

Search for New Optical Crystals by the Chemical Bond Method

XUE Dong-feng¹, Betzler Klaus², Hesse Hartmut²,
Kitamura Kenji³, Ratajczak Henryk^{4,5}, WANG Ji-yang⁶

(1. School of Chemical Engineering, Dalian University of Technology, Dalian 116012, China;

2. Universität Osnabrück, Fachbereich Physik, D-49069, Osnabrück, Germany;

3. Advanced Materials Laboratory, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan;

4. Faculty of Chemistry, University of Wrocław, ul. F. Joliot-Curie 14, 50-383 Wrocław, Poland;

5. Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P. O. Box 937, 50-950 Wrocław 2, Poland;

6. Institute of Crystal Materials, Shandong University, Jinan 250100, China)

(Received 17 March 2004)

Abstract: From the chemical bond viewpoint, dielectric properties of some practical materials with various crystal structures were quantitatively studied. The correlation between constituent chemical bonds and dielectric properties of these crystals was analyzed using the proposed chemical bond method. Furthermore, on the basis of the chemical bond method a combination method was presented for the quantitative determination of dielectric properties of materials with a similar crystal structure. From the current work, we may derive structural information concerning the nonlinearity origin of optical crystals, which is helpful for the nonlinear optical crystal engineering.

Key words: chemical bond method; crystal engineering; nonlinear optics; optical material

CLC number: O742

Document code: A

Article ID: 1000-985X(2004)04-0605-08

利用化学键方法寻找新型光学晶体

薛冬峰¹, Betzler Klaus², Hesse Hartmut²,
Kitamura Kenji³, Ratajczak Henryk^{4,5}, 王继扬⁶

(1. 大连理工大学化工学院, 大连 116012;

2. Universität Osnabrück, Fachbereich Physik, D-49069, Osnabrück, Germany;

3. Advanced Materials Laboratory, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan;

4. Faculty of Chemistry, University of Wrocław, ul. F. Joliot-Curie 14, 50-383 Wrocław, Poland;

5. Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P. O. Box 937, 50-950 Wrocław 2, Poland;

6. 山东大学晶体材料研究所, 济南 250100)

摘要: 利用化学键的观点定量地研究了一些具有各种晶体结构实用材料的介电性质。采用已建立的化学键方法, 分析了这些晶体的介电性质与其组成化学键之间的关系。更进一步, 基于晶体的化学键方法提出了一个组合方法用于定量确定具有相似晶体结构材料的介电性质。从目前的工作中可以推导出光学晶体非线性起源的结构信息, 因此可以在一定程度上帮助人们开展非线性光学晶体工程的研究工作。

关键词: 化学键方法; 晶体工程; 非线性光学; 光学材料

1 Introduction

Crystals are solids in which the elementary building blocks, the atoms or ions, are arranged regularly in a space lattice with specific geometrical symmetry elements. New crystal materials are the lifeblood of solid state research and

Received date: 2004-03-17

Foundation item: Project supported by a Foundation for the Author or of National Excellent Doctoral Dissertation of P. R. China (No. 200322)

Biography: XUE Dong-feng (1968-), Male, from Henan province, Doctor, Professor. E-mail: dfxue@chem.dlut.edu.cn

device technology. Many physical phenomena show up remarkably only in single crystals and can only be studied and understood in single crystals. Therefore, the crystal grower—especially if he develops a proficiency in relating structure, bonding and other chemical-physical considerations to properties of interest—is in a key position in determining the direction and success of solid state research and ultimately technology. It is well known that developing and performing crystal growth processes is quite expensive; anyhow it is always expected from the materials scientist to grow different single crystals according to specific needs. The structure-property relationship of materials is a classical and well-studied research area, which can give an important help in guiding crystal growth research.

