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2007 J. Phys.: Condens. Matter 19 456215

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Temperature dependence of low-lying phonon dephasing by ultrafast spectroscopy (optical Kerr effect) in Ag β -alumina and Tl β -alumina

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Received 30 June 2007, in final form 6 September 2007

Published 15 October 2007

Online at stacks.iop.org/JPhysCM/19/456215

Abstract

Dephasing processes for low-lying phonons of Ag⁺ and Tl⁺ β -alumina were observed in the time domain using the femtosecond pulse laser in the temperature range of 15–350 K. The dephasing dynamics associated with the time evolution of the vibrational coherence state can be directly identified with the phonon decay in the femtosecond transient. In this study, the temperature dependence of the dephasing property was decomposed into three terms in order to understand the correlation between vibration and diffusion: (i) a static structural disorder, (ii) an anharmonic coupling and (iii) an ionic diffusion. The dephasing property of the low-lying phonon in Ag β -alumina as a superionic conductor was compared with that of the isomorphous Tl β -alumina, whose ionic conductivity was about 10³ times less than Ag β -alumina. The magnitude of static disorder shows a large value ($\hbar\Gamma_0 = 0.49$ meV) in Ag β -alumina, which is twice that of Tl β -alumina ($\hbar\Gamma_0 = 0.22$ meV) with the same structure and the same number of excess cations by nonstoichiometry. The coefficient of phonon lifetimes originating from the cubic anharmonicity of a potential well is about five times larger in Ag β -alumina than Tl β -alumina. A strongly temperature dependent decay component is only seen in the superionic conductor Ag β -alumina above 200 K, and is not observed in Tl β -alumina. This is attributed to the phonon dephasing caused by the jump motion of the Ag⁺ ions. The estimated activation energy and pre-exponential factor are $E_a = 71$ meV and $\hbar/\tau_0 = 2.86$ meV in Ag β -alumina, respectively, for the correlation time $\tau_c = \tau_0 \exp(E_a/k_B T)$. The value of $\hbar/\tau_0 = 2.86$ meV, which can be regarded as an attempt frequency for the jump, coincides with the low-lying phonon frequency $\hbar\omega_0 = 2.7$ meV, but the $E_a = 71$ meV is different from that of the dc conductivity ($E_a = 173$ meV). These results, which are strongly

coupled with the elementary excitation from oscillation to ionic diffusion in the picosecond time domain, would be of prime importance for the superionic conduction mechanism.

1. Introduction

A Na β -alumina forms a layered structure in which spinel-type blocks composed of Al and O are separated by a loosely packed plane containing Na and O. Because of the loose packing, space is available for movement of the Na ions in this plane, leading to a high two-dimensional ionic conductivity. The Na ions in β -alumina can be easily exchanged with monovalent ions such as Ag, Tl, K, Rb and Li with the same space group $P6_3/mmc(D_{6h}^4)$ [1]. These monovalent ions are distributed on three different types of sites, commonly referred to as Beavers–Ross (BR), anti-Beavers–Ross (aBR) and mid-oxygen (mO) sites [1]. From the x-ray diffraction results, it is shown that Na [2], K [3] or Rb [4] occupies BR and mO sites as the stable and metastable sites, respectively, while Ag [5] or Tl [3, 4] occupies BR (stable) and aBR (metastable) sites. The lattice constants of Ag and Tl β -alumina are $a = 5.595 \text{ \AA}$, $c = 22.488 \text{ \AA}$, and $a = 5.596 \text{ \AA}$, $c = 22.912 \text{ \AA}$, at room temperature, respectively. Although Ag and Tl β -alumina have nearly the same structural properties, Ag β -alumina shows a fast-ionic conductivity ($0.64 \times 10^{-2} \text{ S cm}^{-1}$ at $23 \text{ }^\circ\text{C}$) [6], and is called a ‘superionic conductor (SIC)’, while the ionic conductivity of Tl β -alumina is as small as $2 \times 10^{-6} \text{ S cm}^{-1}$ at $25 \text{ }^\circ\text{C}$ [7].

An ion in a conventional solid is vibrating its equilibrium position at finite temperature. In an SIC, however, a mobile ion vibrates at the equilibrium site, and then sometimes jumps to the neighboring metastable site, which is followed by successive jumps to give rise to a macroscopic diffusion.

Dispersionless low-lying phonon modes have been observed in most SICs (Na β -alumina $\sim 5.0 \text{ meV}$ [8], $\text{RbAg}_4\text{I}_5 \sim 2.5 \text{ meV}$ [9]). Assuming these low frequency modes to be an attempt frequency for jump diffusion, the evaluated conductivity is in good agreement with the experimental one. Thus the low-lying phonon plays an important role in the ionic diffusion.

