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Pressure-Induced Antifluorite-to-Anticotunnite Phase Transition in Lithium Oxide

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Using synchrotron angle-dispersive x-ray diffraction (ADXD) and Raman spectroscopy on samples of Li$_2$O pressurized in a diamond anvil cell, we observed a reversible phase change from the cubic antifluorite ($\alpha$, Fm-3m) to orthorhombic anticotunnite ($\beta$, Pnma) phase at 50(±5) GPa at ambient temperature. This transition is accompanied by a relatively large volume collapse of 5.4 (±0.8) % and large hysteresis upon pressure reversal ($P_{\text{down}}$ at ~25 GPa). Contrary to a recent study, our data suggest that the high-pressure $\beta$-phase ($B_0 = 188±12$ GPa) is substantially stiffer than the low-pressure $\alpha$-phase ($B_0 = 90±1$ GPa). A relatively strong and pressure-dependent preferred orientation in $\beta$-Li$_2$O is observed. The present result is in accordance with the systematic behavior of antifluorite-to-anticotunnite phase transitions occurring in the alkali-metal sulfides.

1. INTRODUCTION

Lithium oxide (Li$_2$O) is one of simplest ionic oxides and it is isoelectronic to H$_2$O. At ambient pressure it exists in the antifluorite structure [1], characterized by oxygen (O$^{2-}$) ions arranged in an fcc sublattice with lithium (Li$^{1+}$) ions in tetrahedral interstitial sites (Fig. 1a). This structure is in contrast to that of isovalent symmetric ice (ice X), where the oxygen sublattice forms a bcc arrangement [2]. However, a further transformation to an antifluorite phase in ice at some pressure above 150 GPa has been predicted [3, 4], and experiments show changes in vibrational mode coupling [5] and single-crystal x-ray diffraction peak intensity [7] near 150 GPa. Recent studies argue that a new phase is either hexagonal or orthorhombic [6], but the existence and nature of this phase and the pressure at which it is reached are still uncertain [7, 8]. In further similarity to ice, for which a high-pressure, high-temperature superionic phase has been predicted [9], ambient pressure Li$_2$O becomes superionic at temperatures above 1350 K [10], prior to melting at 1705 K [11]. In the superionic phase, oxygen ions constitute a rigid framework while lithium ions move from one tetrahedral site to another via octahedral interstitial sites. Despite its marked similarities to H$_2$O, until very recently the high pressure behavior of Li$_2$O was not addressed in the literature. One report by Kunc et al. [12] identified a high pressure phase transition using powder x-ray diffraction and investigated trends under pressure using ab initio calculations, but so far data at only one pressure point in this high pressure phase has been reported.

Technological applications for this material range from possibilities for hydrogen storage (in combination with Li$_3$N [13]), to use as a blanket breeding material for thermonuclear reactors to convert energetic neutrons to usable heat and to breed tritium necessary to sustain deuterium-tritium reactions [14, 15]. Understanding the behavior of Li$_2$O at high temperatures and pressures is therefore very useful for its applications as well as a potential aid in understanding the behavior of the hot, dense ice structures which are of such great importance to planetary science, geosciences, and fundamental chemistry. Additionally, investigation of this simple material is a reference point for understanding more complex metal-oxides.

In this study, we investigate the high pressure behavior of Li$_2$O at room temperature with ADXD and Raman spectroscopy. We present further and more complete evidence for a phase transition from antifluorite to anticotunnite structure, recently observed for the first time by Kunc et al. [12], and discuss it in light of similarities to trends observed in the alkali metal sulfides.

2. EXPERIMENT

Polycrystalline Li$_2$O powder (99.5% purity, CERAC, Inc.) was loaded into a membrane diamond anvil cell (DAC) of Livermore design. Brilliant cut diamonds with 0.3 mm flats were used with a 0.15 mm diameter sample chamber in a rhenium gasket of 0.05 mm initial thickness to achieve a pressure range of 8 to 61 GPa. No
pressure medium was used in the experiments, as α-Li$_2$O has a low enough bulk modulus that non-hydrostaticity was not predicted to be a serious concern. This assumption turned out to be potentially problematic, as will be shown. In the first experiment copper was included in the sample chamber as an internal pressure indicator and in the second pressure was determined from micron-sized ruby (Al$_2$O$_3$;Cr$^{3+}$) crystals using the quasihydrostatic ruby pressure scale [16]. All sample loadings were performed in an inert environment, as Li$_2$O is hygroscopic.

