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## Modelling the Structure of Nanoparticle-embedding Matrices: Molecular Dynamics in $\text{Li}_2\text{B}_4\text{O}_7$

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*A new model describing interatomic and angular interactions, taking into account periodic properties in borate-type solid phases, is presented and applied to  $\text{Li}_2\text{B}_4\text{O}_7$  through simulations at temperatures ranging from 0 K to the melting point and in the pressure range 0 to 10000 MPa. Simulation reproduces quite well cell lengths, atomic positions and distances in boron-oxygen polyhedrons and the polar nature of the crystal structure. An order-disorder type ferro-paraelectric transition of the second kind is found to occur at a Curie point  $T_C \approx 839$  K, corresponding to jumping of Li atoms between two lattice sites. By increasing or decreasing the pressure, the total energy and the crystal properties for simulations performed at 300 K show a shoulder at  $p_t \approx 5000$  MPa, implying the existence of a reversible second-order phase transition. The cell volume below  $p_t$  follows a Murnaghan law with the bulk modulus  $B_0 = 15.6$  GPa and its first derivative  $B_0' = 4.31$  (at ambient pressure). In contrast to the low-pressure phase where threefold and fourfold boron atoms coexist, in the high-pressure phase all borons are fourfold-coordinated. The present approach can be directly applied to modelling the structure of nanosized systems.*

*Keywords: lithium tetraborate, molecular dynamics, crystal structure, order-disorder ferroelectric transition, pressure-induced phase transition.*

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## Introduction

As transparent magnets, borate glasses containing nanoparticles represent a new class of nanomaterials, promising for technical applications [1]. The parent crystalline phase  $\text{Li}_2\text{B}_4\text{O}_7$  (LTBc) has received much attention because of piezoelectric and nonlinear optical properties (second harmonic generation, SHG) related to its polar crystal structure [2–11].

In this work, a new model describing interatomic and angular interactions, taking into account periodic properties in borate-type solid phases, is presented and applied to LTBc. Starting from the point of view based on DFT calculations with coordination-dependent boron charges [12–14], a parameter set is chosen from structural considerations and tested through various simulations at temperatures ranging from 0 K to the melting point. The description of LTBc is achieved through simulations in the pressure range 0 to 104 MPa. A special attention is paid to structural and dielectric properties of the different crystal phases.

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# 1. Molecular Dynamics and Interaction Model in $\text{Li}_2\text{B}_4\text{O}_7$ System

The potential model is based on two-particle and three-particle potentials. The bond interactions are described by a Born-Mayer repulsion term added to the Coulomb potential:

$$V_{ij} = q_i q_j e^2 / r_{ij} + b_{ij} \exp(-r_{ij} / \rho_{ij}). \quad (1)$$

where  $r_{ij}$  is the interatomic distance between ions  $i$  and  $j$ ,  $e$  is the elementary charge,  $q_i$  and  $q_j$  are the relative effective charges of  $i$  and  $j$  ions,  $b_{ij}$ ,  $\rho_{ij}$  are the repulsive parameters in this potential model. The infinite sum of all  $V_{ij}$  is evaluated by the Ewald sum technique [12] implying real-space calculations inside a sphere of a cutoff radius (*ca* 12 Å) and reciprocal-space calculations outside.

We follow Maslyuk *et al.* [13–15] who found a good agreement between DFT results and experiments (in crystal structure, elastic properties, optical and phonon spectra) by assuming different effective charges for threefold (B3) and fourfold (B4) boron atoms,  $q_{\text{B3}}$  and  $q_{\text{B4}}$ , but invariant for different ternary oxides of the  $[(1-x)\text{B}_2\text{O}_3 + x\text{Li}_2\text{O}]$  system and temperature-independent. The  $x$ -invariance of the boron charges implies a variation of both  $q_{\text{Li}}$  and  $q_{\text{O}}$  with the concentration ratio  $r = [\text{B4}] / ([\text{B3}] + [\text{B4}])$ , satisfying the charge neutrality and adjusted in order to obey to the characteristics of phonon dispersion in ternary crystals [14]. As a consequence, a correlation appears between  $q_{\text{Li}}$  and  $q_{\text{O}}$  charges, as shown in Fig. 1, except for  $\text{Li}_3\text{BO}_3$  ( $x = 0.75$ ) where the absence of direct connectivity between B3 results in stronger Li-O interactions.

