

# Structure–Property Relationships in $\text{Li}_{1-x}\text{H}_x\text{IO}_3$ Type Complex Crystals

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**Chemical bond parameters and the linear and nonlinear optical (NLO) properties of all constituent chemical bonds in  $\text{Li}_{1-x}\text{H}_x\text{IO}_3$  [ $x$  (the amount of hydrogen) = 0.0, 0.28, and 0.34] (LHIO) type complex crystals have been investigated from the chemical bond viewpoint. At the same time, the relationship between the crystal structure and its optical properties has been obtained, based on the calculated results of  $\text{LiIO}_3$ ,  $\text{Li}_{0.72}\text{H}_{0.28}\text{IO}_3$ , and  $\text{Li}_{0.66}\text{H}_{0.34}\text{IO}_3$ . The nonlinear optical properties of LHIO single crystals are found to be particularly sensitive to the  $\text{H}^+$  impurity concentration.** © 1998 Academic Press

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## INTRODUCTION

Single crystals of hexagonal lithium iodate ( $\alpha$ - $\text{LiIO}_3$ , space group  $P6_3$ ) and orthorhombic hydrogen iodate ( $\text{HIO}_3$ ,  $P2_12_12_1$ ) have been of great interest for application in laser technology and in optoelectric devices, owing to their nonlinear optical properties (1–3). However, such applications require crystals of high quality and stability. The growth of both crystals is easily accomplished by isothermal controlled evaporation of supersaturated aqueous solutions. The optical quality of  $\alpha$ - $\text{LiIO}_3$  crystals is restricted by three known factors: the temperature, the evaporation rate, and the pH of the  $\text{LiIO}_3$ – $\text{HIO}_3$ – $\text{H}_2\text{O}$  solution. Single crystals with the best quality are generally grown from neutral or slightly acidic solutions (pH 6–7) with a slow evaporation rate, at about 315 K. Lowering the pH toward 1.5 by adding  $\text{HIO}_3$  can make the growth become easier but these crystals have less optical quality. In earlier works, Ricci and Amron (4) first reported the existence of the lithium iodate–iodic acid solid solution  $\text{Li}_{1-x}\text{H}_x\text{IO}_3$  with  $x$  varying continuously from 0.22 to 0.35, and Hamid *et al.* (5–7) reported a method for the growth of LHIO single crystals and investigated the concentration dependence ( $x$  varies from 0.0 to 0.35) of some of their physical properties. These LHIO solid solutions have been recognized as prospective materials for technical

applications, in particular owing to the largest piezoelectric  $r_{33}$  coefficient within the series of iodates when the  $\text{HIO}_3$  content  $x$  (mole fraction) takes the value 0.30 (7). Unfortunately, investigations of the nonlinear optical properties of these lithium iodate–iodic acid solid solutions have not yet been reported. Therefore, in the present work we study, from the chemical bond viewpoint, the NLO properties of LHIO single crystals and find the concentration dependence of these NLO effects.

Recently, the crystal structures of some LHIO single crystals have been well refined (8–11); this gives us a good chance to find the structure–property relationships in these crystals. This work, at the same time, can also serve as a powerful tool in modifying the physical properties of these complex crystals.

## CHEMICAL BONDING IN LHIO TYPE CRYSTALS

At room temperature, for the special case  $x = 0.0$ , the single-crystal  $\alpha$ - $\text{LiIO}_3$  crystallizes in the space group  $P6_3$  with cell constants  $a = 5.477 \text{ \AA}$ , and  $c = 5.170 \text{ \AA}$  (8, 9). Its crystal structure consists of a lithium ion, which is surrounded by six oxygen atoms in a distorted octahedral arrangement, and a discrete trigonal iodate group with  $1.8021 \text{ \AA}$  I–O bonds. The lithium iodate–iodic acid solutions LHIO crystallize in the same space group ( $P6_3$ ) as  $\alpha$ - $\text{LiIO}_3$ . At room temperature, the lattice parameters are  $a = 5.514 \text{ \AA}$ , and  $c = 4.960 \text{ \AA}$  for  $x = 0.28$  and  $a = 5.5634 \text{ \AA}$ , and  $c = 4.9538 \text{ \AA}$  for  $x = 0.34$  (10, 11). From a statistical viewpoint as shown in Fig. 1, in LHIO single crystals, lithium atoms occupy at random  $(1 - x)$  of their  $\alpha$ - $\text{LiIO}_3$  positions (Wyckoff site  $2a$ ), while the hydrogen atoms do not replace lithium atoms but are randomly distributed in general position ( $6c$ ) around a Li vacancy with the occupation factor of  $x$ . Obviously, if  $x = 0$  (that is, disregarding the hydrogen atoms), Fig. 1 will become a view of the lithium site environment in  $\alpha$ - $\text{LiIO}_3$ .