Among the wide interesting areas of crystal materials, nonlinear optical (NLO) crystals are specially attractive owing to the increasing variety of applications of NLO crystal materials for second harmonic generation (SHG), sum or different frequency mixing, optical parametric oscillation or amplification. These potential applications have resulted in the development of numerous inorganic NLO crystals dominating the single crystal market. Over the past 30 years, the search for new and better NLO materials has never ceased in the endeavor to develop new laser sources and extend applications. Although there have been many theoretical and experimental studies on the NLO properties of molecules and crystals, the knowledge, in this regard, is still not broad enough for general materials scientists to design, tailor and modify artificial crystals for different NLO applications. A better knowledge about the correlation between the crystal (or molecular) structure and corresponding NLO properties can effectively guide the expensive search for new materials in this field.

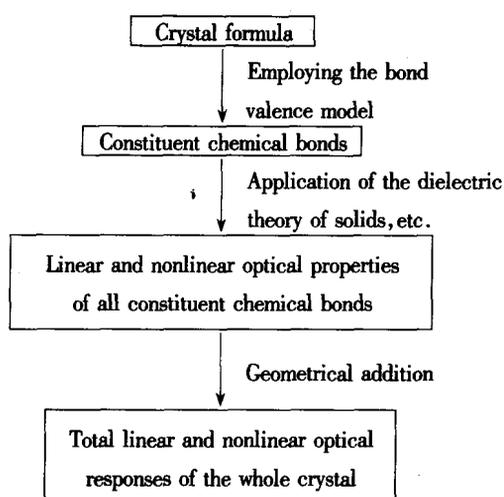
To date, commercial software at the ab initio level (e. g., Gaussian programs) provides functions to predict the NLO-SHG effects of binary crystals. Yet it is still not possible or difficult to use these programs for calculating the nonlinear susceptibilities of solid state materials with complicated crystal structures like KTiOPO_4 and LiNbO_3 . Therefore, inorganic crystals with the complex crystallographic structure have still to be theoretically treated with semi-empirical and empirical approaches at different approximation levels^[1]. The chemical bond method^[2] indicates that properties of constituent chemical bonds might regulate both linear and second order nonlinear optical properties and related effects of an assigned crystal. It might not only form the basis but also provide an opportunity to improve the quality of the observed relationship between the structure and property of solid state materials.

The constitution-property relationship among some dielectric materials with a similar crystallographic structure has shown, that if we combine the chemical bond method and the constitution-property relationship in solid state materials, a powerful tool may be expected to search for new dielectric materials^[3,4]. Therefore, such a work forms a combination method for the calculation and prediction of linear and nonlinear dielectric properties (e. g., refractive indices and SHG tensor coefficients) of solid state materials with similar crystallographic structure.

2 Fundamentals of the chemical bond method

Applying the chemical bond method in order to calculate the optical properties of crystallized solids means to decompose a crystal into its constituent bonds, to calculate properties of these isolated bonds, and finally to add up all these specific or individual contributions. As electric fields in the optical frequency regime show up only slight spatial variations in the regarded volume, for the geometrical addition only the directions, not the absolute positions of chemical bonds have to be taken into account.

The chemical bond method of solids is constructed on the basis of previous theories and models of crystallized solids, such as the dielectric theory of solids proposed by Phillips and Van Vechten^[5,6], the bond charge model proposed by Levine^[7], the bond valence model proposed by Brown^[8], and the chemical bond theory for complex crystals proposed by Xue et al.^[9]. The method can be described as some formal steps, which are sketched in the following scheme (all contained formulas and parameters in the description may be calculated by corresponding crystallographic data).



