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著者	Fujimori Hirotaka, Komatsu Hiroshi, Ioku Koji, Goto Seishi, Yoshimura Masahiro
journal or publication title	Physical Review. B
volume	66
number	6
page range	064306
year	2002
URL	http://hdl.handle.net/10097/53124

doi: 10.1103/PhysRevB.66.064306

Anharmonic lattice mode of Ca_2SiO_4 : Ultraviolet laser Raman spectroscopy at high temperatures

Hiroataka Fujimori,^{*,†} Hiroshi Komatsu, Koji Ioku, and Seishi Goto

Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, Ube 755-8611, Japan

Masahiro Yoshimura

Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan

(Received 29 December 2000; revised manuscript received 26 November 2001; published 29 August 2002)

Raman spectra of Ca_2SiO_4 have been obtained at temperatures up to 1723 K by using a continuous-wave ultraviolet Raman spectroscopic system. At room temperature, the typical Raman spectrum of γ - Ca_2SiO_4 was recorded. In the region of 1073–1123 K, two strong bands of the γ phase around 800 and 900 cm^{-1} disappeared, which indicates the $\gamma \rightarrow \alpha'_L$ transformation. Raman frequencies decreased in the α'_L and α'_H phases with increasing temperature. The measured shifts are used in conjunction with available high-pressure Raman data to calculate the Gruneisen parameter related to pressure variation at constant temperature, the corresponding parameter related to temperature variation at constant pressure, and the anharmonic parameter. Although the anharmonicity is weaker for the bands related to the internal vibrations of Si-O bonds (more than around 400 cm^{-1}), the band related to the lattice vibration mode (around 250 cm^{-1}) shows stronger anharmonic behavior.

DOI: 10.1103/PhysRevB.66.064306

PACS number(s): 63.20.Ry, 78.30.Hv

I. INTRODUCTION

An anharmonic contribution to an equation of state of a substance is one of the current problems of physics. Vibrational spectra are crucial for constraining lattice-dynamical models, for understanding thermodynamic properties, and for constraining phase equilibria. The same spectra recorded at high temperature and high pressure reveal detailed information on bonds and thermodynamic properties at temperatures and pressures that are beyond the range of direct thermodynamic measurements. Direct estimation of anharmonic effects on the heat capacity is difficult for several reasons. In fact, for most minerals, anharmonic effects become noticeable at temperatures above 1000 K. Accurate calorimetric measurements at these temperatures can only be achieved with a few grams of mineral. We must therefore use other investigative methods.

Raman scattering is one of the most powerful tools for observing anharmonicity. However, the measurable region of temperatures is limited in conventional Raman spectroscopy using visible region excitation. This can be explained in terms of the fact that it is difficult to detect weak Raman scattering using a substance at high temperatures in comparison with an intense continuous background due to thermal emission. In such a case continuous-wave 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.^{1,2} Recently, by means of UV Raman spectroscopy, we have observed the phase transition and soft phonon modes in SrZrO_3 around 1200 °C,³ OH vacancies arising in hydroxyapatite at high temperatures,⁴ and the phase transition of hafnia around 2085 K.⁵ In this study we propose that an UV Raman system is very useful to observe anharmonicity at high temperatures.

Silicates are attractive substances since they have long been known as not only hydraulic and refractory materials in

the cement industry but also earth's mantle minerals in the physical geography. Remy, Reynard, and Madon⁶ have reported on the high-temperature Raman spectra of Ca_2SiO_4 in the temperature range of 298–1433 K. In this temperature range, however, it is difficult to estimate anharmonic effects due to the discontinuous change of the spectra associated with the martensitic transformation between α'_L (or β) and γ . Therefore, in this work, Raman spectra of Ca_2SiO_4 have been successfully obtained in the wide range of temperatures up to 1723 K by using a continuous-wave UV Raman spectroscopic system.¹ Moreover, we calculate the Gruneisen parameters γ_{iT} , related to pressure variation at constant temperature from the data of the high-pressure Raman spectra that have been reported in Ref. 7, and the corresponding parameters γ_{iP} , related to temperature variation at constant pressure from the data of the high-temperature Raman spectra in this work. Intrinsic anharmonic parameters can also be derived from these parameters. Intrinsic anharmonicity leads to an important departure from the Dulong and Petit limit of the heat capacity at a temperature above 1000 K. These anharmonic effects can substantially affect the position of calculated equilibrium curves in the phase diagram of Ca_2SiO_4 .