High-pressure behavior of Li$_2$O was investigated by ADXD and Raman spectroscopy, both at ambient temperature. ADXD was performed at the microdiffraction beamline 16IDB of the HPCAT (High Pressure Collaborative Access Team) at the APS (Advanced Photon Source). In these experiments, we used intense monochromatic x-rays ($\lambda = 0.36798$ or $0.41285$ Å) microfocused to about 0.01 mm at the sample using a pair of piezo-crystal controlled bimorphic mirrors. The x-ray diffraction patterns were recorded on a high-resolution image plate detector (MAR 345). The recorded two-dimensional diffraction images (Debye-Scherrer rings) were then integrated to produce high quality ADXD patterns using FIT2D and analyzed with the XRDA [17] and GSAS (EXP/GUI) [18] programs.

Raman spectra were excited using an argon-ion laser ($\lambda = 514.5$ nm) focused to ~0.01 mm. Scattered light (measured in back-scattering geometry) was filtered with a 514.5 nm Super-Notch-Plus filter, analyzed with a single spectrometer (characterized by less than 3 cm$^{-1}$ spectral resolution) consisting of a 1200 grooves/mm ion-etched blazed holographic diffraction grating, and imaged with a liquid nitrogen cooled CCD camera at Lawrence Livermore National Laboratory. A spectral range of 100-1400 cm$^{-1}$ was used.

3. X-RAY DIFFRACTION

Rietveld refinements of the ADXD patterns of Li$_2$O confirm the identity of the antifluorite (α-Li$_2$O) structure (Fig. 2, top panel), which is found to be stable up to 45 GPa. Above this pressure, diffraction peaks from a new phase begin to emerge, as shown in Fig. 3. However, traces of the low-pressure phase are apparent up to nearly 55 GPa. This large coexistence region may be due to pressure gradients in the cell which arise be-

<table>
<thead>
<tr>
<th>Lattice parameters (Å)</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>(61.9 GPa)</td>
<td>4.456(2)</td>
<td>2.7865(6)</td>
<td>5.212(1)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fractional coordinates</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>0.745(1)</td>
<td>0.25</td>
<td>0.600(1)</td>
</tr>
<tr>
<td>Li(1)</td>
<td>0.883(3)</td>
<td>0.25</td>
<td>0.305(2)</td>
</tr>
<tr>
<td>Li(2)</td>
<td>0.305(3)</td>
<td>0.25</td>
<td>0.570(3)</td>
</tr>
</tbody>
</table>
cause of a lack of pressure medium. However, all diffraction peaks remain relatively sharp across the transition, demonstrating that shear stress conditions are relatively uniform. In a homogeneous sample, such a coexistence region may be due to hysteresis arising from nucleation barriers to a first-order transition, or it may indicate that this transition is kinetically hindered or sluggish. These explanations seem more likely, and are consistent with an even larger (25 GPa) hysteresis that was observed upon pressure reversal, as will be shown.

The Cu pattern in the x-ray diffraction diagrams of Fig. 3 is undesirable for a clean refinement of crystal structure, particularly so for the high-pressure phase where several reflections from Cu overlap with those from the sample. We performed an additional experiment without Cu (but with ruby) and carried out a full Rietveld profile refinement of the structure based on the anticotunnite (β-Li2O) structure (PbCl2-type, Pnma, Z = 4) identified in Ref. [12], and also seen in the similar alkali metal sulfide Li3S system [19]. Clearly, the refined results (summarized in Fig. 2, lower panel) are reasonably good even at 61.9 GPa. The origin of the small reflection near 2Θ = 15.7 is unknown, but does not originate from the sample. Refined parameters include cell parameters, profile function, fractional coordinates, thermal parameters, Chebyshev polynomial background and the spherical harmonic (6th order) correction for preferred orientation (PO). The starting atomic coordinates were those determined for Li2S in the Pnma structure at 7.9 GPa; a = 5.92 Å, b = 3.65 Å, c = 6.90 Å, xO = 0.77, xLi1 = 0.98, xLi2 = 0.32, zO = 0.61, zLi1 = 0.36, zLi2 = 0.56. The final refinement converges to R(F2) = 0.1197, with atom positions given in Table 1. At this pressure, a refinement of the PO correction yielded a texture index of 1.5437, indicating a moderate PO in the orthorhombic phase at 61.9 GPa (where a texture index value of 1.0 means no texture and 3.0 is strong texture). This effect is confirmed by the presence of clear intensity variations around the powder diffraction rings shown in Fig. 4. The PO appears to increase from 53 to 61 GPa (these parameters were, however, taken during separate experiments), an effect which may lead to the intensity inversion of the two most prominent peaks which is observed between 53 and 61 GPa in the diffraction spectra. Because of the quality of the data and relatively small number of diffraction peaks available, the refinement was not entirely conclusive, and the resulting structure must, therefore, be viewed as approximate.