Scheme 1 Working procedure of the chemical bond method in solid state matters

3 Application of the dielectric theory of solids to crystals

The only difference between the single-bond and multi-bond crystals is the different coordination environment of constituent ions in the crystallographic frame. In a multi-bond crystal, anionic ions are usually coordinated to more than one kind of cations. According to the chemical bond method, the relation between the crystal formula and its constituent chemical bonds may be expressed as an equation (called as the bond-valence equation^[9]), which shows that the crystal formula is a sum of all constituent bond sub-formulae (corresponding to a structural unit bonded to only one kind of chemical bonds). In the bond sub-formulae, there is also an element ratio, which is closely correlated to the coordination conditions of constituent atoms or ions. Since any chemical bond is a binary unit, the bond sub-formula is binary too. However, the dielectric theory of solids^[5,6] may be reasonably applied to calculations of these binary bond sub-formulae. In the extension of the dielectric theory of solids to multi-bond crystals, the improved concept of some parameters and corresponding modifications have been respectively introduced^[9]. Therefore, in order to apply the dielectric theory of solids to a multi-bond crystal such as LiNbO_3 , the following transfer has to be made, as shown in Figure 1 the crystal structure (a) and constituent chemical bonds (b) of lithium niobate may be well correlated. The crystal formula of LiNbO_3 can thus be written as $\text{LiNbO}_3 = [\text{LiO}_3 + \text{NbO}_3]$, according to the bonding behaviors of such atoms in Fig. 1(b).

As shown previously^[2], the chemical bond method regards certain macroscopic physical properties of a crystal as the

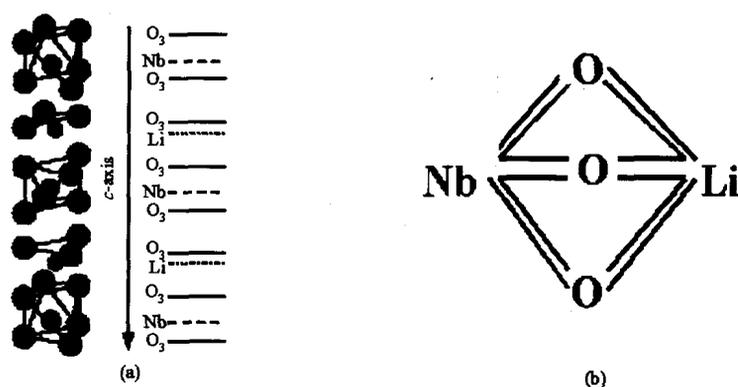


Fig. 1 Crystallographic structure and bond graph of lithium niobate crystals.

(a) crystallographic frame ;(b) bond graph

combination of the contributions of all constituent chemical bonds. According to the relationship between the crystal structure and optical response of crystal materials, the linear and second order nonlinear optical properties of any crystal can be calculated using the appropriate geometric sum of the respective properties of its corresponding constituent chemical bonds. On the basis of the crystallographic structure of an assigned crystal, all related bond parameters can be deduced from the detailed chemical bonding structures of all constituent atoms, its linear and second order nonlinear optical susceptibilities and d_{ij} can thus be written as

$$F_{\mu}^{\mu} = N_{\mu}^{\mu} \chi_{\mu}^{\mu} \quad (1)$$

and

$$d_{ij} = \left\{ \frac{G_{ij}^{\mu} N_{\mu}^{\mu} [(Z_A^{\mu})^* + (Z_B^{\mu})^*] f_i^{\mu} (r_{\mu}^{\mu})^2}{2 d^{\mu} q^{\mu} [(Z_A^{\mu})^* - (Z_B^{\mu})^*]} + \frac{G_{ij}^{\mu} N_{\mu}^{\mu} S (2S - 1) (r_0^{\mu})^2 f_c^{\mu} (r_{\mu}^{\mu})^{\mu}}{d^{\mu} q^{\mu} (r_0^{\mu} - r_c^{\mu})^2} \right\} \quad (2)$$

respectively^[9]. Eq. (2) comes from the extensions of Levine's bond charge model^[7] for complex crystals^[9], which shows contributions of each type of constituent chemical bonds (i. e., μ type) to the total tensor d_{ij} of a multi-bond crystal. Eq. (2) makes it possible to quantitatively calculate NLO coefficients of multi-bond crystals. Parameters used in the above two equations include:

F_{μ}^{μ} Fraction of bonds of type μ composing the crystal; χ_{μ}^{μ} Linear susceptibility contribution from μ type bonds;

N_{μ}^{μ} Number of bonds of type μ per \AA^3 ; χ_{μ}^{μ} Susceptibility of a single bond of type μ ;

