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## Abstract

*In situ* high-pressure energy-dispersive x-ray diffraction measurements on $\alpha$-LiIO$_3$ have been performed by using a diamond anvil cell device with synchrotron radiation up to 75 GPa at room temperature. No new phase was found. The second Birch–Murnaghan equation of state is fitted with $B_0 = 55 \pm 3$ GPa for the zero-pressure bulk modulus, $B_0' = 2.9 \pm 0.4$ for its pressure derivative.

## 1. Introduction

$\alpha$-LiIO$_3$ is a promising optical material exhibiting a large transparent range and strong piezoelectric, photorefractive and non-linear effects [1–6]. $\alpha$-LiIO$_3$ crystallizes in space group $P6_3$ with $a = 5.481$ Å, $c = 5.172$ Å. The iodine atom environments consist of three near oxygen atoms, defining a pyramidal IO$_3^-$ group, and three more distant oxygen atoms completing a distorted octahedron. The features of the I–O network agree with those of other iodine structures, such as NaIO$_3$, KIO$_3$. The stability of $\alpha$-LiIO$_3$ has attracted attention since the 1960s. Both high pressure and high temperature can result in phase transitions. Up to now, many studies, based on DTA and x-ray diffraction [2, 4], have been reported on the complex phase transition of $\alpha$-LiIO$_3$ which relate to the temperature; but little research had been carried out on the phase transition arising from pressure. Shen *et al* [7] studied the phase diagram of $\alpha$-LiIO$_3$ up to 4 GPa, and speculated that $\varepsilon$-LiIO$_3$ would appear under ultrahigh pressure. Hu *et al* [10] carried out research on $\alpha$-LiIO$_3$ under a high pressure of 23 GPa by means of x-ray diffraction with monochromatic Mo radiation; no phase transition occurred.

More details can be obtained by energy-dispersive x-ray diffraction (EDXD) because of its unique high-intensity light as compared with conventional x-rays. In this research, we report on the pressure dependence of the energy-dispersive x-ray diffraction patterns of lithium iodine up to 75 GPa. The structure stability with increasing pressure was studied.

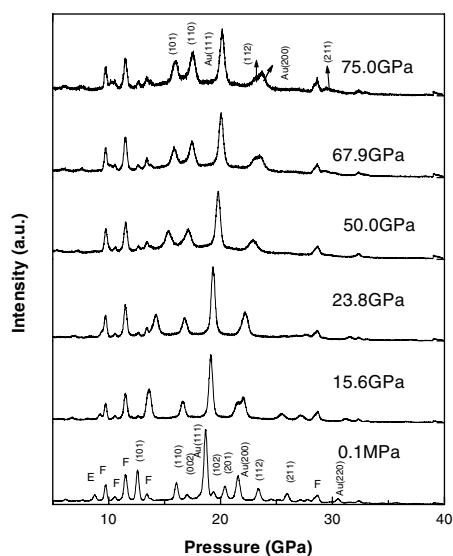[3] Author to whom any correspondence should be addressed.

**Figure 1.** EDXD patterns of $\alpha$-LiIO$_3$ under selected pressures. F: fluorescence; Ec: escape peak (from the detector).

## 2. Experimental details

The primary sample of LiIO$_3$ was grown from a neutral solution [9, 10]. According to the powder x-ray diffraction patterns at ambient pressure, a hexagonal unit cell with $a = 5.481$ Å, $c = 5.170$ Å was adopted.

The *in situ* high-pressure EDXD experiment was carried out in the Beijing Synchrotron Radiation Laboratory (BSRL). Diamond anvils driven by a gear-worm system were used to generate high pressure. The diamond flat was 360 $\mu$m. A hole with a diameter of 100 $\mu$m in the gasket was used as the sample chamber. Specimens were placed in it with Au powder for internal pressure calibration. A mixture of methanol/ethanol (4:1) was used as the pressure medium. The size of the x-ray spot was $80 \times 80$ $\mu$m and the diffraction angle $2\theta$ was 16.212. The applied energy ranged from 5 to 40 keV. A Si–Li solid detector was used to collect the diffraction data.

## 3. Result and discussion

Figure 1 shows the EDXD patterns for $\alpha$-LiIO$_3$ under selected pressures. Seven diffraction lines for the sample are observed clearly, from the pattern taken before pressurization, which can be assigned as (101), (110), (002), (102), (201), (112), and (211). As can be seen, in the lower-energy zone, there are some fluorescence peaks which result from Au, I and the escape peak which is caused by the electronic transition of the detector. No shift of these two kinds of peak occurs during the compression process.

