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First-principles calculations of zone-center phonons in CsB_3O_5: Comparison with experiment

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ABSTRACT

Cesium triborate (CsB_3O_5) crystal is an excellent nonlinear optical material with many advantages. As one part of understanding the properties of CsB_3O_5, the vibrational frequencies at the Brillouin zone center are calculated using a plane-wave pesudopotential method within the framework of the local density approximation. The complete $27A+26B_1+26B_2+26B_3$ vibrational modes are assigned, graphically visualized and classified according to the vibrations of tetrahedral BO_4 and $(B_3O_6)^{3-}$ ring. Comparisons with previous experimental reports are discussed in detail.

1. Introduction

Since the discovery of nonlinear optical (NLO) materials β-BaB_2O_4 (BBO), many new borate-based NLO crystals have been discovered, which have greatly expanded the range of laser wavelengths [1]. For example, LiB_3O_5 (LBO) [2,3], CsB_3O_5 (CBO) [4], $CsLiB_3O_5$ (CLBO) [5,6], BiB_3O_6 [7,8], $Li_2B_4O_7$ [9], and $Sr_2B_2BeO_7$ (SBBO) [10] have been studied as promising NLO materials. Borates are superior in UV applications to other commonly used NLO materials such as potassium dihydrogen phosphate (KDP) or $LiNbO_3$ because of their high UV transmittance at wavelengths down to 155 nm combined with a high damage threshold.

The electronic structures and optical properties of borate crystals have been studied with various theoretical methods [11–14]. The first-principles methods offer much more insight into the understanding of the optical response and microscopic structures of NLO materials [1]. Vibrational spectroscopy has become increasingly important as a tool for understanding the chemical bonding and can be used in an empirical way in the evaluation of the NLO properties. Raman spectroscopy has become a powerful and effective tool for resolving the structure of the local arrangements in borate glass by comparison with analogous crystalline compounds. With the aid of Raman and infrared spectra one can probe the early formation of non-bridging oxygen atoms and give unambiguous evidence for the formation of ring-type metaborate units. Therefore, it is necessary to carry out the detailed theoretical and experimental studies of borate crystals.

Many experimental studies have been carried out to investigate the vibrational spectra of important NLO borate crystals, such as BBO [15,16], LBO [17–19], CBO [20], CLBO [21], BiB_3O_6 [22], and $Li_2B_2O_4$ [23,24]. Usually, one assigns the experimental vibrational frequencies of a borate crystal based on the frequencies of the normal modes of BO_3 and BO_4 reported in other borate crystals and glasses. It should be noted that this method is tentative because of the complexity of the crystal structures of CBO and LBO. Certainly, the classical potential model can be used to study the vibrational properties. In this paper, we presented the results for the zone-center modes of CsB_3O_5 crystal using a plane-wave pseudopotential method within the framework of the local density approximation (LDA). The calculated results are compared with the available experimental data taken from the literature.

2. Crystal structure and computational details

The crystal structure of cesium triborate was determined by Krogh-Moe [25]. The space group is $P2_12_12_1$ and the unit cell dimensions are $a = 6.213$, $b = 8.521$ and $c = 9.170$ Å. The structure, with four chemical formulae in the unit cell, contains a basic

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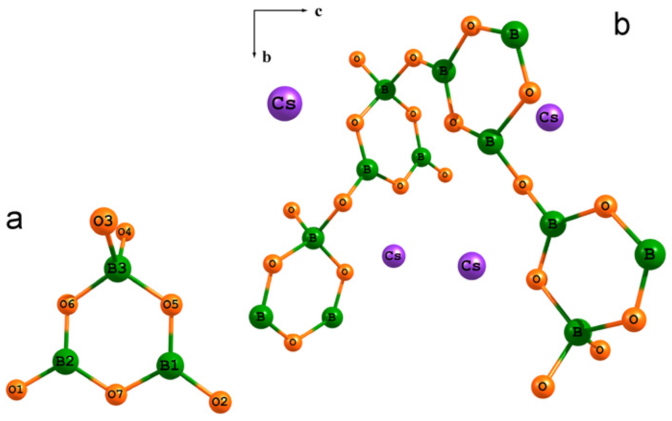

Fig. 1. (a) The basic unit of cesium triborate. (b) Projection along the *a*-axis, showing the structure as a network of borate triangles and tetrahedral (color online).

building block of a $(B_3O_7)^{5-}$ group, as shown in Fig. 1(a). It includes one BO_4 and two BO_3 units, where two of the boron atoms (B_1 and B_2) are threefold coordinated and the third boron atom (B_3) in the ring is fourfold coordinated by oxygen; O_4, O_5, O_6, and O_7 are exocyclic; O_1, O_2, and O_3 are in the ring. The crystal structure of CBO can be described as a continuous three-dimensional network of spiral chains formed from $(B_3O_7)^{5-}$ groups and cesium cations are located at the interstices of the network (see Fig. 1(b)). The average boron–oxygen distance is 1.48 Å for the tetrahedra and 1.38 Å for the triangles.