G_{ij}^{μ} Geometrical contribution of chemical bonds of type μ ;

$(Z_A^{\mu})^*$, $(Z_B^{\mu})^*$ Effective number of valence electrons of A and B ions, respectively;

n Ratio of numbers of two elements B and A in the bond valence equation^[12];

f_i^{μ}, f_c^{μ} Fractions of ionic and covalent characteristics of the individual bonds $f_i^{\mu} = (C^{\mu})^2 / [(E_h^{\mu})^2 + (C^{\mu})^2]$ and

$f_i^{\mu} = 1 - f_c^{\mu}$, where C^{μ}, E_h^{μ} are the average energy gaps due to ionic and covalent effects;

d^{μ} Bond length of the μ type bonds in \AA ; q^{μ} Bond charge of the μ -type bond;

S Exponent in the bond force constant (2.48);

$r_c^{\mu} = 0.35 r_0^{\mu}$ Core radius, where $r_0^{\mu} = d^{\mu} / 2$. and $r_{\mu}^{\mu} = (r_A^{\mu} - r_B^{\mu}) / (r_A^{\mu} + r_B^{\mu})$ Difference in the atomic sizes, where r_A^{μ} and r_B^{μ} are the covalent radii of atoms A and B.

All of the above parameters can be deduced from the detailed chemical bonding structure of all constituent atoms, which are obtained from the corresponding crystallographic structure of the assigned crystal material^[9]. For the lithium niobate crystal at room temperature, its crystallographic structure, site location of constituent atoms and bond graph are described in Fig. 1.

4 Results for some practical NLO crystal materials obtained from the chemical bond method

By means of the described theoretical relationship between the crystal structure and its second order NLO tensor coefficients, we have done quantitative calculations of the nonlinearities for various interesting NLO crystals with typical complex structures (as shown in Table 1). These include several different crystallographic characteristics, which can be regarded as typical for complex NLO crystal materials^[10]. The quantitative analysis can finally yield helpful information in the search for new type NLO crystal materials. Theoretical results obtained by our method are in good agreement with the corresponding experimental data^[10], for example, for KTiOPO_4 crystals we have^[11]

$$d_{31} = -7.92 \times 10^{-9} \text{esu (Calc.) and } 6.06 \times 10^{-9} \text{esu (Expt.)};$$

$$d_{32} = -11.29 \times 10^{-9} \text{esu (Calc.) and } 10.38 \times 10^{-9} \text{esu (Expt.)};$$

$$d_{33} = -40.67 \times 10^{-9} \text{ esu (Calc.) and } 40.35 \times 10^{-9} \text{ esu (Expt.) ,}$$

and for KH_2PO_4 crystals we have ^[12]

$$d_{36} = 0.95 \times 10^{-9} \text{ esu (Calc.) and } 0.93 \times 10^{-9} \text{ esu (Expt.) ,}$$

which emphasizes that our method is widely applicable and can reasonably reflect the microscopic physical characteristics of complex crystals.

Table 1 NLO-dominator analysis of some practical crystals

NLO-dominator	Crystal	NLO-dominator	Crystals
Li-site	LiNbO ₃	F-site	HIO ₃
	LiTaO ₃		LiIO ₃
K-site	KNbO ₃	P-site	KH ₂ PO ₄
	KTiOPO ₄	N-site	NH ₄ H ₂ PO ₄
	KTiOAsO ₄	B-site	BiB ₃ O ₆