In the case of Ag β -alumina, the low-lying phonon was identified as E_{2g} -symmetry with low energy less than 3.5 meV [10–13]. The eigenvector shows that Ag ions vibrate along the conduction plane and aluminum and oxygen are fixed at their equilibrium positions [14]. This mode was confirmed by neutron scattering [8] to be a dispersionless phonon toward the c -direction. It may be characterized as a set of oscillators in the two-dimensional layer between the spinel blocks. Similarly, in the Tl β -alumina, an E_{2g} -symmetry mode corresponding to the low-lying phonon is also observed at 4.7 meV [12, 13].

In the light scattering measurement, the vibrational frequency and its decay are inferred from Raman spectra by analyzing peak positions and band shapes. Raman spectroscopy is a powerful technique to investigate the phonon dynamics, whose frequency shifts and widths yield quantitative values for the frequencies and relaxation times [13]. However, the low-lying phonon of the SIC is so strongly damped and so low in frequency that it often merges into a central peak. In this case the Raman spectral response can be very difficult to distinguish from quasi-elastic response. Therefore, it is difficult to analyze the intrinsic dephasing process from the band width in the SIC.

Instead of frequency response experiments like the Raman scattering, we present here the femtosecond time-resolved observation (optical Kerr effect spectroscopy; OKE) for the low-lying phonons of Ag β -alumina and Tl β -alumina. This method detects the time-dependent third-order polarization, which exhibits underdamped sinusoidal modulations with frequencies

corresponding to all Raman-active modes that are accessible within the pulse width [15, 16]. The modulations are monitored as a transmitted intensity of the polarized probe pulse.

In this study, the low-lying phonon of Ag β -alumina was measured in the time domain by a femtosecond pulse laser to understand the process of motion from oscillation to diffusion in the picosecond time domain. That of Tl β -alumina was also investigated to compare the ion dynamics to the superionic conductor Ag β -alumina.

2. Experimental details

Single crystals of Na β -alumina grown from the melt were provided by Toshiba [17]. The Ag and Tl isomorphs were prepared by an ion exchange procedure to keep the original Na β -alumina specimen in molten AgNO₃ or TlNO₃ at 330 °C for 100 h [1]. The Ag(Tl) β -alumina sample is a clear and colorless single crystal, whose crystallographic axis was identified by the back-reflection Laue method. The chemical formula of M β -alumina used in this work is determined by ICP-AES (Optima3300, PerkinElmer) to be 1.17(M₂O)·11(Al₂O₃) (M = Ag or Tl).

The ultrafast optical Kerr spectroscopy was carried out in two different types of femtosecond pulse laser systems in the temperature range 98–300 K using a liquid nitrogen cryostat and at 17–300 K using a liquid helium cryostat, respectively. The excitation sources of femtosecond pulses were generated by a mode locked Ti:sapphire laser (500 mW and 600 mW in average power) pumped by the output of a CW argon ion laser (20 W and 7 W), routinely yielding a train of 250 and 100 fs duration pulses with a repetition rate of 150 kHz and 80 MHz, respectively. Its central wavelengths were 805 nm in the 150 kHz pulse repetition system and 755 nm in the 80 MHz system. The OKE experiments were performed in a standard Kerr effect geometry [18]. Two femtosecond pulses were overlapped spatially and temporally inside the sample. The main (pump) pulse was used to excite a coherent phonon response through impulsive stimulated Raman scattering (ISRS), and the weak (probe) pulse was used to monitor the phonon oscillation and decay through the time-dependent birefringence, i.e. the optical Kerr effect (OKE) signal, induced by the vibrations. The sample was positioned at the spatially and temporally intersection of the pump and probe beams that were focused into the sample with a lens of 200 mm focal length. The spatial intersection was obtained by passing two beams through a pin hole with a diameter of 50 μ m, and the temporal overlapping of pump pulse and probe pulse was obtained by detecting second-harmonic generation (SHG) light from a β -BaB₂O₄ (BBO) crystal. The probe beam delay with respect to the pump was controlled by the computer-driven translation stage with a maximum resolution of 0.12 fs/step. The pump pulse polarization was adjusted to 45° with respect to the probe beam using a zero-order half-wave plate. The probe beam was passed through a pair of crossed Glan-Laser polarizers that have a specified extinction of better than 10⁵ to control the polarization of the probe beam. Optical heterodyning is achieved by providing a local oscillator field in addition to the signal field at the detector [19]. A $\pi/2$ local oscillator was derived by a slight rotation (<1°) of the quarter-wave plate oriented with its first axis parallel to the polarization of the probe beam. Since the low-lying phonon of β -alumina (point group D_{6h}) belongs to E_{2g} symmetry with an off-diagonal (XY) element, this phonon can be selectively excited by the polarized light configuration as illustrated in figure 1.