II. EXPERIMENTS AND DATA ANALYSIS

A. Sample preparation

It is important to use a compositionally homogeneous sample for measuring vibrational spectra. The solid-state reaction route was used for preparation⁸ of Ca_2SiO_4 . CaCO_3 (55.55% as CaO, Seimi Chemical Co., Inc., Kanagawa, Japan) and SiO_2 (99.89%, Wako Pure Chemical Co., Inc., Tokyo, Japan) powders were manually mixed as ethanol slurries and dried powders in an agate mortar with a pestle for 1 h. The mixed powder was pressed into a lump by hand. This was fired in air at 1773 K in an electric furnace with MoSi_2 heaters and cooled in the furnace.

B. Ultraviolet Raman spectroscopic system

Raman measurements for the Ca_2SiO_4 specimen at various temperatures have been performed by using a continuous-wave UV Raman spectroscopic system designed to measure the Raman scattering from substances at high temperatures.¹ This system is 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 plasma lines from the laser are rejected by a Pellin-Broca prism combined with apertures. Its detail was described elsewhere.¹ It has been reported that the UV excitation provides good-quality Raman spectra with practically flat backgrounds even at 1773 K, in sharp contrast to the conventional visible excitation shown in Ref. 1. The sample was mounted in a furnace with a Pt-Rh heater where the sample was placed and then fixed on a Pt/13% Rh thermocouple with alumina cement. The specimen was heated at a rate of 10 K/min, and then a temperature was kept constant during measurements (within ± 1 K). Each measurement was done in air after a constant temperature was maintained for 10 min. The laser power at the tube level was set at 50 mW. Considering the spectral resolution and the high spectral intensity at high temperatures, the entrance slit width was set at 100 μm , which corresponds to the full width at half maximum of 4.7 cm^{-1} . In the region of 1573–1723 K, the thermal emission backgrounds from the sample and the furnace were measured without the laser line, and then these were subtracted from the Raman spectra at this temperature region. An Hg line was used for Raman-shift calibration for each measurement. No artificial smoothing was used on the acquired Raman spectra.

III. RESULTS AND DISCUSSION

A. Effect of temperature on Raman spectra

At room temperature, the powder x-ray-diffraction pattern of the specimen showed that the sample was γ and single phase,⁹ the typical Raman spectrum of $\gamma\text{-Ca}_2\text{SiO}_4$ was recorded.⁶ With an increase in sample temperature, all bands broadened (Fig. 1). The two strong bands of $\gamma\text{-Ca}_2\text{SiO}_4$ (● in Fig. 1), which reflect atomic displacements around the SiO_4 groups in the γ phase,¹⁰ weakened at 1073 K, and disappeared up to 1123 K. This indicates that the γ -to- α'_L phase transformation completed up to this temperature, which is consistent with the result reported by Remy, Reynard, and Madon.⁶ In the range of 1073–1723 K, the spectra mainly show seven Raman bands: external, ν_2 , $2\nu_4$, $2(\nu_1$ or $\nu_3)$, and ν_3 in order of increasing frequency. The seven Raman bands are assigned later in this paper. Raman spectra associated with the α'_L , α'_H , and α phases are very similar, which corresponds to closely related structures among these polymorphs. The differences just come from the orientation of the SiO_4 tetrahedra and the slight movement of calcium ions.¹⁰ Relations describing dependences of the frequencies on the temperature were obtained by fitting the results by least squares as follows: $\omega_i = \omega_{i0} + (\partial\omega_i/\partial T)_P(T - T_0)$, where subscripts 0 refer to parameter values at 298 K and

