In situ Observation of $BaTa_2O_6$ up to 1573 K by Ultraviolet Laser Raman Spectroscopy

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Raman spectra of $BaTa_2O_6$ have been successfully obtained at temperatures up to 1573 K for the first time, using a continuous-wave ultraviolet Raman spectroscopic system designed to measure the Raman scattering from materials at high temperature. The typical Raman spectra of the orthorhombic phase (Type I) were recorded in the region of room temperature to 1573 K. The present result is described in terms of the parameter related to temperature variation at constant pressure, defined in a similar way to the Gruneisen parameter. Raman bands located above 250 cm^{-1} and the mode at 169 cm^{-1} show smaller values of the parameter than lower frequency modes below 250 cm^{-1} except the mode at 169 cm^{-1}, suggesting that these higher frequency modes and the mode at 169 cm^{-1} are assigned to TaO_6 internal modes.

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1 Introduction

The $BaO–Ta_2O_5$ system has long been studied because of its wide possible applications[1]. $BaTa_2O_6$ is one of the most interesting materials in current technologies due to photocatalytic property[2] and electrical property[3],[4]. The nature of chemical bonds in the crystal structure is one of the most important keys to deciding their physical and chemical properties[3]. Introducing structural perturbations into the structure of these compounds gives valuable insight into the properties of the chemical bonds. Variations of pressure and temperature and substitution of isomorphous ions are available means to introduce structural perturbations.

The structural studies of $BaTa_2O_6$ have been performed using X-ray diffraction (XRD) analysis[5]~[7]. However, XRD reveals structural variation through static atomic displacements. On the other hand, Raman scattering approaches the issue of structural perturbations from a dynamic point of view, through the frequency shifts of vibrational modes. The same vibrational spectra recorded at high temperatures and high pressures reveal detailed information on bonds and crystal physical properties, and also provide constraints on thermodynamic properties at temperatures and pressures beyond the range of direct thermodynamic measurements. However, the measurable region of the temperature is limited under conventional Raman spectroscopy using visible-region excitation[8],[9]. It is difficult to detect weak Raman scattering from substances at high temperatures in comparison with an intense continuous background due to thermal emission. In such a case continuous-wave (CW) ultraviolet (UV) Raman spectroscopy is more suitable for the measurements at high temperatures, because the UV excitation shifts the Raman scattering to shorter wavelengths away from the intense thermal emission peak. Recently, we have used UV Raman spectroscopy to observe the phase transition in $SrZrO_3$ at ~1473 K[10], OH vacancies arising in hydroxyapatite at high temperatures[11], the phase transition of hafnia at

~2085 K[12], an anharmonic lattice mode of Ca_2SiO_4 up to 1723 K[13] and vibrational spectra of Ca_3SiO_5[14].

In the present study, we have successfully observed the Raman spectra of $BaTa_2O_6$ at high temperatures up to 1573 K, which have not yet been reported, using UV Raman spectroscopic system designed to measure the Raman scattering from substances at high temperature. The result is discussed here from the point of view of the properties of the chemical bonds in terms of the parameter γ_{iP}, defined in a similar way to the Gruneisen parameter, γ_{iT}. Moreover, the assignments of the respective bands of the $BaTa_2O_6$ Raman spectrum are predicted through the properties of the chemical bonds. This information would help to understand the relation between the photocatalytic and electrical properties and the structural change.

