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Citation: AIP Advances 3, 122123 (2013); doi: 10.1063/1.4858421
View online: http://dx.doi.org/10.1063/1.4858421
View Table of Contents: http://scitation.aip.org/content/aip/journal/adva/3/12?ver=pdfcov
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Anharmonic behavior and structural phase transition in Yb$_2$O$_3$

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(Received 30 September 2013; accepted 10 December 2013; published online 31 December 2013)

The investigation of structural phase transition and anharmonic behavior of Yb$_2$O$_3$ has been carried out by high-pressure and temperature dependent Raman scattering studies respectively. In situ Raman studies under high pressure were carried out in a diamond anvil cell at room temperature which indicate a structural transition from cubic to hexagonal phase at and above 20.6 GPa. In the decompression cycle, Yb$_2$O$_3$ retained its high pressure phase. We have observed a Stark line in the Raman spectra at 337.5 cm$^{-1}$ which arises from the electronic transition between $^2$F$_{5/2}$ and $^2$F$_{7/2}$ multiplates of Yb$^{3+}$ (4f$^{13}$) levels. These were followed by temperature dependent Raman studies in the range of 80–440 K, which show an unusual mode hardening with increasing temperature. The hardening of the most dominant mode ($T_g + A_g$) was analyzed in light of the theory of anharmonic phonon-phonon interaction and thermal expansion of the lattice. Using the mode Gr"uneisen parameter obtained from high pressure Raman measurements; we have calculated total anharmonicity of the $T_g + A_g$ mode from the temperature dependent Raman data. 

I. INTRODUCTION

The rare earth (RE) sesquioxides [RE$_2$O$_3$] attract an enormous research interest from both technological as well as fundamental point of view. They are excellent host materials for solid state lasers and improved phosphors. They have high thermal stability and toughness suitable for their application in refractors or abrasives. At ambient, the RE oxides exist in three polymorphic phases: for large cationic radius (La to Nd), the hexagonal phase designated as the $A$-type with a space group $P\overline{3}m1$ is the most stable; for the medium cations (Sm to Gd), the monoclinic phase designated as $B$-type with space group $C2/m$ is preferred; and for the small cations (Tb to Lu), the cubic-phase designated as $C$-type with space group $Ia\overline{3}$ is the most stable.

The high pressure studies of RE sesquioxides are a subject of fundamental research; particularly to address the problems of stability and structural transformation, metal-insulator transition, enhancement or collapse of magnetic ordering, and amorphization, etc. Under such conditions the bonding patterns established for the systems near ambient conditions change dramatically, causing profound effects on numerous physical and chemical properties and leading to the formation of new classes of materials. The investigations on pressure induced phase transition of $C$-type RE oxides (e.g. Yb$_2$O$_3$, Er$_2$O$_3$, Sc$_2$O$_3$, Ho$_2$O$_3$, and Y$_2$O$_3$) have been reported by using energy dispersive x-ray diffraction (EDXD). There have also been reports on the high pressure behavior of other RE sesquioxides.

Among the $C$-type RE sesquioxides, Yb$_2$O$_3$ is of particular interest because Ytterbium ($Yb$, f$^{15}$) is one of the anomalous rare earth elements, whose oxide exhibits anomalous wavenumber decrease in the Raman modes, particularly the $T_g + A_g$ mode. The anomalies correlate with...
the thermodynamic properties and weaker bonding in Yb$_2$O$_3$. This weaker bonding is related to unique properties of Yb as a metal, which include minima in melting point and heat of vaporization, as well as relative maxima in atomic radii/volume, and also in compounds with other oxidation states. It is also suggested that these anomalies are caused by the electron-phonon interaction involving low-lying f-states which are below the Fermi level for Ytterbium. In the cubic phase the Yb atoms occupy two octahedral sites; eight atoms in (a) positions with three-fold inversion symmetry C$_3$v, and 24 atoms in (d) positions with two-fold symmetry C$_2$. For the C$_3$v site two oxygen atoms are missing across the body diagonal while for the C$_2$ site they are missing across a face diagonal.