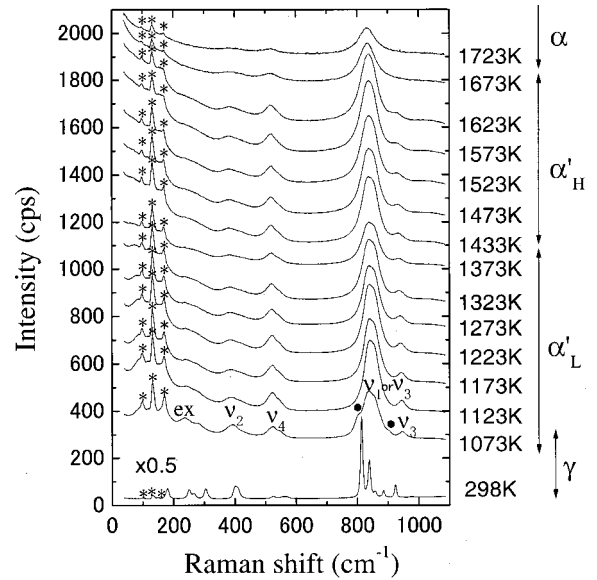


FIG. 1. Temperature dependence of Raman spectra of Ca_2SiO_4 excited by a 363.8 nm UV laser line. Note scale factor to the spectrum at 298 K. The relative change of Raman intensities up to 1123 K has an indefinite factor because of orientational changes of grains, due to the γ -to- α'_L phase transformation. The plasma lines (*) from the laser source appeared. The symbols (●) in the spectrum at 1073 K represent two strong bands of $\gamma\text{-Ca}_2\text{SiO}_4$. The peaks of the considered Raman bands (i) are labeled by external, ν_2 , ν_4 , ν_1 , and ν_3 .

0.1 MPa. The results are presented in Table I and Fig. 2. The pattern decomposition of the Raman bands around 800–900 cm^{-1} (ν_1 or ν_3) was performed by using a commercial profile-fitting program GRAMS, and assuming two Lorentz functions. The Raman bands in this range of frequency are enlarged in Fig. 2(b). All of the bands show a linear frequency decrease with increasing temperature. The value of $(\partial\omega_i/\partial T)_P$ of the band ($\omega_{i0} = 875 \text{ cm}^{-1}$) slightly varied around 1433 K due to probably the α'_L -to- α'_H phase transition.

B. Theoretical approach of anharmonicity

Anharmonicity is responsible for crystal properties, such as the thermal expansivity and temperature-induced shifts of normal-mode frequencies. The temperature and pressure dependences of a given frequency arise from two contributions:^{11,12} (1) a pure-volume contribution due to the compressibility and the thermal expansion (quasi-harmonicity), which cannot be negligible above 300 K, (2) a volume-independent (pure-temperature and -pressure) contribution arising from the higher-order anharmonic interactions (intrinsic anharmonicity), which may become important above 1000 K. Knowing the compressibility and the thermal expansion, it is possible to separate two contributions by performing measurements of both pressure and temperature dependences of a vibrational mode. An infinitesimal change in frequency (ω_i) can be written as

$$d \ln \omega_i = a_i dT + \gamma_{iT} d \ln \rho = c_i dT + e_i dP = f_i dP + \gamma_{iP} d \ln \rho, \quad (1)$$

TABLE I. Slope of the regression lines for the frequency shifts as a function of temperature and pressure, the γ_{iT} , γ_{iP} , and α_i values for the different Raman-active modes. ω_{i0} refers to the frequency at 298 K and 0.1 MPa by extrapolating Raman spectra at high temperatures.