The energies of the two input pulses on the sample were 180 mW (pump):30 mW (probe) in the 150 kHz pulse repetition system with the *l*-N₂ cryostat and 160 mW (pump):40 mW (probe) in the 80 MHz pulse repetition system with the *l*-He cryostat. The pump-induced variation of the local oscillator was detected as a modulation of probe intensity with a Si photodiode and a photomultiplier tube for the 150 kHz system and the 80 MHz system, respectively. The output

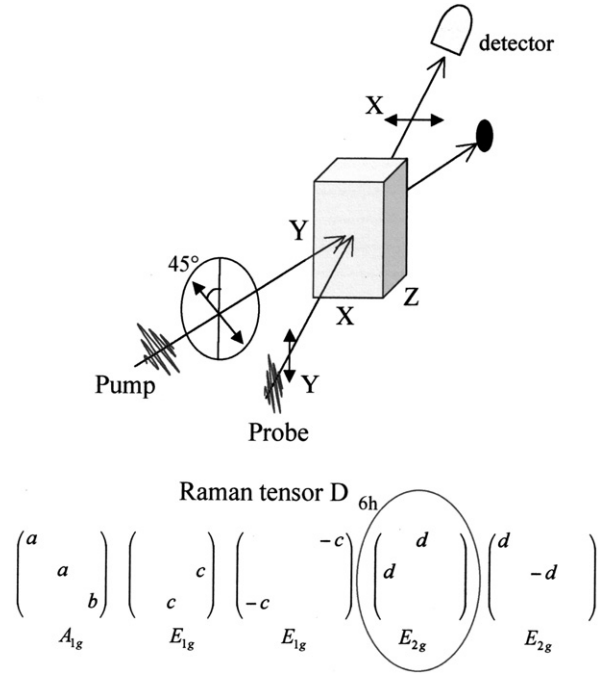


Figure 1. Illustration of experimental configuration for polarized light and Raman tensor for D_{6h} symmetry. The pump linear polarization is oriented at 45° relative to the y -axis of the crystal. The incident probe polarization is along the y -axis. This polarized configuration can excite only the E_{2g} mode as denoted by a hatched Raman tensor.

signal was amplified by a lock-in amplifier referenced to a chopper that modulated the pump beam at a frequency of about 1 kHz.

3. Results

The OKE spectrum for the low-lying mode of A_g β -alumina is shown in figure 2. The impulse response function was assumed to consist of an instantaneous electric response around time $t = 0$ ps and an underdamped sinusoidal oscillation:

$$G(t - t') = A\delta(t - t') + Be^{-\Gamma(t-t')} \sin(\omega_0(t - t') + \phi_0). \quad (1)$$

The signal intensity $I(t)$ is proportional to the response function $G(t - t')$ after convolution with the intensity autocorrelation function of the laser pulse $P(t)$ [15]:

$$I(t) \propto \int_{-\infty}^t G(t - t')P(t') dt'. \quad (2)$$

The values of the frequency ω_0 and dephasing rate Γ in equation (1) were determined by a least-squares fitting procedure as shown in figures 2 and 3. We estimated the uncertainties in our values of ω_0 and Γ to be approximately $\pm 5\%$. The error value was determined by setting one of the parameters of ω_0 and Γ at different fixed values and repeating the fitting procedure with all other parameters allowed to vary; acceptable fits could no longer be obtained when the parameters were shifted by more than 5%.

Figures 4 and 5 show the temperature dependence of the phonon frequency ω_0 and dephasing Γ , respectively. The open circle denotes the data from the 150 kHz pulse repetition

