

Theoretical studies of nonlinear optical properties of compounds $K_4Ln_2(CO_3)_3F_4$ ($Ln=Pr, Nd, Sm, Eu, Gd$)

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$K_4Ln_2(CO_3)_3F_4$ ($Ln=Pr, Nd, Sm, Eu, Gd$) is a special type of frequency doubling compound, whose crystal structure exhibits a scarcity of fluorine ions. This leads to two different coordination polyhedrons in the general position of K(2) atoms: $[K(2)O_6F(1)_2F(2)]$ and $[K(21)O_6F(1)_2]$ in a 2/1 ratio. The chemical bonding structures of all constituent atoms of the compound $K_4Gd_2(CO_3)_3F_4$ (KGCOF) are comprehensively studied; moreover, the relationship between the chemical bonding structure and the nonlinear optical (NLO) properties is investigated from the chemical bond viewpoint. The theoretical prediction of the NLO tensor coefficient d_{11} of KGCOF is in agreement with experimental observation. Theoretical analyses show that the nonlinearity of this crystal type mainly originates from K–O bonds. In addition, the correlation between the NLO tensor d_{11} and the refractive index n_0 of KGCOF is discussed. © 2000 American Institute of Physics.
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I. INTRODUCTION

New efficient nonlinear optical (NLO) materials are required for various applications including, e.g., the field of diode-pumped solid state laser sources. Such harmonic generating materials with NLO coefficients 2 to 3 times larger than that of the standard material potassium dihydrogen phosphate (KDP) are for instance found in the large class of compounds that contain small planar noncentrosymmetric ions. This class includes compounds containing $(BO_3)^{3-}$ or $(NO_3)^-$ ions such as yttrium aluminum borate,¹ neodymium aluminum borate,² potassium lanthanum nitrate, and potassium cerium nitrate.³ The planar carbonate group $(CO_3)^{2-}$ exhibits a high and anisotropic polarizability in calcite,⁴ in plane $\alpha_{\parallel} = 4.20 \times 10^{-24} \text{ cm}^{-3}$ and perpendicular $\alpha_{\perp} = 3.18 \times 10^{-24} \text{ cm}^{-3}$. Regardless of their ultimate application, all these compounds are very interesting from the standpoint of their structure-property relationships. To achieve an “engineering” of NLO materials meeting special applications, it is indispensable to accumulate knowledge and experience in finding and designing new NLO crystals of potential use.

The crystal structure of the compound $K_4Ln_2(CO_3)_3F_4$ ($Ln=Pr, Nd, Sm, Eu, Gd$) has been determined to be acentric by measuring the second harmonic generation (SHG) intensity $I_{2\omega}$ from $K_4Ln_2(CO_3)_3F_4$ powders.⁵ Mercier *et al.*⁵ also found that a powder of $K_4Eu_2(CO_3)_3F_4$ shows a frequency doubling efficiency similar to that of potassium titanium oxide phosphate (KTP). Apart from that, there has been no further study on NLO behaviors of such $K_4Ln_2(CO_3)_3F_4$ compounds, only luminescence properties were concerned.⁶

Structurally it is most interesting that among these $K_4Ln_2(CO_3)_3F_4$ compounds nearly all constituent chemical bonds are disordered in orientations, and that there are some vacancies of fluorine atoms around K(2) atoms which finally lead to two cases of the K(2) coordination polyhedron: $[K(2)O_6F(1)_2F(2)]$ and $[K(2)O_6F(1)_2]$ in 2/1 ratio in the crystal structure frame. Furthermore, an element with high electronegativity—the fluorine atom—enters the crystal structure frame; this will finally make the crystal structure and the corresponding optical properties different from those of the known NLO crystals without the fluorine atom in their crystal structures. Obviously, from the viewpoint of materials science, the potential NLO applications of such crystals containing fluorine atoms have to be considered in the near future. On the other hand, aiming towards new rare-earth-based phosphors, the exploration of mixed systems containing fluoride and carbonate entities⁶ already started. Therefore, it is of great interest to investigate chemical bonding structures and the origin of the NLO properties in this special type of frequency doubling compound.

