Ab initio study of the hygroscopic properties of borate crystals

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The hygroscopic properties of the borate crystals LiB_3O_5, CsB_3O_5, and $CsLiB_6O_{10}$ are studied by density-functional theory. It is found that the absorption energy and the diffusion mechanism of water molecules differ significantly for the three crystals. The deliquescent properties of borate crystals are determined mainly by the stress induced by water absorption. Our calculations are in good agreement with experimental observations.

Borate crystals, including LiB_3O_5 (LBO), CsB_3O_5 (CBO), and $CsLiB_6O_{10}$ (CLBO), show excellent nonlinear optical properties[1–4] and greatly promote the development of the green-ultraviolet lasers.[5–7] However, the hygroscopy of these borate crystals in ambient atmosphere is a significant challenge for their practical application. LBO, CBO, and CLBO crystals all include (B_3O_7) rings, which make up a three-dimensional backbone; the alkali cations reside in the interstices. They have similar structures—hence the term *LBO family*—but their hygroscopic properties are quite different. LBO is the most stable, even submerged in water, while deliquescent phenomenon happens to CBO and CLBO: the surface of CBO develops a white powdery layer, and CLBO cracks along the *a* or *b* axis when exposed to ambient atmosphere. Experiments have been carried out to investigate hygroscopic phenomena of the LBO family, particularly of CLBO crystal. Pan *et al.* reported that the cracking of CLBO crystal in ambient atmosphere results from the anisotropic corrosive effect of water vapor.[8] Morimoto *et al.* proposed that water molecules are dissociated in CLBO crystal.[9] In contrast to Morimoto's result, Kovacs *et al.* recently found using IR absorption spectroscopy that H_2O keeps its molecular configuration in a CLBO crystal.[10] Crystal structural data show that the minimum size of the cavity formed by cations and the surrounding (B_3O_7) frames are about 2.2, 3.2, and 4.0 Å for LBO, CBO, and CLBO, respectively. Intuitively, one may expect that the hygroscopic behaviors are related to the available volumes of cavities in crystals. In addition, because the interstice along the *a* axis in CBO and along the *a* or *b* axes in CLBO is larger than in the other directions, H_2O molecules could easily traverse the crystal along those directions and crack the crystals.[8]

In this paper, we have systematically studied the absorption of water molecules in the LBO family using DFT. First, we find that water is unstable in bulk LBO. The optimal absorption structures of water molecules in CBO and CLBO are determined. H_2O retains its molecular configuration in the bulk, in good agreement with the IR absorption spectra reported by Kovacs for CLBO.[10] We further calculate the diffusion paths of a H_2O molecule though both CBO and

CLBO, their corresponding activation energy barriers, and the stress induced by H_2O absorption. These results provide a coherent and unified picture for the cracking of CBO and CLBO crystals. We conclude that the induced stress is the main reason for the deliquescence of borate crystals.

The first-principles calculation has been performed by the CASTEP package[11] with the ultrasoft pseudopotentials[12,13] and the generalized gradient approximation.[14] The energy cutoff for the basis set was 300 eV, and integrations over the Brillouin zone were performed using the Monkhorst-Pack scheme[15] with $2\times3\times4$, $3\times2\times2$, and $3\times3\times3$ k points for LBO, CBO, and CLBO, respectively. The Broyden, Fletcher, Goldfarb, and Shannon minimizer[16] is used to perform structural optimization and the convergence. The energy change, maximum force, maximum stress, and maximum displacement in the optimization are set as 2×10^{-5} eV/atom, 0.05 eV/Å, 0.1 GPa, and 0.002 Å, respectively.