The crystal structure of β-Li2O can be understood to consist of chains of distorted tricapped trigonal prisms of cations parallel to the y-axis, giving the anion a coordination number of 9 (Fig. 1b). Near the transition, the polyhedral cation-anion distances range from 1.664 Å to 2.246 Å with an average of 1.89 Å. These values are reasonable, based on the Li-O distances quoted for lithium oxide clusters in Ref. [20]. In comparison, in the α-Li2O structure, the anion coordination number is 8 with a cation-anion distance of 1.79 Å near the transition. There is a 5.4 ± 0.3 % volume collapse across the transition.

Fig. 5 shows the pressure-volume data of the two phases, along with the best fit 3rd order Birch-Murnaghan equation of state (EOS) curves. Also shown are experimental data points and calculated EOS curves from Ref. [12]. Fitting parameters are summarized in Table II. Because of a limited pressure range studied for β-Li2O, it was necessary to constrain B′ to equal 4. This approximation was based on the procedure adopted by Grzechnik et al. [19] in the case of Li3S. Variation of this value between 3.5 and 4.5 resulted in at most a 12% difference in B0 and a 1% difference in V0. The agree-
ment between experimental and calculated equations of state for α-Li$_2$O suggest that pressure is reasonably hydrostatic in this phase. Contrary to the results of Kunc et al. [12], under pressure we do not see major broadening of fluorescence line spectra from the ruby pressure calibrant in the α phase, an observation which could indicate that this phase supports substantial shear stress.

Although the single experimental data point shown for the high pressure β phase in Ref. [12], which was also acquired without a pressure medium, agrees well with the present work, there is a dramatic disparity between their calculated equation of state and the experimental one from this study. The β-Li$_2$O pressure-volume data from Ref. [12] are generated from \textit{ab initio} total energy DFT calculations, using the Projector Augmented Waves (PAW) method. In the high pressure phase, the lattice constants and internal positions are determined by a process of ‘relaxing’ these parameters, minimizing all forces at each step. In the experiment, however, the proposed increase in PO with pressure may suggest an increase in stress inhomogeneity as well, a highly non-hydrostatic state which is not well modeled by the ‘relaxed’ structure in the calculation. The use of an optimally hydrostatic pressure medium in a future experiment may indicate just how well the theoretical model approximates reality in this case. It is doubtful that non-hydrostaticity alone can explain away the discrepancy, however. If the value for bulk modulus for the β phase were actually as close to that of the α phase as theory predicts, it is unlikely that non-hydrostatic effects would cause such a large ‘error’ in the experimental equation of state of the β but not the α phase.

Although the dramatic factor-of-two increase in bulk modulus across this phase transition appears anomalously large, actually a similar (and larger) increase is recorded for the antifluorite-antitcotunnite transition in Li$_2$S [19] and, although values for bulk modulus are not quoted, it appears that a similar effect is seen in Na$_2$S [21]. An examination of the pressure evolution of the a, b and c lattice parameters, shown in the inset of Fig. 5, may explain the large increase in bulk modulus. We find that the b-axis is much stiffer (almost three times greater) than the a and c axes. Thus, the trigonal prism chains shown in Fig. 1b are seen to be very rigid and to strongly resist compression. This is consistent with the sizable directional effects which are apparent from the intensity variations of the diffraction rings in Fig. 4.

### 4. RAMAN SPECTROSCOPY

The pressure-induced changes in Raman spectra of Li$_2$O give further evidence of a phase transition beginning near 49 GPa upon increasing pressure, as shown in Fig. 6. The low-pressure α phase has four formula units per unit cube. Factor group analysis gives one Raman active optical phonon mode T$_{2g}$, which describes motion of the Li sublattice. This mode is seen in the Raman spectrum near 575 cm$^{-1}$ at low pressure. At the phase transition from α to β there is a considerable lowering of symmetry and consequently a significant increase in number of modes. The β phase has four formula units per unit cube, and factor group analysis yields 6A$_g$ + 3B$_{1g}$ + 6B$_{2g}$ + 3B$_{3g}$ Raman active phonon modes. In the Raman spectrum of the β phase, we see three prominent bands (near 750, 800 and 830 cm$^{-1}$) and at least seven weaker bands at lower Raman shifts, not counting even weaker features appearing as shoulders of these bands. Since the sample is powder, a precise mode assignment for the Raman peaks is difficult. The observation of fewer modes than predicted by group theory is likely due to accidental degeneracy, insufficient instrumental resolution, and/or diminishingly weak intensity.