It is well known that Raman scattering is one of the most powerful techniques to investigate the phonon spectrum, electron phonon coupling, structural phase transitions, and anharmonic behavior of the optical modes. Raman spectroscopic investigations of the high pressure phases of nanocrystalline Eu$_2$O$_3$, Y$_2$O$_3$, Gd$_2$O$_3$, Sm$_2$O$_3$, and Dy$_2$O$_3$ have already been reported. Meyer et al. have reported the structural phase transition of C-type Yb$_2$O$_3$ to the monoclinic B-type at 13 GPa in high pressure EDXD measurement and the same was observed at 20 GPa in high pressure Mössbauer measurement at 4.2 K. Hoekstra et al. obtained B-type Yb$_2$O$_3$ from C-type at 40 kbar and 1000°C and the transition was found to be irreversible. Recently Yusa et al. also demonstrated the conversion of C-type Yb$_2$O$_3$ into A-type at 19.6 GPa through an intermediate B-type phase which was observed at 15.9 GPa. Recently Lonappan reported high pressure Raman data on single crystal Yb$_2$O$_3$. However, to the best of our knowledge, there are no reports on combined studies on high pressure Raman scattering to investigate the phase transition as well as the anharmonic behavior of optical phonons as a function of temperature. In this article, we are reporting a detailed Raman scattering investigation of Yb$_2$O$_3$ as a function of pressure as well as temperature.

II. EXPERIMENTAL

Commercially available Yb$_2$O$_3$ powder was used for the present study and no pre-treatment was done. The slow scan XRD of the Yb$_2$O$_3$ powder was carried out by Bruker D-8 Advance powder X-Ray diffractometer using Cu $k_\alpha$ ($\lambda = 1.5404$ Å) radiation.

The high-pressure Raman scattering studies were carried out with a single stage Jobin-Yvon Spex monochromator using an Ar$^+$ ($\lambda = 514.5$ nm) ion laser. The Raman signal was detected by water cooled photomultiplier tube (PMT). A Mao-Bell type diamond anvil cell (DAC) with octagonal flats having about 400 $\mu$m diameter culets was used to generate high pressure up to 28 GPa. The sample was loaded in the drilled gasket hole along with a few small ruby chips (5–10 $\mu$m) for monitoring the pressure. The pressure transmitting medium used was methanol: ethanol in the ratio of 4:1.

Temperature dependent Raman measurements were performed in the backscattering geometry using the Jobin-Yvon T64000 Triple-mate instrument coupled with the Ar$^+$ 514.5 nm laser line. A charge-coupled device system with the accuracy of (0.5 cm$^{-1}$) was used to collect the scattered data. The sample temperature was varied from 80–440 K by using a continuous flow LN$_2$ optical cryostat in which the sample compartment was maintained at a pressure of $\sim 10^{-6}$ torr using a turbo-molecular pump.

III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction pattern obtained from the sample under investigation. The diffracting peaks agreed well with the JCPDS data card number 43–1037 for cubic phase of Yb$_2$O$_3$. The crystallite size of Yb$_2$O$_3$ was estimated as $\sim 96$ nm by using Debye-Scherrer relation.

The Raman spectrum of Yb$_2$O$_3$ powder obtained under ambient conditions is shown in Figure 2. As mentioned, the cubic Yb$_2$O$_3$ belongs to the space group Ia$\overline{3}$($T_d^3$) having 16 formula units per primitive cell. There are 32 Yb-ions, 24 in (d) sites with C$_2$ symmetry, and 8 in (b) sites with site symmetry C$_3$v. There are 48 oxygen atoms in the body-centered cell having
site symmetry $C_{1}$. The irreducible representations of vibrations of atoms occupying the sites are:

$$C_{2} (Yb) : A_g + A_u + E_g + E_u + 5T_g + 5T_u$$

(1a)
C₃i \left( \text{Yb} \right): A_u + E_u + T_u \quad (1b)

C₁ \left( \text{O} \right): 3A_g + 3E_g + 9T_g \quad (1c)

The eight rigid Yb atoms at C₃i site do not contribute to the Raman active optical modes, but give acoustic branch of A_u + E_u and infrared active T_u mode. Hence, the 22 Raman active optical modes of cubic Yb₂O₃ at ambient are:

\[ \Gamma = 4A_g + 4E_g + 14T_g \quad (2) \]

However, smaller numbers of modes are observed in the Raman spectra; this may be due to the fact that some of the observed modes are actually superposition of closely spaced different type of modes, which are un-separated owing to a weak factor-group interaction.⁶

As shown in Figure 2, we have observed five distinct lines (I₁–I₅) at 269.2, 301.9, 337.5, 363.8, and 613.5 cm⁻¹, and a wide shoulder in the range of 400–545 cm⁻¹. The lines (I₁–I₅) are assigned as the T_g + E_g, E_g, \( \Gamma_e(C₃i) \), T_g + A_g, and T_g, respectively; the observed line I₃ at 337.5 cm⁻¹ is referred to as a Stark level assignment for Yb³⁺ ion in C₃i site.²⁵ In the case of C-type Yb₂O₃, the Yb³⁺ ion in C₃i sites have electronic configuration Yb³⁺(Xe 4d¹⁰4f¹³5s²5p⁶), the spin-orbit and crystal-field interaction splits the f-orbital into the multiplets of \( 2F_{7/2} \) and \( 2F_{5/2} \) levels. The electronic transition from the ground state of \( 2F_{7/2} \) to the \( 2F_{5/2} \) level gives the Stark line at 337.5 cm⁻¹.²⁶

