

The prospect of beryllium–oxygen group to search for new nonlinear optical crystals

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Abstract

The prospect of beryllium–oxygen anionic group, especially $(\text{BeO}_3)^{4-}$ anionic group, as the basic structural unit to search for new nonlinear optical (NLO) crystals is evaluated by anionic group theory and density functional theory. Our calculations reveal that the birefringence of the crystals containing only beryllium–oxygen anionic group is too small to satisfy the conditions of good NLO crystals for vacuum ultraviolet (VUV) applications, although the microscopic NLO coefficients of coplanar $(\text{BeO}_3)^{4-}$ group is comparable to that of $(\text{BO}_3)^{3-}$ group.

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1. Introduction

With the development of solid laser devices, investigations of new nonlinear optical (NLO) crystals have become a hotspot of material science in the past two decades. A good NLO material should satisfy some conditions [1]: (i) a relatively large efficient second harmonic generation (SHG) coefficient (d_{eff}) in the required spectroscopic region, $d_{\text{eff}} \geq d_{36}(\text{KDP}) = 0.39 \text{ pm/V}$ for ultraviolet (UV) and vacuum ultraviolet (VUV) NLO crystals and $d_{\text{eff}} \geq 10 \cdot d_{36}(\text{KDP})$ for visible NLO crystals; (ii) a moderate birefringence Δn , ranged from 0.06 to 0.1, to achieve phase-matchable condition; (iii) a wide transparency range; (iv) resistance to high laser intensity; and (v) good chemical stability and mechanical properties. On the study of various NLO crystals such as perovskite, tungsten–bronze type, iodate, phosphate, molybdate and nitrite crystals, Chen [2] proposed a the-

oretical model called ‘the anionic group theory’ for the NLO susceptibility of NLO crystals. This theory rests on the following two assumptions: (i) the overall SHG coefficient of the crystal is the geometrical superposition of the microscopic second-order susceptibility of the anionic groups, and the contribution from the essentially spherical cations is negligible; (ii) the microscopic second-order susceptibility of the basic anionic group can be calculated from the localized molecular orbitals of this group using quantum chemistry calculation methods.

Using the anionic group theory, the structural origin of NLO effects of borate NLO crystals for UV and VUV applications including $\beta\text{-BaB}_2\text{O}_4$ (BBO) [3], LiB_3O_5 (LBO) [4], were clearly elucidated. Moreover, $\text{KBe}_2\text{BO}_3\text{F}_2$ (KBBF) [5] and $\text{Sr}_2\text{Be}_2\text{B}_2\text{O}_7$ (SBBO) family [6–9] were discovered with the help of this theory. Boron can be coordinated by three and four oxygen atoms to form triangular $(\text{BO}_3)^{3-}$ and tetrahedral $(\text{BO}_4)^{5-}$ anionic groups. Our pervious studies shown that the $(\text{BO}_4)^{5-}$ anionic group is not suitable as a good structural unit for NLO crystal due to its small microscopic

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second-order susceptibility, while the coplanar $(\text{BO}_3)^{3-}$ anionic group is a best candidate for that [1,10].

In addition, density functional theory (DFT) provides a more favorable approach to study the mechanism of the linear and nonlinear optical effects using the band wave functions. We have used this theory and perturbation theory to calculate the linear refractive indices and SHG coefficients of various NLO crystals such as BBO [11], LBO [12], KBBF [13], SBBO family [14], and SrBe_3O_4 [15]. Our calculated values are in good agreement with the experimental results. Meanwhile, a real-space atom-cutting method has been used to investigate the influence of cations and anionic groups to optical responses [11]. The method means that if the contribution of ion A to the n th-order polarizability is denoted as $\chi^{(n)}(\text{A})$, we can obtain it by cutting all ions except A from the original wavefunctions, i.e., $\chi_{\text{A}}^{(n)} = \chi_{\text{All ions expt. A are cut}}^{(n)}$.

The comparison of the calculated SHG values of these two methods and the experimental results for BBO, LBO, CBO, and CLBO crystals are listed in Table 1. Obviously, both anionic group theory and DFT are reliable to calculate the optical properties of various crystals. Moreover, Our previous study based on DFT theory proved that the contribution of anionic group to the SHG effect is dominant (>80%), and that of cations can be negligible in the first-order approximation [10–12].