In  $\alpha$ - $\text{LiIO}_3$ , there are three types of constituent chemical bonds, Li–O(*s*), Li–O(*l*), and I–O bonds, where the italic letters *s* and *l* in the parentheses mean the short and long chemical bonds, respectively. However, in LHIO single

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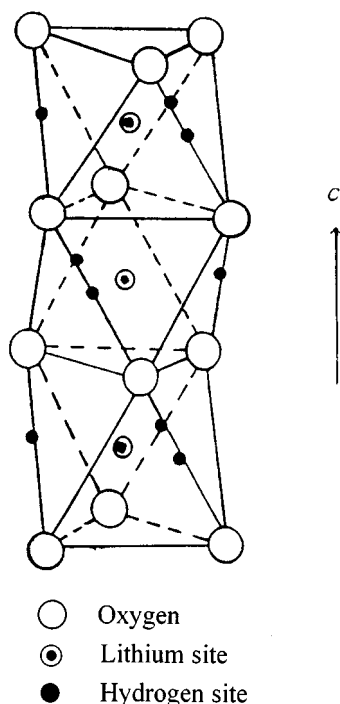


FIG. 1. Stereoscopic drawing of the lithium site environment in  $\text{Li}_{1-x}\text{H}_x\text{IO}_3$  single crystals by using the statistic neutron diffraction data, where  $x = 0.28$  and  $0.34$ . The coordination environment of the Li atoms is a slightly elongated octahedron. Each  $\text{LiO}_6$  octahedron shares two opposite faces with two neighboring octahedra and the resulting arrangement is an infinite string of  $\text{LiO}_6$  octahedra extending along the  $c$  direction. Hydrogen sites are located on three of the six lateral edges of the distorted oxygen octahedron around the lithium site.

crystals, there are seven types of constituent chemical bonds,  $\text{Li-O}(s)$ ,  $\text{Li-O}(l)$ ,  $\text{I-O}$ ,  $\text{H-O}(s)$ ,  $\text{H-O}(l)$ ,  $\text{I-O}'$ , and  $\text{I-O}''$  bonds, where  $\text{O}$ ,  $\text{O}'$ , and  $\text{O}''$  indicate different sites of oxygen atoms in their crystal structures. Since in LHIO crystals, both Li and H atoms are randomly distributed in the given sites, only regular  $\text{IO}_3$  pyramidal groups are nearly identical to those of  $\alpha\text{-LiIO}_3$ . From a microscopic viewpoint, there are  $100(1-x)$   $[\text{LiIO}_3]$  structural units and  $100x$   $[\text{HIO}_3]$  structural units in  $100 \text{Li}_{1-x}\text{H}_x\text{IO}_3$  formula structural units. Therefore, these LHIO single crystals are composed of the two structural units  $\text{LiIO}_3$  and  $\text{HIO}_3$  according to the mole ratio  $[(1-x)/x]$ , which can be written as  $\text{Li}_{1-x}\text{H}_x\text{IO}_3 = (1-x)[\text{LiIO}_3] + x[\text{HIO}_3]$ . For the  $100(1-x)$   $[\text{LiIO}_3]$  structural units, their chemical bonding situation is the same as that of  $\alpha\text{-LiIO}_3$ —two constituent groups  $\text{LiO}_6$  and  $\text{IO}_3$ , with each oxygen atom coordinated to one I atom and two Li atoms. On the other hand, in the  $100x$   $[\text{HIO}_3]$  structural units, there are two other constituent groups— $\text{HO}_2$  and  $\text{IO}_3$ . In fact, we can first fix a H atom in one site of six possible positions ( $6c$ ) and then analyze different coordination environments of all oxygen atoms in LHIO. In any case, oxygen atoms in the  $[\text{HIO}_3]$  structural units are

divided into two types according to their different coordination conditions, which are labeled  $\text{O}'$  and  $\text{O}''$ , respectively. The  $\text{O}'$  atom is bonded to one H atom and one I atom; however, the  $\text{O}''$  atom is bonded to only one I atom. By changing the hydrogen site, all possible cases can be taken into account.