The shoulder region (400–545 cm⁻¹) is effectively the combination of two peaks at 442.3 and 521.2 cm⁻¹. The peak at 442.3 cm⁻¹ is corresponding to the T_g mode and other one is unidentified; however this mode persists and its intensity increases gradually with increase of pressure; which will be discussed later.

Pressure dependent Raman measurement of Yb₂O₃ sample taken at room temperature, is shown in Fig. 3. It is observed that the most intense I₅ peak at 363.8 cm⁻¹ progressively loses intensity and disappears at and above \( \sim 21 \text{ GPa} \), and the emerging peaks at \( \sim 510 \text{ cm⁻¹} \) dominate. When the pressure increases, new Raman modes emerge at \( \sim 483.5 \) and 517.8 cm⁻¹ at and above 11.3 GPa, particularly these two modes consistently increase their intensity and further develop in to well defined peaks. One can see from Fig. 3 that the main peak (363.8 cm⁻¹) of cubic Yb₂O₃ phase coexists with the emerging modes of new phase in a wide pressure region. At the maximum

\[ \text{FIG. 3. Pressure dependent Raman spectra of Yb}_₂\text{O}_₃ \text{ at room temperature; left inset shows the deconvolution of 515 cm}^{-1} \text{ peak at 27.4 GPa.} \]
We have calculated the mode Gr"uneisen parameters using the following equation.

\[ \gamma_i = \frac{B_0}{\omega_0} \left( \frac{d\omega}{dP} \right) \]

where, \( \omega \) is the mode frequency at ambient. The pressure coefficients of the observed cubic phase Raman modes (as listed in Table I) are obtained from the linear fitting using the equation:

\[ \omega = \omega_0 + (d\omega/dP) P \]

Out of these, the bending vibrations occur at low wave-numbers, typically between 100 and 200 cm\(^{-1}\), while the stretching vibrations occur at higher wave-numbers between 400 and 550 cm\(^{-1}\). In analogy with the previously reported modes for the hexagonal phases,\(^{27}\) the mode at \( \sim 484.8 \) may be identified as the \( A_{1g} \) and the mode at \( \sim 512.6 \) cm\(^{-1}\) may be assigned to the \( E_g \) mode. It may be pertinent to point out here that according to Shaack and Koningston,\(^{6}\) \( Yb_2O_3 \) is known to behave differently from all other rare earth sesquioxides where the Raman lines are considerably broadened. This observation is consistent with the present result.

The irreducible representations of the vibrations of the atoms in hexagonal \( Yb_2O_3 \) are:

\[ C_{3v} (Yb) : A_{1g} + A_{2u} + E_g + E_u \] (3a)

\[ C_{3v} (O) : A_{1g} + A_{2u} + E_g + E_u \] (3b)

\[ D_{3d} (O) : A_{2u} + E_u \] (3c)

Hence, the Raman active optical modes of the hexagonal \( Yb_2O_3 \) are:

\[ \Gamma = 2A_{1g} + 2E_g \] (4)

On decompression, as the pressure is released, the observed peaks shift towards lower frequency side and the intensity decreases as shown in Fig. 5. However, the starting cubic phase is not recovered at total release. Instead the most prominent band at about \( 513 \) cm\(^{-1}\) at \( 27.4 \) GPa splits into a doublet on total release, with peaks centered at \( 493 \) and \( 525 \) cm\(^{-1}\). This observation further confirms the formation of hexagonal (A) phase at high pressure, which is irreversible on decompression.

The relationship between cubic (-) and monoclinic (\( B \)) structures is not simple because the rare earth atoms are displaced with respect to the oxygen during transition from \( C \) to \( B \). The \( C \) to \( B \) transformation is reconstructive while \( C \) to \( A \) is displacive. It seems that...
the slightly different experimental conditions seem to favor either B or A phase. The B to A or A to B transition requires lesser energy as it is displacive type. In this context, it is relevant to mention here that Zhang et al. also reported a phase diagram for Gd$_2$O$_3$ according to which at low temperatures, the cubic to hexagonal phase transition is favored with application of pressure while at high temperatures, the monoclinic phase is favored. Since the kinetics of phase transformation depend in general on the pressure, temperature and the amount of non-hydrostatic stresses as well as the existence of defects; the barrier heights for transformation would also depend on these parameters.