To optimize the absorption structure, a water molecule has been placed initially on various sites in LBO, CBO, or CLBO. With the expectation that the water molecule may break the weak bond between (B_3O_7) rings and lead to crystal collapse, the O atom of H_2O is put at a position 1.3 Å from a B atom in the (B_3O_7) ring, and one H atom of H_2O is placed 1.0 Å from the O atom between (B_3O_7) rings. Then the systems are relaxed. The calculated geometries for the three crystals all show that the water molecules move, contrary to initial expectation, into the interstices. In another run, a water molecule was put near a cation as a starting point. Finally, the same optimized geometries are reached as shown in Fig. 1, in which the water molecule forms four bonds with surrounding atoms. Thus the water molecule is fully saturated by these bonds. The absorption energy of a water molecule is obtained by the minimized total energy of the absorption systems, subtracting those of separate crystals and gaseous water molecules. They are $+1009$, -489, and -676 meV for LBO, CBO, and CLBO, respectively. This result clearly shows that a water molecule is not stable in LBO, and the systems gain energy after water absorption for CBO and CLBO. Furthermore, a water molecule is more stable in CLBO than in CBO; the absorption energy in
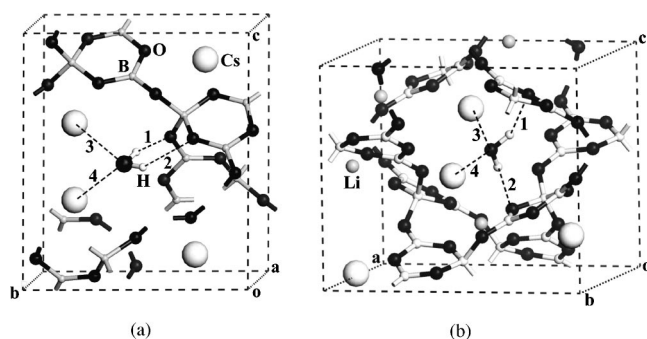
FIG. 1. (Color online) The absorption sites of a water molecule in CBO (a) and CLBO (b) crystal cells. Their dimensions are $(6.21 \times 8.52 \times 9.17)$ Å^3 and $(10.49 \times 10.49 \times 8.940)$ Å^3 for CBO and CLBO crystal cells, respectively. The purple, light blue, yellow, and red balls represent Cs, Li, B, and O atoms in a crystal, and the green and white balls represent O and H atoms in a water molecule.

CLBO approaches that in bulk ice (~ -720 meV). The volumes of CBO and CLBO unit cells with an absorbed water molecule are expanded about 13% and 7%, respectively, relative to the cases without water absorption.

In CBO, the two H-bond lengths between the H atoms and the two nearest O atoms in the (B_3O_7) rings are about 1.77 and 2.25 Å [white dashed lines in Fig. 1(a)], corresponding to a strong and a weak H bond, respectively. The distances between the two Cs atoms and the O atom of H_2O are about 3.05 and 2.89 Å [green dashed lines in Fig. 1(a)], which are within the range of the Cs-O bond length. The H_2O molecule is almost symmetrical, with $d_{H1-O}=0.97$ Å and $d_{H2-O}=0.99$ Å, and the H1-O-H2 angle is compressed to 101.1°. In CLBO, the two H bonds between H and the O in the (B_3O_7) backbone are 1.91 and 1.94 Å [white dashed lines in Fig. 1(b)], respectively. Both are strong H bonds. The Cs-O bond lengths between the O of H_2O and the Cs atoms are 3.10 and 3.05 Å [green dashed lines in Fig. 1(b)]. The H_2O molecule is symmetrical with $d_{H1-O}=d_{H2-O}=0.98$ Å, and the H1-O-H2 angle is expanded to 107.0°.

To study whether H_2O tends to dissociate when absorbed in the LBO family, an additional initial position was considered, in which one H is separated from the O by a distance of 2.0 Å and the O remains in a normal OH group with the other H. This dissociated H-OH configuration recovered to form a water molecule again at the end. Therefore a water molecule is a stable configuration when absorbed in borate crystals, which contrasts with Morimoto's result,[9] but is supported by Kovacs' recent measurement.[10] Our results rule out the possibility that the absorbed water may break the weak bond between (B_3O_7) rings, and cause the collapse. It suggests that the deliquescence is due mainly to mechanical reasons, rather than a chemical reaction.