Analogy with the boron–oxygen groups, beryllium and oxygen can also form four coordinated $(\text{BeO}_4)^{6-}$ and three coordinated $(\text{BeO}_3)^{4-}$ anionic groups. Moreover, beryllium–oxygen compounds would have short cutoff wavelengths in UV region since beryllium is a

light element. In this work, the microscopic second-order susceptibilities of $(\text{BeO}_4)^{6-}$ and $(\text{BeO}_3)^{4-}$ groups are calculated by GAUSSIAN'92 ab initio calculation method [16], and compared with those of $(\text{BO}_3)^{3-}$ and $(\text{BO}_4)^{5-}$ groups. Furthermore, the linear and nonlinear optical effects of the beryllium–oxygen compounds, which contain only beryllium–oxygen anionic group including $(\text{BeO}_3)^{4-}$ group, are theoretically studied by CASTEP package [17,18]. We believe that these results may help experimentalists to evaluate the prospect of beryllium–oxygen group in searching for nonlinear optical crystals.

2. Methods and computational details

At beginning of this work, GAUSSIAN'92 package is used to study the microscopic second-order susceptibilities of $(\text{BeO}_4)^{6-}$ group and $(\text{BeO}_3)^{4-}$ group. The formulae for the microscopic SHG coefficients are given in [10].

To investigate the contribution of beryllium–oxygen groups to linear and nonlinear optical effects, we search all crystals which contains only the $(\text{BeO}_3)^{4-}$ group and/or $(\text{BeO}_4)^{6-}$ group in inorganic crystal structure database (ICSD) [19]. There are six compounds: $\text{K}_4\text{Be}_2\text{O}_4$ ($P1121/b$, $a = 7.098 \text{ \AA}$, $b = 10.577 \text{ \AA}$, $c = 5.706 \text{ \AA}$, $\gamma = 131.3^\circ$) [20], $\text{K}_4\text{Be}_3\text{O}_5$ ($C12c1$, $a = 10.381 \text{ \AA}$, $b = 7.228 \text{ \AA}$, $c = 10.788 \text{ \AA}$, $\beta = 118.4^\circ$) [21], $\text{Na}_6\text{Be}_8\text{O}_{11}$ ($P\bar{1}$, $a = 5.321 \text{ \AA}$, $b = 6.424 \text{ \AA}$, $c = 8.391 \text{ \AA}$, $\alpha = 101.7^\circ$, $\beta = 96.4^\circ$, $\gamma = 105.8^\circ$) [22], Na_2BeO_2 ($P1211$, $a = 11.520 \text{ \AA}$, $b = 5.308 \text{ \AA}$, $c = 7.882 \text{ \AA}$, $\beta = 99.3^\circ$) [23], SrBe_3O_4 ($P\bar{6}2c$, $a = b = 4.596 \text{ \AA}$, $c = 8.930 \text{ \AA}$, $\gamma = 120.0^\circ$) [24], and Y_2BeO_4 ($Pmcn$, $a = 3.532 \text{ \AA}$, $b = 9.899 \text{ \AA}$, $c = 10.400 \text{ \AA}$) [25,26]. The basic structural features of the six crystals are shown in Fig. 1, their unit cells contain 2, 4, 1, 8, 2 and 4 formula unit, respectively. In Y_2BeO_4 crystal, the anionic group is coplanar $(\text{BeO}_3)^{4-}$ group. In $\text{K}_4\text{Be}_2\text{O}_4$ crystal two $(\text{BeO}_3)^{4-}$ groups are linked as the anionic group, while in the other crystals, $(\text{BeO}_3)^{4-}$ group is linked to tetrahedral $(\text{BeO}_4)^{6-}$ group as the basic structural unit. According to their space group symmetry, only Na_2BeO_2 and SrBe_3O_4 have SHG effects.

CASTEP, a plane-wave pseudopotential total energy package based on the DFT, is employed to solve the electronic and band structures as well as linear and nonlinear optical properties of these crystals. The optimized pseudopotentials in the Kleinman–Bylander form [27] allows us to use small plane-wave basis set without compromising the accuracy required by our study. The formulae of SHG coefficients are given in [11]. With the ab initio calculation method, the contributions of beryllium–oxygen group to the optical properties of crystals could be recognized and understood. This is the goal of this Letter.

