Raman spectroscopic study of benitoite-type compounds

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Raman scattering measurements were performed in the benitoite-type BaTiSiO$_5$, BaZrSiO$_5$, BaSnSiO$_5$ and tetragermanate-type BaGeO$_5$ phases in order to elucidate the spectroscopic and structural features of D$_2$/vG(T$_3$O$_9$)-type compounds (expressed by Smith’s notation) with the GO$_6$ octahedral unit isolated by the T$_3$O$_9$ ring. The Raman band assignments in middle and high wavenumber region were also carried out. In addition, the wavenumber of antisymmetric stretching vibration mode, $\nu_{as}$, for Si–O–G bond was calculated by means of combination of the simple molecular model and Badger’s rule, and compared with the experimental results. It was suggested that the $\nu_{as}$ was governed by the force constant of T–O$_6$ bond, which was connected with the G$^{4+}$.

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1. Introduction

Crystals with the octahedral units (GO$_6$) isolated by the three-membered rings (T$_3$O$_9$) are expressed as the D$_2$/G(T$_3$O$_9$), where D, G, T, and v correspond to the ions with the coordination number of more than nine (polyhedral unit), six (octahedral), four (tetrahedral), and the valence of the cation of D, respectively, by the notation proposed by Smith et al. Benitoite (BaTiSiO$_5$), bazirite (BaZrSiO$_5$) and wadeite (K$_2$ZrSiO$_5$), and tetragermanate-type BaGeO$_5$ and BaTiGeO$_5$ belong to the D$_2$/G(T$_3$O$_9$)-type in the case of T = Si and Ge, respectively. The D$_2$/G(SiO$_6$)-type compounds are regarded as a significant phase for optical materials. For example, the benitoite shows a clear blue and red photoluminescence at room temperature. In addition, Takahashi recently reported that the synthetic bazirite including tetrahedral Ge unit, i.e., octahedral GeO$_6$ unit, is still controversial. Therefore, the D$_2$/G(SiO$_6$)-type compounds have a great potential for blue emitting and long-lasting phosphors without lanthanide elements. On the other hand, second-order optical nonlinearity of LiNbO$_3$-class has been accomplished in transparent fresnoite-type BaTiGeO$_5$-crystallized glasses, and the BaTiGeO$_5$/BaGeO$_5$ phase plays an important role for formation of the Ba$_2$TiGe$_2$O$_8$ phase in the BaO–TiO$_2$–GeO$_2$ system glasses. However, nature of the D$_2$/G(T$_3$O$_9$)-type phases, particularly the spectroscopic features, were not fully clarified yet. Therefore, in this study, we measured the Raman spectra in several D$_2$/G(T$_3$O$_9$)-type compounds, i.e., BaTiSiO$_5$, BaZrSiO$_5$, BaSnSiO$_5$ and BaGeO$_5$, and discussed the structural features of D$_2$/G(T$_3$O$_9$)-type phase based on the Raman information. Furthermore, we attempted to calculate the wavenumber of antisymmetric stretching vibration mode by combination of the simple molecular model and Badger’s rule.

Particularly, the BaGeO$_5$ phase consists of the GeO$_6$ octahedron and GeO$_5$ ring. The Raman band with respect to the six-coordinated Ge unit, i.e., octahedral GeO$_5$ unit, is still controversial. Therefore, it is expected that the Raman measurement of BaGeO$_5$ phase provides a knowledge regarding the vibration of GeO$_5$ unit in the inorganic materials, e.g., oxide crystal and glass.

2. Experimental

Polycrystalline samples of BaZrSiO$_5$, BaSnSiO$_5$ and BaGeO$_5$ phases were synthesized by a solid-state reaction. A natural mineral of BaTiSiO$_5$, i.e., benitoite, which was produced from San Benito, California, was also used as a sample. Formation of crystalline phases in sintered samples was examined by an X-ray diffraction analysis using Cu Kα radiation. Raman spectra of the samples were measured using an Ar$^+$ laser operating at 514.5 nm. The scattered light was detected using the system consisting of a triple grating monochromator and a liquid-nitrogen-cooled CCD device detector (Horiba Jobin Yvon, T64000). The measurements were performed at room temperature.

3. Results and discussion

3.1 Raman scattering spectra

The BaZrSiO$_5$, BaSnSiO$_5$ and BaGeO$_5$ polycrystalline phases with high crystallinity and free from any impurity phases were successfully synthesized, i.e., single phase formation. Figure 1 show the Raman scattering spectra of a natural benitoite (BaTiSiO$_5$), and synthetic bazirite (BaZrSiO$_5$) and pabstite (BaSnSiO$_5$), and tetragermanate-type BaGeO$_5$. In this study, we noticed the Raman band in the range of 500 to 1100 cm$^{-1}$.