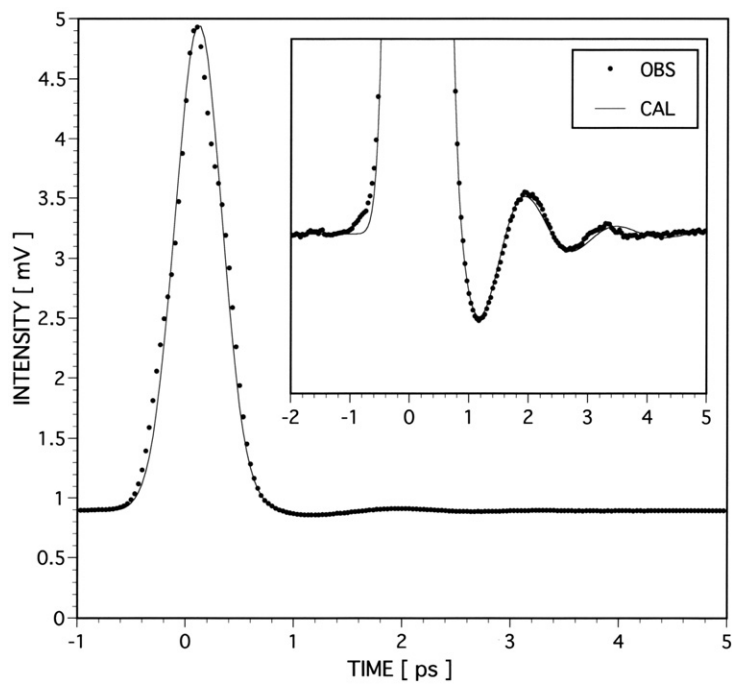


Figure 2. Comparison of an experimental OKE spectrum with a calculated one (solid curve) in Ag β -alumina at 97.7 K.

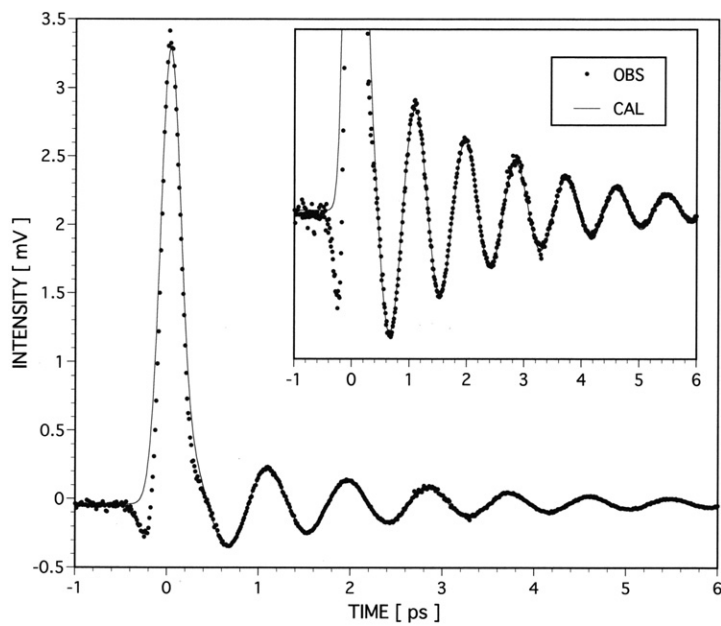


Figure 3. Comparison of an experimental OKE spectrum with a calculated one (solid curve) in Tl β -alumina at 294 K.

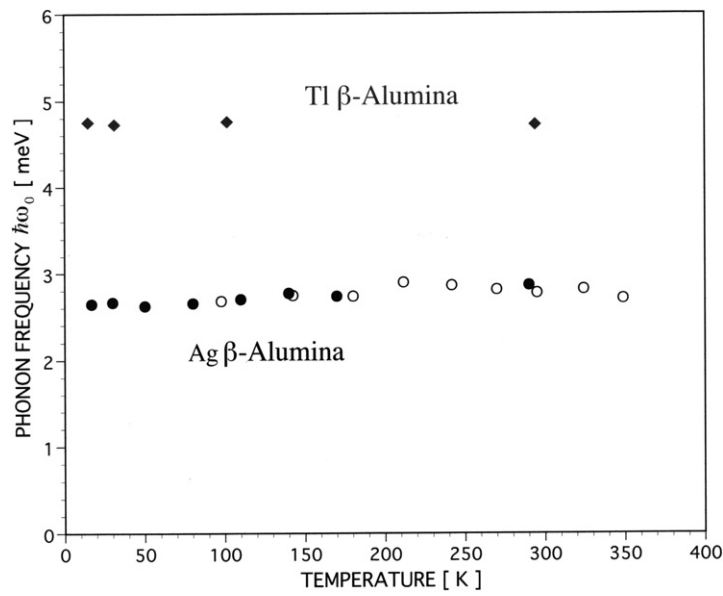


Figure 4. The temperature dependence of the phonon frequency $\hbar\omega_0$. The data were measured by two types of pulse repetition systems (150 kHz and 80 MHz), which are denoted by open and full symbols, respectively.

