

[illegible]

計畫參與主人員：田力耕

- 本成果報告包括以下應繳交之附件：

- ☐赴國外出差或研習心得報告一份
- ☐赴大陸地區出差或研習心得報告一份
- ☐出席國際學術會議心得報告及發表之論文各一份
- ☐國際合作研究計畫國外研究報告書一份

執行單位：淡江物理系

中文摘要:

SHG(Second Harmonic Generation)是一種可以從長波長的來源得到短波長的方法，LBO (LiB_3O_6) 是具有 SHG 特性的重要材料。而 LBO, CBO, 及 CLBO 都是有著陰離子團(B_3O_6)的晶體，只是具有不同的陽離子。能隙基本上也是決定了在 NLO 的過程中，最後射出 SHG 光束的一個關鍵。現在我們有興趣知道對於這三種晶體的能隙大小的趨勢關係。在這個工作中我們採用了虛擬晶體方法，這是一種利用人造的晶體結構來研究材料性質的方法。再利用第一原理計算來研究實驗所無法達到的地步。

英文摘要:

Second Harmonic Generation (SHG) is a way to obtain short wavelength laser beam from a longer wavelength source. LBO (LiB_3O_5) is a very important crystal which exhibits good SHG properties. LBO, CBO, CLBO is a class of crystals which share the same composition of anion group (B_3O_5), but just differ by their cations. Band gap fundamentally determines the window of wavelength of the out-coming SHG beam and it is also related to the damage threshold of the crystal during the NLO process. Now, we are interested to know what makes the band gap of these three crystals different, and what are the factors determine the trend of their gaps. In this work we have adapted the so called Virtual Crystal Approach, which means investigating the properties of materials based on artificially constructed crystal structures. By using *ab initio* method, one will than be able to explore a wider configuration space that are not accessible

to by usual experimental techniques.

計劃緣由與目的:

With the usual natural light sources, the polarisability of a material is linearly proportional to the magnitude of electric field. The invention of laser makes extremely high intensity light beam available, allowing the material to interact with electromagnetic wave within the non-linear response regime. Second harmonic and sum harmonic effect can happen under such condition to provide sources of short wavelength light. The refractivity is also related to the polarisability of a medium, and therefore the refractive index also depends on the intensity of light. Material of such kind can be used as a modulator.

LBO (LiB_3O_5) is a very important crystal which exhibits good SHG properties LBO, CBO, CLBO is a class of crystals which share the same composition of anion group B_3O_5 , but just differ by their cations. Studying how their physical quantities vary may provide clues to understand how structural and constitutional change can affect quantities that are important in SHG crystal design, which are (1) the band gap, (2) the birefringence and (3) the second order susceptibility of the crystals. The later two are important for achieving phase matching condition and create non-linear effect, respectively. Our *ab initio* study of these two quantities are reported separately.

Although band gap may not seem to be

relevant to NLO properties so much as birefringence and $\chi^{(2)}$ do, it fundamentally determines the window of wavelength of the out-coming SHG beam and it is also related to the damage threshold of the crystal during the NLO process. Band gap sometimes turn out to be the most critical factor in the NLO material design. In this paper, we are interested to know what makes the band gap of these three crystals different, and what are the factors determine the trend of their gaps. This is not a trivial question which can be addressed by the apparent chemical composition of the crystals. For example, the trend of gap variation, $E_g(\text{LBO}) > E_g(\text{CBO}) > E_g(\text{CLBO})$, can not be explained by just considering whether the cation in the system is Li or Cs. The understanding of the physical origin of this gap variation will be very important for the band gap engineering of similar materials.

Given that LBO, CBO, and CLBO share the common chemical composition except the group IA elements, it is still natural to suspect that the cationic effect play major role in causing gap variation. One may imagine that such effect could come directly from the individual electronic properties of cation affecting either the edge of conduction band or valence band, or both. Alternatively, it can be an indirect effect as the different size of cation altering the packing style of BO framework in these three crystals, results in different gap values. The later is not an unreasonable guess, after all our previous calculations already indicates that the density of states near the

gap are dominated by Boron and Oxygen. In this work we have adapted the so called Virtual Crystal Approach, which means investigating the properties of materials based on artificially constructed crystal structures. By using *ab initio* method, one will than be able to explore a wider configuration space that are not accessible to by usual experimental techniques. With such an approach, essential structural components are removed or replaced and their electronic structure and optical properties calculated. The differences in computed results will help one to identify the component which gives the most important contribution to the desired properties (in this case band gap) and eventually lead to an understanding of the mechanism.

結果與討論：

Energy gaps of LBO, CBO, CLBO crystals are not determined by the electronic structure of the neutral Boron-Oxygen framework itself. Instead, the valence electron of IA elements, which is donated to oxygen site and making the BO framework charged, play crucial role in the determination of the band gap in these borate NLO crystals.