2 Experimental procedure

A compositionally homogeneous sample is important for measuring the Raman spectra. For this reason, the polymerized complex method was used to synthesize $BaTa_2O_6$, which is a proper method for synthesis of polycrystalline samples due to different metal ions dispersing homogeneously at atomic level[15]. $TaCl_5$ (Junsei chemical Co., LTD, Japan) was used as a source of tantalum, which was precisely weighed and dissolved into methanol in nitrogen atmosphere in order to avoid hydrolysis. The $TaCl_5$ methanol solution was added into a mixture of ethylene glycol (Kanto Kagaku Co., Ltd., Japan) and anhydrous citric acid (Wako Pure Chemical Co., Inc., Japan). $BaCO_3$ (78.48 % as BaO content, Seimi Chemical Co., Inc., Japan) was placed in this solution. A quantity of three times the anhydrous citric acid was used when the charge balance was taken into account assuming charged valences of Ta ions, Ba ions and $C_6H_8O_7$ to be $+5$, $+2$ and -3, respectively. Above procedures were carried out with stirring at room temperature. After adding all needed chemicals, the mixture was heated up to ~403 K with stirring until all chemicals added were dissolved into the solution. For promoting ester reaction, the temperature was raised up to 473 K. As the solution became concentrated, it became highly viscous, accompanied by a change in color from colorless to yellow. The pyrolysis of the polymerized complex was carried out in air at 723 K in order to remove most organics. The obtained powder was treated thermally at 1073 K for 2 hours. The treated powder was pressed to be pellet shape. This pellet sample was sintered at 1273 K for 24 hours. X-ray diffraction was used to identify the phase of the sintered powder of $BaTa_2O_6$.

Raman measurements for the $BaTa_2O_6$ sample at various temperatures were performed using a new CW UV Raman spectroscopic system based on an ultraviolet argon-ion laser (363.8 nm), a spatial filter, a triple monochromator, and a two-dimensional charge-coupled device detector. The sample was set in a furnace with a Pt–Rh heater, where the sample was fixed onto a Pt–13 %Rh thermocouple with alumina cement. The sample was heated at a rate of 10 K/min. Each measurement was conducted in air after a constant temperature had been maintained for 10 minutes. The laser power at tube level was at 130 mW, and the entrance slit width was set at 100 μm, which corresponds to a full-width-at-half-maximum of 4.7 cm^{-1}. An Hg line was used for Raman-shift calibration for each measurement. At 1573 K, the background of thermal emission from the sample and the furnace was measured without the laser line, and then that was subtracted from the Raman spectrum measured at this temperature. At room temperature, the Raman spectrum of the sample was finally measured again after the furnace was cooled down. No artificial smoothing was used on the acquired Raman spectra.

3 Results

It is currently accepted that four phases of $BaTa_2O_6$ can exist at atmospheric pressure. $BaTa_2O_6$ is structurally characterized by layer networks of TaO_6 octahedra[6],[7]. Orthorhombic phases probably have a structure in which pairs of edge-sharing octahedra are joined at corners. In the tetragonal phase, the octahedra may share only corners. In the hexagonal phase, there are both a network of edge-sharing pairs and corner sharing octahedra. Two kinds of orthorhombic phases were reported: type I and type II as described in Refs. 5 and 16. Layden[5] has reported that the orthorhombic (type I), tetragonal, and hexagonal phases were obtained when the specimen was quenched from below 1423 K, between about 1423 K and 1573 K, and from 1573 K to its melting point, respectively. At room temperature, the powder XRD pattern of the present sample (**Fig. 1**(a)) showed that the sample was the orthorhombic phase (Type I) and the single phase.

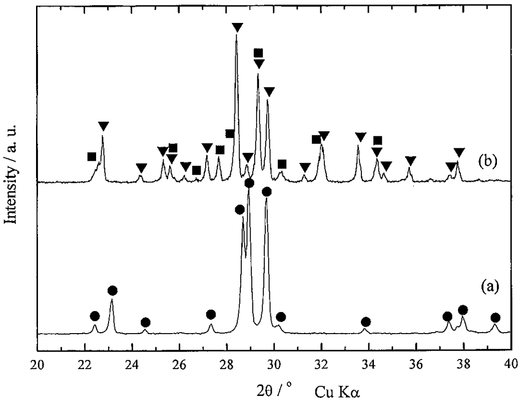

Fig. 1 XRD patterns of the $BaTa_2O_6$ samples at room temperature (a) before and (b) after the sample has been heated for Raman measurement up to 1673 K and then cooled down in the furnace. The symbols, ●, ▼, and ■, denote the diffraction peaks from orthorhombic, hexagonal, and tetragonal phases, respectively.

