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Molecular dynamics study of the ternary compound $Li_3AlB_2O_6$*

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A new compound with the same chemical composition as $Li_3AlB_2O_6$ but with a different x-ray powder diffraction pattern as reported before was synthesized and studied experimentally by M. He, Chen X L *et al* (*J. Solid State Chem.* **163**, 369 (2002)), but there lacks first principles study on the structure of it. Using conjugant gradient (CG) molecule dynamics (MD) simulation with a full relaxation of the atomic positions and of the shape and size of the cell, the structure of $Li_3AlB_2O_6$ is studied from first principles. For the density functional, the local density approximation (LDA) and the generalized gradient approximation (GGA) forms are used respectively. Both the LDA and GGA results support the experimental structure of M. He *et al*. The result of MD simulation using GGA agrees with the experimental result much better. The energy bands are also studied, the band gap given by LDA and GGA are 5.65 eV, 5.34eV, respectively.

Keywords: aluminium borate, $Li_3AlB_2O_6$, structure, molecule dynamics simulation
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1. Introduction

Recently, great effort has been devoted to find some new materials that possess a unique combination of nonlinear-optical, acoustic optical and physical properties, which promise a wide variety of practical applications. One such important application is the development of powerful and tunable ultraviolet lasers, which rely on the frequency doubling of lasers in the visible range.[1] Frequency doubling of lasers depends on the development of nonlinear optical materials. Few such materials are available; those most widely used at present are the inorganic crystals containing borates. Because planar $[BO_3]^{3-}$ has high polarizability and excellent transparency in the ultraviolet region, borates are attractive candidates in the search for new nonlinear optical materials.[2] Therefore, important advances have been achieved in the synthesis and characterization of inorganic borates during the past years.[3−5] More important, the anisotropy of polarizability of planar $[BO_3]^{3-}$ group indicates that borates are also potential birefringent materials if their $[BO_3]^{3-}$ groups are in suitable configuration, so a great deal of research has focused on many ternary borate and other multi-component systems.[5−7]

Because Al is similar to B in outer electronic structure and often has tetra-coordination, it may act like tetrahedrally coordinated B in compounds. The ternary system Li_2O–Al_2O_3–B_2O_3 has been investigated by many researchers, and the ternary phase diagram of it was first reported by Kim and Hummel in 1962, but only two kinds of ternary borates ($Li_4Al_4B_6O_{17}$ and Li_2AlBO_4) were observed.[8] Abdullaev *et al* identified six ternary compounds, $Li_2Al_2B_4O_{10}$, Li_2AlBO_4, Li_3 AlB_2O_6, $Li_2Al_2B_2O_7$, $Li_2Al_4B_4O_{13}$ and $Li_4Al_2B_4O_{11}$ in 1983.[9] However, only $Li_3AlB_2O_6$ was structurally characterized among all these compounds.[10] In 1997, Chryssikos *et al* [10] confirmed the existence of $Li_3AlB_2O_6$ and reported its infrared and Raman spectra. But they obtained different results for the thermal stability of this compound. He *et al*[11,12] reinvestigated this ternary system experimentally, and found a new compound with the same chemical composition as $Li_3AlB_2O_6$ but with a

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different x-ray powder diffraction pattern. There is no ab initio research on this new founded structure, especially on its electronic structure in literature to our knowledge.

The purpose of our work is studying the structure of the compound $Li_3AlB_2O_6$ from first principles using SIESTA (Spanish Initiative Electronic Simulations with Thousands of Atoms).[13,14]

2. Method

The local orbital atomic simulation code SIESTA was chosen for its speed with large systems, its large assortment of molecular dynamics methods, and its capability to use either the LDA or one of several versions of the GGA.

We run SIESTA in the MD simulation mode using the CG minimization method to finally relax the atom and lattice vectors. In our MD simulation process, the reference structure is the experimental structure, which has been solved and refined from single-crystal and power x-ray diffraction data by He *et al.*[12] The compound $Li_3AlB_2O_6$ crystallizes in a triclinic unit cell (space group $P\bar{1}$) with lattice parameters a=4.876(8)Å, b=6.191(16)Å, c=7.910(20)Å, α=74.46°, β=89.44°, and γ=89.52°. There are 2 formulas per unit cell and 12 atoms in the asymmetric unit.

Both LDA and GGA are used in our computation. For LDA, the Ceperley–Alder exchange-correlational potential is used.[15] For GGA, the Perdew, Burke and Enzerhof (PBE) exchange-correlational energy functional is selected.[16,17] In all the computations, ATM3 pseudopotentials for Al, Li, B and O atoms are used.[18] Valence electrons are described by linear combinations of numerical pseudoatomic orbitals using a split-valence multiple-ζ with polarization and diffuse orbitals.[19,20] The energy convergence is carefully tested with respect to k-point sampling over the irreducible part of the zone using a uniform grid of k-points suggested by Monkhorst and Pack.[21] We have done a number of conjugant gradient (CG) minimization runs for different numbers of k-points. And the k-points are generated from Monkhorst–Pack method with $N_1 = N_2 = N_3$. Energy convergence tests find that the convergence starts at N_i=3. In order to provide a sufficient accuracy in the calculations of the total energy and forces, all the results given below are obtained using 24 atom cells and $4 \times 4 \times 4$ shifted k-point grid. It was found that the total energies calculated with the $4 \times 4 \times 4$ shifted k-point grid converged to an accuracy of 0.1 meV per atom, and the forces acting on atoms were less than 10^{-4} eV/Å.

Convergence tests comparing the size of the orbital basis set, between single-zeta, double-zeta, and double-zeta with polarization showed that the double-zeta basis was rather good, so we choose the best one, double-zeta with polarization (DZP). The basis with an energy shift of 0.02 Rydberg was sufficient for energy convergence, with an energy cut off of 200 Rydbergs for the real-space grid.