## THEORETICAL METHOD

According to the chemical bond theory of complex crystals (12) and the modified bond charge model (13, 14), the linear optical property of a complex crystal can be ascribed to a linear combination of contributions of all constituent chemical bonds; however, its nonlinear optical property should be regarded as the geometrical superposition of these contributions. This connection between macroscopic physical properties of a complex crystal and its constituent chemical bonds can be constructed by using its bond-valence equation, which is deduced from the detailed crystal structure (12). For example, in a complex crystal  $A_aB_bD_dG_g$  (crystal molecular formula) any kind of the chemical bond  $A-B$  can be written as

$$[N(B-A)a/N_{CA}]A[N(A-B)b/N_{CB}]B, \quad [1]$$

where  $A$ ,  $B$ ,  $D$ , and  $G$  are different constituent elements in the crystal formula and  $a$ ,  $b$ ,  $d$ , and  $g$  are the numbers of the corresponding element.  $N(B-A)$  is the number of  $B$  ions in the coordination group of an  $A$  ion,  $N_{CA}$  is the nearest coordination number of the atom  $A$  in the crystal.

Formula [1] also can be rewritten as

$$mAB_n, \quad [1']$$

where the prefix  $m = N(B-A)a/N_{CA}$  represents the ratio of the number of  $B$  ions to the total ions surrounding the central  $A$  ion and the subscript  $n = [N(A-B)bN_{CA}]/[N(B-A)aN_{CB}]$  represents the ratio of the number of  $B$  ions to  $A$  ions.

By using formula [1'], we can write each item of the bond-valence equation of a complex crystal, and then the complex crystal is decomposed into forms that can be quantitatively calculated by means of the dielectric theory of solids (15–17).

The total linear susceptibility  $\chi$  can be written in terms of the contributions  $\chi^\mu$  of the various types of bonds (15)

$$\chi = n_r^2 - 1 = \sum_{\mu} F^{\mu} \chi^{\mu} = \sum_{\mu} N_b^{\mu} \chi_b^{\mu}, \quad [2]$$

where  $n_r$  is the refractive index,  $F^{\mu}$  is the fraction of bonds of type  $\mu$  composing the crystal,  $N_b^{\mu}$  is the number of chemical

bonds of type  $\mu$  per  $\text{cm}^3$ , and  $\chi_b^\mu$  is the susceptibility of a single bond of type  $\mu$ .

The linear susceptibility of any chemical bond labeled  $\mu$  is described as (16, 17)

$$\chi^\mu = \frac{(\hbar\Omega_p^\mu)^2}{(4\pi)[(E_h^\mu)^2 + (C^\mu)^2]}, \quad [3]$$

where  $E_h^\mu$  and  $C^\mu$  are the homopolar and heteropolar parts of the total average energy gap. Figuratively speaking,  $E_h^\mu$  and  $C^\mu$  measure the average energy gaps due to covalent and ionic effects. Quantitatively, both parameters can be calculated from (12, 15)

$$E_h^\mu = 39.74/(d^\mu)^{2.48} \quad [4]$$

$$C^\mu = 14.4b^\mu \exp(k_s^\mu r_0^\mu) [(Z_A^\mu)^*/r_0^\mu - n(Z_B^\mu)^*/r_0^\mu], \quad [5]$$

where  $n$  is the ratio of the numbers of the two elements  $B$  and  $A$  in the subformula (12),  $r_0^\mu = d^\mu/2$ ,  $\exp(k_s^\mu r_0^\mu)$  is the Thomas-Fermi screening factor and  $(Z_A^\mu)^*$  is the effective valence electron number of the  $A$  ion (12).  $b^\mu$  is a correction factor depending on the crystal structure; if the refractive index of a crystal is known, its value can be deduced from foregoing equations (13–15).