In the middle wavenumber range, the remarkable Raman peaks were observed in the range of ~500–650 cm$^{-1}$. Although the octahedral G site in the D$_2$/G(SiO$_6$)-type phase was occupied by different species, the large and sharp peak positions were almost identical (578 cm$^{-1}$, 579 cm$^{-1}$ and 574 cm$^{-1}$) for benitoite, bazirite and pabstite phases, respectively. In the high wavenumber range, the BaTiSiO$_5$, BaZrSiO$_5$ and BaSnSiO$_5$ phases indicated the peculiar bands in the range of ~900–1000 cm$^{-1}$, mainly 937 cm$^{-1}$, 957 cm$^{-1}$ and 994 cm$^{-1}$, respectively. In addition, the small bands were also seen in the range of ~1000–1100 cm$^{-1}$. Furthermore, the Raman spectrum in the BaGeO$_5$ phase

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revealed the remarkable Raman peak in the middle range of ~500–600 cm⁻¹, and two typical bands in the high wavenumber region, i.e., 817 cm⁻¹ and 876 cm⁻¹.

3.2 Interpretation of Raman band

Referring to the crystal structure of benitoite, the Si⁴⁺ takes the tetrahedral coordination, having four bonds to oxygen atoms, and constructs the three-membered ring, i.e., SiO₄. Each two Si–O bonds link to other SiO₄ units in the ring plane (Si–Oeq; the suffix means equatorial), and the other two bonds perpendicular to the ring plane (Si–Oax; axial) connect with the octahedral TiO₆ units with the longer Ti–O bond than the Si–O, which are situated at the upper and lower position than the SiO₄ ring. Therefore, the Si atom in the beniteite structure have the two bridging oxygen (Si–Oax–Si) in the Si₃O₉ ring and two non-bridging oxygen (Si–Oeq–Si) in the Si₃O₉ ring, and antisymmetric stretching of Si–Oeq–Si in the Si₃O₉ ring, and antisymmetric stretching of Ge–O–Ge and stretching mode of Si–O–Si and the stretching mode of Si–O–Ti. Taking into account the description of Roman numeral indicates the coordination number) in tita

Furukawa and White also described that the antisymmetric stretching mode of the Si–O–Si and the stretching mode of Si–O–non-bridging bonds lie in the range of 1000–1200 cm⁻¹. Therefore, the small Raman bands observed in the range of ~1000–1100 cm⁻¹ are ascribed to the antisymmetric stretching mode of Si–Oeq–Si in the SiO₃ ring.

Su et al. measured the Raman spectra in a number of titanosilicates with different Ti-coordinate states and structural units, and investigated the relationship between the Raman shifts and the local bonding configurations around Si and Ti. It is proposed that the strong Raman band around 900–1000 cm⁻¹ is assigned to the stretching mode of Si⁴⁺–O–Ti⁶⁺ (The superscript of Roman numeral indicates the coordination number) in titanosilicates, i.e., the TiO₆ units isolated by SiO₄ tetrahedra. Indeed, they also have measured the Raman spectrum of benitoite, and concluded that the strong band around 940 cm⁻¹ was attributed to the stretching of Si–O–Ti. Taking into account the description by Furukawa and White, it is strongly suggested that the peculiar Raman bands of benitoite in the range of ~900–1000 cm⁻¹ are due to the antisymmetric vibration mode of Si⁴⁺–Oeq–Ti⁶⁺. This is quite credible because McKeown et al. also assigned the Raman band group in the range of ~900–1000 cm⁻¹ to the vibration modes concerning with the Si–Oeq. Therefore, the strong Raman bands appeared at 957 cm⁻¹ for the bazirite and 994 cm⁻¹ for the pabstite are ascribed to the antisymmetric stretching mode of Si⁴⁺–Oeq–Si in the SiO₃ ring, and antisymmetric stretching of Si⁴⁺–Oeq–G⁻ (G: Ti, Zr and Sn) and stretching mode of Si⁴⁺–Oeq–Si, respectively.