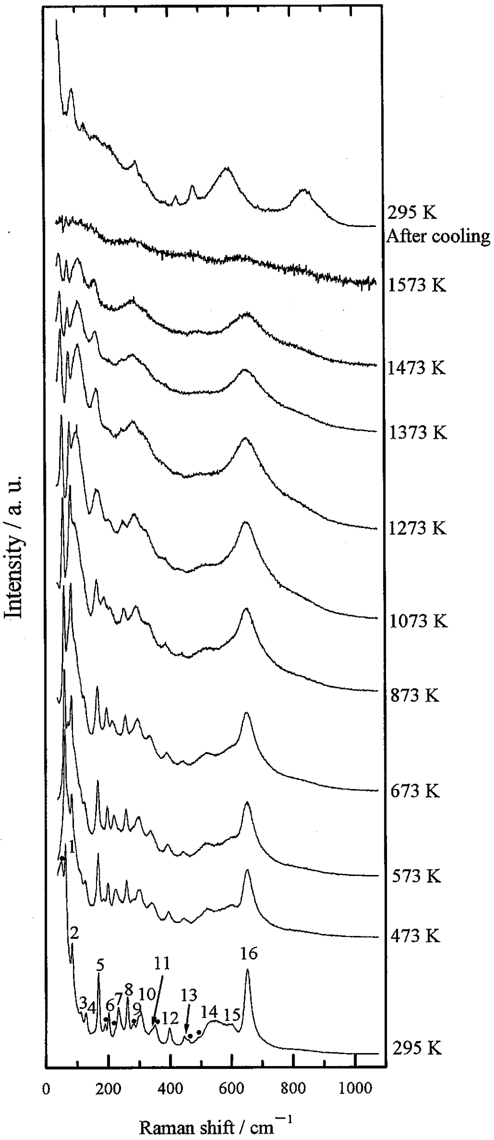

Fig. 2 Temperature dependence of the Raman spectra of $BaTa_2O_6$ excited by the 363.8 nm UV laser line. Peaks of considered Raman bands are labeled by $i=1$ to 16 with small peaks (●).

Fig. 2 shows the result of Raman spectra measured at high temperatures. Raman spectrum at 298 K shows the typical spectrum of the orthorhombic $BaTa_2O_6$ (Type I)[17]. The spectra showed sixteen Raman bands and more, $i=1$ to $i=16$, in order of increasing frequency. With an increase in sample temperature, all bands broadened and showed a continuous shift, however, did not change significantly up to 1573 K. According to the XRD pattern of the sample quenched from 1573 K, there would be present of a mixture of Raman spectra of the orthorhombic (Type I) and the tetragonal phase at 1573 K. At 1673 K, the full-width at the half-maximum of the Raman spectrum was too large to observe. The spectra did not return to the initial pattern at 298 K after the sample had been heated up to 1673 K and then cooled down in the furnace. The XRD pattern of the sample after cooling shows the hexagonal phase with a small amount of the tetragonal phase (Fig. 1(b)). Two-phase coexistence and hysteresis are characteristic of first-order transition. This interpretation is consistent with the fact that transitions among those phases are reconstructive[6]. The overcoming of an energy barrier is responsible for the occurrence of the phase transitions.

Pattern decomposition of the Raman bands was performed assuming the Lorentzian functions. Relations describing the dependencies of the frequencies on temperature were obtained by fitting the results by the least-squares rule, as follows:

$$\omega_i = \omega_{i0} + (\partial\omega_i/\partial T)_P(T - T_0) \qquad (1)$$

where the subscripts "0" refer to the parameter values extrapolated at 298 K and 0.1 MPa. The results are presented in **Table 1** and **Fig. 3**.

