ge_4O_{14}$ (designated as BGG) and $Na_2CaGe_6O_{14}$ (NCG). The BGG and NCG polycrystalline samples were synthesized by fully-crystallization of the glasses with the stoichiometric composition of the BGG and NCG.[13)] The formations of the single phases of the BGG and NCG crystals were confirmed by powder X-ray diffraction analysis. The obtained polycrystalline samples were ground, pressed into pellets at 10^3 kg/mm² and re-sintered at 1000°C for 12 h in air. These samples were polished on both sides to a thickness of about 0.2 mm in order to fit the sample box on a heat stage for temperature control of the samples.

2.2 Second-harmonic generation and Raman spectral measurements

Temperature dependence of the SH intensity for the langasite-type crystalline samples was measured on the basis of powder technique developed by Kurtz and Perry.[14)] The SH intensity measurement was carried out using the fundamental wave of a Q-switched Nd: yttrium-aluminum-garnet (YAG) laser at the wavelength of 1064 nm (Quanta-Ray, Spectra-Physics) as the incident light. The temperature around the langasite-type crystalline samples was adjusted using the heat stage (LK–600PM, Linkam Scientific Instruments, Ltd.) in the range from room temperature (*R.T.*) to 550°C. The SH signal generated from the samples was detected by a photomultiplier tube after shutting off the incident light (1064 nm). The temperature dependence of the Raman scattering spectra was measured by excitation of an Ar^+ laser operating at 488.0 nm (ILT 5000, Ion Laser Technology, Inc.). The output power of the laser is ~15 mW. The temperature control of the samples was also performed by the heat stage. The range of the wavenumber in the Raman spectral measurements was 250–1200 cm^{-1}.

3. Results

Figure 1 shows the SH intensities as a function of temperature for the langasite-type phases in this study, together with the result for the $BaTiO_3$ polycrystalline phase as an example. For the $BaTiO_3$ phase, the SH intensity curve is drastically

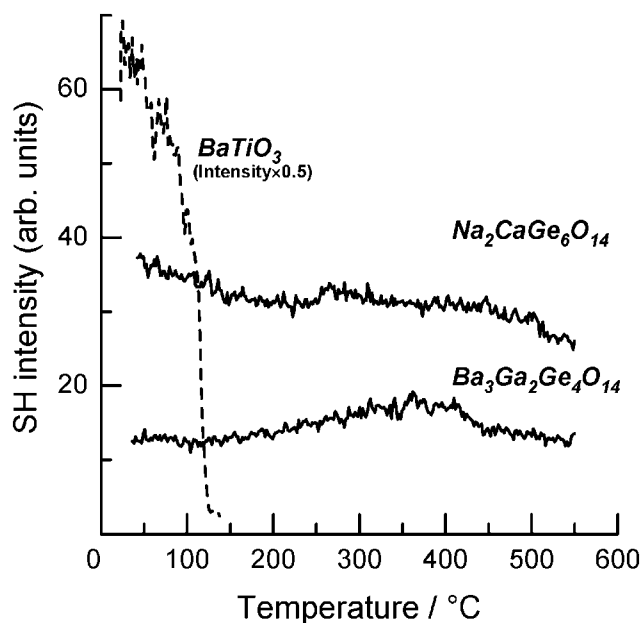Fig. 1. Temperature dependence of SH intensities in langasite-type $Ba_3Ga_2Ge_4O_{14}$ and $Na_2CaGe_6O_{14}$ crystalline phases (solid line). The $BaTiO_3$ phase synthesized by a solid-state reaction is also included in this figure (dashed line). The value of the SH intensity for the $BaTiO_3$ phase is multiplied by 0.5 in order to better fit in this graph.

Fig. 2. Raman scattering spectra of langasite-type $Ba_3Ga_2Ge_4O_{14}$ and $Na_2CaGe_6O_{14}$ phases. The spectrum of the $La_3Ga_5SiO_{14}$ phase synthesized by a solid-state reaction at 1350°C is also included.

decreased with the increasing temperature, and eventually reaches a minimum at ∼125°C. On the other hand, the langasite-type crystalline phases showed no significant changes in the SH intensities unlike the $BaTiO_3$ sample (Fig. 1). However, a small "hump" and "discontinuity" could be observed around 370°C and 270°C in the SH intensity curves of the BGG and NCG phases, respectively.