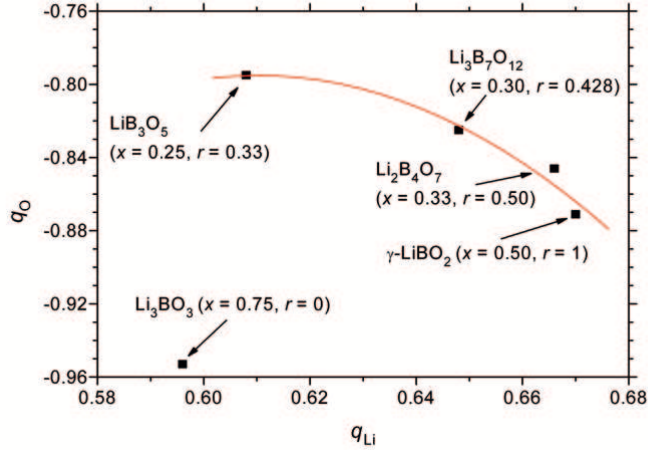


Fig. 1. Correlation between lithium and oxygen effective relative charges for different ternary oxides  $[(1-x)\text{B}_2\text{O}_3 + x\text{Li}_2\text{O}]$ ;  $r$  is the fraction of fourfold boron. The full squares are fitted values by Maslyuk *et al.* [14]; the full curve is a guide for the eye

For angular interactions involving an ion  $i$ , we choose a truncated harmonic potential:

$$V_{ijk} = \frac{1}{2} A_{ijk} (\vartheta_{ijk} - \vartheta_{ijk}^0)^2 \exp[-(r_{ij}^8 + r_{ik}^8) / \rho_{ijk}^8] \quad (2)$$

where  $A_{ijk}$  represents the strength of the angular interactions,  $\vartheta_{ijk}$  is the angle formed by the

ions  $i, j, k$ ,  $\vartheta_{ijk}^0$  is the equilibrium angle and  $\rho_{ijk}$  is the truncating parameter. In LTbc we distinguish four angular interactions, resulting from:

- (i) the presence of (B3) and (B4) involving  $\vartheta_{ijk}^0 = 120^\circ$  and  $\vartheta_{ijk}^0 = 109.47^\circ$  respectively;
- (ii) the oxygen angular connectivity which is different between two tetrahedrons ( $\vartheta_{ijk}^0 \approx 135^\circ$ ) and between a tetrahedron and a triangle ( $\vartheta_{ijk}^0 \approx 120^\circ$ ).

The entire parameter set used in the simulations described below is collected in Table 1. All values come from Maslyuk et al. [15] except for the  $b_{OO}$  coefficient which is adjusted through a MD equilibration at 0 K with respect to the crystallographic data of [16], extrapolated from the 80–300 K range to 0 K. Our  $b_{OO}$  value ( $9.1 \times 10^5$  kJ/mol) appears less repulsive than that given in [15] ( $1.37 \times 10^7$  kJ/mol).