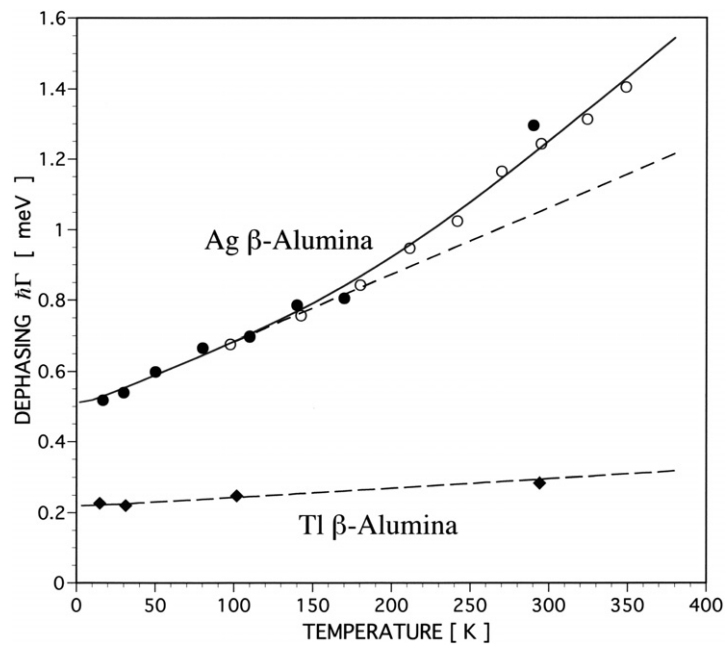


Figure 5. The temperature dependence of dephasing Γ . The data were measured by two types of pulse repetition systems (150 kHz and 80 MHz), which are denoted by open and full symbols, respectively. The solid curve is calculated using equation (6) and the dashed curve represents the three-phonon anharmonic decay with Γ_0 : $\Gamma = \Gamma_0 + C \left(1 + \frac{2}{\exp(\hbar\omega_0/2k_B T) - 1}\right)$.

system with the *l*-N₂ cryostat and the both closed symbols are from the 80 MHz system with the *l*-He cryostat. We observed no significant temperature dependence in ω_0 within the uncertainties. The evaluated frequency ω_0 of Ag β -alumina ($\hbar\omega_0 = 2.7$ meV) is in fairly good agreement with the values of 3.6 meV [10], 3.3 meV [11], 2.9 meV [12] and 2.2 meV [13] reported by Raman scattering measurements. In the Tl β -alumina, the phonon decays slightly as a single sinusoidal wave with the phonon energy 4.7 meV in figure 3. The previous Raman studies reported two bands (3.6 and 4.7 meV) regarded as the low-lying phonon [12, 13]. Colombari *et al* suggested that a band at 4.7 meV was characterized by a single Tl at a BR site, indicating it was the E_{2g} normal mode defined by the dynamical matrix. A band at 3.6 meV was interpreted as an impurity mode, which was a coupled vibration by two Tl ions near mO sites. From the other viewpoint, other symmetry modes (e.g., A_{1g}) could be considered to be mixed by the structural disorder. We could not observe any mode at 3.6 meV.

4. Discussion

The dynamics of mobile ions in SICs is a combination of the short-time local vibration and the long-time diffusive motion in the periodic potential made by the surrounding ions. The local vibration is a consequence of the non-random nature of the ion dynamics, and the jump-diffusive motion can be regarded as a random aspect which can be introduced into the generalized Langevin equation formalism by an extended friction term or a memory function form as [20]

$$m_e \ddot{Q} + m_e \Gamma_0 \dot{Q} + m_e \omega_0^2 \int_0^t M(t-t') \dot{Q}(t') dt' = R(t); \quad (3)$$

Q is the displacement of the local mode. In the case of the low-lying phonon in β -alumina the main term of Q is the displacement of the Ag(Tl) ion along the conduction plane and the effective mass m_e is its mass [14]. ω_0 is a harmonic frequency and $M(t)$ the memory function. The memory function can be evaluated by the projection operator technique to extract the correlating part of the random force to the observable. $R(t)$ is a random fluctuation force and Γ_0 is a friction to the oscillator which includes a static disorder in the crystal at $T = 0$ K. A simple expression of this equation (3) as Ag(Tl) ions move around the minima of the periodic potential is appropriate for the low-lying phonon, because the dispersionless feature is approximately regarded as an independent oscillator on the behavior of the upward and downward spinel blocks composed of aluminum and oxygen. In particular, Bruesch *et al* [20] assumed an exponential form for $M(t)$, which can be written as $M(t) = \exp(-t/\tau_c)$, where τ_c is the critical time between oscillatory and diffusive behavior. It corresponds to an oscillating particle with its average position obeying a diffusion equation. With the Fourier-Laplace transform $M(\omega) = \tau_c/(1 - i\omega\tau_c)$ of the memory function $M(t)$, frequency dependent dephasing $\Gamma(\omega)$ is given by

$$\Gamma(\omega) = \Gamma_0 + \frac{\tau_c \omega_0^2}{1 + (\omega\tau_c)^2}. \quad (4)$$

On the other hand, in the case of nonsuperionic conductors, the main relaxation mechanism of a phonon is a mode coupling decay due to the anharmonicity. The decay of the optical phonon into two longitudinal acoustic phonons gives the damping term as [21]

$$\Gamma_{CA} = C \left(1 + \frac{2}{\exp(\hbar\omega_0/2k_B T) - 1} \right). \quad (5)$$

This equation is an approximate expression for the temperature dependence of the damping constant based on three phonon processes (cubic anharmonicity in second order) and the simple Klemens model [22].

