Strong optical phonon mode of natural seraphinite probed by terahertz time-domain spectroscopy

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***Abstract*—The natural seraphinite has the optical phonon modes in the frequency range from 0.1 to 2 THz. The observed absorption modes at 0.8, 1.2, and 0.96 THz are understood as infrared active phonon modes of $A_u(z)$ and $B_u(x, y)$ symmetries, respectively. The 0.96 THz mode is, in particular, strong and narrow comparable to the reported 0.53 THz mode in α-lactose monohydrate. Experiments carried out by THz time-domain spectroscopy shows a good agreement with theoretical analysis based on the phonon-polarition dispersion relation.**

I. Introduction

THZ frequency range has been attracted for a few decades due to the state of the art technology of THz waves.

In this paper, we report the optical phonon modes of seraphinite in THz frequency range. Seraphinite is a particular form of a clinochlore mineral with gem-grade quality, which contains Mg with the chemical formula of $(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$ [1]. Figure 1(a) shows the atomic structure of seraphinite comprised of a monoclinic layered structure in the space group C2/m at room temperature [2] . The substructure of seraphinite consists of two different electrically charged layers, a talc-like nagative layer and a brucite-like positive layer [3]. Since the layers are electrically charged, the pseudo random piling in clinochore could induce polariton behaviors by illuminated light. We find that the absorptions at 0.8, 1.2, and 0.96 THz frequencies are the phonon-polariton coupled modes [4] for infrared (IR)-active optic phonons with $A_u(z)$ and $B_u(x, y)$-symmetries [5], respectively, at 26.64, 39.96, and 31.97 cm^{-1}.

II. Experimental procedure

Experiments were conducted by a conventional THz-TDS to obtain the index of refraction and the extinction coefficient [6].

Samples were prepared with two different cuts, parallel ($\parallel$)-cut with thickness of 0.8 mm and perpendicular ($\perp$)-cut with thickness of 0.96 mm, with respect to the feather-like pattern. The sample rotation was carried out by a motorized rotation mount and the sample was attached on the aluminum metal holder with a hole diameter of 5 mm.

III. Results

When the measured transmitted THz waveforms were compared with and without the sample, the complex refractive index ($\widetilde{n} = n + i\kappa$) and the extinction coefficient ($\alpha = 2\omega\kappa/c$, c is the speed of light.) of seraphinite are obtained from the transmission amplitude spectrum and spectral phase difference [6].

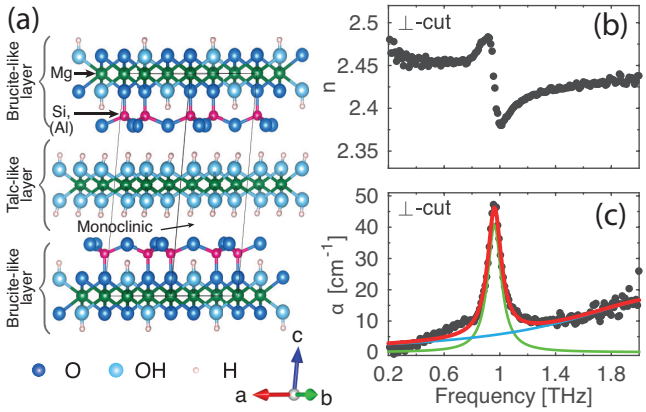

Fig. 1. (a) Atomic structure of seraphinite with position parameters from Ref. [2]. (b, c) The measured refractive index and the extinction coefficient of $\perp$-cut seraphinite at 120°. The fitted red sold line has a Q-factor of 8 at 0.96 THz.

Predicted by the factor group analysis [5], [7], the seraphinite with the space group of C2/m has the dipole momenta of A_u and B_u modes, which are inclined at the z-axis and placed in the ab-plane, respectively. The principle coordinates $(x,\ y,\ z)$ of this crystal are related to the crystallographic coordinates $(a,\ b,\ c)$ as follows: $x||a$, $y||b$, and $\angle(a, c)$= 96.35(5)° [2].

Figures 1(b) and (c) show the measured optical constants of the investigated $\perp$-cut seraphinite measured at azimuthal angle of 120 °. A strong absorption peak is shown at 0.96 THz with a bandwidth of 0.12 THz (FWHM). The corresponding quality (Q= $\nu/\Delta\nu$) factor of 8.14 is comparable to the Q factor of alpha-lactose monohydrate [8] when the extinction coefficient is fitted to two Lorentzian functions (green and blue solid lines) shown in Fig. 1(c). The extracted parameters are summarized in Table I.

TABLE I
THE CHARACTERISTICS OF 0.96 THZ MODE OF $\perp$-CUT SERAPHINITE.

Materials	ν [THz]	$\Delta\nu$ [THz]	Q-factor	References
Seraphinite	0.960	0.120	8.14	This work
α-Lactose	0.525	0.069	7.60	Ref. [8]