To investigate the anharmonic behavior of optical phonons, we have studied the temperature dependent Raman spectra of Yb$_2$O$_3$ in the range of 80–440 K. The spectrum of Yb$_2$O$_3$ at 80 K (Fig. 6) shows modes at 281.3, 306.4, 332.7, 357.8, 419.9, and 435.6 cm$^{-1}$, corresponding to the $T_g + E_y$, $E_y$, $\Gamma_{el}$, $T_g + A_y$, and two $T_g$, respectively. It is interesting to observe the electronic contribution ($\Gamma_{el}$) at 332.7 cm$^{-1}$. It is also significant to point out that the shoulder region i.e. 400–550 cm$^{-1}$ region which showed very weak peaks at ambient shows well defined peaks at 80 K.

The temperature dependent micro-Raman study of Yb$_2$O$_3$ indicates more complex behavior. Observed from the Fig. 7 is the unusual hardening of $T_g + A_y$ mode at 357.8 cm$^{-1}$ upon heating;
whereas the modes at 281.3, 306.4, 419.9, and 435.6 cm$^{-1}$ do not show any significant shift within the temperature range 80–440 K; but they gradually lose their intensity, become broadened, and finally disappear above 370 K. The considerable change is observed in the most intense peak $T_g + A_g$ at 357.8 cm$^{-1}$. The frequency shift for this mode in the temperature range 80–190 K is low; however, there is a significant shift of frequency ($\sim 7$ cm$^{-1}$) above 200K and up to 440 K. A dashed straight guide line in Fig. 7 gives better recognition of frequency shift. From Fig. 8 too, where the
FIG. 7. Temperature dependent phonon behavior of Yb$_2$O$_3$ in the range 80–440 K.

Experimental points are plotted, one can see the anomalous mode hardening as the peak frequency shifts towards higher frequency side with increasing temperature.

It is known that the variation of the frequency of normal modes with change in temperature at a constant pressure arises from contributions from volume expansion and anharmonicity. The latter in turn arises from cubic and quartic anharmonicities (self-energy shift). The complete expression for the frequency as a function of temperature can be explained as:

\[ \omega(T) = \omega_0 + (\Delta \omega)_{\text{latt}} + (\Delta \omega)_{\text{anh}} \]  

(7)

Where, \( \omega_0 \) is the harmonic frequency, which was obtained as 357.8 cm\(^{-1} \), extrapolating the experimental data down to 80 K; the quasi-harmonic term \( (\omega)_{\text{latt}} \) accounts for the lattice expansion contribution; and \( (\omega)_{\text{anh}} \) is the intrinsic (true) anharmonic contribution due to cubic and quartic anharmonicities. In the most solids of positively expanding lattice, phonon mode softening results as a function of increase in temperature. The quasi-harmonic contribution can be explained as:

\[ (\Delta \omega)_{\text{latt}} = \omega_0 \left\{ \exp \left[ -\gamma_i \int_0^T 3\alpha(T) dT \right] - 1 \right\} \]  

(8)

Where, \( \gamma_i \) (= 1.543) is the mode Gr"uneisen parameter of the \( T_g + A_g \) mode obtained from the pressure dependent data above, and \( \alpha \) (= 6.6 \times 10^{-6}/K) is the linear thermal expansion coefficient of Yb$_2$O$_3$. The anharmonic contribution \( (\omega)_{\text{anh}} \) arises from the phonon-phonon interaction due to the lowest-order cubic and quartic terms in the inter-atomic potential. The anharmonic contribution as a function of temperature can be explained as:

\[ (\Delta \omega)_{\text{anh}} = A \left[ \frac{2}{\exp(\hbar\omega_0/2kT) - 1} - 1 \right] + B \left[ \frac{3}{\exp(\hbar\omega_0/3kT) - 1} + \frac{3}{\exp(\hbar\omega_0/3kT) - 1}^2 \right] \]  

(9)

The first term describes the coupling of an optical phonon to two low-energy phonons (three phonon process); the second term is due to the coupling of three phonons (four-phonon process).
A and B are the fitting parameters. The multi-phonon processes associated with the cubic terms give rise to a negative frequency shift; whereas, the shift associated with quartic anharmonicity can be either positive or negative. The resultant frequency shift due to phonon-phonon interaction may be either positive or negative depending on the relative magnitudes of the anharmonic terms in the inter-atomic potential.