The Raman spectra of the BGG and NCG crystalline phases are shown in **Fig. 2**, together with that of $La_3Ga_5SiO_{14}$ phase. The BGG and NCG phases indicated significantly simple and clear Raman spectra, allowing us to distinguish each Raman band. However, in the $La_3Ga_5SiO_{14}$ phase, the Raman bands in the spectrum are vague in the lower and middle wavenumber regions in spite of its high crystallinity, which was confirmed by the powder XRD. The BGG and NCG phases are quite appropriate for the investigation of the Raman shift as a function of temperature, therefore, these phases have been selected as the specimen in this study.

The temperature dependence of the typical peak shift of the Raman bands in the BGG and NCG phases are shown in **Fig. 3**. The SH intensity curves of the BGG and NCG phases are shown together with Fig. 3. In the middle and higher wavenumber regions, the Raman peaks were monotonically shifted to lower wavenumbers, corresponding to the increase in the bond distance due to the thermal vibration. On the other hand, in the lower wavenumber region of both samples (∼300 cm^{-1}, and ∼280 and ∼400 cm^{-1} for the BGG and NCG phases, respectively), the response of the Raman shifts to the temperature also revealed the hump or the discontinuity at 400°C and 200–300°C in the BGG and NCG phases, respectively.

4.   Discussion

It is known that the $BaTiO_3$ crystal has a ferroelectric-paraelectric phase transition around 125°C, i.e., Curie point (T_c), and its spontaneous polarization, P_s, decreased as the temper-
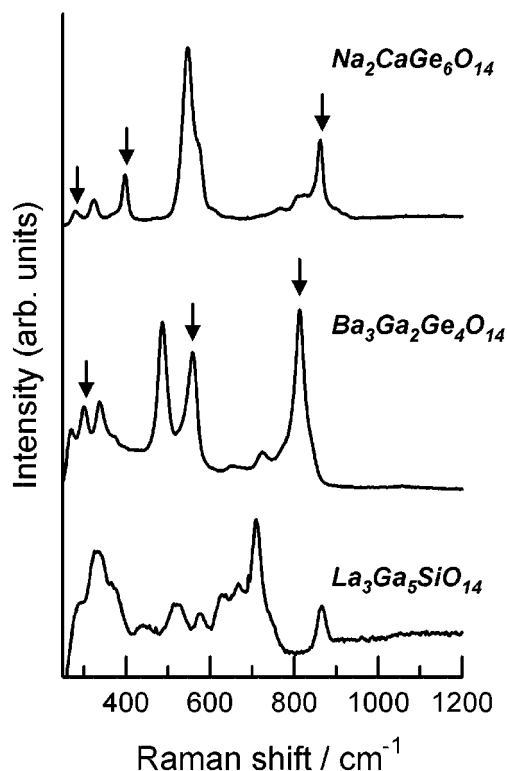
ature reached the T_c, and finally disappeared at the T_c according as Curie–Weiss' law, i.e., $P_s \propto (T_c - T)^{1/2}$. This result for the $BaTiO_3$ phase clearly indicates that the measurement of the SH intensity as a function of temperature is valid for this experimental system. In this study, the behavior of the SH intensity curves are quite similar to the response of the Raman shifts at elevated temperature; the position of the hump and the discontinuity of the SH intensity curves is well overlapped at that of Raman shift. Therefore, it is considered that the hump detected in the SH intensity curves implies a structural change.

The anomalous Raman shift around ∼300 cm^{-1} in the BGG phase and ∼280 and ∼400 cm^{-1} in the NCG phase could also be confirmed. According to the Raman spectroscopic studies, these Raman bands could be assigned to the Ba–O (∼300 cm^{-1}), Na–O (∼280 cm^{-1}) and Ca–O vibration modes (∼400 cm^{-1}).[15]-[20] The chemical formula of the langasite-type crystals is represented by $A_3BC_3D_2O_{14}$, where elements A and B occupy the deca- and octahedral sites, respectively, and elements C and D occupy the different tetrahedral sites. In the langasite structure, the large atoms, such as alkali, alkari earth and lanthanide elements, occupy the decahedral A-site. Meanwhile, the Raman scattering originated in the dipole moment of the crystal, and then the polarization could be modulated by the atomic displacement due to the lattice vibration in the crystal. This means that the peak shift in the Raman band exactly corresponds to the change in the bond distance. Hence, the hump and discontinuity seen in the Raman band shifts of the langasite-type phases most likely originated from the anomalous motion of the A–O bond.