Polarized IR absorption spectrum is a sensitive technique to determine the orientation of water molecule in single crystal by measuring the vibration modes.[17] For the symmetric vibration, the dipole moment changes along the axis of symmetry of H_2O, while for the asymmetric vibration the change is perpendicular to the axis of symmetry within the plane of the water molecule. Kovacs et al. reported that the angle γ_s between the c axis of CLBO and the symmetric vibration
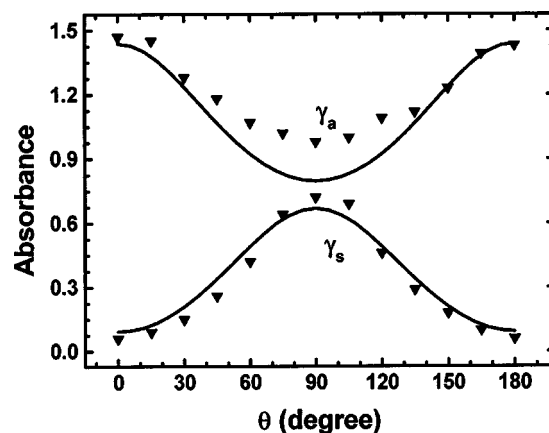

FIG. 2. The polarization angle dependence of symmetric vibration and asymmetric vibration. θ is the angle between the polarization direction of radiation and c axis of CLBO. The continuous lines represent the theoretical values and triangles represent the experimental values by Kovacs et al. (Ref. 10).

axis of H_2O is about 86°, and the angle γ_a between the c axis and the asymmetric vibration axis is about 49°.[10] We offer a correction: the angle γ_a should be about 40°, which has been confirmed by the authors recently.[18] The two angles, $\gamma_s \approx 83°$ and $\gamma_a \approx 35°$, are determined from our optimized geometry, and then the polarization angle dependence of the symmetric and asymmetric vibration are calculated using formulas in Ref. 17 to compare with the experimental data[10] in Fig. 2. The curve for γ_s is in excellent agreement with, and for γ_a closes to the experimental results. We also obtain that the orientation of a water molecule in CBO is $\gamma_s \approx 75°$ and $\gamma_a \approx 71°$, and an experimental study is expected.

The water diffusion mechanism in CBO and CLBO is studied by a constrained minimization scheme. In this approach, we fix the oxygen atom of a water molecule along the direction with the largest vacancy—the a axis for CBO and the a or b axes for CLBO-and then minimize the total energy with respect to all remaining degrees of freedom. Because of the symmetry of CLBO, the H_2O diffusion path along its a axis is equivalent to that along its b axis. The typical diffusion paths of H_2O along the a axis in a CBO
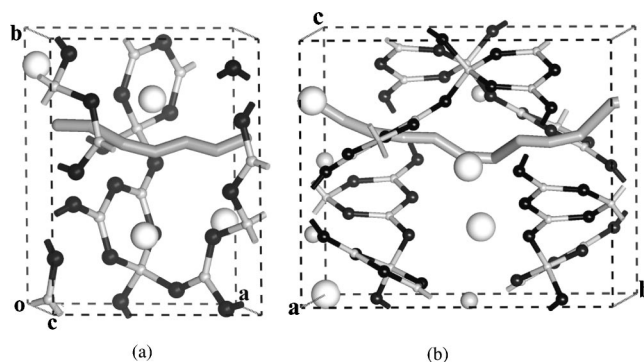

FIG. 3. (Color online) The representative results for the diffusion of a water molecule in CBO and CLBO crystals. The green lines denote the diffusion path of H_2O along the a axis in a CBO crystal (a), and along the b axis in a CLBO crystal (b).

TABLE I. The absorption energies, potential barriers, and volume expansions for one water molecule per unit cell in LBO family crystals.

Crystal	Absorption energy (meV)	Energy barrier (meV)	Volume expansion
LBO	+1008		
CBO	−489	827	13%
CLBO	−676	223	7%

crystal and along the *b* axis in a CLBO crystal are shown in Figs. 3(a) and 3(b), respectively. A water molecule diffuses along the green pathway in the channel formed by Cs atoms and the (B_3O_7) backbone in CBO [Fig. 3(a)], with a rather high energy barrier of 827 meV. A similar path for CLBO is shown in Fig. 3(b) with a much lower energy barrier of 223 meV. These very different activation barriers result in the different diffusion behaviors of water molecules in CBO and CLBO. The water molecule is much more difficult to overcome the high energy barrier to enter the inner of crystal in CBO, and thus hygroscopy happens only at its surface. On the other hand, in CLBO water molecules move along the *a* or *b* axes more easily, and cracks developed along these directions, which agrees with the experiment by Pan.[8] It is also interesting to note that when a water molecule diffuses along the *a* or *b* axis in CLBO, it walks around the Cs atoms locally in the interstices, as shown in Fig. 3(b). Table I lists the absorption energies, activation barriers, and volume expansions for one water molecule per unit cell in crystals of the LBO family.