The BaGe₄O₉ phase is a tetragermanate-type phase, i.e., AGe₄O₉ (A: Sr, Ba and Pb), which are structurally similar to benitoite, i.e., the isolated GeO₆ octahedron and GeO₄ ring, but not isostructural because of the different space group, i.e., P31c. It is reported that the Raman bands at ~525 cm⁻¹ and ~700–900 cm⁻¹ were attributed to the symmetric stretching mode of Ge–O–Ge, and antisymmetric stretching mode of Ge–O–Ge and stretching mode of Ge–O’, respectively. In addition, Henderson and Fleet assigned the band at ~515 cm⁻¹ to the symmetric stretching.
of Ge–O–Ge bond associated with the GeO₄ ring in vitreous GeO₂. Furthermore, Verweij and Buerster reported the strong Raman peaks observed at 499 cm⁻¹ and 517 cm⁻¹ are also assigned to the GeO₄ ring mode in the wadeite-type K₂Ge₄O₉, which is constructed by the octahedral GeO₆ unit and GeO₄ ring. Therefore, the Raman bands at ~500–600 cm⁻¹ were assigned to the symmetric stretching of Ge–Oeq–Ge in the GeO₄ ring. On the other hand, the large Raman band at ~500–600 cm⁻¹, corresponding to the GeO₄ ring vibration mode, in the BaGe₄O₉ phase indicated the splitting into four peaks. This is possibly due to the distortion of GeO₄ rings coming from the low symmetry of tetragermanate-type phase (P21/c) compared to that of benitoite-type phase. Concerning the Raman spectra in the high wavenumber region, by analogy to the assignment of silicate O due to the difference of ionic radius, e.g., bond length of Zr–O and Sn–O should be longer than that of Ti–O. Nevertheless, the BaGe₄O₉ phase indicated the splitting into four peaks. This is possibly due to the distortion of Ge₃O₉ rings coming from the low symmetry of tetragermanate-type phase (P21/c) compared to that of benitoite-type phase. Concerning the Raman spectra in the high wavenumber region, by analogy to the assignment of silicate series, the distinguishable bands at ~820 cm⁻¹ and ~880 cm⁻¹ in the BaGe₄O₉ phase are attributed to the antisymmetric stretching mode of GeIV–Oa and stretching mode of GeIV–Oeq–GeIV, respectively.

### 3.3 Interaction between GO₆ and Si(Ge)O₄ ring

As before mentioned, the Raman band in the range of 900–1000 cm⁻¹ is related to the isolated octahedral GO₆ unit in the titanoclastics, namely Si₃O₉–Ge–SiVII bond (G: Ti, Zr and Sn). The Ti and Zr are categorized into the group four element (Sn belongs to the group fourteen), and the Ti⁴⁺ with octahedral coordination in the benitoite could be totally replaced by Zr⁴⁺ and Sn⁴⁺, maintaining the same structure (i.e., bazirite and pabstite, respectively). At first, we speculated that in the bazirite and pabstite, the peculiar Raman peak, corresponding to the antisymmetric stretching vibration mode of Si₃O₉–G₆–SiVII, appeared at low wavenumber compared to that of benitoite phase because the bond length of Zr–O and Sn–O should be longer than that of Ti–O due to the difference of ionic radius, e.g., r(Ti⁴⁺), r(Zr⁴⁺) and r(Sn⁴⁺) for 0.0745 nm, 0.0860 nm and 0.0830 nm, respectively. Nevertheless, the BaZrSi₃O₉ and BaSnSi₃O₉ phases indicated the Raman band of Si₃O₉–Ge–SiVII with higher wavenumber than the BaTiSi₃O₉. In order to elucidate it, we attempted to calculate the wavenumbers of antisymmetric stretching vibration modes, νₐs, in the D₃h(G(Ti)O₆)-type compounds.

When we treat the chemical bond as the weights linked by spring, (i.e., on the assumption of Hooke’s law), the frequency concerning the antisymmetric stretching mode of Si(Ge)–O–G bond can be expressed as the following equation:

\[
ν_{αs}^2 = \frac{1}{8π^2c^2} \left( \frac{k_{GGO} - k_{GO}}{μ_{GGO}} + \frac{k_{GGO} - k_{GGO}}{μ_{GGO}} + 4k_{GGO} - k_{GGO}(\cos θ)^2 \right),
\]

where \( ν_{αs} \) is the antisymmetric stretching frequency, \( c \) is light velocity, and \( k, μ \) and \( θ \) correspond to the force constant, reduced mass and bond angle of the Si(Ge)–O–G bond, respectively (the suffix of parameters indicates the type of bond). \( m \) is the mass of oxygen atom. The \( k \) for each Si(Ge)–O and G–O bonds was calculated on the basis of Badger’s rule, i.e.,

\[
r_e = (C_k/κ)^{1/3} + d_d,
\]

where \( r_e \) is the equilibrium bond distance, and \( C_k \) and \( d_d \) are the constants, which depend on the rows in the periodic table. Although this is a semi-empirical equation, it enables us to calculate the force constant of chemical bond with high accuracy by means of the bond distance and its constituent elements.