According to Phillips' suggestion (16), one can define the fraction of ionic and covalent character of the individual bonds  $f_i^\mu$  and  $f_c^\mu$ , by

$$f_i^\mu = \frac{(C^\mu)^2}{(E_h^\mu)^2 + (C^\mu)^2}, \quad f_c^\mu = \frac{(E_h^\mu)^2}{(E_h^\mu)^2 + (C^\mu)^2}. \quad [6]$$

The total NLO tensor coefficient  $d_{ij}$ , can be expressed as (15)

$$d_{ij} = \sum_\mu d_{ij}^\mu = \sum_\mu F^\mu [d_{ij}^\mu(C) + d_{ij}^\mu(E_h)], \quad [7]$$

where  $d_{ij}^\mu$  is the total macroscopic nonlinear contribution of the constituent chemical bonds of type  $\mu$ .  $d_{ij}^\mu(C)$  is the ionic fraction of the nonlinear optical coefficient, and  $d_{ij}^\mu(E_h)$  the covalent fraction,

$$F^\mu d_{ij}^\mu(C) = \frac{G_{ij}^\mu N_b^\mu(0.5) \{[(Z_A^\mu)^* + n(Z_B^\mu)^*]/[(Z_A^\mu)^* - n(Z_B^\mu)^*]\} f_i^\mu (\chi_b^\mu)^2}{d^\mu q^\mu} \quad [8]$$

$$F^\mu d_{ij}^\mu(E_h) = \frac{G_{ij}^\mu N_b^\mu s(2s-1) [r_0^\mu/(r_0^\mu - r_c^\mu)]^2 f_c^\mu (\chi_b^\mu)^2 \rho^\mu}{d^\mu q^\mu}, \quad [9]$$

where  $\rho^\mu = (r_A^\mu - r_B^\mu)/(r_A^\mu + r_B^\mu)$  is the difference in the atomic sizes,  $r_A^\mu$  is the covalent radius of the atom  $A$ ,  $r_c^\mu$  is the core

radius, and  $q^\mu$  is the bond charge of the  $\mu$ th bond, which is also associated with the detailed crystal structure (13, 14).  $G_{ij}^\mu$  is the geometrical contribution of chemical bonds of type  $\mu$ ,

$$G_{ij}^\mu = 1/n_b^\mu \sum_\lambda \alpha_i^\mu(\lambda) \alpha_j^\mu(\lambda), \quad [10]$$

where the sum on  $\lambda$  is over all  $n_b^\mu$  bonds of type  $\mu$  in the unit cell and  $\alpha_i^\mu(\lambda)$  is the direction cosine with respect to the  $i$ th coordinate axis of the  $\lambda$ th bond of type  $\mu$  in this cell.

## RESULTS AND DISCUSSION

Restrictions imposed by the crystal symmetry (8–11) and the Kleinman symmetry conditions (18) on the nonlinear optical coefficients make two independent NLO tensor coefficients  $d_{31}$  and  $d_{33}$  allowed in LHIO single crystals.

On the basis of the detailed structure information (8–11) and the analysis of chemical bonding situations of LHIO type crystals, we can decompose these complex crystals as

$$\text{Li}_{1-x}\text{H}_x\text{IO}_3 = (1-x)[\text{LiIO}_3] + x[\text{HIO}_3]. \quad [11]$$

Then the bond-valence equations of these two structural units can be written separately as

$$\text{LiIO}_3 = \frac{1}{2}\text{LiO}(s)_2 + \frac{1}{2}\text{LiO}(l)_2 + \text{IO} \quad [12]$$

$$\text{HIO}_3 = \frac{1}{2}\text{HO}'(s) + \frac{1}{2}\text{HO}'(l) + \frac{2}{3}\text{IO}'_{3/2} + \frac{1}{3}\text{IO}'_3. \quad [13]$$

The first term, in Eq. [12],  $\frac{1}{2}\text{LiO}(s)_2$ , means there is a structural unit only bonded with the short Li–O bonds in  $[\text{LiIO}_3]$ , which occupies half of the number of Li–O bonds in the constituent  $\text{LiO}_6$  group (including three short Li–O bonds and three long Li–O ones). Since the refractive index of  $\alpha\text{-LiIO}_3$ ,  $n_r = 1.86$  at  $1.064\ \mu\text{m}$  (1), is known, the detailed chemical bond parameters, linearities  $\chi^\mu$ , and nonlinear optical contributions of individual bonds can be quantitatively determined. From Table 1, we can see that in  $\alpha\text{-LiIO}_3$  most parts of the linear and nonlinear optical contributions are from I–O bonds; comparatively speaking, Li–O bonds play a less important role. From the comparison of the calculated and experimental  $d_{ij}$  tensor coefficients of  $\alpha\text{-LiIO}_3$  listed in Table 2, we find the agreement in both values and signs is very good.