Table 1. Parameters of the potential model used in MD simulations of  $\text{Li}_2\text{B}_4\text{O}_7$  crystal

Elements	Atomic charges in $e$ units (from [14])		
Li	$q_{\text{Li}} = 0.666$		
B3	$q_{\text{B3}} = 1.072$		
B4	$q_{\text{B4}} = 1.223$		
O	$q_{\text{O}} = -0.846$		
Interactions	Parameters and their values (from [14]), except $b_{OO}$ )		
Li - O	$b_{\text{LiO}} = 137631$ kJ/mol	$\rho_{\text{LiO}} = 0.236$ Å	
B3 - O	$b_{\text{B3O}} = 51846$ kJ/mol	$\rho_{\text{B3O}} = 0.198$ Å	
B4 - O	$b_{\text{B4O}} = 112389$ kJ/mol	$\rho_{\text{B4O}} = 0.198$ Å	
O - O	$b_{\text{OO}} = 910000$ kJ/mol	$\rho_{\text{OO}} = 0.183$ Å	
O - B3 - O	$A_{\text{OB3O}} = 0.3580$ kJ/mol/rad <sup>2</sup>	$\vartheta_{\text{OB3O}}^0 = 120.07^\circ$	$\rho_{\text{OB3O}} = 2.4$ Å
O - B4 - O	$A_{\text{OB4O}} = 0.1587$ kJ/mol/rad <sup>2</sup>	$\vartheta_{\text{OB4O}}^0 = 109.41^\circ$	$\rho_{\text{OB4O}} = 2.4$ Å
B3 - O - B4	$A_{\text{B3OB4}} = 0.00758$ kJ/mol/rad <sup>2</sup>	$\vartheta_{\text{B3OB4}}^0 = 120.67^\circ$	$\rho_{\text{B3OB4}} = 2.4$ Å
B4 - O - B4	$A_{\text{B4OB4}} = 0.1149$ kJ/mol/rad <sup>2</sup>	$\vartheta_{\text{B4OB4}}^0 = 135.68^\circ$	$\rho_{\text{B4OB4}} = 2.4$ Å

Simulation boxes of 13000 atoms ( $5 \times 5 \times 5$  cells with 8 formula units) were prepared using experimental crystallographic data [17, 18] based on the tetragonal space group I41cd (Table 2) with  $c$ -axis as the polar direction. The MD-simulations were performed with DL\_POLY [19] in the Berendsen isothermal and isobaric (NpT or  $N\sigma$ T isostress ensembles) under periodic boundary conditions, with a time step of 0.5 fs. The Berendsen thermostat was used with a time constant of 0.05 ps. The barostat time constant of 5 ps was necessary to ensure stability of the simulations. The structure was relaxed by energy minimization coupled to a heat bath at 0 K in the NvT-ensemble. Then a series of equilibration simulations was performed at atmospheric pressure in NpT conditions, by temperature steps of 20 K below 300 K and of 50 K above 300 K. In this series the experimental room-temperature  $c/a$  ratio from [17] was used. Above 400 K,

simulations were also made with the  $c/a$  ratio deduced from [16]. Besides, in order to verify that the tetragonal symmetry is conserved, some simulations were made in the  $N\sigma T$  ensemble (where  $b/a$  and  $c/a$  are free to vary). In the  $NpT$  simulations, fractional coordinates of oxygen atoms O4 were fixed accordingly to symmetry rules of the space group. The simulations at pressures up to 10 GPa were performed at room temperature.

## 2. Molecular Dynamics and Interaction Model in $\text{Li}_2\text{B}_4\text{O}_7$ System

### 2.1. Structural Results

The  $NpT$  and  $N\sigma T$  simulations consistently demonstrate the stability of the quadratic cell. Table 2 compares the lattice parameters  $a$ ,  $c$  obtained from the simulations at 300 K with the experimental data. Fig. 2 shows the experimental (a, [17]) and the simulated structure (b) viewed

Table 2. Lattice parameters at 300 K: comparison between experiments [17, 18] and simulations