In our experimental observation, the resultant shift towards higher frequency side; i.e. the positive quartic anharmonicity dominates over the volume expansion effect and third order anharmonicity in the studied temperature range of 80–440 K. The Raman profile of $T_g + A_g$ mode obtained at different temperatures was fitted by using damped harmonic oscillator (DHO) model as:

$$I(\omega) = \frac{[\chi_0 \Gamma_0 \omega_0^3 (\bar{n} + 1)]}{[(\omega_0^2 - \omega^2)^2 + \omega^2 \Gamma^2]}$$

Where, $\omega_0$ is the peak frequency, $\Gamma_0$ is the line width, $\chi_0$ is related to the peak intensity, and $n = \exp(-\frac{\hbar \omega}{k_B T}) - 1$, is the Bose-Einstein factor of phonon frequency $\omega$. It is well known that the bands related to first order Raman scattering should have different temperature dependencies. For the first order Stokes process, the intensity is directly proportional to $(\bar{n} + 1)$, hence, simple Lorentz function is not suitable for the fitting of Raman profile as a function of temperature.

As mentioned, the temperature dependent frequency shift of $T_g + A_g$ in Fig. 8 shows strong frequency hardening with increasing temperature up to $\sim 350$ K, i.e. below the Debye temperature ($T_D$) 385K of Yb$_2$O$_3$. Above the Debye temperature, the hardening process slows down. We have fitted the experimental data points (solid circles) by using equation (7) and the solid line depicts the fitted curve. The error bars represent the standard error of measuring the experimental frequency at different temperatures. The temperature dependent parameters so obtained, are listed in the Table II.

At lower temperatures ($T < T_D$) the main contribution to the hardening is due to the positive quartic anharmonicity. We have calculated the total anharmonicity (listed in Table II) of $T_g + A_g$ mode using
TABLE II. Best-fit values for anharmonic constants, true and quasi-harmonic contribution in $T_g + A_g$ mode of Yb$_2$O$_3$.

<table>
<thead>
<tr>
<th>Raman Mode</th>
<th>$\omega_0$ (cm$^{-1}$)</th>
<th>A (cm$^{-1}$)</th>
<th>B (cm$^{-1}$)</th>
<th>$\frac{d\omega}{dT}$ (cm$^{-1}$K$^{-1}$)</th>
<th>$\left(\frac{1}{\omega_0} \frac{d\omega}{dT}\right)_p$ (K$^{-1}$)</th>
<th>$\left(\frac{1}{\omega_0} \frac{d\omega}{dT}\right)_V$ (K$^{-1}$)</th>
<th>$\gamma_i\alpha$ (K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g + A_g$</td>
<td>356.8</td>
<td>-0.21</td>
<td>0.63</td>
<td>0.033</td>
<td>$8.17 \times 10^{-5}$</td>
<td>$9.19 \times 10^{-5}$</td>
<td>$1.02 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

the formula$^{34}$

$$
\left(\frac{1}{\omega_i} \frac{d\omega_i}{dT}\right)_p = \left(\frac{1}{\omega_i} \frac{d\omega_i}{dT}\right)_V - \gamma_i\alpha
$$

The first term on the right hand side describes the true anharmonic contribution and second, quasi-harmonic term. Above the Debye temperature, the hardening process slows down due to the increasing opposite effect of quasi-harmonicity arising from the thermal expansion and cubic anharmonicity.

IV. CONCLUSIONS

We have investigated the response of the optical phonons of cubic Yb$_2$O$_3$ powder as a function of pressure and temperature. The cubic Yb$_2$O$_3$ transforms to the hexagonal phase at and above 20.6 GPa. However, the mixed phase of cubic and hexagonal was identified at and above $\sim$11 GPa. The phase transition is irreversible as observed after release of pressure. We have identified the sharp intra-band electronic transition between the split unfilled f-orbital of Yb$^{3+}$ ions sitting at $C_{3v}$ sites. The temperature dependencies of the optical modes of Yb$_2$O$_3$ show an unusual hardening with increasing temperature. Using the mode Gruneisen parameter calculated from the high pressure data, we have calculated the true anharmonicity and quasi-harmonicity of the most dominating $T_g + A_g$ mode of Yb$_2$O$_3$, the temperature dependent data analysis reveals that this mode is truly anharmonic, i.e. $(\Delta \omega)_{anh}$ is the dominant factor, and leads to the unusual/anomalous mode hardening observed in the present case and this phenomenon arises from dominating quartic phonon-phonon interaction.

ACKNOWLEDGMENTS

The authors are grateful to CSIR for research grant (network project NWP-45) and Director, National Physical Laboratory for encouragement. We are thankful to Dr. S. M. Sharma and Mr. H. Poswal in BARC, Mumbai for facilitating high pressure Raman measurements.