Since  $b^\mu$  ( $b^\mu = \beta(N_c^\mu)^p$ , where  $N_c^\mu$  is the average coordination number) is a structural correction factor of a complex crystal, its value depends on the coordination environments of all constituent elements. Therefore, the value of  $b^\mu$  is related to the detailed crystal structure. By using the similar structural correction factor  $b^\mu$  of  $\alpha\text{-LiIO}_3$  and  $\text{HIO}_3$  (14) as well as combining Eqs. [11]–[13], the chemical bond parameters and the linear and nonlinear optical contributions

TABLE 1

Chemical Bond Parameters and Linear and Nonlinear Contributions of Each Type of Bond to the Total Linearity and Nonlinearity of  $\alpha$ -LiIO<sub>3</sub>, at 1.064  $\mu$ m

	LiIO <sub>3</sub>		
	Li-O(s)	Li-O(l)	I-O
$d^u$ (Å)	2.0795	2.1515	1.8021
$E_h^u$ (eV)	6.4668	5.9433	9.2235
$C^u$ (eV)	6.7213	6.2912	10.9929
$f_{\epsilon}^u$	0.4807	0.4716	0.4131
$\chi^u$	0.9111	0.9579	5.5097
$\chi_b^u$	0.5410	0.5688	3.2716
$q^u/e$	0.3633	0.3547	1.2728
$G_{31}^u$	0.1922	-0.1901	0.1820
$d_{31}^u$ ( $\times 10^{-9}$ esu)	-2.2024	2.3104	-19.2914
$G_{33}^u$	0.2088	-0.2478	0.0998
$d_{33}^u$ ( $\times 10^{-9}$ esu)	-2.3918	3.0111	-10.5810

(to the total linearity and nonlinearity, at 1.064  $\mu$ m) of each type of constituent chemical bond in LHIO single crystals can be quantitatively determined (see Tables 3 and 4).

Theoretically, their linear dielectric behaviors and nonlinear optical responses are predicted on the basis of the foregoing discussion, i.e., by combining Eqs. [12] and [13] according to the mole ratio  $[(1-x)/x]$ . At room temperature, the refractive indices of Li<sub>0.72</sub>H<sub>0.28</sub>IO<sub>3</sub> and Li<sub>0.66</sub>H<sub>0.34</sub>IO<sub>3</sub> are predicted as 1.92 and 1.94 at 1.064  $\mu$ m, respectively. It is well known that the linear optical property (i.e., the dielectric constant) of a crystal is mainly determined by the heavy constituent ion. It is known that  $n_r^z(\text{HIO}_3) = 1.9508$  at 1.065  $\mu$ m (19). Thus, the dielectric constants in LHIO single crystals are to a great extent ascribed to

TABLE 2

Comparison of Calculated and Experimental  $d_{ij}$  Values of  $\alpha$ -LiIO<sub>3</sub> at 1.064  $\mu$ m

	$d_{ij}$	
	$d_{31}$ ( $\times 10^{-9}$ esu)	$d_{33}$ ( $\times 10^{-9}$ esu)
Calculated	-19.183	-9.962
Experimental	-18.0 <sup>a,c</sup>	-11.5 $\pm$ 1.0 <sup>b,c</sup>

<sup>a</sup>The absolute value used here is the average of experimental data of various measurements (in units of  $10^{-9}$  esu): 16.5  $\pm$  2.3 (ref 2), 17.85  $\pm$  1.5 (ref 20), 18.0 (ref 21), and 18.0 (ref 22).

<sup>b</sup>The absolute value is taken from ref 20,  $d_{33}(\alpha\text{-LiIO}_3) = (12.4 \pm 1.0) d_{36}(\text{KDP})$ .  $d_{36}(\text{KDP}) = 0.93 \times 10^{-9}$  esu is a primary standard of second-order nonlinear coefficients.

<sup>c</sup>The signs of experimental  $d_{ij}$  tensors are known to be negative (23).

the I<sup>5+</sup> cation and their refractive indices at 1.064  $\mu$ m are approximately between 1.86 and 1.9508. It is obvious that our theoretical predictions are very reasonable.

From Tables 3 and 4, we can find that values of the bond length  $d^u$  and the geometric characteristic  $G_{ij}^u$  of constituent chemical bonds do not change dramatically, and are comparable with those of  $\alpha$ -LiIO<sub>3</sub> for the corresponding Li-O and I-O bonds. On the other hand, it also can be seen that chemical bond parameters are similar to those of  $\alpha$ -LiIO<sub>3</sub> (see Table 1) and of HIO<sub>3</sub> (see ref 14); however, the linear and nonlinear optical contributions of the corresponding constituent chemical bonds of LHIO single crystals have an obviously increasing tendency as the H<sup>+</sup> concentration increases from 0.0 to 0.34. We also find that H-O'(l) bonds play a rather important role in NLO contributions to the total nonlinearity of LHIO.