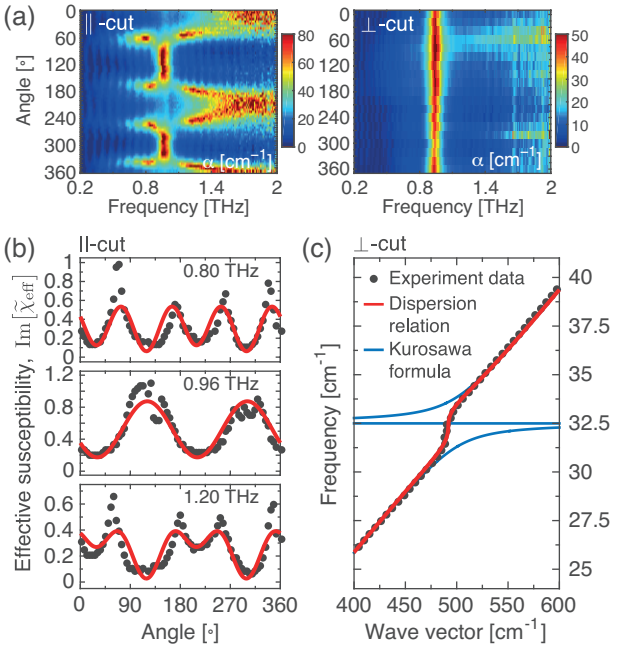

Fig. 2. (a) The extinction coefficients of ∥-cut and ⊥-cut seraphinites measured by varying the azimuthal angle from 0° to 360° with respect to the THz polarization. (b) $\chi_{\rm eff}$ of the ∥-cut seraphinite. $\chi_{\rm eff}$ for A_u (0.8 THz, 1.2 THz) and for B_u (0.96 THz) modes are fitted to Eq. (1) and Eq. (2) represented by the red solid line, respectively. (c) The Phonon-polariton dispersion curve of ⊥-cut seraphinite measured at azimuthal angle of 120 °.

The experimental results in Fig. 2 show that the investigated seraphinite has a biaxial birefringence and angle dependent behavior, thus the dielectric function should be defined by a tensor with a similar form in Ref. [7]. The extinction coefficients of ∥-cut and ⊥-cut seraphinite shown in Fig. 2(a) were measured by varying the azimuthal angle.

The isotropic excitation behavior in the ⊥-cut seraphinite can be explained by the fact that A_u modes are not excited and only B_u modes are excited when the incident wave propagates along the z direction to the ⊥-cut crystal. Therefore 0.96 THz mode is assigned to B_u modes. However, the ∥-cut seraphinite exhibits the anisotropic excitation behavior, which can be explained by the polarizability, since the angle dependence (θ) of the polarizability ($\tilde{P}(\omega,\theta) = \epsilon_0 \tilde{\chi}_{\rm eff}(\omega,\theta)\tilde{E}$) is the same as that of the effective susceptibility defined by $\tilde{\chi}_{\rm eff}(\omega,\theta) = \{n(\omega,\theta) + i\kappa(\omega,\theta)\}^2 - 1$ [9]. Then the angle dependence of $\mathrm{Im}[\tilde{\chi}_{\rm eff}]$ shown in Fig. 2(b) can be described by the third-order and linear polarizability in the forms

$$P^{(3)}(\theta) \propto c_{11}\sin^4\theta + c_{12}\cos^4\theta + 6c_{13}\cos^2\theta\sin^2\theta, \quad (1)$$

$$P^{(1)}(\theta) \propto c_{21}\sin^2\theta + c_{22}\cos^2\theta, \quad (2)$$

where the coefficients are denoted by c_{ij}.

IV. Discussion

The absorption modes at 0.8, 1.2, and 0.96 THz are understood as the IR-active phonon modes from its monoclinic structure, which can be described by the phonon-polariton dispersion relation expressed as a factorized relative dielectric function of its poles and zeros [10]. And the Kurosawa formula is obtained with zero damping from the factorized dielectric function [11]. When we denote the parameter $\epsilon_{\rm exp}$ by a dielectric constant at the highest frequency throughout the measured frequency range, the modified phonon-polariton dispersion for a single mode is given by [4], [10]

$$\widetilde{k}(\omega) = \frac{\omega}{c}\left[\epsilon_{\rm exp}\,\frac{{\Omega_{\rm LO}}^2 - \omega^2 - i\omega\Gamma_{\rm LO}}{{\Omega_{\rm TO}}^2 - \omega^2 - i\omega\Gamma_{\rm TO}}\right]^{1/2}, \quad (3)$$

where $\Omega_{\rm TO}$ ($\Omega_{\rm LO}$) and $\Gamma_{\rm TO}$ ($\Gamma_{\rm LO}$) are the resonant frequency and the damping constant of the transverse optical (longitudinal optical) mode, respectively.

Figure 2(c) shows the phonon-polariton dispersion curve extracted from the measurement of the ⊥-cut sample at $\theta = 120°$ using $\mathrm{Re}\big[\widetilde{k}(\omega)\big] = \omega/c\cdot\sqrt{n^2(\omega)+\kappa^2(\omega)}$, which is shown in comparison with the theoretical dispersion relation using the real part of Eq. (3). The measured data shows a good agreement with the phonon-polariton dispersion. The fitting parameters are estimated from the measurement as $\Omega_{\rm TO} = 32.5 \pm 0.17$ cm^{-1}, $\Omega_{\rm LO} = 32.6 \pm 0.17$ cm^{-1}, $\Gamma_{\rm TO} = 2.74$ cm^{-1}, $\Gamma_{\rm LO} = 2.67$ cm^{-1}, and $(\varepsilon_{\rm exp})^{1/2} = 2.44$.

V. Conclusion

In summary, we have reported a spectral fingerprint of crystal seraphinite in THz frequency range. In our measurements conducted with THz-TDS, the strong IR-active modes at 0.80, 0.96, and 1.20 THz in seraphinite have been found. The 0.96 THz mode has, in particular, exhibited a strong and narrow (Q=8) absorption. The polarization-dependent THz-TDS measurements have revealed the $A_u(z)$-symmetry of the 0.80 and 1.20 THz modes and the $B_u(x,y)$-symmetry of the 0.96 THz mode. Theoretical interpretation based on the phonon-polariton dispersion relation has shown an excellent agreement with the observed phonon mode at 0.96 THz. It is expected that THz spectroscopy may be useful for identification and characterization of various gemstones.

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