	Experimental	Simulation
$a$ (Å)	$9.479 \pm 0.003$ [17]	9.586(1)
	$9.470 \pm 0.006$ [18]	
$c$ (Å)	$10.280 \pm 0.004$ [17]	10.431(1)
	$10.28 \pm 0.01$ [18]	

along the  $c$ -axis. Firstly, we can see that the simulation reproduces quite well the cell lengths with a small departure ( $\Delta a/a = 1.12\%$ ,  $\Delta c/c = 1.47\%$ ). Secondly, the calculated distances between B3 and O atoms,  $d(\text{B3} - \text{O}) = 1.279 \text{ \AA}$ , are shorter, while those between B4 and O,  $d(\text{B4} - \text{O}) = 1.500 \text{ \AA}$ , are slightly longer in comparison with the mean experimental values [17]:  $d(\text{B3} - \text{O}) = 1.373 \text{ \AA}$  and  $d(\text{B4} - \text{O}) = 1.476 \text{ \AA}$ , respectively. Nevertheless, the whole crystal structure is quite well reproduced.

### 2.2. Thermodynamical Results

Temperature dependences of the total energy ( $E_{\text{tot}}$ ) and the cell volume ( $v$ ) are shown, respectively, in Figs. 3–4. Both curves can be fitted with second-order polynomials, see the legends of Figs. 3–4.

Thus, no phase transition is found below 700 K, in agreement with X-ray diffractometric [16] and IR spectroscopic studies [2]. Burak and Moroz [20] have claimed having observed an isostructural phase transition at 235 K: no such transitions have been detected in our simulations.

Finally, the melting point is found between 950 and 1050 K. This uncertainty comes from the choice of the starting  $c/a$  ratio in the simulations. Nevertheless, these values are not too much below the thermal determinations of Shastry and Hummel [21] (see Fig. 5).

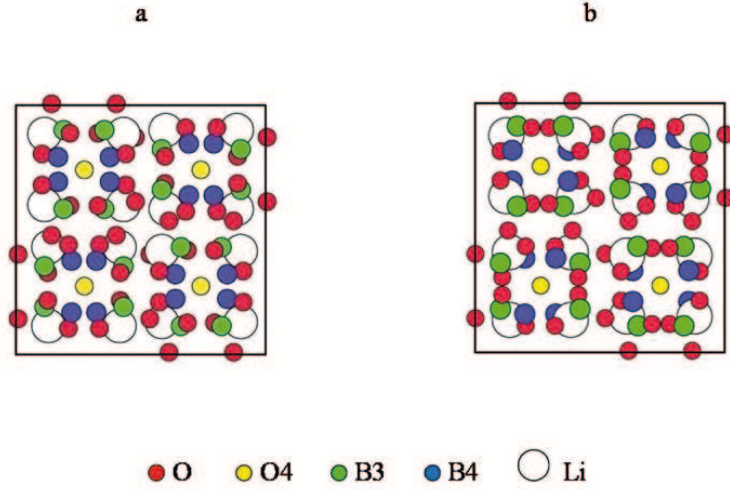


Fig. 2. Experimental (a, in accordance with the crystal structure determined by Krogh-Moe [17]) and simulated (b) room-temperature crystal structure viewed along the  $c$ -axis

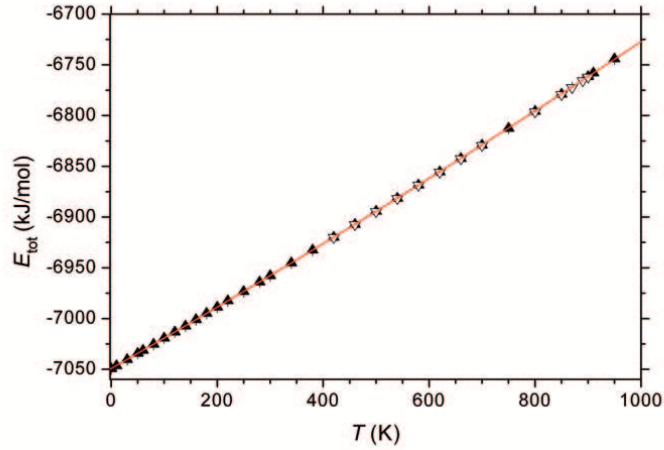


Fig. 3. Temperature dependence of the total energy in NpT simulations ▲:  $c/a$  ratio from [17]; ▽:  $c/a$  from [16]. The full line is the corresponding fit:  $E_{\text{tot}} = -7049.40 + 0.2992T + 2.20 \times 10^{-5}T^2$