TABLE 3

Chemical Bond Parameters and Linear and Nonlinear Contributions of Each Type of Bond to the Total Linearity and Nonlinearity of Li<sub>0.72</sub>H<sub>0.28</sub>IO<sub>3</sub> at 1.064  $\mu$ m

	Li <sub>0.72</sub> H <sub>0.28</sub> IO <sub>3</sub>						
	LiIO <sub>3</sub>			HIO <sub>3</sub>			
	Li-O(s)	Li-O(l)	I-O	H-O'(s)	H-O'(l)	I-O'	I-O''
$d^u$ (Å)	2.1046	2.1753	1.7899	1.2894	1.7421	1.7899	1.7899
$E_h^u$ (eV)	6.2772	5.7834	9.3802	21.1576	10.0315	9.3802	9.3802
$C^u$ (eV)	6.4648	6.0601	10.9299	4.3449	2.5298	13.1811	3.8719
$f_{\epsilon}^u$	0.4853	0.4766	0.4241	0.9595	0.9402	0.3362	0.8544
$\chi^u$	1.0057	1.0565	5.8878	0.7618	1.4022	1.8630	7.6489
$\chi_b^u$	0.5807	0.6100	3.3995	0.7918	1.4573	1.9362	7.9494
$q^u/e$	0.3474	0.3389	1.2294	2.1102	1.7879	3.1205	4.3976
$G_{31}^u$	0.1922	-0.1921	0.1836	0.1352	-0.1353	0.1836	0.1836
$d_{31}^u$ ( $\times 10^{-9}$ esu)	-2.7378	2.9078	-23.6168	0.8206	-2.3932	-1.2687	-33.7848
$G_{33}^u$	0.1758	-0.2139	0.1059	0.5478	-0.5473	0.1059	0.1059
$d_{33}^u$ ( $\times 10^{-9}$ esu)	-2.5043	3.2388	-13.6146	3.3241	-9.6794	-0.7314	-19.4763

**TABLE 4**  
**Chemical Bond Parameters and Linear and Nonlinear Contributions of Each Type of Bond to the Total Linearity and Nonlinearity of  $\text{Li}_{0.66}\text{H}_{0.34}\text{O}_3$  at 1.064  $\mu\text{m}$**

	$\text{Li}_{0.66}\text{H}_{0.34}\text{IO}_3$						
	$\text{LiIO}_3$			$\text{HIO}_3$			
	Li-O(s)	Li-O(l)	I-O	H-O'(s)	H-O'(l)	I-O'	I-O''
$d^\mu$ ( $\text{\AA}$ )	2.1055	2.2212	1.8033	1.3314	1.7168	1.8033	1.8033
$E_h^\mu$ (eV)	6.2706	5.4915	9.2083	19.5408	10.4022	9.2083	9.2083
$C^\mu$ (eV)	6.4293	5.7881	10.6771	4.1099	2.6004	12.9874	3.8136
$f_c^\mu$	0.4875	0.4737	0.4265	0.9576	0.9412	0.3345	0.8536
$\chi^\mu$	1.0307	1.1167	6.1058	0.8121	1.3594	1.8788	7.7456
$\chi_h^\mu$	0.6050	0.6555	3.5843	0.8581	1.4364	1.9852	8.1845
$q^\mu/e$	0.3434	0.3296	1.2017	2.0746	1.8019	3.1017	4.3764
$G_{31}^\mu$	0.1913	-0.1919	0.1842	0.1377	-0.1383	0.1842	0.1842
$d_{31}^\mu (\times 10^{-9} \text{ esu})$	-2.9639	3.2890	-26.5721	0.9493	-2.3553	-1.2999	-35.2028
$G_{33}^\mu$	0.1576	-0.2193	0.1085	0.5381	-0.5353	0.1085	0.1085
$d_{33}^\mu (\times 10^{-9} \text{ esu})$	-2.4427	3.7595	-15.6459	3.7103	-9.1155	-0.7654	-20.7278