It is reported that the size of the atom occupying at the A-site significantly influences the d_{11} of the piezoelectric
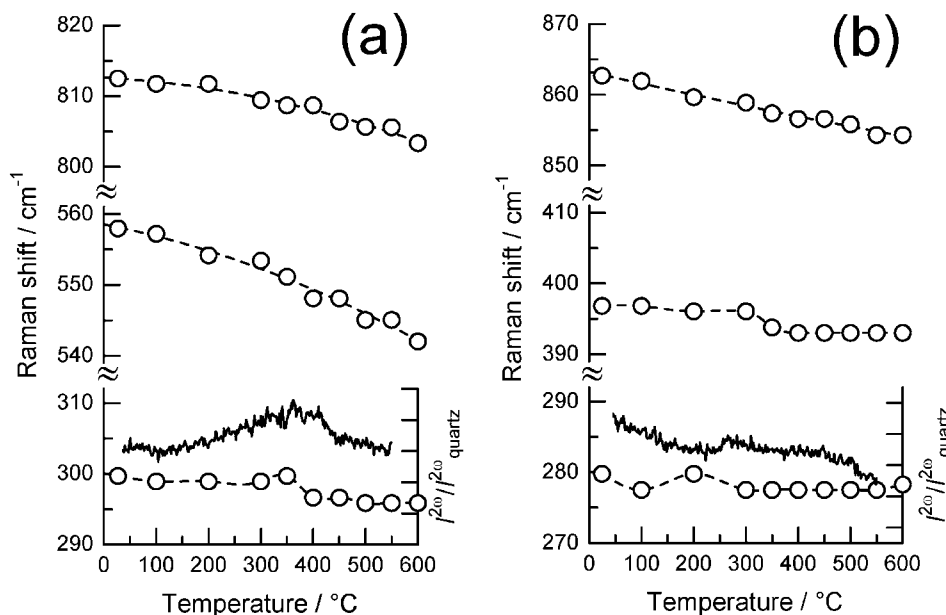
Fig. 3. Variation in the peak shift as a function of temperature of the langasite-type (a) $Ba_3Ga_2Ge_4O_{14}$ and (b) $Na_2CaGe_6O_{14}$ phases. The peaks plotted in Figs. 3(a) and (b) are indicated by the arrows in Fig. 2.

constant[21] and the second-order optical nonlinearity.[13] In principle, the SH signal observed from the langasite-type poly-crystalline samples is coming from only the d_{11} element of the second-order optical nonlinear coefficient of the corresponding single crystal, because the point group of the langasite-type crystal is D_3 (32).[14] In this study, it was strongly suggested that the anomaly, that is, the small hump and discontinuity observed in the SH intensity curves in the temperature range of $R.T.$–550°C, directly reflects the anomalous behavior of the A–O bond in the langasite structure. However, it is still not clear why the A-site indicates such an anomalous behavior. Therefore, more detail investigations, for example, high-temperature X-ray and its Rietveld analyses, are necessary. Further study is now in progress.

Pavlovska et al. reported that under compression, the volume of the AO_8 decahedra with weak bonds was first decreased.[22] In addition, the displacement of a part of La atom was recently found in the langasite-type crystal.[23] These reports suggest that the A-site is a possible site to trigger the structural change. Mill et al. described that the isomorphous phase transitions, e.g., jumpwise changes in atomic coordinates, formation of a new position, etc., are possible in the langasite structure in the high temperature region.[24] Therefore, it is probable that the anomaly detected in the Raman spectral measurement indicates the isomorphous phase transition proposed by Mill et al.

5. Summary

In this paper, we presented the anomalous temperature behavior of the langasite-type $Ba_3Ga_2Ge_4O_{14}$ (BGG) and $Na_2CaGe_6O_{14}$ (NCG) crystalline phases based on optical and spectroscopic measurements. The anomalous behaviors were detected at ∼370°C and ∼270°C in the BGG and NCG phases, respectively, using the second-harmonic intensity measurement as a function of temperature. In addition, the similar anomaly could also be confirmed at 350°C and 200–300°C in the Raman shift of the BGG and NCG phases, respectively. It was strongly suggested that these behaviors originated in the motion of the A-site in the langasite struc-

ture. It was considered that our study revealed this intrinsic peculiarity in the langasite-type crystal using an optical technique for the first time.