### 2.3. Non-linear Properties

For each simulation run, the dielectric polarization vector ( $\mathbf{P}$ ) has been calculated. Its component along the  $c$ -axis ( $P_z$ ) is found to decrease with increasing temperature above 200 K

Table 3. Mean fractional coordinate of Li atoms along the c-axis and its spatial fluctuation, as a function of temperature below and above the phase transition

$T$ (K)	$z_{\text{Li}}$	$\Delta z_{\text{Li}}$
300	0.8724	0.0013
400	0.8744	0.0013
800	0.8773	0.0022
850	0.8780	0.0030
910	0.8769	0.0041

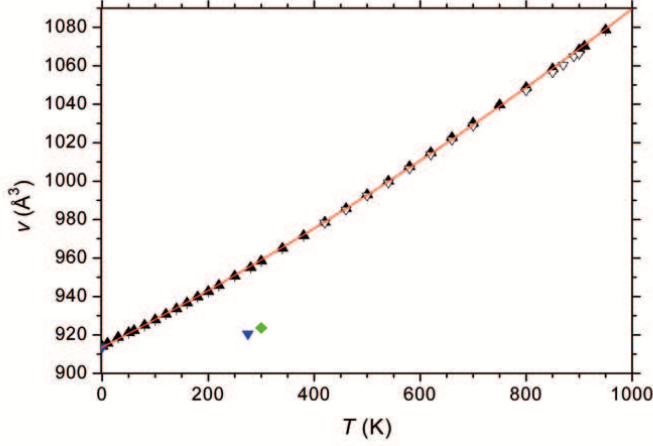


Fig. 4. Temperature dependence of the cell volume in NpT simulations. ▲:  $c/a$  ratio from [17]; ◆: experiment [17]; ▽:  $c/a$  from [16]; ▼: experiment [16]. The full line is the corresponding fit:  $v = 913.7 + 0.140 T + 3.6 \times 10^{-5} T^2$

(Fig. 5), according to the empirical law

$$P_z^2 = 165 + 0.13 (839 - T). \quad (3)$$

One can see that  $P_z$  does not vanish above  $T = 839$  K (its "remnant" value is  $P_z \approx 13 \mu\text{C cm}^{-2}$ ). Meanwhile,  $P_x$  and  $P_y$  also have non-zero values which are temperature-independent, so that above  $T = 839$  K all three components of  $\mathbf{P}$  become comparable. This behaviour is an artifact due to border effects. Indeed, in contrast to the other simulations made (see Section II),  $\mathbf{P}$  is calculated within the simulation box without applying periodic boundary conditions.

As shown in Fig. 5,  $P_z^2$  behaves similarly to the second-harmonic generation coefficient ( $s_{33}$ ) measured by Furusawa et al. [7]. These authors found a linear temperature dependence of  $s_{33}$  above room temperature and, extrapolating this dependence, suggested the existence of a second-order transition at  $T_0 \approx 863$  K. Because no soft mode associated with a displacive-type

phase transition was observed by Raman spectroscopy in the temperature range 300–900 K [11], Furusawa et al. concluded that this second-order phase transition could be of order-disorder type. The present simulations show that fluctuations of the fractional coordinate of Li along the  $c$ -axis drastically increase in the temperature range 850–950 K (see Table 3). This behaviour can be explained assuming that in this range the Li atoms are jumping between two different sites in a crystallographic supercell. So, our simulations confirm the possibility of a second-order ferroelectric  $\rightarrow$  paraelectric phase transition in LTBC, the Curie point  $T_C \approx 839$  K given by eq. (3) corresponding to an order-disorder transition.