The quantitative analysis of the different individual contributions to the total nonlinear response of a crystal yields the most dominant contributing subgroup. Furthermore, conclusions can be drawn regarding the sensitive lattice sites. An overview about the crystals investigated so far is given in our previous publication^[10], in which the dominant subgroups contributing to the NLO response and the

sensitive lattice sites of the crystals are also listed. From the presented dominant NLO contributor of each crystal listed in Table 1, it is easy for us to find some structural information concerning the nonlinearity origin of an assigned crystal. For example, which are the most important constituent groups, chemical bonds, and the sensitive lattice site in the crystal structure that can produce the most important effect on the total nonlinearity of an assigned crystal. Thus this result also gives us a powerful tool in modifying NLO properties of the existing NLO crystals according to our needs, e. g., by using the same or similar dominant subgroups and for the modification of the NLO properties of existing NLO crystals by substituting the ions at the NLO sensitive lattice sites. When we substitute ions in the sensitive lattice sites with corresponding selected ions, the NLO responses of this crystal would be modified by a big margin, thus we can realize the aim to modify NLO responses of the assigned crystal according to the specific need. Therefore, our work in a sense, presents us a useful theoretical method to understand NLO properties of a crystal from a microscopic viewpoint. Our method is also helpful for us to design and synthesize new type NLO materials, as well as modify the macroscopic physical properties of crystals according to our specific needs. It should be noted that our chemical bond method is different from the anionic group theory, due to that the chemical bond method treats any solid as a network of bonds that have respective contributions to various macroscopic properties of the bulk material, while the anionic group theory (i. e., the localized molecular orbital model for NLO effect in crystals) regards macroscopic properties of any crystal as the dominant contribution of its anionic group in the crystallographic frame. Therefore, the anionic group theory has to face the problem to suitably select the dominant anionic group in the crystallographic frame and the chemical bond method need not do it.

5 Inorganic crystals with hydrogen bonds

Hydrogen bonds in general exist widely in solids, not only in almost all organic crystals but also in many inorganic crystals. Previous studies have shown that the hydrogen bonds are a robust motif which can serve as an important constituent part of solids, but nevertheless offer considerable geometrical diversity^[13]. The combination of robustness and geometrical flexibility offers wide scope for the construction of a range of different molecular packing arrangements based on the hydrogen bonds. The previous works concerning the calculation of SHG coefficients of crystals with hydrogen bonds, such as the crystals HIO₃, NH₄H₂PO₄, K[B₅O₆(OH)₄]·2H₂O and K₂La(NO₃)₅·2H₂O, etc., have shown us that the hydrogen bonding is a special kind of functional chemical bonds, whose linear and nonlinear optical properties as well as chemical bonding geometries should be paid much attention in the NLO crystal designing. At the same time, we also quantitatively explained the important effect of the hydrogen bonds on the optical nonlinearities of some inorganic crys-

tals^[14]. It is quite helpful and necessary for us to investigate the behavior of these hydrogen bonds in different hydrogen bonded systems, especially for the inorganic crystalline solids. We also believe that the current work can provide us some helpful information on the successful search for new excellent inorganic molecular crystals with hydrogen bonds.

In this work two representatives of molecular crystals with hydrogen bonds in the crystallographic frame are studied, $\text{Na}_2\text{SeO}_4 \cdot \text{H}_2\text{SeO}_3 \cdot \text{H}_2\text{O}$ and $\text{KH}(\text{Cl}_3\text{CCOO})_2$. In Figure 2 and 3 the chemical bonding behaviors of all constituent atoms in both crystals are schematically described. By using the chemical bond method two crystals are quantitatively studied, the calculated results for the assigned hydrogen bonds and total NLO tensors of the whole crystal are shown in Table 2 and 3. From both tables we can find that if hydrogen bonds in the crystallographic frame can show their good NLO contributions (limited by corresponding geometries) the corresponding crystal would have better NLO effects (e. g., the case of $\text{Na}_2\text{SeO}_4 \cdot \text{H}_2\text{SeO}_3 \cdot \text{H}_2\text{O}$ crystal), on the other hand, if hydrogen bonds can not show their good NLO contributions the corresponding crystal would have worse NLO effects (e. g., the case of $\text{KH}(\text{Cl}_3\text{CCOO})_2$ crystal). Therefore, the key point in employing hydrogen bonds for the structural design of SHGNLO materials is to optimize their bonding geometry in the respective crystallographic frame.