In this work, we systematically calculate linear and nonlinear optical responses of $K_4Gd_2(CO_3)_3F_4$ (KGCOF) by using the chemical bond method⁷ which was developed from the dielectric theory of solids^{8,9} and the bond charge model,¹⁰ as well as the chemical bond theory of complex crystals.¹¹ In the case of KGCOF, we deduce the crystal optical properties from the microscopic properties of all kinds of constituent chemical bonds by studying the detailed chemical bonding structures of the whole crystal (i.e., the so-called derived bond valence equation). The role of each constituent group can be quantitatively determined, analyzing the optical nonlinearity of KGCOF at long wavelengths ($\sim 1.0 \mu\text{m}$). Ac-

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According to the analyses of this representative crystal, the application prospect of this new structural family of fluoride carbonates is evaluated: $K_4Ln_2(CO_3)_3F_4$ with $Ln=Pr, Nd, Sm, Eu, Gd$.

II. THEORETICAL METHOD

According to the dielectric theory of solids,^{8,9} the linear susceptibility of any bond can be expressed as

$$\chi^\mu = (4\pi)^{-1} (\hbar \Omega_p^\mu / E_g^\mu)^2. \quad (1)$$

where Ω_p^μ is the plasma frequency, and E_g^μ is the average energy gap between the bonding and the antibonding states.

For multibond crystals, the total linear susceptibility χ can be divided into contributions χ^μ from various types of bonds,¹⁰

$$\chi = n_0^2 - 1 = \sum_\mu F^\mu \chi^\mu = \sum_\mu N_b^\mu \chi_b^\mu, \quad (2)$$

where n_0 is the refractive index, F^μ is the fraction of μ type bonds composing the crystal, N_b^μ is the number of bonds of type μ per cm^3 , and χ_b^μ is the susceptibility of a single bond of type μ .

The energy gap E_g^μ may be separated into the homopolar and heteropolar parts as $(E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2$,⁸ and E_h^μ and C^μ can be calculated from^{10,11}

$$F^\mu d_{ij}^\mu(C) = \frac{G_{ij}^\mu N_b^\mu (0.5) \{ [(Z_A^\mu)^* + n(Z_B^\mu)^*] / [(Z_A^\mu)^* - n(Z_B^\mu)^*] \} f_i^\mu (\chi_b^\mu)^2}{d^\mu q^\mu}, \quad (7)$$

$$F^\mu d_{ij}^\mu(E_h) = \frac{G_{ij}^\mu N_b^\mu s (2s - 1) [r_0^\mu / (r_0^\mu - r_c^\mu)]^2 f_c^\mu (\chi_b^\mu)^2 \rho^\mu}{d^\mu q^\mu}, \quad (8)$$

where $\rho^\mu = (r_A^\mu - r_B^\mu) / (r_A^\mu + r_B^\mu)$, is the difference in the atomic sizes, r_A^μ the covalent radius of the atom A, and $r_c^\mu = 0.35r_0^\mu$ the core radius; q^μ is the bond charge of the μ th bond,² and G_{ij}^μ is the geometrical contribution of chemical bonds of type μ .^{2,10}

III. RESULTS AND DISCUSSION

The structural characteristics of the family $K_4Ln_2(CO_3)_3F_4$ ($Ln=Pr, Nd, Sm, Eu, Gd$) have been determined by Mercier *et al.*⁵ who investigated crystals fabricated by hydrothermal growth ($T=740^\circ C$, $P=220$ MPa, $t=24$ h). The x-ray diffraction data show that the crystal structure of all members of this family is very similar, the structure of the Gadolinium compound KGCOF is rhombohedral $R32$, $Z=3$, with $a_H=9.0268$ Å, $c_H=13.684$ Å. The restrictions imposed by the crystal symmetry yield an NLO tensor for

$$E_h^\mu = 39.74 / (d^\mu)^{2.48}, \quad (3)$$

$$C^\mu = 14.4b^\mu \exp(-k_s^\mu r_0^\mu) [(Z_A^\mu)^* - n(Z_B^\mu)^*] / r_0^\mu, \quad (4)$$

where n is the ratio of numbers of two elements B and A in the bond valence equation,¹¹ d^μ is the bond length of the μ type bonds, and $r_0^\mu = d^\mu / 2$. $\exp(k_s^\mu r_0^\mu)$ is Thomas-Fermi screening factor; $(Z_A^\mu)^*$ is the effective valence electron number of A ion,¹¹ and b^μ is a structural correction factor.^{2,10-12}

According to Phillips' suggestion,⁸ one can define the fractional ionicity f_i^μ and covalency f_c^μ of the individual bonds by

$$f_i^\mu = (C^\mu)^2 / (E_g^\mu)^2 \quad \text{and} \quad f_c^\mu = (E_h^\mu)^2 / (E_g^\mu)^2. \quad (5)$$

Chemical bond nonlinearities have been evaluated on the basis of linear results by means of the bond charge model of Levine.¹⁰ The complete expression for the total SHG coefficient d_{ij} is written as

$$d_{ij} = \sum_\mu d_{ij}^\mu = \sum_\mu F^\mu [d_{ij}^\mu(C) + d_{ij}^\mu(E_h)], \quad (6)$$

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

$K_4Ln_2(CO_3)_3F_4$ type crystals of the general form¹³

$$d = \begin{pmatrix} d_{11} & -d_{11} & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & -d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (9)$$

with only two independent coefficients d_{11} and d_{14} . Furthermore, according to the Kleinman symmetry condition,¹⁴ d_{14} turns out to be zero; thus only d_{11} has to be considered.