i	ω_{i0} (cm ⁻¹)	$\left(\frac{\partial\omega_i}{\partial P}\right)_T$ (cm ⁻¹ /GPa) ^a	γ_{iT}	$\left(\frac{\partial\omega_i}{\partial T}\right)_P$ (cm ⁻¹ /K)	γ_{iP}	$\alpha_i \times 10^5$ (K ⁻¹)
External	251(4)	4.7(5)	3.1(7)	-0.014(3)	1.0(2)	12(6)
ν_2	399(3)	1.8(1) or 1.6(3)	0.75(12) or 0.67(19)	-0.013(2)	0.5(1)	1.3(16) or 0.8(20)
ν_4	530(1)	1.15(8)	0.36(6)	-0.0092(8)	0.29(3)	0.4(7)
ν_4	547(5)	1.3(2)	0.4(1)	-0.007(3)	0.2(1)	1(1)
ν_1 or ν_3	854.8(9)	4.72(8)	0.9(1)	-0.0224(5)	0.44(2)	3(1)
ν_1 or ν_3	875(3)	4.56(14)	0.9(1)	-0.018(2)	0.36(4)	3(1)
ν_3	970(3)	4.50(8)	0.77(9)	-0.031(2)	0.55(5)	1(1)

^aData from Ref. 7.

$$c_i = \left(\frac{\partial \ln \omega_i}{\partial T} \right)_P, \quad (2)$$

$$e_i = \left(\frac{\partial \ln \omega_i}{\partial P} \right)_T, \quad (3)$$

$$\gamma_{iT} = \left(\frac{\partial \ln \omega_i}{\partial \ln \rho} \right)_T = e_i K_T = \frac{K_T}{\omega_i} \left(\frac{\partial \omega_i}{\partial P} \right)_T, \quad (4)$$

$$\gamma_{iP} = \left(\frac{\partial \ln \omega_i}{\partial \ln \rho} \right)_P = -\frac{c_i}{\alpha} = -\frac{1}{\alpha \omega_i} \left(\frac{\partial \omega_i}{\partial T} \right)_P, \quad (5)$$

$$a_i = \left(\frac{\partial \ln \omega_i}{\partial T} \right)_V = -\alpha (\gamma_{iP} - \gamma_{iT}), \quad (6)$$

$$f_i = \left(\frac{\partial \ln \omega_i}{\partial P} \right)_V = \left(-\frac{1}{K_T} \right) (\gamma_{iP} - \gamma_{iT}), \quad (7)$$

where ρ is the molar density, α is the volume thermal expansion of the crystal, and K_T is the bulk modulus that characterizes the incompressibility of the structure.

1. Gruneisen parameters γ_{iT} and the corresponding parameters γ_{iP}

γ_{iT} is the Gruneisen parameter of a considered bond (i) related to pressure variation at constant temperature. γ_{iP} is the constant-pressure parameter with temperature variation defined in a similar way as γ_{iT} . c_i is the frequency shift due to temperature increase at constant pressure (c_i is generally negative). In the same way e_i is the frequency shift due to pressure at constant temperature (generally positive). Values of γ_{iT} and γ_{iP} for each Raman-active mode estimated from Eqs. (4) and (5) are summarized in Table I and Figs. 3(a) and 3(b). $(\partial\omega_i/\partial T)_P$ and $(\partial\omega_i/\partial P)_T$ are estimated from the spectra of α'_L , α'_H , and α -Ca₂SiO₄ in this work and those of β -Ca₂SiO₄ in Ref. 7, respectively. Because the Raman spectra vary continuously due to the similarity of the crystal structures among the polymorphs of Ca₂SiO₄ with the excep-