Both edges of band gap are mainly contributed from the electronic structure on Oxygen site, which is sensitive to the local environment introduced by different IA elements, as shown in the present work by using partial crystal construction (crystal fragment method). Among local geometrical factors, correlation can be found between band gap and the size of cation cavity,

whereas the effects of bond length and bond angle around oxygen are not important.

From the step by step augmentation of the fragments of Borate framework in LBO, CBO and CLBO (and observing the gap changes), the gap trend of the three crystals can be reproduce by all size of models, from a very small cluster to the entire BO framework. This strongly suggests that the gap variation among these borate crystals is a local effect controlled mainly by the distance between cation and oxygen. This also explains the correlation between the sort of "cavity" size and the trend of band gap.

Being an unoccupied state, LUMO band is more delocalised than HOMO one and therefore its eigenvalue is more sensitive to the geometry of the local environment determined by neighbouring atoms. The LUMO band electron, mainly from oxygen s-state, is more tightly confined in the cage in LBO than in CBO. The mechanism of gap variation can therefore be understood as the size effect of cation, through the packing of borate framework, indirectly fine-tuning the the energy level of the state at the bottom of the conduction band.

The overall picture is therefore the following : the size of cation affect how they are packed together with B_3O_5 framework in crystals. The force balance between atoms in unit cell further determined the equilibrium position of cations relative to nearby oxygen atoms. The band gap of $B_3O_5+1e^-$ system, which is mainly due to the local Op-Os transition, is sensitive to oxygen-cation distance and

results in the gap variation of LBO, CBO and CLBO crystals.

計畫成果自評:

1. 由於有部分的資料遺失才會造成計畫的時間拖長。
2. 本身要研究 Bandgap 和結構之間，是不簡單的問題。
3. 現在撰稿的進度正在進行了，預計再兩個月之後，將會投稿。

參考文獻：

- [1] P.Hohenberg and W. kohn, Phys. Rev. 136, B864 (1964)
- [2] C. T. Chen, Y. C. Wu, A. D. Jiang, B. C. Wu, G. M. You, R. K. Li, and S. J. Lin, J. Opt. Soc. Am. B 6, 616 (1989)
- [3] Y. C. Wu, T. Sasaki, S. Nakai, A. Yokotani, H. Tang, and C. T. Chen, Appl. Phys. Lett. 62 2614 (1993)
- [4] Y. Mori, I. Kuroda, S. Nakajima, T. Sasaki, and S. Nnakai, Appl. Phys. Lett. 67, 1818 (1993)
- [5] J. Lin, M. H. Lee, Z. P. Liu, C. T. Chen, and C. J. Pickard, Phys. Rev. B 60, 13380 (1999)
- [6] Z.S. Lin, J. Lin, Z.Z. Wang, C.T. Chen, M-H. Lee, Phys. Rev. B 62, 1757 (2000)
- [7] CASTEP 3.5 program Molecular Simulation, Inc. j (1997)
- [8] M. C. Payne, M. P. Teter, D. C. Allan,

T. A. Arias, J. D. Joannopoulos, Review
of Modern Physics. V.64 N.4, 1045
(1992)

[9] V. Heine The Pseudopotential concept
Solid State Physics. Vol 24, p 1,
Academic Press, New York, 1970

[10] W. Kohn and L. J. Sham, Phys. Rev.
140, 1133A (1965)

[11] L. J. Sham and W. Kohn, Phys. Rev.
B. 145, 5611 (1966)

[12] Perdew, J. P. Wang Y. Phys. Rev. B.
46, p 6671 (1992)

[13] A. M. Rappe, K. M. Rabe, E.
Kaxiras, and J. D. Joannopoulos, Phys. Rev.
B 41, 1227 (1990)

[14] J. S. Lin, A. Qteish, M. C. Payne,
and V. Heine, Phys. Rev. B 47, 4174
(1993)

[15] R. W. Godby, M. Schluter, and L. J.
Sham, Phys. Rev. B 37, 10 159 (1988)

[16] C. S. Wang and B. M. Klein, Phys.
Rev. B 24, 3417 (1981); M. S. Hybertsen
and S. G. Louie, ibid. 34, 5390 (1986)

[17] S.G. Louie, S. Froyen and M.L.
Cohen, Phys. Rev. B 26, 1738 (1982)

[18] M-H. Lee, PhD. Thesis, University
of Cambridge (1995)

[19] Pseudopotential Database
Information, CASTEP Module, Cerius2
3.5, Molecular Simulation Inc.

[20] L. J. Sham, M. Schluter, Phys. Rev.
B. 32, 3883 (1985)

[21] J.P. Perdew, Int. J. Quantum Chem.
497-523, Suppl. 19 (1985)

[22] A. Seidl, A. Goerling, P. Vogl, J.A.
Majewski and M. Levy, Phys. Rev. B 53,
3764 (1996)

[23] I.N. Remediakis and E. Kaxiras,
Phys Rev B 59, 5536 (1999)

[24] L. Fritsche, J. Phys.: Condens.
Matter 8, 2237 (1996)