Research Article

Temperature Dependence of the Raman Frequency of an Internal Mode for SiO₂-Moganite Close to the α - β Transition

Mustafa Cem Lider and Hamit Yurtseven

Department of Physics, Middle East Technical University, 06531 Ankara, Turkey

Correspondence should be addressed to Hamit Yurtseven, hamit@metu.edu.tr

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The temperature dependence of the 501 cm⁻¹ frequency of the vibrational mode is analyzed for SiO₂-moganite. The experimental data for the heating and cooling cycles of moganite from the literature is used for our analysis. The coexistence of α - β moganite is obtained over a finite temperature interval, and the α - β moganite transition at around 570 K is studied, as observed experimentally.

1. Introduction

SiO₂-moganite has been studied using various techniques over the years since it was discovered [1, 2] and approved as a mineral species in 1999. Its structure has been determined in some previous studies [3, 4]. It exhibits a displacive phase transition from the low temperature α -moganite (monoclinic) to the high temperature β -moganite at around 573 K. Its space group in the α phase is I2/a whereas in the β phase it is Imab. During the phase transformation, hysteresis occurs for the cooling and heating cycles, which indicates a first-order type as opposed to the α - β transition in quartz ($T_C = 846$ K). This transition in quartz is considered to be of a second order in the presence of the soft modes [5]. It has been observed that the 207 cm⁻¹ mode disappears completely above the α - β quartz [6]. More recently, the experimental analyses have identified a first-order character to the phase transition between α -quartz and the intermediate incommensurate phase [7–9]. In our recent study, we have calculated the temperature dependence of the Raman frequency shifts and the linewidths for the optical lattice vibrations of the 128 cm⁻¹ and 466 cm⁻¹ in the α -phase of quartz from the anharmonic self-energy [10]; we have also calculated [11] the temperature dependence of the damping constant (Raman bandwidths) for the lattice modes of 147 cm⁻¹ and 207 cm⁻¹

close to the α - β transition in quartz by considering the soft mode behavior in this crystal.

In regard to the SiO₂-moganite system, there is no indication of soft mode behavior in this mineral. Using hard mode spectroscopy [12], it has been observed that the 501 cm⁻¹ Raman mode is the highest intensity mode in moganite [13] whereas in quartz the highest intensity mode occurs at 465 cm⁻¹. It has also been pointed out that a relatively intense mode at 463 cm⁻¹ in moganite overlaps the 465 cm⁻¹ mode in quartz [13]. As observed experimentally [13], the 501 cm⁻¹ mode can be associated with the structural phase transition in moganite. Its spontaneous vibrational displacement is expected to vary linearly with the square of the order parameter, which is usually the case in the behavior of hard modes in the Raman spectra for a second-order transition [12].

In the previous study [13], the temperature dependence of the Raman frequency and bandwidth for this symmetric stretching bending vibration (501 cm⁻¹ B_{3g} mode) have been measured for the α - β transition in moganite experimentally. The temperature dependence of the unit cell volume of moganite has also been measured for the α - β transition in this mineral previously [13].

In this study, we calculate the Raman frequency of this internal mode using the volume data [13] through the mode

TABLE 1: Values of the coefficients for the experimental unit-cell volume [13] according to (3) for the α - β phases of moganite. The V_1 value which was obtained by extrapolating the $V(T)$ data [13] at around $T = 303$ K is also given here.

V ($\text{\AA}^3$)	a ($\text{\AA}^3$)	$b \times 10^{-2}$ ($\text{\AA}^3/\text{K}$)	$-c \times 10^{-6}$ ($\text{\AA}^3/\text{K}^2$)	V_1 ($\text{\AA}^3$)	Temperature interval (K)
α - β phase	111.71	1.09	6.61	114.41	$297.5 < T < 868.3$

Grüneisen parameter for the α - β transition in moganite. By determining the mode Grüneisen parameter using the vibrational frequency [13] and the unit cell volume [13] data, the Raman frequencies of the 501 cm^{-1} mode are predicted for the α - β transition in moganite.

In Section 2 we give our calculations and results. Discussion and conclusions are given in Sections 3 and 4, respectively.

2. Calculations and Results

The Raman frequency ν can be calculated from the crystal volume V through the isobaric Grüneisen parameter γ_p defined as

$$\gamma_p = - \left(\frac{\partial \ln \nu / \partial T}{\partial \ln V / \partial T} \right)_p, \quad (1)$$

where T and p are the temperature and pressure, respectively.