The pressure-induced shifts of the distinguishable Raman bands are plotted in Fig. 7, observed in both up (solid circles) and down (open circles) strokes of pressure. Experimental data and theory curves from Ref. [12] are also shown, for comparison. Data points are fit with an equation of state derived from valence force field theory which was previously shown to be physically realistic [22]. The frequency shifts with pressure of the

### TABLE II: Birch-Murnaghan EOS fitting parameters. Volumes are given per formula unit.

<table>
<thead>
<tr>
<th>$B_0$ (GPa)</th>
<th>$V_0$ (Å$^3$)</th>
<th>$B'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>Ref. [12]</td>
<td>This work</td>
</tr>
<tr>
<td>α</td>
<td>90(1)</td>
<td>75(7)$^a$</td>
</tr>
<tr>
<td>β</td>
<td>188(12)</td>
<td>80.8(18)$^b$</td>
</tr>
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</table>

$^a$Experimental results
$^b$Calculated results

FIG. 6: Raman spectra upon increasing (a) and decreasing (b) pressure. Cosmic radiation spikes were removed from two of the spectra.
FIG. 7: (Color online) The shift in pressure of Li$_2$O Raman bands. Solid lines are fits to the experimental data from this study. Red dotted lines represent the calculated theoretical pressure dependence of the Raman frequencies from Ref. [12]. In the cubic phase, the theoretical curve lines up exactly with the experimental result from this study. Vertical dashed lines approximate the phase transition pressure upon increasing and decreasing pressure.

TABLE III: Frequencies, pressure coefficients, and Grüneisen parameters (all calculated at 50 GPa), for the plotted Raman modes of Li$_2$O.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Frequency (cm$^{-1}$)</th>
<th>Pressure Coefficient ( \frac{1}{\omega} \frac{d\omega}{dP} ) (10$^{-3}$ GPa$^{-1}$)</th>
<th>Grüneisen Parameter ( \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-Li$_2$O</td>
<td>758</td>
<td>5.5(5)</td>
<td>1.3(1)</td>
</tr>
<tr>
<td>$\beta$-Li$_2$O</td>
<td>829</td>
<td>4.8(4)</td>
<td>1.8(2)</td>
</tr>
<tr>
<td></td>
<td>799</td>
<td>3.4(4)</td>
<td>1.3(2)</td>
</tr>
<tr>
<td></td>
<td>747</td>
<td>2.5(4)</td>
<td>0.9(2)</td>
</tr>
<tr>
<td></td>
<td>632</td>
<td>3.7(4)</td>
<td>1.4(2)</td>
</tr>
<tr>
<td></td>
<td>557</td>
<td>5.1(5)</td>
<td>1.9(2)</td>
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<tr>
<td></td>
<td>488</td>
<td>3.6(4)</td>
<td>1.3(2)</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>4(1)</td>
<td>1.4(2)</td>
</tr>
<tr>
<td></td>
<td>411</td>
<td>5(1)</td>
<td>1.9(2)</td>
</tr>
<tr>
<td></td>
<td>357</td>
<td>5.1(5)</td>
<td>1.9(2)</td>
</tr>
<tr>
<td></td>
<td>342</td>
<td>2.7(8)</td>
<td>1.0(2)</td>
</tr>
</tbody>
</table>

5. DISCUSSION

The mechanism for the antifluorite-anticotunnite phase transition is already well understood because of the numerous well-known pressure-induced fluorite-cotunnite transitions that occur [23, 24]. If one pictures the antifluorite structure as (111) planes of anions separated by pairs of (111) planes composed of ions from the cation sublattice, the mechanism for the transition can be seen as a displacement of the anions in the [111] directions, half to the adjacent upper plane and half to the adjacent lower plane, accompanied by rotations and distortions of the Li triangular polyhedra within the planes (Fig. 8). This transition has the advantage of increasing the oxygen coordination number from 8 to a more stable 9, increasing the average O-Li separation distance from 1.78 Å to 1.89 Å, and increasing the packing through the 5.4 % volume collapse from 17.56 Å$^3$/formula unit.