According to the chemical bond theory of complex crystals,¹¹ macroscopic optical properties of KGCOF can be ascribed to contributions of each type of its constituent chemical bond. Therefore, how to deal with each type of constituent chemical bond is the key of this problem. According to the chemical bonding structure of KGCOF, its crystal formula can be decomposed as follows (i.e., the bond valence equation of KGCOF),

$$\begin{aligned}
K_4Ln_2(CO_3)_3F_4 = & \frac{1}{2}K(1)O(1)_{8/5} + \frac{1}{4}K(1)O(11)_{8/5} + \frac{1}{4}K(1)F(1)_{8/5} + \frac{2}{9}K(2)O(1s)_{9/5} + \frac{2}{9}K(2)O(1l)_{9/5} + \frac{2}{9}K(2)O(11s)_{9/5} \\
& + \frac{2}{9}K(2)O(11l)_{9/5} + \frac{2}{9}K(2)O(2)_{9/5} + \frac{2}{9}K(2)O(21)_{9/5} + \frac{4}{9}K(2)F(1)_{9/5} + \frac{2}{9}K(2)F(2)_3 + \frac{1}{4}K(21)O(1s)_{8/5} \\
& + \frac{1}{4}K(21)O(1l)_{8/5} + \frac{1}{4}K(21)O(2)_{8/5} + \frac{1}{4}K(21)F(1)_{8/5} + \frac{4}{9}GdO(1)_{9/5} + \frac{2}{9}GdO(11)_{9/5} + \frac{4}{9}GdO(2)_{9/5} \\
& + \frac{2}{9}GdO(21)_{9/5} + \frac{2}{9}GdF(1)_{9/5} + \frac{4}{9}GdF(2)_3 + \frac{2}{3}CO(1)_{3/5} + \frac{2}{3}CO(11)_{3/5} + \frac{2}{3}CO(2)_{3/5} \\
& + \frac{2}{3}C'O(1)_{3/5} + \frac{1}{3}C'O(21)_{3/5},
\end{aligned} \tag{10}$$

where K(1), C', etc. are marked according to the detailed chemical bonding situations, so that we can distinguish them from each other and then calculate properties of each type of chemical bond. The fourth term $\frac{2}{9}K(2)O(1s)_{9/5}$ indicates that in KGCOF there is a structural unit only having the short K(2)–O(1) bonds (2.7462 Å), which occupies 2/9 of number of chemical bonds in the constituent K(2) potassium cation cluster [K(2)O₆F(1)₂F(2)]. There are six different structural types of polyhedrons in K₄Ln₂(CO₃)₃F₄ type compounds: [K(1)O₆F(1)₂], [K(2)O₆F(1)₂F(2)], [K(21)O₆F(1)₂], [LnO₆F(1)F(2)₂], [CO(1)O(11)O(2)], and [C'O(1)₂O(21)].

There are three kinds of coordination polyhedrons of potassium atoms in KGCOF, K(1) and K(21) have eight atoms around them respectively, and K(2) has nine atoms. In the calculation of the chemical bonding structures of the K atoms, we find that in one unit cell of K₄Ln₂(CO₃)₃F₄ type crystals there are three additional F(2) fluorine atoms needed to coordinate to three K(2) atoms, therefore, in the real crystal structure frame there are vacancies in F(2) sites around K(2) atoms. On an average result from the single crystal x-ray diffraction,⁵ the ideal coordination condition of K(2) atoms in one crystal formula is surrounded by three fluorine atoms, however, the real case is that there are 2.66 fluorine atoms bonded to K(2) atoms, i.e., [K(2)O₆F(1)₂F(2)_{0.66}]. Here, it should be pointed out that we should at first know clearly about the chemical bonding condition of all constituent atoms, if we want to study the structure-property relationship of an assigned crystal by means of the chemical bond method. Therefore, in order to calculate microscopic properties of each type of constituent chemical bond of KGCOF, we have to mark each site again and calculate chemical bonding structures of all atoms again, on the base of the given set of atomic coordinates.⁵ This is mainly caused by 0.34 vacancies in F(2) sites around K(2) atoms, which makes the chemical bonding condition of all constituent atoms become complicated. The reasonable and successful solution dealing with such problems is to divide K(2) sites into two different kinds of positions, and treat them separately. According to this idea, two different polyhedron, [K(2)O₆F(1)₂F(2)] and [K(21)O₆F(1)₂] are then constructed by us, and the ratio of number of both polyhedron is 2. Each atom in Eq. (10) is clearly marked by taking its coordination difference into account. Obviously, these three potassium sites [K(1), K(2), and K(21)] have different coordination environments in KGCOF, especially for K(2) with three coordinated fluorine atoms. The 9 coordinated Gd cation has the