Table 1

The comparison of calculated SHG value of both theoretical methods and the experimental results for BBO, LBO, CBO, and CLBO crystals (unit: pm/V)

Crystal	d_{ij}	Calculated		Experimental
		Anionic group theory ^a	DFT	
BBO	d_{22}	1.73	-1.39^b	$\pm 1.60^d$
	d_{31}	~ 0	0.058	∓ 0.11
	d_{33}	~ 0	0.032	~ 0
LBO	d_{31}	-0.94	-0.505^c	$\mp 0.67^e$
	d_{32}	1.00	0.582	± 0.85
	d_{33}	0.20	0.014	± 0.04
CBO	d_{14}	-0.68	-0.577	$\pm 0.75^a$
CLBO	d_{36}	-0.57	-0.546	$\pm 0.67^f$

^a Ref. [1].

^b Ref. [11].

^c Ref. [12].

^d Ref. [3].

^e V.G. Dmitries, G.G. Gurzadyan, D.N. Nikogosyan, Handbook of Nonlinear Optical Crystals, Springer, New York, 1995.

^f J. Shoji, H. Nakamura, R. Ito, T. Kondo, M. Yoshimura, Y. Mori, T. Sasaki, J. Opt. Soc. Am. B 18 (2001) 302.

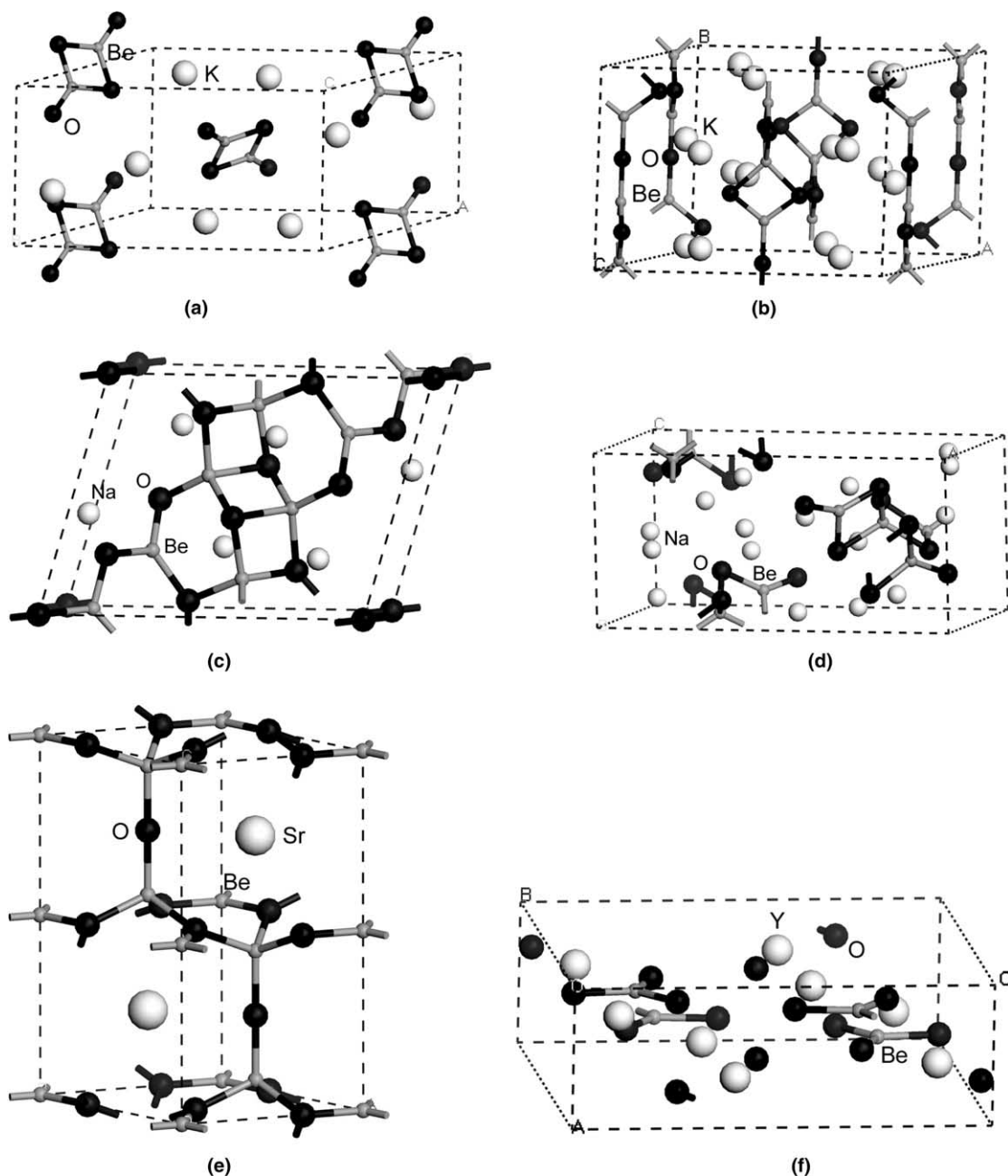


Fig. 1. Unit cell of crystals in which the anionic group only contain $(\text{BeO}_3)^{4-}$ group and/or $(\text{BeO}_4)^{6-}$ group. (a) $\text{K}_4\text{Be}_2\text{O}_4$, (b) $\text{K}_4\text{Be}_3\text{O}_5$, (c) $\text{Na}_6\text{Be}_8\text{O}_{11}$, (d) Na_2BeO_2 , (e) SrBe_3O_4 , and (f) Y_2BeO_4 .

3. Results and discussions

The microscopic second susceptibilities of $(\text{BeO}_3)^{4-}$ and $(\text{BeO}_4)^{6-}$ groups calculated by means of the GAUSSIAN'92 method are listed in Table 2. The values of $(\text{BO}_3)^{3-}$ and $(\text{BO}_4)^{5-}$ groups are also shown in Table 2 as a comparison. These calculations support two obvious conclusions as follows. (1) The coplanar $(\text{BeO}_3)^{4-}$ group has the comparable microscopic SHG coefficients with that of coplanar $(\text{BO}_3)^{3-}$ group. Therefore, the coplanar $(\text{BeO}_3)^{4-}$ group is suitable as the basic unit for SHG effects. (2) Analogy with $(\text{BO}_4)^{5-}$ group, the

microscopic SHG coefficients of $(\text{BeO}_4)^{6-}$ is too small to satisfy the condition for good NLO crystals.

Table 2

Comparison of the microscopic second susceptibilities of $(\text{BeO}_3)^{4-}$, $(\text{BeO}_4)^{6-}$, $(\text{BO}_3)^{3-}$ and $(\text{BO}_4)^{5-}$ anionic groups (unit: 10^{-31} esu, $\lambda = 1064$ nm)