FIG. 8: (Color online) (a) $\alpha$-Li$_2$O along the (111) plane, showing the transition mechanism to $\beta$-Li$_2$O (b). For the cubic structure shown in (a), all oxygen ions are coplanar, located midway between planes of lithium ions which are separated by 1.032 Å near 50 GPa. For the orthorhombic structure shown in (b), half the oxygen ions have moved into the lower plane of Li ions (shown as colored polyhedra) and half into the upper (empty), with the planes separated by 1.402 Å near 50 GPa.
to 16.61 Å\(^3\)/formula unit near 50 GPa. At this pressure, the α-Li\(_2\)O phase lattice parameter is \(a = 4.126\) Å while the β-Li\(_2\)O phase parameters are given by \(a = 4.518\) Å, \(b = 2.808\) Å, \(c = 5.246\) Å. Accompanying this transition is a remarkable 100 GPa increase in bulk modulus, for which an inhomogeneous stiffening of the material along the b-axis is at least partially responsible. The repulsion between closely spaced and highly charged ions also contributes to the overall stiffening of the crystal lattice, and threatens to destabilize the structure unless the coordination number is high around the most highly charged (O\(^{2-}\)) ions. Therefore, a transition to an Ni\(_4\)In-type structure is expected at higher pressure, as it would further increase the anion coordination number to 11.

An examination of the known behavior of alkali-metal chalcogenides under pressure may allow us to understand and predict the behavior of this class of materials. Although Li\(_2\)O is the first alkali-metal oxide which has been shown to possess a pressure-induced antifluorite-anticotunnite transition, it is common in alkali-metal sul-
fides [19, 21, 25]. Li\(_2\)S, Na\(_2\)S, K\(_2\)S, and Rb\(_2\)S have all been shown or are predicted to undergo an antifluorite to anticotunnite transition, at lower and lower pressures with increasing cation mass until, in Cs\(_2\)S, the anticotun-
nite phase is stable at ambient conditions (Fig. 9). These compounds are predicted to undergo a second transition from the anticotunnite to a hexagonal Ni\(_2\)In-type phase at even higher pressure [25] and so it is likely that Li\(_2\)O will do the same, although the calculations of Kunc et al. [12], indicate that this will not occur below 100 GPa.

Alkali metal oxides K\(_2\)O, Na\(_2\)O and Rb\(_2\)O also have the antifluorite structure at ambient conditions [26, 27]. The only alkali metal oxide exception is Cs\(_2\)O, which has been seen to possess the CdCl\(_2\) structure [28] which, however, is a simple rhombohedral distortion of the fluorite structure. No high-pressure studies have been performed on these materials, but we can reasonably expect that they will follow the same series of transitions that have been observed here. Ice also, in the past, has been predicted to exist in the antifluorite structure at sufficiently high pressure [3, 4]. Since then this proposition has been called into question, but the actual high pressure structure re-
mains to be seen experimentally, and is most currently not predicted to exist below 170 GPa [8]. Ice VII gradually becomes "symmetric" ice-X at the pressure range of 40-90 GPa, with a bcc oxygen sublattice, similar to that of ice VII but with hydrogen atoms occupying the central position between adjacent oxygen atoms. The possi-
bilità of a transition of ice X to a phase similar to that of α-Li\(_2\)O could indicate a systematic pressure-induced structural behavior for all alkali-metal chalcogenides.

6. CONCLUSION

A recently discovered pressure-induced antifluorite-
anticotunnite phase transition, seen for the first time in an alkali-metal chalcogenide [12], was investigated in de-
tail using x-ray diffraction and x-ray Raman scattering. Several new properties of the high pressure phase were discovered. A dramatic increase in bulk modulus was seen for the first time, and the source of the high pressure phase’s rigidity identified to be related to an inhomoge-
neous stiffening of one of the crystal lattice parameters. A consequent preferred orientation which increases with pressure in the orthorhombic phase was identified as re-
sponsible for an inversion in the intensities of two of the most prominent x-ray diffraction peaks. The pressure-
induced shift in the Raman bands of both phases was observed, and found to be consistent with our observation of a large bulk modulus increase. The x-ray diffraction and Raman data both point towards a strong hysteresis across this transition, which is consistent with a kineti-
cally hindered or sluggish first-order transition, or one in which a large volume change and a large change in bulk modulus can serve as nucleation barriers for the transi-
tion. Comparisons were drawn between Li\(_2\)O and a series of alkali metal sulfides, allowing us to make confident predictions about the high pressure behavior of the rest of the alkali-metal chalcogenides and even, perhaps, the beha-

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