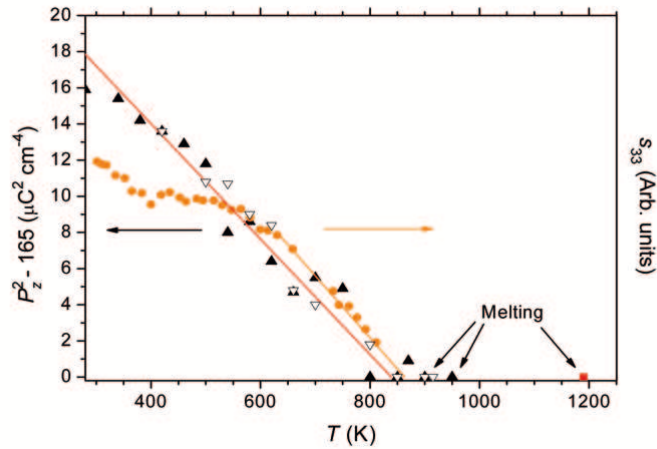


Fig. 5. Square of the calculated  $P_z$ -component of the dielectric polarization compared with the second-harmonic generation coefficient  $s_{33}$  as a function of temperature.  $\blacktriangle$  and  $\nabla$  have the same meaning as in the preceding figures ;  $\circ$  :  $s_{33}$  values from [7];  $\bullet$  : the melting point  $T_{\text{fus}} = 1190$  K [21]. The full line is the fit, see eq. (3); the dashed line shows an extrapolation of high-temperature  $s_{33}$  values

### 3. Simulations at Room Temperature

#### 3.1. Low-pressure Phase

Pressure dependences of the total energy and the cell volume are shown, respectively, in Figs. 6–7. By increasing the pressure  $p$ , all these quantities unambiguously show a leap occurring at  $p_t \approx 5000$  MPa, and by decreasing the pressure one passes through exactly the same values. These smooth ‘discontinuities’ and the absence of pressure hysteresis imply the existence of a second-order pressure-induced phase transition, and one can see that this transition is quite reversible.

In the low-pressure phase (called thereafter I - [LTBc]),  $E_{\text{tot}}$  can be fitted with the following equation:

$$E_{\text{tot}} = -6957.83 - 0.0021p + 1.27 \times 10^{-4}p^2 \quad (4)$$

Particularly interesting is the fact that in the I - phase, which is stable at ambient pressure,

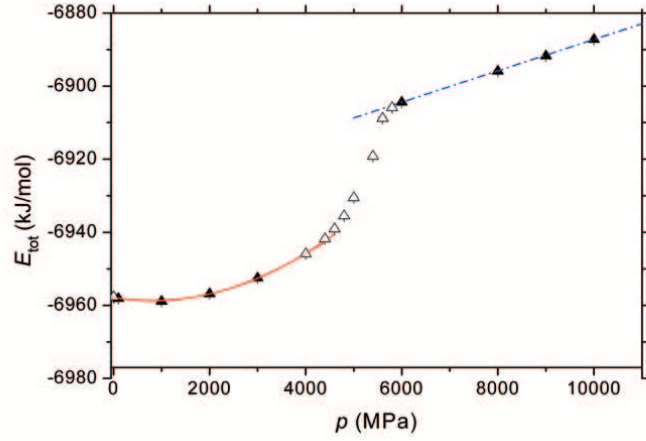


Fig. 6. Pressure dependence of the total energy at room temperature.  $\blacktriangle$  and  $\triangle$ : NpT simulations with increasing and decreasing the pressure, respectively. The full and dash-dotted lines are the corresponding fits, eqs. (4) and (7)

the calculated  $v(p)$  dependence can be fitted by the following equation (see Fig. 7):