tion of γ -Ca₂SiO₄, $(\partial\omega_i/\partial T)_P$ and $(\partial\omega_i/\partial P)_T$ can be evaluated over the phase transitions among them. The value of $\alpha \equiv 1/V_0(\partial V/\partial T)_P$ was $5.9(2) \times 10^{-5}$ K⁻¹, which was obtained by a linear least-squares fit for the molar volume of β , α'_L , and α'_H -Ca₂SiO₄ as a function of temperature in Ref. 13. The bulk modulus of β -Ca₂SiO₄, $K_T \equiv -V(\partial P/\partial V)_T = 166(15)$ GPa,¹³ was used. The γ_{iT} and γ_{iP} parameters are proportional to the equilibrium length of a considered bond (i), r_i , and the local thermal expansion coefficient of a considered bond (i), α_i , respectively; $\gamma_{iT} \propto K_T r_i^3$ and $\gamma_{iP} \propto \alpha_i / \alpha$.¹² For the higher-frequency bands [$i = \nu_2, 2\nu_4, 2(\nu_1$ or $\nu_3)$, and ν_3], the values of γ_{iT} and γ_{iP} parameters are smaller than for the lower-frequency mode ($i = \text{external}$), which represents shorter equilibrium bond distance and smaller α_i , reflecting their relative incompressibilities, weak expansivities, and strong bonds. The bulk modulus of SiO₄ tetrahedral units is larger than that of the crystal; the incompressibility of 220–500 GPa was estimated for the general Si-O bonds.^{14,15} The thermal expansion coefficient of tetrahedral units is smaller than that of the crystal; the thermal expansion coefficient of $\alpha_i \approx 0$ K⁻¹ for the general Si-O bonds has been estimated from the systematics in olivine structures.¹⁶ This result shows that these high-frequency modes involve stretching and bending motions of the Si-O bonds ($r_i \approx 1.6$ Å)^{9,10,17–19} in the SiO₄ tetrahedra (internal modes). On the other hand, both γ_{iT} and γ_{iP} are larger for the lower-frequency band of $i = \text{external}$ than the bands $i = \nu_2, 2\nu_4, 2(\nu_1$ or $\nu_3)$, and ν_3 , which represents the oscillator having the longer equilibrium bond length and larger α_i , reflecting its relative compressibility, strong expansivity, and weak bond. The weaker bond is caused by a lower charged atom and a higher coordination number. This band can be assigned to a lattice vibration mode (a translational lattice mode of Ca (Ca-O bond, $r_i \approx 2.3$ – 2.9 Å)^{9,10,17–19} or Si and/or a rotational lattice mode of SiO₄, etc.). Overall pressure- and temperature-induced volume changes are taken up by weaker bonds in the crystal structure. These results are supported by deducible assignments from ²⁸Si-³⁰Si and ⁴⁰Ca-⁴⁴Ca isotopic shifts.²⁰

Raman and IR spectra can generally be described in terms of internal modes and external lattice modes. Modes derived from motions in the SiO₄ group are considered as the inter-