Table 1 Slopes of Regression Lines for Frequencies as a Function of Temperature, and $\alpha \cdot \gamma_{iP}$ Values for each Raman-Active Mode.

i	ω_{i0} (cm^{-1})	$(\partial \omega_i / \partial T)_P$ (cm$^{-1}\cdot$K^{-1})	$\alpha \cdot \gamma_{iP} \times 10^4$ (K^{-1})
1	64.49(7)	−0.01374(7)	2.128(9)
2	85.9(1)	−0.01140(8)	1.327(8)
3	114.4(7)	−0.0122(7)	1.11(6)
4	129.3(5)	−0.0122(6)	0.94(4)
5	168.89(8)	−0.0057(1)	0.336(6)
6	203.0(2)	−0.0204(3)	1.00(1)
7	233.5(3)	−0.0385(4)	1.65(1)
8	261.9(1)	−0.0139(2)	0.531(6)
9	297.3(9)	−0.018(1)	0.59(4)
10	307(1)	−0.016(1)	0.51(4)
11	341(1)	−0.017(1)	0.49(3)
12	398.6(4)	−0.0167(5)	0.42(1)
13	447(1)	−0.012(1)	0.26(3)
14	534(1)	−0.030(1)	0.55(2)
15	600(2)	−0.013(3)	0.22(5)
16	652.8(1)	+0.0033(1)	−0.051(2)

Numbers in parentheses represent standard deviation in the last digit of numerical values. ω_{i0} refers to the frequency at 298 K and 0.1 MPa estimated by extrapolating Raman shifts in the whole range of temperature.

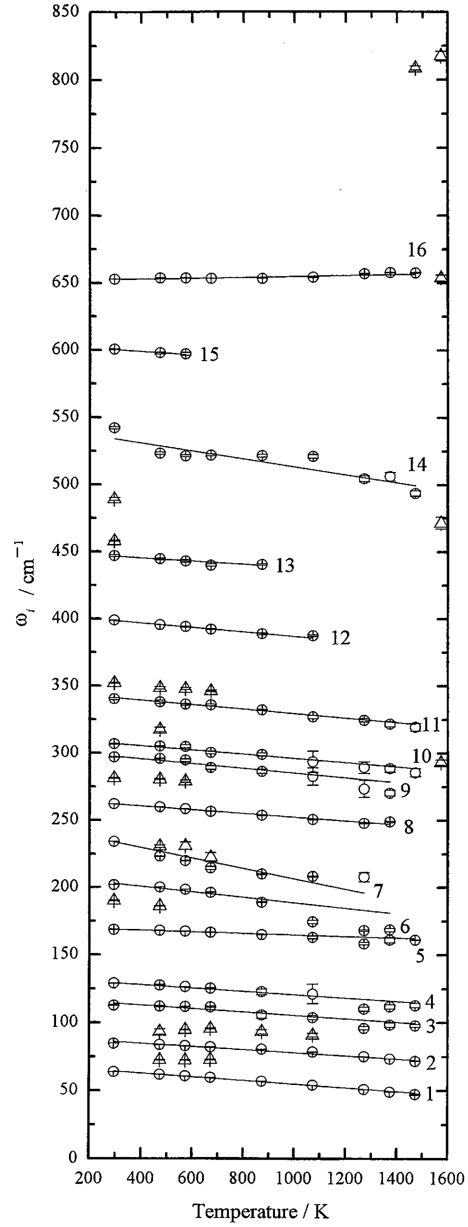

Fig. 3 Temperature dependence of the Raman bands of $BaTa_2O_6$ at room pressure. Straight lines represent fits by least-squares regression with weights $w = (\text{error})^{-2}$ on the considered Raman bands ($i = 1$ to 16) denoted by symbols (○). The frequencies of bands other than the ith considered ones are plotted using symbols (△).