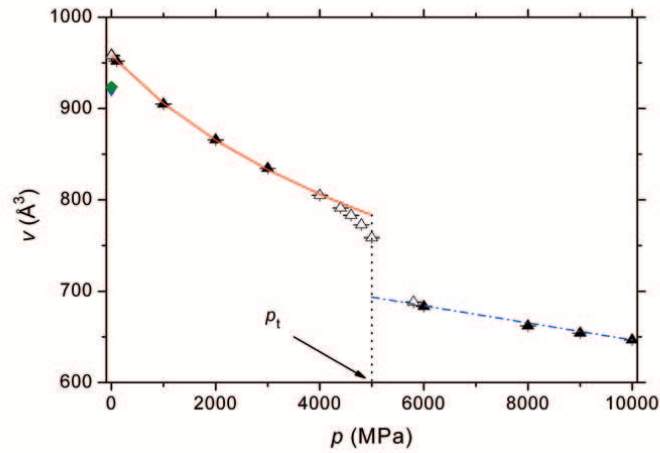


Fig. 7. Pressure dependence of the cell volume with increasing ( $\blacktriangle$ ) and decreasing ( $\triangle$ ) the pressure in NpT simulations at room temperature.  $\blacklozenge$ : experiment [17];  $\blacktriangledown$ : experiment [16]. The full and dash-dotted lines are the corresponding fits, eqs. (5) and (8)

$$v = 958.5 \left(1 + \frac{p}{3610}\right)^{-0.232}. \quad (5)$$



This equation of state is of the Murnaghan type [22]:

$$v(p) = v_0 \left( 1 + \frac{B_0'}{B_0} p \right)^{-\frac{1}{B_0'}} \quad (6)$$

where, in our case, at atmospheric pressure the bulk modulus is  $B_0 = 15.6$  GPa and its first derivative is  $B_0' = 4.31$ .

### 3.2. High-pressure Phase

In contrast with the low-pressure phase, in the high-pressure phase (called thereafter as II [LTBc])  $E_{\text{tot}}$  and  $v$  depend linearly on the pressure:

$$E_{\text{tot}} = -6930.2 + 0.0043 p \quad (7)$$

and

$$v = 740.3 - 9.37 \times 10^{-3} p. \quad (8)$$

The II-polymorph structure is illustrated in Fig. 8: the mean atomic fractional coordinate values show that the symmetry operations of the space group I41cd are conserved, in agreement with the second-order character of the  $\text{I} \leftrightarrow \text{II}$  phase transition. This pressure-induced phase transition

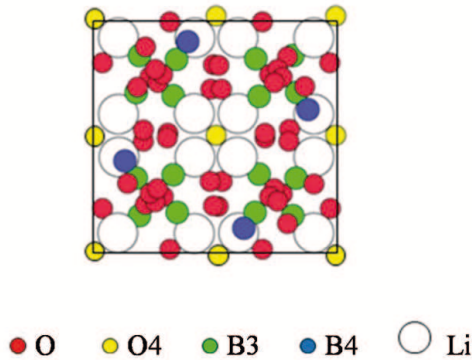


Fig. 8. Calculated high-pressure crystal structure of  $\text{Li}_2\text{B}_4\text{O}_7$  at room-temperature viewed along the  $c$ -axis

obeys to the usual increase of the boron coordination: all B-atoms are in B4 conformation ( $r = [\text{B4}] / ([\text{B3}] + [\text{B4}]) = 1$ ), as in the II -  $\text{B}_2\text{O}_3$  high-pressure form studied by Prewitt and Shannon [23]. The II - [LTBc] phase involves two kinds of boron-oxygen tetrahedrons (see Fig. 9). The former B3 atoms are at the centre of distorted tetrahedrons with an average B-O distance 1.390 Å. The former B4 atoms remain at the centre of distorted tetrahedrons, but with larger average B-O distance (1.512 Å), nearly equal to its value in the I - [LTBc] polymorph (1.497 Å). The oxygen O4 associated with the short B - O distance is coordinated by only two B4 atoms, whereas the other oxygens are coordinated by three borons. The resulting boron-oxygen network has a tetrahedral linkage similar to that in II -  $\text{B}_2\text{O}_3$  and produces cages for Li atoms. Note that the B3 to B4 transformation has been obtained without any change in the force field between the low- and high-pressure phases.