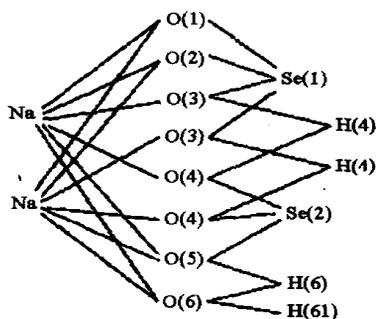


Fig. 2 The bond graph of $\text{Na}_2\text{SeO}_4 \cdot \text{H}_2\text{SeO}_3 \cdot \text{H}_2\text{O}$ single crystal. Each line represents a chemical bond. The sequence number labeled on constituent atoms corresponds to the lattice site in the crystallographic literature^[15]

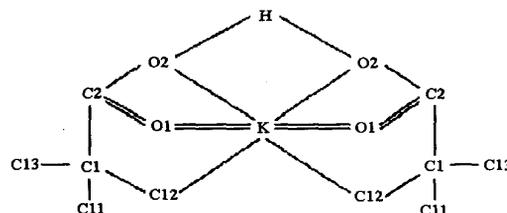


Fig. 3 The bond graph of the $\text{KH}(\text{Cl}_3\text{CCOO})_2$ single crystal. Each line represents a chemical bond. The sequence number labeled on constituent atoms corresponds to the lattice site in the crystallographic literature^[16]

Table 2 Bond properties of hydrogen bonds of $\text{Na}_2\text{SeO}_4 \cdot \text{H}_2\text{SeO}_3 \cdot \text{H}_2\text{O}$ molecular crystal.

Hydrogen bond parameters	H—O	NLO tensor of the crystal
Bond length d^μ (Å)	1.776	
Bond susceptibility μ	2.448	
Bond NLO tensor d_{31}^μ (pm/V)	0.055	$d_{31} = -1.726$
Bond NLO tensor d_{32}^μ (pm/V)	1.573	$d_{32} = -0.612$
Bond NLO tensor d_{33}^μ (pm/V)	4.439	$d_{33} = 0.709$

Table 3 Bond properties of hydrogen bonds of $\text{KH}(\text{Cl}_3\text{CCOO})_2$ molecular crystal

Hydrogen bond parameters	H—O	NLO tensor of the crystal
Bond length d^μ (Å)	1.839	
Bond susceptibility μ	0.617	
Bond NLO tensor d_{36}^μ (pm/V)	-0.0002	$d_{36} = -0.209$

6 Doped LiNbO_3 single crystals

LiNbO_3 (abbreviated as LN) is a typical non-stoichiometric crystal usually grown from the congruent melt. The crystals exhibit typical structural vacancies (i. e., empty octahedra) and lattice vacancies at Li sites (due to the intrinsic de-

fects such as Nb_{Li} antisites) in their structure. Therefore, various dopants such as rare earth and transition metal ions can be easily introduced into the crystal frame of LN, preferably at Li sites. Many of these dopants lead to useful variations in the crystal properties which facilitate various important applications. Nominally pure LN devices suffer from the so-called optical damage when exposed to high intensity illumination due to the photorefractive effect. The problem can be greatly reduced by co-doping LN single crystals with MgO at a concentration of about 5 mol %. Moreover, it has been shown that the photorefractive damage in LN single crystals can be prevented by co-doping with ZnO more efficiently than with MgO. Obviously, clearly knowing about the important effect from various dopants in the LN crystallographic frame on its optical properties, is essential for us all to determine the responses of corresponding crystal materials and further to evaluate their optoelectronic capabilities.