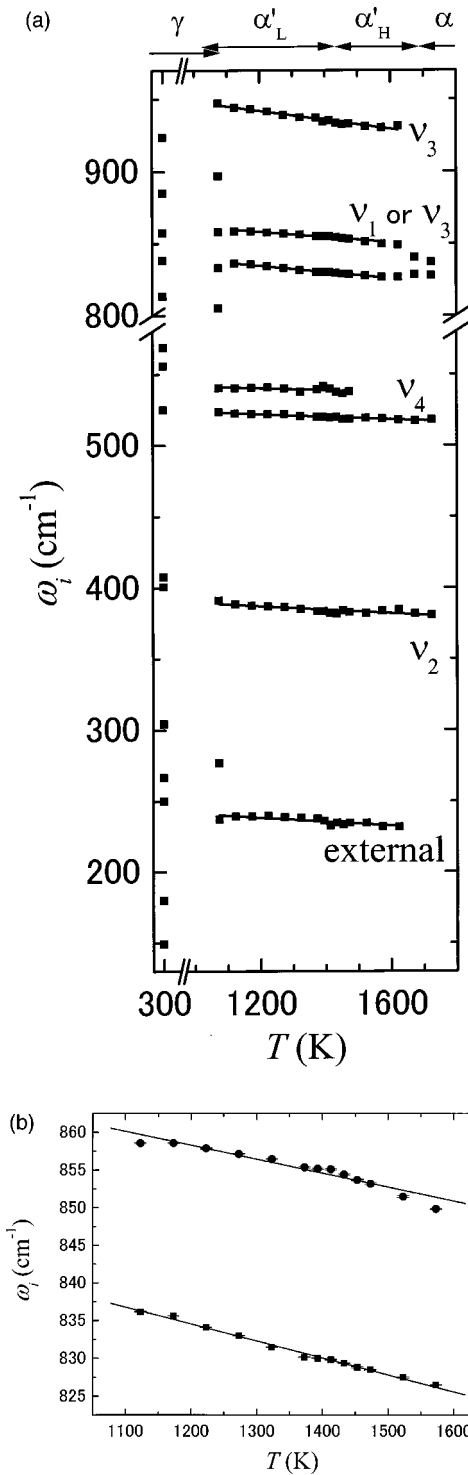


FIG. 2. Temperature dependence of the Raman bands of Ca_2SiO_4 at room pressure (a) in the entire range of the frequency measured (b) around 850 cm^{-1} . Straight lines represent fits by least-squares regression.

nal modes to distinguish them from the external modes involving Ca and Si lattice vibrations. For the isolated SiO_4^{4-} tetrahedral ion with the T_d symmetry, the four normal vibrational modes have been predicted to occur at the following wave numbers: 777 cm^{-1} [ν_1 (A_1) symmetric stretching],

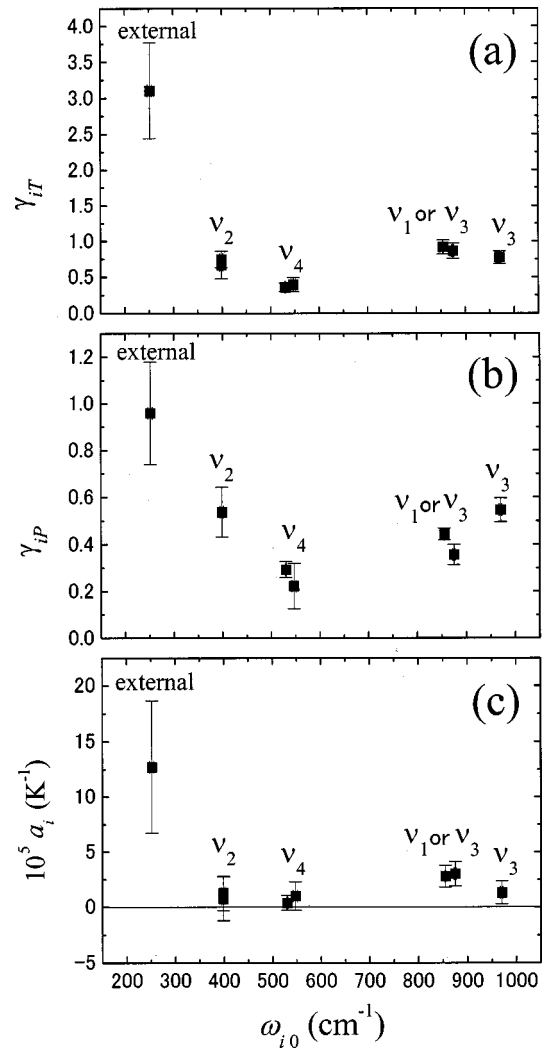


FIG. 3. Values of (a) γ_{iT} , (b) γ_{iP} , and (c) a_i for the Raman bands of Ca_2SiO_4 . γ_{iT} and γ_{iP} parameters are proportional to the equilibrium length of a considered bond (i), r_i ; $\gamma_{iT} \propto KTr_i^3$ and the local thermal expansion coefficient of a considered bond (i), α_i ; $\gamma_{iP} \propto \alpha_i/\alpha$, respectively. The zero lines in (a) and (b) represent pure harmonic behavior. The zero line in (c) represents pure harmonic or quasiharmonic behavior.