4 Discussion

We discuss the present results here in terms of the temperature-varied parameter at constant pressure associated with the Gruneisen parameter. In the following equations, γ_{iT} is the Gruneisen parameter of a considered mode (i), related to pressure variation at constant temperature, and γ_{iP} the constant-pressure parameter with temperature variation, defined in a way similar to γ_{iT}[18),19)].

$$\gamma_{iT} = \left(\frac{\partial \ln \omega_i}{\partial \ln \rho}\right)_T = \frac{K_T}{\omega_i}\left(\frac{\partial \omega_i}{\partial P}\right)_T \qquad (2)$$

$$\gamma_{iP} = \left(\frac{\partial \ln \omega_i}{\partial \ln \rho}\right)_P = -\frac{1}{\alpha \omega_i}\left(\frac{\partial \omega_i}{\partial T}\right)_P \qquad (3)$$

Here, ρ is the molar density, α the volume thermal expansion of the crystal, and K_T the bulk modulus, which characterizes the incompressibility of the structure. These parameters are crucial to assigning Raman bands. Values of $\alpha \cdot \gamma_{iP}$ for each Raman-active mode, estimated from Eq. (3), are summarized in Table 1. In this study, the $\alpha \cdot \gamma_{iP}$ parameter was estimated as a substitute of γ_{iP} because the value of α is not yet reported. The value for $(\partial\omega_i/\partial T)_P$ is estimated from the spectra observed at high temperatures. The γ_{iP} parameter is proportional to the local thermal expansion coefficient of a considered bond (i), α_i; $\gamma_{iP} \propto \alpha_i/\alpha$[19].

Raman and IR spectra generally can be described in terms of internal modes and external lattice modes. Modes derived from motions into the TaO_6 group are considered to be the internal modes, to distinguish them from the external modes involving Ba and Ta lattice vibrations. For the higher frequency bands ($i=8$ to 16) and the band at 169 cm^{-1} ($i=5$), the values of the $\alpha \cdot \gamma_{iP}$ parameter are smaller than for the lower frequency modes ($i=1$ to 7 except $i=5$), which represents smaller α_i values, reflecting their relative incompressibility, weak expansivity, and strong bonds. The thermal expansion coefficient of the tetrahedral units is smaller than that of the crystal[20]. This result shows that these high frequency modes above 250 cm^{-1} and the band at 169 cm^{-1} can involve stretching and bending motions of the Ta—O bonds in the TaO_6 octahedra (internal modes).

On the other hand, $\alpha \cdot \gamma_{iP}$ is larger for the lower frequency bands of $i=1$ to 7 except $i=5$ than for the bands of $i=5$ and $i=8$ to 16, which indicates that the oscillators have a larger α_i value, reflecting their relative compressibility, strong expansivity, and weak bonds. The weaker bonds are caused by lower charged atoms and higher coordination numbers. All the Ba ions are accommodated in sixteen coordinated sites. Thus, these bands can be mainly assigned to lattice vibrational modes (translational lattice modes of Ba or Ta and/or rotational lattice modes of TaO_6). Overall pressure- and temperature-induced volume changes are taken up by weaker bonds in the crystal structure. These results are qualitatively supported by the force field calculated from a vibrational analysis[16]. Translational lattice modes of Ba or Ta and rotational lattice modes of TaO_6 were predicted to occur in the regions of 71–124 cm^{-1} and 244–353 cm^{-1}, which is corresponding to $i=1$ to 4 and $i=6$ to 7, respectively.

5 Conclusions

In the present study, the Raman spectra of $BaTa_2O_6$ were successfully obtained at temperatures up to 1573 K for the first time, using a new system of UV Raman spectroscopy. The typical Raman spectra of the orthorhombic phase (Type I) were recorded at the room temperature and high temperatures. The present results have been discussed in terms of the constant-pressure parameter with temperature variation, defined in a similar way to the Gruneisen parameter. For the Raman bands located above 250 cm^{-1} and the band at 169 cm^{-1}, the values of the parameter are smaller than for the lower frequency modes bellow 250 cm^{-1} except the band at 169 cm^{-1}, indicating that these higher frequency modes and the band at 169 cm^{-1} are assigned to the internal vibrations of the TaO_6 octahedra.