Table 4 Bond properties of constituent chemical bonds of the lithium niobate crystal

Bond parameters	Chemical bonds	
	Li—O	Nb—O
Bond length d^{μ} (Å)	2.063	2.130
Bond susceptibility μ	2.705	5.603
Bond NLO tensor d_{22}^{μ} (pm/V)	0.775	0.201
Bond NLO tensor d_{31}^{μ} (pm/V)	8.559	1.152
Bond NLO tensor d_{33}^{μ} (pm/V)	2.322	1.892

As listed in Table 4, in LN single crystals the Li sites are NLO-SHG sensitive lattice sites. Therefore it is important to study the effect of dopants, introduced at these sites (corresponding to the case of the stoichiometric LN), on the nonlinear optical properties of LN. We also perform the calculations for the +2 and +3 valence dopants Mg^{2+} , Zn^{2+} and In^{3+} occupying the Li^{+} sites. The results are summarized as following equations,

$$\text{for } Mg^{2+} \text{ and } Zn^{2+} \text{ dopants:} \quad d_{22} = 2.71 (1 - 0.026 c_{Mg} - 0.023 c_{Zn}) \text{ pm/V} \quad (3)$$

$$d_{31} = -4.12 (1 - 0.028 c_{Mg} - 0.026 c_{Zn}) \text{ pm/V} \quad (4)$$

$$d_{33} = -22.9 (1 - 0.027 c_{Mg} - 0.024 c_{Zn}) \text{ pm/V} \quad (5)$$

$$\text{While for the } In^{3+} \text{ dopant:} \quad d_{22} = 2.71 (1 - 0.064 c_{In}) \text{ pm/V} \quad (6)$$

$$d_{31} = -4.12 (1 - 0.097 c_{In}) \text{ pm/V} \quad (7)$$

$$d_{33} = -22.9 (1 - 0.082 c_{In}) \text{ pm/V} \quad (8)$$

where c represents the respective molar percentages of oxides MgO, ZnO and In_2O_3 . The NLO tensors are calculated at the wavelength 1079 nm.

The effects of Mg^{2+} and Zn^{2+} doping on the NLO response of LN crystals are quite similar, which are different from that of the In^{3+} dopant. It can be seen that the NLO effect decreases with doping concentration increasing. The slight differences between these two +2 valence dopants can be ascribed to small differences in the ionic characteristics between Mg and Zn showing up in the calculation. Generally speaking, the decreasing tendency of NLO effects of LN crystals is strongly dependent on the valence of the selected dopant.

For a comparison we also studied the influence of dopants occupying Nb^{5+} sites and calculated the effect of the Nb/Ta replacement in the $LiNb_{1-y}Ta_yO_3$ type mixed single crystals with $y = 0.00, 0.81, 0.92, 0.97$, and 1.00. The results are also compared with those of $Li_{1-5x}Nb_{1+x}O_3$ type single crystals with intrinsic defects, to get an estimate for the different magnitudes in which the results for Nb replacing Li are included^[17]. It is clear that doping on the Li sites affects the NLO properties of LN very much stronger than doping on Nb sites.

7 A combination method for dielectric constants of materials with the similar crystal structure

By the chemical bond method, the constitution-property relationship of dielectric materials with various crystallographic structures can be deduced on the basis of the correlation between constituent chemical bonds and corresponding

optical properties of crystal materials. Quantitatively, the linear dielectric constant of a solid, ϵ , may be expressed in terms of the respective polarizability of its constituent atoms^[3,4,18], where the contained parameters only change with different constituent atoms when we deal with a certain group of solids with a similar crystal structure.

Combining the chemical bond method with the relationship between dielectric responses and the average atomic number of constituent atoms of crystals, we can get a combination method in calculating and predicting dielectric properties of materials with the similar crystal structure. Such a combination method is more efficient in the search for novel optical materials, due to that it may clearly indicate a property-trend in a series of materials with a similar crystallographic structure.

8 Conclusions

Starting from the chemical bonding structure of all constituent atoms in the crystallographic frame (deduced from the experimental structural data), chemical bond parameters, linear and nonlinear optical properties of each type bond, all independent second order NLO tensor coefficients d_{ij} of an assigned crystal can be quantitatively calculated by the chemical bond method. The chemical bond method, in a sense, presents a useful tool to understand the (constituent) bond-property and constitution-property correlations in the crystal materials. Further, a combination method on the basis of the chemical bond method may produce us a more powerful tool or guide in the search for new type optical materials.

Acknowledgements: The first author thanks all previous coauthors for their numerous helpful discussions.

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