References

1) Andreev, I. A. and Dubovik, M. F., *Sov. Tech. Phys. Lett.*, Vol. 10, pp. 205–207 (1984).

2) Hornsteiner, J., Born, E. and Riha, E., *Phys. Stat. Solidi (a)*, Vol. 86, pp. R3–R4 (1997).

3) Takeda, H., Uecker, R., Kumatoriya, M., Shimamura, K., Reiche, P. and Fukuda, T., *Cryst. Res. Technol.*, Vol. 32, pp. 939–945 (1997).

4) Adachi, M., Sawada, Y., Funakawa, T. and Karaki, T., *Ferroelectrics*, Vol. 273, pp. 89–94 (2002).

5) Uda, S., Wang, S.-Q., Konishi, N., Inaba, H. and Harada, J., *J. Cryst. Growth*, Vol. 275, pp. 251–258 (2005).

6) Lakin, E. E., Dubovik, M. F. and Krasnopol'skii, I. V., *Inorg. Mater.*, Vol. 25, pp. 1043–1044 (1989).

7) Stade, J., Bohatý, L., Hengst, M. and Heimann, R. B., *Cryst. Res. Technol.*, Vol. 37, pp. 1113–1120 (2002).

8) Wang, Z., Cheng, X., Yuan, D., Pan, L., Guo, S., Xu, D. and Lv, M., *J. Cryst. Growth*, Vol. 249, pp. 240–244 (2003).

9) Wang, Z., Yuan, D., Xu, D., Lü, M., Cheng, X. and Pan, L., *Mater. Res. Bull.*, Vol. 39, pp. 987–992 (2004).

10) Abrahams, S. C., Kurtz, S. K. and Jamieson, P. B., *Phys. Rev.*, Vol. 172, pp. 551–553 (1968).

11) Baskaram, N. and Chang, H., *Mater. Chem. Phys.*, Vol. 77, pp. 889–894 (2002).

12) Takahashi, Y., Kitamura, K., Benino, Y., Fujiwara, T. and Komatsu, T., *Mater. Sci. Eng. B*, Vol. 120, pp. 155–160 (2005).

13) Takahashi, Y., Saitoh, K., Benino, Y., Fujiwara, T. and Komatsu, T., *J. Ceram. Soc. Japan*, Vol. 112, pp. 61–64 (2004).

14) Kurtz, S. K. and Perry, T. T., *J. Appl. Phys.*, Vol. 39, pp.

3798–3813（1968）.

15) Takahashi, Y., Kitamura, K, Inoue, S., Benino, Y., Fujiwara, T. and Komatsu, T., *Jpn. J. Appl. Phys.*, in press.

16) Shaw, C. M. and Shelby, J. E., *Phys. Chem. Glasses*, Vol. 32, pp. 48–54 (1991).

17) Markgraf, S. A. and Sharma, S. K., *J. Am. Ceram. Soc.*, Vol. 75, pp. 2630–2632 (1992).

18) Markgraf, S. A. and Sharma, S. K., *J. Mater. Res.*, Vol. 8, pp. 635–647 (1993).

19) Verweij, H. and Buster, J. H. J. M., *J. Non-Cryst. Solids*, Vol. 34, pp. 81–99 (1979).

20) Xia, H. R., Meng, X. L., Cheng, X. F., Li, L. X., Zhu, L. and Zheng, W. Q., *Mater. Sci. Eng. B*, Vol. 100, pp. 107–112 (2003).

21) Iwataki, T., Ohsato, H., Tanaka, K., Morikoshi, H., Sato, J. and Kawasaki, K., *J. Eur. Ceram. Soc.*, Vol. 21, pp. 1409–1412 (2001).

22) Pavlovska, A., Werner, S., Maximov, B. and Mill, B., *Acta Crystallogr.*, Vol. B58, pp. 939–947 (2002).

23) Pugacheva, A. A., Maksimov, B. A., Mill, B. V., Pisarevskii, Yu. V., Kondakov, D. F., Chernaya, T. S., Verin, I. A., Molchanov, V. N. and Simonov, V. I., *Crystallogr. Rep.*, Vol. 49, pp. 53–59 (2004).

24) Mill, B. V., Makshimov, B. A., Pisarevskii, Yu. V., Danilova, N. P., Pavlovska, A., Werner, S. and Schneider, J., *Crystallogr. Rep.*, Vol. 49, pp. 60–69 (2004).