In calculation, the BaTiSi₃O₉, BaZrSi₃O₉, BaSnSi₃O₉, BaGe₄O₉ and K₂ZrSi₃O₉ (wadeite) were selected because these crystal structures and atomic positions were known. Here, the K₂ZrSi₃O₉ was also included because the structure of wadeite is considerably related to that of benitoite (but not isostructural), and the Raman spectrum was already reported. Figure 2 shows the calculation model for antisymmetric vibration mode in the BaGSi(Ge)₃O₉ phases. In here, we noticed only the interaction of SiIV–Oax and GVI–Oax, i.e., distances of the Si(Ge)IV–Oax and GVI–Oax (r(Si(Ge)IV–Oax) and r(GVI–Oax)) and bond angle of the SiIV–Oax–GVI (θ(Si(Ge)IV–GVI)). The parameters used in the calculation, and the calculated wavenumber (νₐs) are summarized in Table 1. The relation between the calculated and observed values of

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<tr>
<th>Bond Angle, θ(Si(Ge)IV–GVI), Reduced Mass, μ, Bond Length, r, Force Constant Estimated by Badger’s Rule, k, and Calculated and Observed Frequencies, νₐs and νₐs, in BaGSi(Ge)₃O₉ (G: Ge, Ti, Zr, Sn) and K₂ZrSi₃O₉ Phases</th>
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<tr>
<td>BaTiSi₃O₉</td>
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<td>ionic radius of GIV⁺/Å⁺</td>
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<td>r(Si(Ge)IV–Oax)</td>
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* The ionic radii in this table are cited from the data by Shannon (Ref. 19). Coordination number is six.
** Averaged values.
*** After McKeown et al. (Ref. 21).
wavenumber of antisymmetric stretching vibration mode is shown in Fig. 3. A good correlation between the \(v_{\text{as}}^{\text{cal}}\) and \(v_{\text{as}}^{\text{obs}}\) was obtained in spite of the use of simple calculation model. Moreover, it was demonstrated that the peak position of antisymmetric stretching vibration mode was irrespective of the ionic radius of \(G^{4+}\) in the octahedral unit, but closely related to the force constant of Si(Ge)–O bond (\(k_{\text{Si(Ge)–O}}\)) in the Si(Ge)–O ring (inset of Fig. 3).

Although we could explain the peak position of \(v_{\text{as}}\) in the \(D_{2h}\) \(G(T_3O_9)\)-type phase, the change in Raman intensity of the \(v_{\text{as}}\) related to the structure of these compounds. In the high wavenumber range, in which the bands for antisymmetric stretching vibration mode are observed in the Raman spectra.

4. Summary

We synthesized the \(D_{2h}\) \(G(T_3O_9)\)-type compounds, i.e., \(\text{BaTiSi}_3\text{O}_9\), \(\text{BaZrSi}_3\text{O}_9\), \(\text{BaSnSi}_3\text{O}_9\), and \(\text{BaGeO}_3\), and measured their Raman scattering spectra, and their band assignment was also carried out for the purpose of spectroscopic understanding to the structure of these compounds. In the high wavenumber region, the peculiar bands at \(\sim 900–1000 \text{ cm}^{-1}\) are ascribed to the antisymmetric stretching vibration, \(v_{\text{as}}\), of Si–O\(_{ax}\)–G (G: Ti, Zr and Sn). In the \(\text{BaGeO}_3\) phase, the Raman bands at \(\sim 820 \text{ cm}^{-1}\) is attributed to the \(v_{\text{as}}\) of Ge\(^{IV}\)–O\(_{ax}\)–Ge\(^{VI}\). Furthermore, we attempted to calculate the wavenumbers of \(v_{\text{as}}\) of Si(Ge)–O\(_{ax}\)–G (G: Ge, Ti, Zr and Sn) on the basis of the crystallographic data and Badger’s rule in the \(D_{2h}\) \(G(T_3O_9)\)-type phases. The calculated values of \(v_{\text{as}}\) indicated a good correspondence with the peak position of \(v_{\text{as}}\) observed in this study. It was concluded that the peculiar Raman peaks observed in the range of 900–1000 \text{ cm}^{-1}\) for the silicate series and of 790–850 \text{ cm}^{-1}\) for the germinate series corresponded to the \(v_{\text{as}}\) mode in the \(D_{2h}\) \(G(T_3O_9)\)-type phases. It was also verified that the \(v_{\text{as}}\) was governed by the force constant of Si(Ge)–O\(_{ax}\).

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