448 cm^{-1} [ν_2 (E) doubly degenerate in-plane bending], 935 cm^{-1} [ν_3 (F_2) triply degenerate asymmetric stretching], and 607 cm^{-1} [ν_4 (F_2) triply degenerate out-of-plane bending].²¹ Since the site symmetry of the SiO_4 group is modified in the crystalline lattice, the spectra will be varied by the selection rules. However, the internal modes originate from the ν_1 , ν_2 , ν_3 , and ν_4 modes of the isolated ion. When compared with vibrational modes of the isolated SiO_4^{4-} tetrahedral ion, the bands $\omega_{i0} = 399, 530, 547,$ and 970 cm^{-1} probably correspond to the modes derived from the $\nu_2, \nu_4, \nu_4,$ and ν_3 internal modes of the SiO_4 tetrahedra, respectively. The two bands $\omega_{i0} = 855$ and 875 cm^{-1} may be due to the ν_1 or ν_3 internal mode of the SiO_4 group. It is difficult to assign the external lattice mode $\omega_{i0} = 251\text{ cm}^{-1}$ to the Ca or Si mode. Several vibrational band assignments have been performed on Mg_2SiO_4 .^{22,23}

2. Anharmonic parameters a_i

a_i corresponds to an intrinsic anharmonic parameter. It expresses a change in frequency induced by temperature at constant volume. f_i is also an intrinsic anharmonic term expressing a frequency change due to a pressure change at constant volume. In the pure harmonic approximation $a_i = f_i = c_i = e_i = \gamma_{iP} = \gamma_{iT} = 0$. In the quasiharmonic approximation all the bonds in a given crystal volume behave harmonically, but their equilibrium lengths can change. It follows that $a_i = f_i = 0$, $\gamma_{iP} = \gamma_{iT}$, and $c_i/e_i = -\alpha K_T$. Pressure and temperature affect vibrational frequencies only through volume changes. In this approximation γ_{iP} and γ_{iT} bear the same information. In a true anharmonic model none of the above parameters is equal to zero and they can all be calculated from the experimental measure of c_i and e_i . $a_i \neq 0$ implies that frequency changes are not driven by volume changes alone.

The difference between quasiharmonicity and intrinsic anharmonicity can be explained by studying the frequency shift of a given mode in response to pressure, temperature, and volume changes. It appears that the anharmonicity calculated from Eq. (6) is higher for the low-frequency mode (i = external) than for the high-frequency modes [$i = \nu_2, 2\nu_4, 2(\nu_1$ or $\nu_3)$, and ν_3], reflecting the important instability of the low-frequency mode [Table I and Fig. 3(c)], which would be caused by its weaker and softer bond as described in Sec. III B 1. The internal modes of the SiO_4 tetrahedra will be more stable due to their stronger and harder bonds. Generally the a_i parameter is negative or close to zero.²⁴ Our results must be considered with caution in the absence of complete measurements of a_i of all the crystal vibrational modes

(acoustic, IR, and Raman active) under pressure and temperature. However, it is the certain fact that the a_i parameter for the lattice vibration mode (low-frequency mode) is located far from zero.

IV. CONCLUSION

In this study Raman spectra of Ca_2SiO_4 have been obtained at temperatures up to 1723 K by using a system of UV Raman spectroscopy. The intrinsic anharmonic behavior of Ca_2SiO_4 has been studied by using data of high-temperature and high-pressure spectroscopic measurements. The measure of a_i allows calculations of intrinsic anharmonic effects on the heat capacity at constant volume and the departure from the Dulong and Petit limit. The ultraviolet Raman technique would open a door for powerful tools that can be used to study anharmonicity, for which accurate thermochemical measurements at high temperature cannot be achieved.

ACKNOWLEDGMENTS

The authors are thankful to Professor Masato Kakihana and Professor Masatomo Yashima (Tokyo Institute of Technology) for their help on the UV Raman system for high-temperature measurements. We are greatly indebted to Dr. Akihiko Nakatsuka (Yamaguchi University) and Dr. Cesar R. Foschini (Massachusetts Institute of Technology) for their valuable comments. The present work has been supported partly with the cooperative program in Materials and Structures Laboratory at Tokyo Institute of Technology and Japan Cement Association.

*Corresponding author. Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, 2-16-1, Tokiwadai, Ube, Yamaguchi, 755-8611, Japan. FAX: +81-836-85-9601. Electronic address: fuji@amse.yamaguchi-u.ac.jp and hiro@hiro-fuji.net

[†]Also at: Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139. Electronic address: hirofuji@mit.edu

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