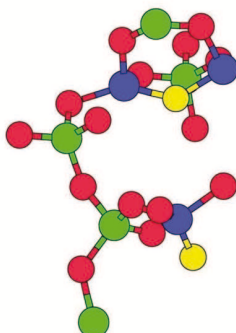


Fig. 9. Boron-oxygen tetrahedral linkage in the high-pressure form of  $\text{Li}_2\text{B}_4\text{O}_7$ . The atom symbols are the same as in Fig. 2 and Fig. 8

By analogy with *ab initio* calculations on II -  $\text{B}_2\text{O}_3$  [24,25], one can assume that II - [LTBc] is more ionic than I - [LTBc]. Therefore, the Coulomb contribution to the total energy is the driving force for the transformation from I - [LTBc] to II - [LTBc] structures.

## 4. Conclusions

A model describing interatomic and angular interactions with boron charge depending on the coordination has been used in molecular dynamics of the polar  $\text{Li}_2\text{B}_4\text{O}_7$  crystal phase as a function of temperature under constant pressure and as a function of pressure at constant temperature. The simulations performed under atmospheric pressure provide a good description of the crystal structure and confirm the order-disorder ferroelectric transition of the second kind below the melting point, previously inferred from the second-harmonic generation experiments. The calculations performed at room temperature predict a pressure-induced phase transition preserving the crystal symmetry. The corresponding mechanism is the same as for the  $\text{B}_2\text{O}_3$  oxide where all threefold borons become fourfold under pressure.

The consistent approach in molecular dynamics is a powerful tool to predict crystal structure and to assure a continuity of physical properties between crystalline, glassy and nanometric phases.

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## Моделирование структуры матриц, включающих наночастицы: молекулярная динамика в $\text{Li}_2\text{B}_4\text{O}_7$

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*Представлена новая модель описания межатомных и угловых взаимодействий в твердофазных кристаллических боратах с учетом периодичности структуры. Модель применена для моделирования свойств  $\text{Li}_2\text{B}_4\text{O}_7$  в диапазоне температур от 0 К до точки плавления и давлений от 0 до 10000 МПа. Моделирование весьма хорошо воспроизводит размеры ячейки, атомные позиции и расстояния в боро-кислородных полиэдрах, а также полярный характер кристаллической структуры. Предсказан сегнето-параэлектрический переход второго рода типа порядок-беспорядок при температуре Кюри ( $T_C \approx 839\text{K}$ ), обусловленный прыжками атомов лития между двумя позициями в решетке. С увеличением или уменьшением давления полная энергия и свойства кристалла при 300 К показывают наличие ступени при  $p_t \approx 5000$  МПа, предполагающей существование обратимого фазового перехода второго рода. При давлениях ниже  $p_t$  объем ячейки следует закону Мурнагана (Murnaghan) с объемным модулем  $B_0 = 15.6$  GPa и его первой производной  $B_0' = 4.31$  (при атмосферном давлении). В отличие от фазы низкого давления, в которой сосуществуют трех- и четырехкоординированные атомы бора, в фазе высокого давления весь бор четырехкратно координирован. Настоящий подход непосредственно применим для моделирования структуры наноразмерных систем.*

*Ключевые слова: тетраборат лития, молекулярная динамика, кристаллическая структура, сегнетоэлектрический переход типа порядок-беспорядок, индуцированный давлением фазовый переход.*