Thus, using the temperature dependence of the volume the Raman frequency can be predicted by solving (1) as

$$\gamma_p(T) = \nu_0 + \nu_1 \exp \left[-\gamma_p \ln \left(\frac{V(T)}{V_1} \right) \right], \quad (2)$$

where ν_1 and V_1 are the values of the Raman frequency and crystal volume, respectively, at a constant temperature. ν_0 represents the background frequency of the Raman mode considered.

We calculated here the temperature dependence of the 501 cm^{-1} vibrational frequency for heating and cooling cycles of moganite using the unit-cell volume data of this crystal [13]. For this calculation, we first analyzed the unit-cell volume data [13] at various temperatures for the α - β phases of moganite according to a quadratic equation

$$V = a + bT + cT^2, \quad (3)$$

where a , b , and c are constants. Table 1 gives the values of those coefficients from our fit. We plot the observed unit-cell volume [13] as a function of temperature for the α - β phases of moganite according to (3) with the coefficients given in Figure 1.

In order to predict the temperature dependence of the 501 cm^{-1} vibrational mode of moganite in the α - β phases, from the unit-cell volume data [13], we needed to determine the isothermal mode Grüneisen parameter γ_p according to (2). For this determination, we used the experimental data [13] for the Raman mode of 501 cm^{-1} in the α - β phases of moganite. For the heating and cooling cycles of the 501 cm^{-1} vibrational frequency for the temperature interval of 300 to 900 K in the α - β phases of moganite, a quadratic equation

$$\nu(T) = a_0 + a_1 T + a_2 T^2 \quad (4)$$

FIGURE 1: Experimental unit-cell volume [13] as a function of temperature for the the α - β phases of moganite. Solid curve represents (3) fitted to the experimental data.

was used with constants a_0 , a_1 , and a_2 . By fitting (4) to the experimental frequencies [13], the values of the coefficients were determined for both heating and cooling cycles, as given in Table 2. Thus, from this fit of (4) to the experimental vibrational data [13] and the experimental data for the unit-cell volume [13], we were able to determine the value of the isobaric mode Grüneisen parameter as $\gamma_p = 0.75$ for this Raman mode. By assuming that the Grüneisen parameter (γ_p) remains constant throughout the α - β phases of moganite, the Raman frequencies of the 501 cm^{-1} mode were then calculated at various temperatures using the unit-cell volume data [13] according to (2). From our fitting, the background frequency was obtained as $\nu_0 = 0.72 \text{ cm}^{-1}$ for both heating and cooling cycles in moganite. Values of V_1 and ν_1 which were obtained from the extrapolations of the $V(T)$ and $\nu(T)$ data at $T = 303$ K are given in Tables 1 and 3, respectively. In Figures 2 and 3, we plot our calculated vibrational frequencies of 501 cm^{-1} mode as a function of temperature for the cooling and heating cycles, respectively, in the α - β phases of moganite. The observed frequency data [13] are also given in those plots.

3. Discussion

We calculated here the Raman frequencies of the symmetric stretching-bending mode (B_{3g}) as a function of temperature from the experimental unit-cell volume data [13] for the α - β transition in moganite, as shown in Figure 2 (cooling) and Figure 3 (heating). These figures show that our predicted frequencies of this particular internal mode agree with

TABLE 2: Values of the coefficients from the fit of (4) to the experimental data [13] for heating and cooling cycles for the vibrational frequency of 501 cm^{-1} in the α - β phases of moganite.

Vibrational frequency ω (501 cm^{-1})	a_0 (cm^{-1})	$-a_1 \times 10^{-2}$ (cm^{-1}/K)	$a_2 \times 10^{-5}$ ($\text{cm}^{-1}/\text{K}^2$)	Temperature interval (K)
Heating	507.0	2.57	1.29	$301.6 < T < 873.8$
Cooling	506.84	2.63	1.39	$303.5 < T < 875.3$

TABLE 3: Values of the isobaric mode Grüneisen parameter γ_p , extrapolated value ν_i at around $T = 303 \text{ K}$ and background frequency ν_0 for the vibrational frequency indicated in the α - β phases of moganite.