Table 1. Values of the parameters in equation (6).

	$\hbar\Gamma_0$ (meV)	$\hbar C$ (meV)	\hbar/τ_0 (meV)	E_a (meV)
Ag β -alumina	0.49	0.0184	2.86	71
Tl β -alumina	0.22	0.0036	—	—

When the phonons couple to diffuse motion, the temperature dependence of total dephasing Γ has the following form [23]:

$$\Gamma = \Gamma_0 + \Gamma_{CA}(T) + \Gamma_D(T) = \Gamma_0 + C \left(1 + \frac{2}{\exp(\hbar\omega_0/2k_B T) - 1} \right) + \frac{\tau_c \omega_0^2}{1 + (\omega\tau_c)^2}. \quad (6)$$

There are multiple sources of dephasing Γ in equation (6). A static disorder Γ_0 represents inhomogeneity, which in some cases is due to static variation in the vibrational frequency. Anharmonicity Γ_{CA} is energy relaxation, i.e. vibrational damping, through which vibrational energy is lost and vibrational excited states decay to the ground state. Ionic diffusion gives some fluctuations in frequency and phase to the vibration. The stochastic modulation process of the frequency fluctuation is associated with the dephasing in the inhomogeneous medium [24]. The phase fluctuation gives rise to ‘pure’ dephasing, through which phase coherence among an ensemble of oscillators is lost due to vibrational phase shifts that may be modeled as sudden jumps of the phase by certain amounts at random times. Γ_D represents the dephasing containing all these effects from the ionic diffusion.

The temperature dependence of the dephasing Γ was determined by the fitting procedure (see table 1 and figure 5). Since we directly measured the low-lying phonon in this experiment, the observation frequency ω corresponds to the phonon eigenfrequency ω_0 , i.e. $\omega = \omega_0$. The second term $\Gamma_{CA}(T)$ resulting from the cubic anharmonic coupling is linearly increasing with temperature (dashed curves in figure 5). The third term of $\Gamma_D(T)$ as the diffusive behavior plays a significant role in Ag β -alumina above 200 K. On the other hand, this component is negligibly small in Tl β -alumina due to the low diffusivity of Tl.

4.1. The static disorder Γ_0

Γ_0 is the decaying factor of the coherent phonon extrapolated to $T = 0$ K, which is probably due to the dephasing of the coherence by static disorder of an imperfect crystal containing impurities or dislocations. The low-lying phonon is composed of the vibration of the Ag(Tl) on the BR regular position, surrounded by the 17% excess Ag(Tl) ions deviated from the stoichiometric composition. The amount of excess charges is compensated for the Al³⁺ vacancies or excess O²⁻ ions in the spinel blocks.

The excess Ag ions in Ag β -alumina occupy 2b sites (aBR) with the interatomic distance 3.23 Å between Ag(BR) and Ag(aBR) [5]. The excess Tl ions in Tl β -alumina are distributed at 2b sites (aBR) and 6h sites near aBR with the occupancy factor 0.21(2) and 0.51(2) as the number per unit cell at room temperature, respectively [3, 4]. These interatomic distances are 3.23 Å for Tl(BR)–Tl(aBR) and 2.36 Å for Tl(BR)–Tl(6h).

The values of $\hbar\Gamma_0$ were evaluated to be 0.49 meV and 0.22 meV in Ag and Tl β -alumina, respectively, as shown in table 1. It is quite interesting to note that the $\hbar\Gamma_0 = 0.49$ meV of Ag β -alumina is much larger than the $\hbar\Gamma_0 = 0.22$ meV of Tl β -alumina. The Pauling ionic radii were reported to be 1.26 Å for Ag⁺ and 1.44 Å for Tl⁺ [25]. It is suggested that the excess Ag ions at the aBR site interrupt the normal vibratory motion of Ag at the BR site strongly rather than the Tl–Tl interaction in Tl β -alumina, even though the ionic radius of Ag is smaller than Tl.