similar case to that of K(2), having three fluorine atoms around it.

From the Eq. (10), we find there are 26 types of constituent chemical bonds in KGCOF. By using the above theories, chemical bond parameters, linear, and nonlinear optical properties of each type of constituent chemical bond are quantitatively calculated. Calculated results of KGCOF are listed in Table I, under the consideration of the refractive index $n_0 = 1.70$ at the long wavelength ($\sim 1.0 \mu\text{m}$). From Table I, we can see that the dominant contributions to the total nonlinearity of KGCOF are from K–O bonds in [K(1)O₆F(1)₂] and [K(21)O₆F(1)₂] groups, although Gd–O and C–O bonds also have some contributions. This case is similar to the theoretical results of potassium titanium oxide phosphate and potassium titanium oxide arsenate.¹²

From the listed G_{11}^{μ} values of each type of bond in Table I, we can find that the disordered orientations of constituent chemical bonds finally lead to a strong cancellation among the same kind of bonds, and each type of bond only has a small geometrical contribution. This is also the reason that this family of compounds cannot have a strong NLO response, and this should be avoided in the future material designing. On the other hand, from the standpoint of the structural characteristic this new family of compounds presents us a good example in “crystal engineering.” That is, we should pay enough attention to the chemical bonding situation of all constituent atoms and try our best to put them in the selected positions (or sites) so that we can obtain an ideal bonding orientation, which will finally lead to little cancellation among G_{ij}^{μ} .

In order to find the dependence of the tensor coefficient d_{11} of KGCOF on the frequency, we have calculated the NLO tensor coefficients for different refractive indices in the long wavelength regime ($\sim 1.0 \mu\text{m}$), calculated results are listed in Table II. We just do this, because we do not know its exact linear optical properties in advance, and we believe this also can help us to understand its NLO behaviors. From Table II, we can see that the nonlinear optical tensor coefficient d_{11} of KGCOF is about three times larger than that of KDP, which agrees with the estimation of its powder test.⁵ Just as some rare earth crystals we have investigated, e.g., Ln₂(MoO₄)₃, Ln=Pr, Nd, Sm, Eu, Gd, Tb and Dy;¹⁶ Ca₄LnO(BO₃)₃, Ln=La, Nd, Sm, Gd, Er, and Y,¹⁷ the rare earth elements have similar chemical and physical properties and the similar chemical bonding situation in the Ln sites, which finally lead to similar NLO properties.^{16,17} Therefore,

TABLE I. Chemical bond parameters, linear, and nonlinear optical properties of each type of chemical bond in KGCOF.