Vibrational frequency	γ_p	ν_i (cm^{-1})	ν_0 (cm^{-1})
501 cm^{-1}	0.75	500.1	0.72

FIGURE 2: Vibrational frequency calculated as a function of temperature according to (2) for the cooling cycle in the α - β phases of moganite. Observed vibrational frequencies are also shown here.

the observed frequencies [13] except in the hysteresis region where the high- and low-temperature modifications coexist over a finite transition interval. It has been suggested that there occurs an intermediate phase over a 1.3 K interval between the α and β phases in quartz [14]. The intermediate phase may also occur for the α - β transition in moganite. However, since the experimental unit-cell volume [13] does not give any indication of an intermediate phase in moganite as shown in Figure 1, the Raman frequencies of the 501 cm^{-1} mode which were calculated through (2) do not also show such an intermediate phase over the α - β transition in this material. This intermediate phase which can exist in moganite has been considered in quartz [14] as consisting of ordered arrays of Dauphine microtwins. However, the moganite twins result from the loss of mirror symmetry, whereas the Dauphine twins of quartz result from a loss of 2-fold symmetry along the c -axis.

FIGURE 3: Vibrational frequency calculated as a function of temperature according to (2) for the heating cycle in the α - β phases of moganite. Observed vibrational frequencies are also shown here.

As studied previously, the α - β transition in moganite is the displacive transition, and it can be associated with the internal mode of 501 cm^{-1} , as observed experimentally [13]. It has been pointed out that the variations observed for the 501 cm^{-1} peak strongly support the structural transition in moganite [14]. Thus, as a hard mode the square of the Raman frequency and also of the linewidth should be associated with the order parameter linearly, as suggested previously [13]. In fact, the observed behavior of the Raman frequency for the 501 cm^{-1} mode, which increases with decreasing temperature (Figures 2 and 3), indicates the temperature dependence of the order parameter for the α - β transition in moganite. Also, the linewidths of this Raman mode decrease with decreasing temperature, as observed experimentally [13], which can be associated with the order parameter in moganite. As stated previously, a linear variation of the order parameter with square of the frequency (spontaneous vibrational displacement) and of the linewidth (spontaneous vibrational broadening) is considered for a second-order transition in the hard mode Raman spectroscopy [15]. In the presence of the coexistence of the α and β phases, and also a possible intermediate phase in moganite, which indicates a first-order displacive transition the temperature dependence of the Raman frequency and of the linewidth for the 501 cm^{-1} mode can be examined within the framework of a second-order transition in this mineral. In fact, we examined the temperature dependence of the Raman bandwidths of this

mode by calculating the damping constant in terms of the order parameter below the transition temperature ($T_C = 573$ K) for the α - β transition in moganite. By calculating the temperature dependence of the order parameter ($T < T_C$) from the molecular field theory [16], the Raman bandwidths of the 501 cm^{-1} mode were predicted using the soft mode-hard mode coupling model [17, 18] and the energy fluctuation model [19] for the α - β transition in moganite. Our calculation of the damping constant of the 501 cm^{-1} mode failed using both models studied since it diverges as the α - β transition temperature was approached, which was not in agreement with the observed [13] Raman bandwidths. This is due to the fact that the vibrational frequency decreases anomalously as the T_C is approached from the low-temperature phase which is essentially the soft mode behavior according to a power-law formula:

$$\omega \sim (T_C - T)^{1/2}. \quad (5)$$

Our calculation indicated that the 501 cm^{-1} mode does not exhibit a soft mode behavior for the α - β transition in moganite. For the α - β transition in quartz, we were able to predict the divergence of the 147 cm^{-1} and 207 cm^{-1} Raman modes in the vicinity of the transition temperature ($T_C = 846$ K) using the models considered above, as studied in our recent work [11]. We also indicated in that work [11] that the 147 cm^{-1} Raman mode exhibits a soft mode behavior for the α - β transition in quartz. In the case of moganite, the temperature dependence of the vibrational frequency and of the linewidth of the 501 cm^{-1} mode can be further investigated to explain its α - β transition.

4. Conclusions

The temperature dependence of the Raman frequency for the internal mode (501 cm^{-1}) was calculated using the unit-cell volume data through the mode Grüneisen parameters for the α - β transition in moganite. Our calculated Raman frequencies of this mode agree with the observed data in a large temperature interval for this mineral. This shows that the observed behavior of the internal mode associated with the displacive α - β transition in moganite can be predicted adequately by the method of calculation given in this study.

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