$(\text{BeO}_3)^{4-}$		$(\text{BeO}_4)^{6-}$		$(\text{BO}_3)^{3-}$		$(\text{BO}_4)^{5-}$	
$\chi_{111}^{(2)}$	0.348	$\chi_{123}^{(2)}$	−0.112	$\chi_{111}^{(2)}$	0.472	$\chi_{123}^{(2)}$	−0.140
$\chi_{122}^{(2)}$	−0.348	$\chi_{113}^{(2)}$	0.003	$\chi_{122}^{(2)}$	−0.472	$\chi_{113}^{(2)}$	0.006
		$\chi_{223}^{(2)}$	−0.011			$\chi_{223}^{(2)}$	−0.014

Table 3

The static linear and nonlinear optical coefficients of crystals which only contain beryllium–oxygen anionic group including $(\text{BeO}_3)^{4-}$ group

Crystal	Refractive indices				The largest SHG coefficients (pm/V)
	n_x	n_y	n_z	Δn	
$\text{K}_4\text{Be}_2\text{O}_4$	1.5813	1.5858	1.5859	0.0046	–
$\text{K}_4\text{Be}_3\text{O}_5$	1.5843	1.5854	1.6116	0.0273	–
$\text{Na}_6\text{Be}_8\text{O}_{11}$	1.5725	1.5826	1.5922	0.0197	–
Na_2BeO_2	1.6306	1.6395	1.6269	0.0126	$d_{22} = 0.957$
SrBe_3O_4	1.7066	1.7066	1.7233	0.0167	$d_{22} = 0.415$
Y_2BeO_4	1.7976	1.7817	1.7668	0.0288	–

Furthermore, Table 3 lists the calculated linear and nonlinear optical coefficients for all crystals in which the anionic group only include $(\text{BeO}_3)^{4-}$ group and/or $(\text{BeO}_4)^{6-}$ group by CASTEP. The SHG coefficients of SrBe_3O_4 and Na_2BeO_2 are larger than $d_{36}(\text{KDP})$, so suit-

able in the UV region. However, the birefringences of the six crystals are all less than 0.03, which is far smaller than the condition of the birefringence ($0.06 \leq \Delta n \leq 0.1$) for NLO crystals. On the other hand, the real-space atom-cutting method reveals that the birefringences of coplanar $(\text{BO}_3)^{3-}$ group in crystals are larger than 0.07 [13,14]. The real-space atom-cutting method is not adopted to further analyses the contribution of respective group and cation to the birefringence since the birefringence of these beryllium–oxygen crystals is too small. The crystals only containing beryllium–oxygen anionic group, therefore, would not be good candidates for NLO crystals.