All the results given below are obtained using 24 atom cells and $4 \times 4 \times 4$ shifted k-point grid with a full relaxation of the atomic positions and of the shape and size of the cell.

3. Results and discussion

After more than 30 CG molecule dynamics simulations with a full relaxation of the atomic positions and of the shape and size of the cell, we get the final structure of $Li_3AlB_2O_6$ compound. Both the LDA and GGA results are listed in Table 1, the experimental structure of He *et al*[12] is also listed. It can be found that our MD simulations agree with the experimental result fairly well. It can also be seen that the LDA lattice constants are too small relative to experiment, and the GGA functional produced a much improved agreement with experiment.

For LDA, the optimized structure has a cell volume 204.47Å^3; for GGA, the optimized structure has a cell volume 241.04Å^3, while the cell volume of experimental result is 230.04Å^3. According to the cell volume given by MD simulations, the result of GGA method agrees with the experimental result better.

Table 1. The calculated equilibrium lattice parameters and the experimental results of He *et al.*

Method	a/Å	b/Å	c/Å	α/(°)	β/(°)	γ/(°)
Exp.	4.876	6.191	7.910	74.46	89.44	89.52
LDA	4.914	5.433	7.371	82.99	88.97	89.29
GGA	4.949	6.292	8.063	73.84	88.98	89.06

Generally speaking, in actual simulations the GGA has proven to yield improved total energies, atomization energies, energy barriers and structural energy differences over the same calculations with the LDA. The LDA often leads to bonds that are too short; the GGA stretches and softens bonds, which is sometimes an over correction.[22] In Table 2, for some selected geometric parameters, the experimental results of Ref.[12] are compared with our MD simulation results using LDA(CA) and GGA(PBE) density functional respectively.

Table 2. Selected Geometric Parameters (Å, (°)).

Atom distance	Exp.[a)]	LDA	GGA	Distance/ Angle	Exp.[a)]	LDA	GGA
Al–O4	1.728(5)	1.720	1.740	Li1–O5^{i}	1.920(8)	1.900	1.920
Al–O5^{i}	1.746(4)	1.730	1.760	Li1–O3^{v}	1.937(7)	1.905	1.930
A1–O3^{ii}	1.764(5)	1.750	1.770	Li1–O1^{ii}	2.011(8)	1.970	2.300
A1–O1	1.789(5)	1.810	1.780	O4–A1–O5^{i}	117.8(2)	119.87	117.68
B1–O2	1.330(6)	1.330	1.340	O4–A1–O3^{ii}	110.9(2)	104.42	106.46
B1–O3	1.395(6)	1.390	1.410	O5–A1–O1^{ii}	102.6(2)	99.03	103.25
B1–O1	1.412(6)	1.410	1.430	O2–B1–O3	121.9(4)	122.01	122.00
B2–O6^{iii}	1.336(6)	1.330	1.350	O2–B1–O1	122.2(4)	122.60	122.30
B2–O4	1.398(6)	1.390	1.410	O6^{iii}–B2–O4	121.7(4)	122.02	122.44
B2–O5	1.400(6)	1.410	1.420	O6^{iii}–B2–O5	122.0(4)	122.58	122.32

[a)] The experimental value for atom distances and angles are taken from Ref.[12], the label of atoms and the corresponding code are also from Ref.[12].

Two trends are evident from Table 2. First, for Al, B, and O atoms, the distances between Al and O, B and O are predicted very well with LDA functional and GGA functional. The LDA-predicted distances are a little smaller than the experimental, while the distances are larger for the GGA yet without much improvement over LDA when compared with the experiment. Second, for the distances between Li and O atoms, the LDA predicted values have a large deviation from experiment, yet the GGA values drastically improved the agreement with experiment. The main reason is the large nonlocal effect of Li, and it is very similar with the case when Perdew *et al*[23] performed GGA calculations on Li and Na, Jaffe *et al*[24] on Li, Na and K. The large nonlocal effect of alkalis metal mainly comes as follows: the interstitial electron density is quite low compared with other metals, though very uniform. Hence, there is a large gradient of the density, relative to the density itself, between the core and interstitial regions, leading to large gradient corrections. It is believed that GGA-predicted lattice constants of alkalis metal show a large improvement over the LDA, but the agreement with experiment is still not perfect. So, it must be very careful when one optimizes the structure of complex compounds as $Li_3AlB_2O_6$ using density functional theory, especially when one studies the polarization property of such complex compounds, because a small difference in the structure may cause large difference in electronic polarization.[25,26]

The energy bands are also studied by using LDA and GGA (PBE) functional respectively. Both LDA and GGA computations predict $Li_3AlB_2O_6$ as insulators with large band gap, the values are 5.65eV (LDA) and 5.34 (GGA). 31 k-points including special symmetry point Γ, R, U and V are chosen to compute the band structure curves, and it is found that the energy bands are very flat and dense.

4. Summary

The density functional theory local orbit code SIESTA is used to study the structure of the ternary compound $Li_3AlB_2O_6$, through CG molecule dynamics simulations with a full relaxation of the atomic positions and of the shape and size of the cell, we get the optimized structure of $Li_3AlB_2O_6$ from first principles. Both the LDA and GGA results support the experimental structure of He *et al.* According to the lattice constants and the final positions of the atoms, the result of MD simulations using GGA agrees with the experimental result much better than that of LDA on the whole. One possible reason is the large nonlocal effect of Li. The electronic structure computation predicts $Li_3AlB_2O_6$ as insulators with large band gap of 5.65eV (LDA) and 5.34eV (GGA), and the energy bands are very flat and dense.

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