In this paper, the calculations were carried out using Materials Studio (Castep modulus) [26] developed by Accelrys Software Inc. First-principles method based on the density functional theory [27] (DFT) and the LDA [28] was used in our study to calculate the zone-center modes of CBO crystal. The exchange correlation potential within the LDA is calculated using the scheme of Ceperly–Alder as parameterized by Perdew–Zunger [29].

We employ pseudopotentials to describe electron–ion interactions and plane-wave basis sets to represent electronic wave functions. The electron–ion interactions are described by the norm-conserving pseudopotentials proposed by Hamann [30,31]. The number of plane waves included in the basis is determined by a cutoff energy of 500 eV, and the numerical integration of the Brillouin zone is performed using a $3 \times 2 \times 2$ Monkhorst–Pack k-point sampling [32]. The atomic positions and unit cell parameters are fully relaxed until all the forces and the stress are smaller than 0.02 eV/Å and 0.04 GPa, respectively. The displacements and frequencies of the normal vibrational modes at the Brillouin zone center are calculated using the density functional perturbation theory (DFPT) [33]. The convergence criteria for self-consistent field iterations and phonon convergence (the variation in the electronic second-order energy in the linear response scheme in the DFPT calculations) tolerance were 0.1 E−07 eV/atom and 0.1 E−04 eV/A^2, respectively.

3. Results and discussion

A group theoretical analysis of the vibrational modes of the CBO crystal at $q = 0$ predicts the following decomposition according to the irreducible representations of the point group D_2:

$$\Gamma = 27A + 27B_1 + 27B_2 + 27B_3$$

All of the optical modes, $27A+26B_1+26B_2+26B_3$, are Raman active. Modes B_1–B_3 are also infrared active, so they must be optical polar modes. The polarizations of B_1, B_2, and B_3 modes are parallel to the *z*-, *y*-, and *x*-axis, respectively.

Table 1
Calculated and measured frequencies (cm^{-1}) of A modes in CBO crystal

A mode		
Cal.	Expt.	Assignment
28	32	Translation Cs
55	46	Translation Cs
56	59	Translation Cs
85	73	T. of Cs, L. of $(B_3O_6)^{3-}$
105	97	$(B_3O_6)^{3-}$ ν_1
165	158	$(B_3O_6)^{3-}$ ν_1
156	139	T. of $(B_3O_6)^{3-}$
273	270	T. of $(B_3O_6)^{3-}$
282	290	L. of $(B_3O_6)^{3-}$
364	382	Bending BO_4
395	397	Bending BO_4
476	482	
513	529	$(B_3O_6)^{3-}$ ν_4
557	568	
640	660	$(B_3O_6)^{3-}$ ν_6
685	700	$(B_3O_6)^{3-}$ ν_7
702	726	$(B_3O_6)^{3-}$ ν_9
743	757	$(B_3O_6)^{3-}$ ν_8
882	879	BO_4 ν_3
946	956	
956	978	$(B_3O_6)^{3-}$ ν_{10}
998	995	BO_4 ν_3
1095		Bending of ring $(B_3O_6)^{3-}$ ν_{11}
1267	1244	$(B_3O_6)^{3-}$ ν_{12}
1368	1353	ν_{as}(O6–B2–O7) ν_{as}(O2–B1–O7)
1376	1397	ν_{B2-O1} ν_{B1-O5}
1426	1445	ν_{B1-O2}

We fully optimized the structure of CBO crystal. The optimized lattice parameters are $a = 6.181$, $b = 8.529$, and $c = 9.211$ Å, which are in good agreement with the experimentally measured values [25]. From the calculated results we can see the complexity of vibrational modes of the CBO crystal due to its network structure. Besides the three translation modes with zero frequency, the 105 phonon frequencies at the Brillouin zone center were calculated and listed in Tables 1–4. Based on the calculated results we can perform the symmetry analysis by comparing the basis functions of the irreducible representations with the eigenvectors resulting from the dynamical matrix. The corresponding experimental Raman and infrared data taken from Ref. [20] are also given in Tables 1–4. As can be seen from Table 1, a few frequencies predicted by calculated results are absent in the experimental spectra because of the small intensities. A good agreement between most theoretical and experimental vibrational modes is obtained. In general, the deviation from experimental results is 2–32 cm^{-1}. The maximal difference between the experimental and measured frequencies is 32 cm^{-1} for the scattering band of B_3 mode at 474 cm^{-1}.

For many crystals, the types of vibrational modes can be divided into two parts, external and internal modes, and this separation can greatly help the interpretation of infrared and Raman spectra of complex crystal. Internal modes are vibrations which can be associated with those of a molecular unit, shifted by the interaction with crystalline environment. In CBO crystal, the higher frequency parts of the external-vibration spectra overlap with the lower frequency parts of the internal-vibration spectra because the $(B_3O_7)^{5-}$ units are not isolated. Despite its deficiencies, it can still be useful to divide the vibrations into two categories. Some vibrational modes can still be approximately attributed to characteristic vibrations of the $(B_3O_7)^{5-}$ group. As a first approximation, the non-planar triborate group $(B_3O_7)^{5-}$ can be equivalent to a planar six-membered ring $(B_3O_6)^{3-}$ if the two oxygen atoms O_6 and O_7 out of the plane of six-membered ring are replaced with one atom O* in the plane [17]. On the other hand,