A correlation function of solid electrolytes with disordered structures obeys a universal function in the middle frequency range. This is the well known Kohlrausch–Williams–Watts (KWW) function, which is also currently called a ‘stretched exponential’ in the Jonscher regime of the conductivity [26, 27] or a non-BPP behavior in the NMR spectrum [28]. Meyer *et al* [29, 30] found that the combined effect of disorder and Coulomb interaction reproduces the typical non-BPP behavior by Monte Carlo simulation. The strong interaction among the Ag ions and the static disorder will be of the essence in those characteristic properties for the fast-ionic conductivity in Ag β -alumina.

4.2. The anharmonicity Γ_{CA}

The coefficient C of Γ_{CA} caused by an anharmonic effect is about five times larger in Ag β -alumina than Tl β -alumina as shown in figure 5 and table 1. Matsubara proposed a cubic anharmonic thermal vibration to explain specific heat data for superionic conductor α -CuI as well as a statistical disorder model of the Cu ions [31]. It suggested that the anomalously large ionic conductivity of cuprous halides at high temperature was due to a phonon driven diffusion process of Cu ions within the shallow anharmonic potential [32, 33].

The Ag cation at the BR site exhibited a large anisotropic vibration in Ag β -alumina, which will be regarded as a cubic anharmonicity, but Roth made a refinement analysis using the effect of the statistical disorder distribution [5]. The strong cubic anharmonicity from the value of Γ_{CA} is consistent with this large anisotropic vibration, and it suggests that the Ag ions can move easily through the β -alumina rather than Tl.

The constant parameter C shows an inverse lifetime at 0 K in the anharmonic decay. Let us express the C values in terms of the mode Grüneisen parameter γ_G to help view the amount of the cubic anharmonicity. The ratio of γ_G of Ag β -alumina to Tl β -alumina is given approximately as [22]

$$\frac{\gamma_G^{\text{Ag}}}{\gamma_G^{\text{Tl}}} \approx \sqrt{\frac{C_{\text{Ag}}}{C_{\text{Tl}}} \left(\frac{\omega_0^{\text{Tl}}}{\omega_0^{\text{Ag}}} \right)^5 \frac{m_{\text{Ag}}}{m_{\text{Tl}}}} = 4.5, \quad (7)$$

where m is the atomic mass and we eliminated the ratio of the volume or the phonon velocity parameters on the assumption that these values of Ag(Tl) β -alumina are almost the same as each other. The calculation shows that the magnitude of the mode-Grüneisen parameter for the low-lying phonon in Ag β -alumina is 4.5 times larger than that of Tl β -alumina.

4.3. The ionic diffusion Γ_D

A temperature dependent decay component of the third term Γ_D in equation (6) is seen in a superionic conductor Ag β -alumina, but is not observed in Tl β -alumina, which is a poor ionic conductor. Γ_D is attributed to the phonon dephasing caused by the jump motion of the Ag^+ ions. The τ_c in equation (4) means a characteristic time of changing an oscillatory phase by jumping of one Ag^+ ion from a normal position to another site. Since τ_c is associated with the jump process of an ion through a potential barrier, it follows the Arrhenius type formalism $\tau_c = \tau_0 \exp(E_a/k_B T)$, where E_a is the activation energy and τ_0^{-1} is the attempt frequency at $T \rightarrow \infty$ K. The present \hbar/τ_0 and E_a is evaluated to be 2.86 meV and 71 meV, respectively, as in table 1.

The value of \hbar/τ_0 coincides with the phonon frequency energy $\hbar\omega_0 = 2.7$ meV. It is consistent with the strong coupling between the low-lying phonon and the ionic diffusion.

The activation energy of Ag^+ migration in Ag β -alumina has been also evaluated to be 105 meV from quasi-elastic light scattering [34], 122 meV from NMR [35] and 173(3) meV

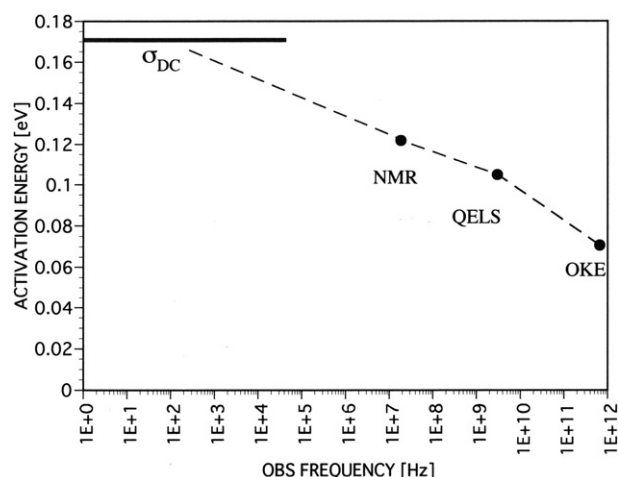


Figure 6. The observation frequency dependence of the activation energy: σ_{DC} [6], NMR [35], QELS [34] and OKE (present study).