	d^μ (Å)	E_h^μ (eV)	C^μ (eV)	f_c^μ	χ^μ	χ_b^μ	q/e	G_{11}^μ	d_{11}^μ
K1-O1	2.8161	3.0486	4.9019	0.2789	2.7349	1.1484	0.1340	0.0652	-1.1732
K1-O11	2.8161	3.0486	4.9019	0.2789	2.7349	1.1484	0.1340	-0.3861	3.4735
K1-F1	2.6615	3.5068	12.3961	0.0741	1.1939	0.5013	0.4559	0.0000	0.0000
K2-O1s	2.7462	3.2447	5.8029	0.2382	1.8914	0.7942	0.1538	0.0740	-0.2012
K2-O11	3.0588	2.4835	4.5581	0.2289	2.2658	0.9514	0.1362	-0.0543	0.1946
K2-O11s	2.7462	3.2447	5.8029	0.2382	1.8914	0.7942	0.1538	0.0606	-0.1648
K2-O11l	3.0588	2.4835	4.5581	0.2289	2.2658	0.9514	0.1362	0.0897	-0.3215
K2-O2	2.8600	2.9339	5.3030	0.2344	2.0218	0.8490	0.1472	0.0756	-0.2265
K2-O21	2.8601	2.9336	5.3026	0.2343	2.0219	0.8490	0.1472	-0.0336	0.1008
K2-F1	2.8762	2.8930	11.6096	0.0585	0.9307	0.3908	0.4604	-0.1572	-0.0290
K2-F2	2.5710	3.8210	19.4811	0.0370	0.4261	0.1789	0.6233	-0.4271	-0.0097
K21-O1s	2.7462	3.2447	5.1856	0.2814	2.6214	1.1007	0.1382	-0.0226	0.1890
K21-O1l	3.0588	2.4835	4.0625	0.2720	3.1571	1.3257	0.1204	0.1374	-1.6043
K21-O2	2.8601	2.9336	4.7338	0.2775	2.8081	1.1791	0.1314	0.1005	-0.9473
K21-F1	2.8762	2.8931	10.3010	0.0731	1.3841	0.5812	0.4195	-0.3794	-0.0603
Gd-O1	2.4535	4.2910	13.4101	0.0929	1.9431	0.8159	0.4154	-0.2658	-0.3745
Gd-O11	2.4534	4.2914	13.7423	0.0889	1.9432	0.8159	0.4342	0.2439	0.1744
Gd-O2	2.6245	3.6307	9.4333	0.1290	2.1716	0.9119	0.2716	-0.0044	-0.0050
Gd-O21	2.6244	3.6311	9.6033	0.1251	2.1747	0.9132	0.2801	-0.0088	-0.0055
Gd-F1	2.2113	5.5527	23.0754	0.0547	1.5692	0.6589	0.8218	0.0000	0.0000
Gd-F2	2.3061	5.0037	52.3530	0.0091	0.3568	0.1498	2.6206	-0.0288	-0.0003
C-O1	1.2737	21.8103	69.3987	0.0899	1.9831	0.8327	1.7891	0.1254	0.0846
C-O11	1.2737	21.8103	69.3987	0.0899	1.9831	0.8327	1.7891	-0.4437	-0.2995
C-O2	1.2944	20.9555	66.9283	0.0893	2.0340	0.8541	1.7591	-0.4376	-0.3113
C'-O1	1.2737	21.8103	69.3987	0.0899	1.9831	0.8327	1.7891	-0.4297	-0.2900
C'-O21	1.2944	20.9555	66.9283	0.0893	2.0340	0.8541	1.7591	0.1250	0.0044

^aNote. All d_{11}^μ tensor coefficients are in units of 10^{-9} esu.

the $K_4Ln_2(CO_3)_3F_4$ family crystals also have the same nonlinear optical responses as KGCOF.

IV. CONCLUSION

Chemical bonding structures and coordination environments of constituent atoms of KGCOF are investigated by using the experimental structural data. Nonlinear optical responses of the new structural family $K_4Ln_2(CO_3)_3F_4$ ($Ln = Pr, Nd, Sm, Eu, Gd$) have been theoretically studied from the structure-property correlation viewpoint. Using the chemical bond method, we have quantitatively calculated chemical bond parameters, linear and nonlinear optical properties of each type of bond of KGCOF (regarded as the representative crystal for this structural family), and the contributions of each type of bond to the total nonlinearity are also determined. The nonlinearity of this $K_4Ln_2(CO_3)_3F_4$ family arises mainly from K-O bonds, thus we can modify their NLO responses by “tuning” K sites in their crystal structures. Their not large NLO response are ascribed to the

strong cancellation of geometrical contributions among their constituent chemical bonds which is caused by the disordered bonding orientations of constituent atoms. The dependence of the NLO tensor coefficient d_{11} of KGCOF on the frequency is also studied. The results of this article can be used as a guide in the crystal engineering of $K_4Ln_2(CO_3)_3F_4$ family structural crystals.

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TABLE II. Theoretical predictions of the nonlinear optical tensor coefficient d_{11} of KGCOF at long wavelengths ($\sim 1 \mu m$) for refractive indices ranging from 1.70 to 1.90. The values are in reasonable agreement with the experimental data of Ref. 5 where an efficiency of about 50% of that of KTP was found [KTP: $|d_{31}| = 6.06 \times 10^{-9}$ esu, $|d_{32}| = 10.38 \times 10^{-9}$ esu (Ref. 15)].

n_0	1.70	1.75	1.80	1.85	1.90
d_{11} (10^{-9} esu)	-1.76	-2.33	-3.03	-3.89	-4.91

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