Theoretical predictions of  $d_{ij}$  tensors of  $\text{Li}_{0.72}\text{H}_{0.28}\text{IO}_3$  and  $\text{Li}_{0.66}\text{H}_{0.34}\text{IO}_3$  at 1.064  $\mu\text{m}$  are summarized in Table 5. From Table 5, we can find that in both crystals,  $\text{Li}_{0.72}\text{H}_{0.28}\text{IO}_3$  and  $\text{Li}_{0.66}\text{H}_{0.34}\text{IO}_3$ , their nonlinear optical tensor coefficients  $d_{ij}$  at 1.064  $\mu\text{m}$  increase with increasing  $x$ . At the same time, we also realize that with the increasing  $\text{H}^+$  concentration in the crystal structure of these LHIO type single crystals, nonlinear optical responses become much larger than those of  $\alpha\text{-LiIO}_3$ .

From Tables 3 and 4, we can find that in these three crystals,  $\alpha\text{-LiIO}_3$ ,  $\text{Li}_{0.66}\text{H}_{0.34}\text{IO}_3$ , and  $\text{Li}_{0.72}\text{H}_{0.28}\text{IO}_3$ , chemical bond parameters and linear and nonlinear optical contributions of all kinds of constituent chemical bonds to the total linearity and nonlinearity at 1.064  $\mu\text{m}$  have similar values. However, it is easy to find that the linear and nonlinear optical contributions of these constituent chemical bonds have an increasing tendency, with  $x$  varying from 0.0 to 0.34. These interesting changes are certainly caused by the amount of hydrogen in the crystal lattice; therefore, the optical properties of these LHIO type single crystals are obviously sensitive to the  $\text{H}^+$  impurity concentration.

**TABLE 5**  
**Comparison of Theoretically Predicted  $d_{ij}$  Tensor Values of  $\text{Li}_{1-x}\text{H}_x\text{IO}_3$  ( $x = 0.0, 0.28, 0.34$ ) Type Crystals at 1.064  $\mu\text{m}$**

	$d_{ij}$	
	$d_{31} (\times 10^{-9} \text{ esu})$	$d_{33} (\times 10^{-9} \text{ esu})$
$\text{LiIO}_3$	-19.183	-9.962
$\text{Li}_{0.72}\text{H}_{0.28}\text{IO}_3$	-27.137	-16.711
$\text{Li}_{0.66}\text{H}_{0.34}\text{IO}_3$	-30.212	-18.603

In the earlier work of Hamid (7), the quasi-static piezoelectric constants were measured for several  $x$  (0.0, 0.015, 0.04, 0.18, and 0.30). Hamid found that for  $x \geq 0.18$ , the piezoelectric constant increases with increasing  $x$ . The measured data of independent piezoelectric tensor components show that the larger piezoelectric coefficients  $r_{31}$  and  $r_{33}$  within the series of iodates will be displayed compared with those of  $\alpha\text{-LiIO}_3$  ( $x = 0.0$ ) when  $x$  takes the value of 0.30 in the LHIO type single crystals (7). Compared with these experimental observations on LHIO type single crystals, we can find from Table 5 the increasing tendency of our theoretical predictions of  $d_{ij}$  tensors is reasonable. Unfortunately, the high-frequency dielectric constants and NLO responses of these LHIO samples have not yet been measured; therefore, in the present paper, we show the predicted behavior of the dielectric properties and NLO responses in both crystals,  $\text{Li}_{0.72}\text{H}_{0.28}\text{IO}_3$  and  $\text{Li}_{0.66}\text{H}_{0.34}\text{IO}_3$ .

## CONCLUSION

Starting from the crystal structures of LHIO type single crystals, we have investigated the chemical bonding situations and the linear and nonlinear optical properties of these crystals. Although the crystal structures do not undergo any dramatic change with different incorporated amounts of hydrogen in the crystal lattice, these small amounts of hydrogen surely change the chemical bonding situations of all constituent elements and thus affect their linear and nonlinear optical contributions. It can be seen that H-O bonds play an important role in the nonlinear optical contributions to the total nonlinearity of LHIO. Theoretical predictions show nonlinear optical responses of these crystals are very sensitive to the  $\text{H}^+$  impurity

concentration and increase with increasing  $x$  from 0.0 to 0.34; the linear optical properties, however, are not as sensitive and exhibit a range from 1.86 to 1.94. Thus, this work in a sense gives us a useful guide in modifying crystal physical properties, especially in the field of the crystal engineering.

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