from dc conductivity [6]. The discrepancy among these values depends on the time- (frequency) scale of the observation; they are decreasing systematically as the frequency is increased as shown in figure 6. It suggests that the different motions between the local hopping such as back-and-forth jumps and the long-range diffusion yield the different activation energies. Sato and Kikuchi [36] theoretically discussed the cation diffusion and ionic conductivity in the β -alumina using the path probability method under the pair approximation. The model system is divided into two sublattices, BR and aBR. Cations preferentially occupy BR sites, whose potential energy is lower than aBR sites and those cations interact with the ions in the nearest-neighbor sites (BR or aBR) with the interaction energy ε . They show that the long-range diffusion is expressed by some extra factors V and W in the conventional random walk approach. The factor V , which is called the *vacancy availability factor*, is the probability that a vacant site comes at the nearest-neighboring site to jump. The factor W , which is called the *effective jump frequency factor* or the *bond-breaking factor*, is the contribution from the surrounding mobile cations. The slope of W depending on $1/T$ is significantly added to the intrinsic activation energy of the cation jump. Since the present study observes the fastest time domain in the ionic motion, the obtained 71 meV is probably corresponding to the intrinsic activation energy for the jump. The difference between 71 meV from the OKE and 173(3) meV from the conductivity is due to the factor W associated with the many-body problem in the long-range diffusion. This is proof that the diffusive motion of the Ag^+ ions does not behave as the free random walk in the superionic conductor $Ag \beta$ -alumina.

5. Conclusion

Low-lying phonons of Ag^+ and Tl^+ β -alumina were observed in the time domain using a femtosecond pulse laser. We investigated the $Ag \beta$ -alumina as a superionic conductor and compared the phonon property with that of $Tl \beta$ -alumina, whose ionic conductivity was about 10^3 times less than $Ag \beta$ -alumina. The dephasing factor Γ of the low-lying phonon was determined in the temperature range of 15–350 K. The temperature dependence of Γ was decomposed into three terms of a static disorder, an anharmonic coupling and an ionic diffusion.

The magnitude of static disorder shows a large value ($\hbar\Gamma_0 = 0.49$ meV) compared with the phonon frequency $\hbar\omega_0 = 2.7$ meV in Ag β -alumina. This value is larger than that of Tl β -alumina ($\hbar\Gamma_0 = 0.22$ meV) with the same structure and with the same number of excess cations by nonstoichiometry. It indicates that the excess Ag ions at the aBR site interrupt the normal vibratory motion of Ag at the BR site strongly rather than the Tl–Tl interaction in the Tl β -alumina.

The phonon lifetimes Γ_{CA} of Ag(Tl) β -alumina originating from the cubic anharmonic vibration were estimated by the temperature dependence of Γ . It was found that the mode-Grüneisen parameter of the low-lying phonon of Ag was 4.5 times larger than that of Tl.

The decay component Γ_D of the third term in equation (6) significantly appeared above 200 K in Ag β -alumina, but in Tl β -alumina did not appear due to the low ionic diffusivity. The pre-exponential factor τ_0 in the characteristic time τ_c of changing a oscillatory phase by the jump motion of Ag ions can be equal to the attempt frequency at $T \rightarrow \infty$ K on the Arrhenius type formalism. The obtained value of $\hbar/\tau_0 = 2.86$ meV coincides with the phonon frequency energy $\hbar\omega_0 = 2.7$ meV. It is consistent with the strong coupling between the low-lying phonon and the ionic diffusion. The activation energy E_a for the jump motion of Ag ions was found to be 71 meV. It decreases systematically with an increase in the observed frequency; 173(3) meV (conductivity) > 122 meV (NMR) > 105 meV (QELS) > 71 meV (OKE). The present observed frequency was taken into the phonon frequency which was the fastest in the ionic motion. The energy difference of about 100 meV between OKE and conductivity will be related to the *effective jump frequency factor* in the many-body interacting system.

These present results, which are strongly coupled with the elementary excitation from oscillation to ionic diffusion in the picosecond time domain, would be of prime importance for the superionic conduction mechanism.

Acknowledgments

The authors thank Professor A Imai of AICHI Institute of Technology for preparing the β -alumina sample. The authors wish to acknowledge the contributions of Mr I Tanaka in the procedure of polishing the crystal. This work was supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, through Grant in Aid for Scientific Research on Priority Areas 439.

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