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Shortest chemical bond length as a criterion for searching new noncentrosymmetric phosphate crystals

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Abstract

A set of available experimental data on crystal structure of simple and binary phosphates, >270 compounds, have been observed with using criterion of the shortest chemical bond between cations and oxygen. A correlation between the magnitude of nonlinear optical susceptibility $\chi^{(2)}$ and the combination of chemical bonds has been discussed. Criteria for searching phosphate compounds with high $\chi^{(2)}$ have been revealed.

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Keywords: Noncentrosymmetric crystals; Phosphate; Structure; Nonlinear optical susceptibility

1. Introduction

A great number of phosphate crystal materials are known presently and tens of new compounds related to this oxide family appear every year. Many phosphate crystals possess noncentrosymmetric structure and are characterized by high nonlinear optical, electrooptical and piezoelectric properties. As an example, well-known families of $KTiOPO_4$ (KTP) and APO_4 (A = Al, Ga) can be pointed [1–3]. For the overwhelming majority of noncentrosymmetric phosphates, however, only synthesis conditions and crystal structure are reported. Material properties of the dominant part of the compounds remain unknown because of great efforts needed for single-crystal growth. The phosphates with noncentrosymmetric properties reported up to now are collected in Table 1. It is evident that the most complete information is available on nonlinear optical properties due to the fact that the average level of $\chi^{(2)}$ can be estimated by powder SHG intensity with method presented in [4]. So, the problem is how to ascertain the materials exhibiting the most promise for high properties, nonlinear optical in particular, among the discovered crystal phases or, in more wide formulation, how to understand the combination of atoms optimal for generating new crystal phase with high properties. Theoretical methods developed for calculation of nonlinear optical susceptibilities yield the reliable results for relatively simple binary compounds [5–8] and frequently contradict in estimations made for more complex oxides [9,10]. Moreover, as it seems the theoretical prediction of crystal structure of a new compound is practically impossible [11]. In this situations the search for empirical dependencies suitable for practical estimations appears to be reasonable. Earlier many helpful empirical correlations between different physical and chemical properties have been revealed for solids [12–16]. As to symmetry, to offer nonlinear optical properties the crystal should be of noncentrosymmetric structure. It is evident that the characteristics of ideal crystal are defined by sort and number of atoms included into elementary cell and chemical bonds between them. So, it seems be reasonable to search for some universal correlations between nonlinear optical properties of the compounds and chemical bonds in crystal lattice.

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Table 1
The acentric properties and shortest oxide bonds of the simple and binary phosphates

N	Chemical formula (1)	Symmetry (2)	*L* (pm)		P_s (μC/cm^2) (5)	*d* (pC/N) (6)	*r* (pm/V) (7)	$\chi^{(2)}$ (pm/V) (8)
			M–O (3)	M–O (4)				
1	$KTiOPO_4$	C_{2v}	267.7	171.6	27		36.3	13.7
2	$K_{0.84}(Ti_{0.92}Nb_{0.08})OPO_4$	C_{2v}	268.6	175.2				13.7
3	$(K_{0.535}Rb_{0.465})TiOPO_4$	C_{2v}	272.0	171.7				13.7
4	$RbTiOPO_4$	C_{2v}	274.7	171.4	30			13.5
5	$TlTiOPO_4$	C_{2v}	268	174	49			12.5
6	$NaTiOPO_4$	C_{2v}	239.8	171.7				∼5.06
7	Tl_3PO_4	C_6	252.9	252.9				∼0.4–3
8	$K(Mg_{1/3}Nb_{2/3})PO_5$	D_4	257.8	189.0				∼1.8
9	$FePO_4$, 294 K	D_3	179.3	179.3				∼1.52
10	δ_1-$LiZnPO_4$	C_{2v}	192.5	189				∼1.5
11	$Rb_3Ti_3O(P_2O_7)(PO_4)_3$	C_{2v}	279.1	179.4				∼1.41
12	α-$CsTi_3P_5O_{19}$	C_s	305.8	180.9				∼1.2
13	KH_2PO_4, 77 K	C_{2v}	278.3	143	4.75			∼1.12
14	$K_{0.15}Ag_{0.85}TiOPO_4$	C_{2v}	233.8	172				∼1.06
15	$Pb_6[PO_4][B(PO_4)_4]$	S_4	204	146				∼1.06
16	$K_{0.66}Na_{0.34}Nb_2PO_8$	D_3	289	186				∼0.88
17	$Tl_{0.79}Na_{0.21}Nb_2PO_8$	D_3	286	185.1				∼0.88
18	KH_2PO_4	D_{2d}	282.5	142				0.88
19	$KGeOPO_4$	C_{2v}	262.5	179.1				∼0.73
20	$Na_5Ti(PO_4)_3$	D_3	235.9	188.2				∼0.7
21	$Zn_3(BO_3)(PO_4)$	C_s	198.0	136.3				0.69
22	$KSnOPO_4$	C_{2v}	261.1	195.7	0.0224			∼0.6
23	$GaPO_4$	D_3	181.0	181.0		4.5		0.5
24	$Ca_9In(PO_4)_7$	C_{3v}	226.1	212.8				∼0.47
25	$AlPO_4$	D_3	173.2	173.2		3.3		0.4
26	$NaTh_2(PO_4)_3$	C_s	232	227	0.01			∼0.31
27	$Na_3Sc_2(PO_4)_3$	C_s	222	201.6				∼0.22
28	BPO_4	S_4	140	140				∼0.014