In order to understand the deliquescence of CBO and CLBO, the induced stress of water absorption is calculated, in which the cells are fixed at their original volumes without water. When a water molecule is added to a cell, we obtain the induced stresses of 4.94 and 2.64 GPa for the optimized CBO and CLBO structures, respectively. Furthermore, the stresses for one water molecule absorbed in two (three) cells are reduced to 3.29 (2.93) GPa and 1.96 (1.55) GPa for CBO and CLBO, respectively. We may estimate the induced stress with respect to the water content in crystals in the following way. The crystal with water absorption will be distorted by strain ε from its condition without water, thus exhibiting an excess energy $\Delta E = 1/2B\varepsilon^2$ and a stress $G = B\varepsilon$, where B is the bulk modulus. Then we have $G \propto \sqrt{\Delta E}$. Assuming the excess energy is proportional to the number of water molecules in the bulk, the stress G is proportional to the square root of the water content, i.e., the stress is $G \propto \sqrt{1/N_{cell}}$, N_{cell} is the number of cells absorbing a single water molecule. The calculated stress for the two crystals agrees with this square-root ratio very well, as shown in Fig. 4.

Experiments provide Mohs hardness measurements of CBO and CLBO at about 5 and 4, corresponding to maximum tensile stresses of 1.9 and 1.1 GPa,[19,20] respectively. Clearly, our results indicate that the water-induced stress is
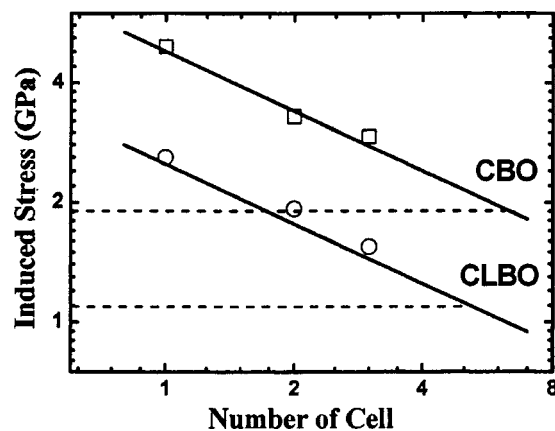

FIG. 4. The induced stress *G* vs the number of cells in which one water molecule is absorbed in CBO and CLBO crystal (log-log plot). The squares and circles indicate the calculated stress for CBO and CLBO, respectively. The solid lines are the theoretical curves and the dash lines denote the values of crack in experiment.

large enough to result in cracking. Thus we believe that volume expansion induced by water absorption is the main mechanism of the deliquescence of CBO and CLBO crystals. If the square-root relation holds, we estimate that CBO and CLBO would crack when the water content exceeds one water molecule in each six (CBO) or five (CLBO) cells; see Fig. 4. In Kovacs' experiment, the crystal can be kept in a humid atmosphere with water content of about 0.1 mol water molecules per mol CLBO, which corresponds to one water molecule per five cells.[10] Our theoretical prediction is therefore consistent with the experimental result.

In summary, we present a systematic study of the different hygroscopic properties of borate crystals by first-principles calculations. It is found that H_2O keeps water molecule configuration in the LBO family. Based on the calculated absorption energy, water is unstable in LBO, but likes to be absorbed in CBO and CLBO by greatly lowering energy. The diffusion mechanism of a water molecule in borate crystals is controlled by an activation barrier, which results in the different hygroscopic behaviors in CBO and CLBO. The deliquescent phenomenon is mainly due to the induced stress of the water involved. The existence of strong absorption, a low activation barrier, and the large induced stress are the predominant factors, which determine the deliquescence and even lead to cracking of crystals. These findings for the borate crystals are consistent with recent experiments. We believe our results have important implications for understanding the hygroscopic properties of other materials.

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