Upon applying of pressure, the (201) peak of the sample shifts gradually to the Au(200) one, coincides with it completely at 23.8 GPa and then passes through it at 67.9 GPa. The (211) peak cannot be distinguished from the neighbouring fluorescence from the iodine between 32 and 50 GPa. So figure 2 does not show the $d$-value for the (201) peak in the range from 23.8 to 50 GPa, or the $d$-value for the peak (211) in the range from 23.8 to 67.9 GPa. In the pressure
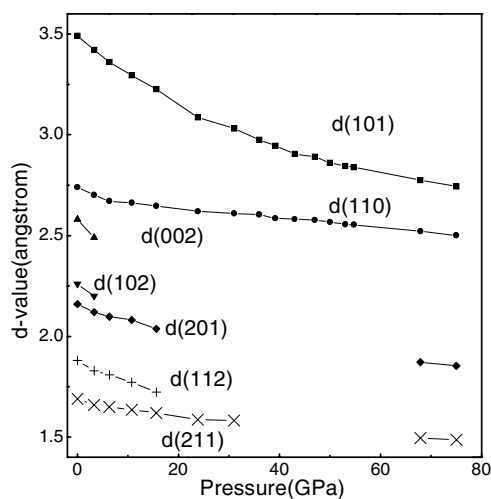
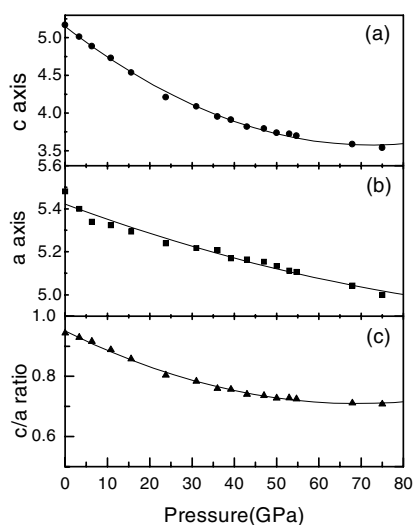**Figure 2.** The $d$-spacing with pressure.



**Figure 3.** Evolution of the lattice parameters with increasing pressure. (a) $a$-axis, (b) $c$-axis, (c) axis ratio $c/a$.

range explored, no new peak appears, and the decrease in peak intensity is common for most substances. Thus, there is no evidence for phase transitions at pressures up to 75 GPa.

As a function of pressure, the interplanar spacing of $\alpha$-LiIO₃ decreases with increasing pressure, as shown in figure 2. The rates of decrease of the $d$-values for different peaks are greatly different. (002), (102), (201), (112) move towards the high-energy side more quickly than (110), (211). These results indicate that the compaction of the lattice is anisotropic. The compressibility of the face (101) is different in the different pressure zones. All the $d$-values show gradual and not abrupt changes on applying pressure.

Figure 3 shows that the $c$-axis is more compressible than the $a$-axis, which is in accordance with the data in figure 2.
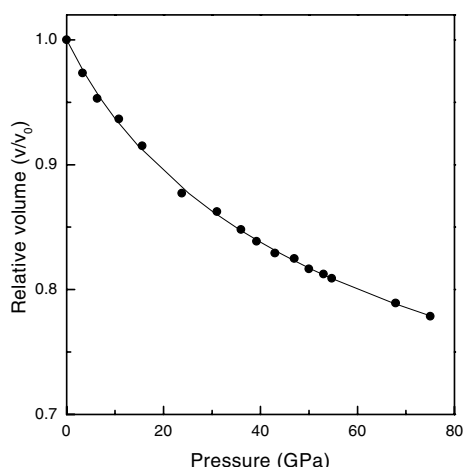
**Figure 4.** The relationship of the relative volume to increasing pressure. The circles are data from our experiment; the line is drawn by fitting the data with the Birch–Murnaghan equation of state.

Figure 4 shows that the relative volume monotonically decreases with increasing pressure to 75 GPa. The second-order Birch–Murnaghan equation of state is used to fit the pressure–volume data:

$$P = 3/2 B_0 x (1+x)^{5/2} (1 - \zeta x + \eta x^2),$$
$$x = [(v/v_0)^{-2/3} - 1], \qquad \zeta = -3/4(B'_0 - 4),$$
$$\eta = 3/8[B_0 B''_0 + (B'_0)^2 - 7B'_0 + 143/9].$$

The bulk modulus $B_0$ and its pressure derivative $B'_0$ thus obtained are $B_0 = 55 \pm 3$ GPa, and $B'_0 = 2.9 \pm 0.4$ respectively; these are consistent with Hu's results ($B_0 = 39.2$ GPa, $B'_0 = 2.87$).

## 4. Conclusions

In summary, we performed *in situ* high-pressure energy diffraction measurements on $\alpha$-LiIO$_3$ at room temperature up to 75 GPa, to study the stability and compressibility of $\alpha$-LiIO$_3$. It is shown that $\alpha$-LiIO$_3$ keeps stable up to 75 GPa. Pressure has different effects for different interplanar distances, which means that the lattice is compressed anisotropically.

We fit the second Birch–Murnaghan equation of state and get the bulk modulus $B_0 = 55 \pm 3$ GPa, and $B'_0 = 2.9 \pm 0.4$.

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