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References

1) T. A. Vanderah, R. S. Roth, T. Siegrist, W. Febo, J. M. Loezos, W. Wong-Ng, *Solid State Sci.*, **5**, 149 (2003).
2) H. Kato, A. Kudo, *Chem. Phys. Lett.*, **295**, 487 (1998).
3) G. K. Layden, *Mat. Res. Bull.*, **3**, 349 (1968).
4) Y.-H. Lee, Y.-S. Kim, D.-H. Kim, B.-K. Ju, M.-H. Oh, *IEEE Transaction on Electron Devices*, **47**, 71 (2000).
5) G. K. Layden, *Mat. Res. Bull.*, **2**, 533 (1967).
6) F. Galasso, G. Layden, G. Ganung., *Mat. Res. Bull.*, **3**, 397 (1968).
7) C. R. Feger, R. P. Ziebarth, *Chem. Mater.*, **7**, 373 (1995).
8) M. Yashima, M. Kakihana, R. Shimidzu, H. Fujimori, M. Yoshimura, *Appl. Spectrosc.*, **51**, 1224 (1997).
9) H. Fujimori, M. Kakihana, K. Ioku, S. Goto, M. Yoshimura, *Appl. Phys. Lett.*, **79**, 937 (2001).
10) H. Fujimori, M. Yashima, M. Kakihana, M. Yoshimura, *Phys. Rev. B*, **61**, 3971 (2000).
11) H. Fujimori, H. Toya, K. Ioku, S. Goto, M. Yoshimura, *Chem. Phys. Lett.*, **325**, 383

(2000).

12) H. Fujimori, M. Yashima, M. Kakihana, M. Yoshimura, *J. Am. Ceram. Soc.*, **84**, 663 (2001).
13) H. Fujimori, H. Komatsu, K. Ioku, S. Goto, M. Yoshimura, *Phys. Rev. B*, **66**, 064306 (2002).
14) H. Fujimori, H. Komatsu, K. Ioku, S. Goto, T. Watanabe, *J. Am. Ceram. Soc.*, **88**, 1995 (2005).
15) M. Kakihana, *J. Sol-Gel Sci. Technol.*, **6**, 7 (1996).
16) Y. Repelin, E. Husson, N. Q. Dao, H. Brusset, *Mat. Res. Bull.*, **15**, 985 (1980).
17) Y. Repelin, E. Husson, H. Brusset, *Spectrochimica Acta*, **35A**, 937 (1979).
18) P. S. Peercy, B. Morosin, *Phys. Rev. B*, **7**, 2779 (1973).
19) P. Gillet, F. Guyot, J.-M. Malezieux, *Phys. Earth Planet. In.*, **58**, 141 (1989).
20) Y. Zhao, D. J. Weidner, *Phys. Chem. Minerals*, **18**, 294 (1991).

$BaTa_2O_6$の紫外レーザーラマン分光法による1573 Kまでのその場観察

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高温下における材料のラマンスペクトルを測定するために設計された連続波の紫外ラマン散乱装置を用いて，$BaTa_2O_6$の1573 Kまでのラマンスペクトルを得た．室温から1573 Kまでの範囲で，典型的な斜方相(Type I)のラマンスペクトルが観測された．本結果をグルーナイゼンパラメータと同様に定義された等圧下における温度変化に関連したパラメーターによって説明すると，250 cm^{-1}以上のラマンモードと169 cm^{-1}のモードは，169 cm^{-1}を除く250 cm^{-1}以下の低周波数モードよりもパラメーターの値は小さい．このことは高周波数モードと169 cm^{-1}のモードが，TaO_6内部振動モードに帰属されることを示唆している．