Fig. 2a presents the charge-density distribution in the plane of the $(\text{BeO}_3)^{4-}$ group of Y_2BeO_4 as an example, while that in the plane of the $(\text{BO}_3)^{3-}$ group of $\text{BaAl}_2\text{B}_2\text{O}_7$ (BABO) [14] is shown in Fig. 2b as a comparison. It is clear that the charge density in the $(\text{BO}_3)^{3-}$ group is a whole, it is difficult to separate the B and O ions. The bonding between B and O is covalent with a π conjugated orbital. The anisotropy of response for $(\text{BO}_3)^{3-}$ group to the light is large because covalent bond is highly directional. Conversely, there are no apparent overlaps between the orbitals of Be and three O atoms. This means that the bonding between Be and O is little covalent, where ions are held together by a nondirectional columbic attraction. Therefore, the response of $(\text{BeO}_3)^{4-}$ group to the light is more isotropy.

4. Conclusion

The prospect of beryllium–oxygen anionic group, especially $(\text{BeO}_3)^{4-}$ anionic group, as the basic structural unit in NLO crystals is evaluated by anionic group theory and DFT. The GAUSSIAN'92 method reveals that the microscopic second susceptibilities $(\text{BeO}_4)^{6-}$ anionic group is very small, while that of coplanar $(\text{BeO}_3)^{4-}$ is comparable with that of $(\text{BO}_3)^{3-}$. Moreover, the linear and nonlinear optical coefficients of all crystals in which the anionic group is only $(\text{BeO}_3)^{4-}$ group and/or $(\text{BeO}_4)^{6-}$ group are calculated using CASTEP package. The theoretic results show that the birefringence of these crystals is too small to satisfy the conditions of good NLO crystals, although their SHG coefficients are suitable. Therefore, the beryllium–oxygen anionic group is not a good candidate as searching for NLO crystals.

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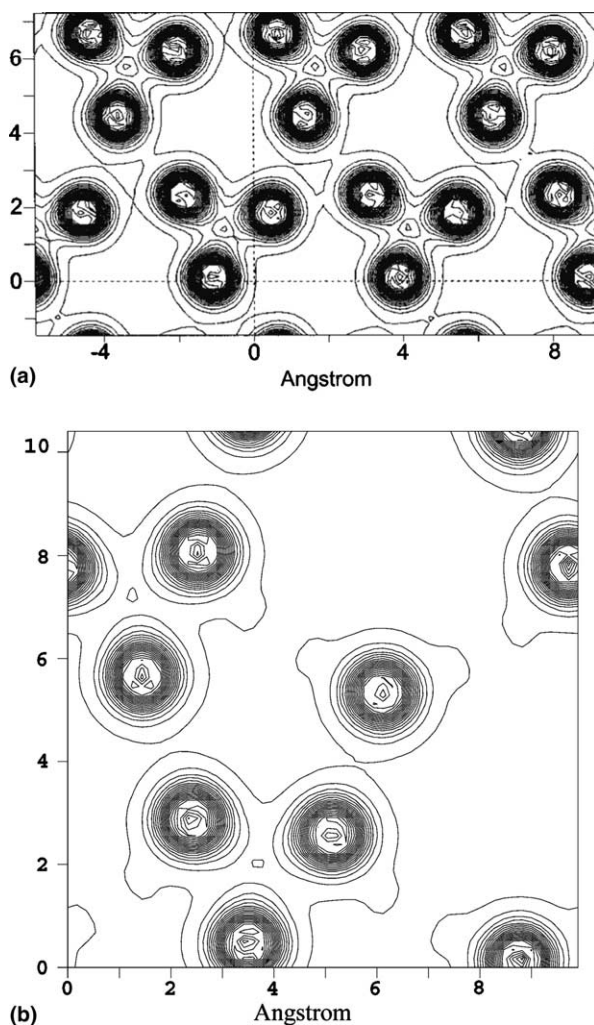


Fig. 2. (a) Charge density in the $(\text{BeO}_3)^{4-}$ plane of Y_2BeO_4 crystal, (b) Charge density in the $(\text{BO}_3)^{3-}$ group plane of BABO crystal.

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