P_s, spontaneous polarization; *d*, maximum piezoelectric coefficient; *r*, maximum electrooptic coefficient; $\chi^{(2)}$, maximum nonlinear optical susceptibility.

The absence of inversion center in crystal lattice is defined by two factors, namely the distortion of oxygen environment around cation M and asymmetric linkage of MO_x groups with the oxygen polyhedra containing another cations. As it appears, the length of the shortest chemical bond *L*(M–O) can be reasonably used as a parameter to characterize the acentricity of MO_x structural groups. The rules governing the linkage of polyhedra of different cations in crystal lattice, however, are less clear and it is a difficult task to formulate geometrical parameter to describe numerically the "acentricity rate". To be useful for comparison of very numerous and dissimilar oxide structures the criterion should be simple and independent of crystal symmetry. Previously it has been shown on the examples of binary oxides and noncentrosymmetric molybdate and tungstate oxides that the value of *L*(M–O) can be taken as a universal characteristic to describe the empirical relations between crystal structure and noncentrosymmetric material properties [17–19]. Binary oxide crystals $E_nM_mO_p$ can be noncentrosymmetric only if the length *L*(E–O) is shorter than 198 nm and has necessarily a center of symmetry if $L(M–O) > 198$ nm. The aim of this study is to search for the correlation between the magnitude of nonlinear optical susceptibility and chemical bond lengths for presently known simple and binary noncentrosymmetric phosphates, omitting compounds containing crystal water groups and halogen ions.

2. Symmetry and statistics

At the moment our collection of noncentrosymmetric phosphates includes 272 compounds for which crystal structure has been solved by experimental methods of X-ray or neutron analysis. To keep the place the complete table of the phosphates is not presented here. Powder or single-crystal structure data are considered only if these are published and $R(F) < 0.15$. Any oxide containing phosphorus was classified as "phosphate" if in crystal lattice at least one cation position was filled with phosphorus ions by ≥20%. In binary phosphates, if cation M has few different crystal lattice positions with the same coordination, the value of *L*(M–O) is defined by the shortest bond length within all these positions. In the simple phosphates, if some positions of cation M in crystal lattice are different in coordination, this compound is classified as formal "binary" and these positions are considered as different formal cations characterized by different *L* values. Chemical composition of binary phosphates can be described by formulas $M_nM_mP_pO_t$,

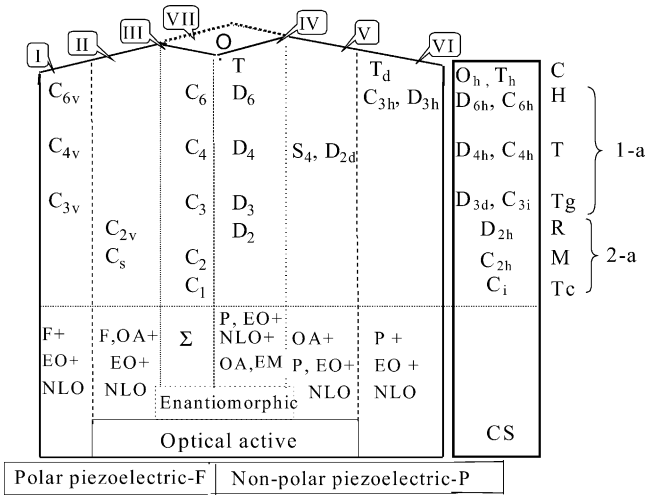

Fig. 1. Relationships between symmetry dependent properties and crystal classes. The notations are: C, cubic; H, hexagonal; T, tetragonal; Tg, trigonal; R, rhombic; M, monoclinic; Tc, triclinic; F, pyro- or ferro-electric (polar piezoelectric); P, piezoelectric; EO, electrooptic; NLO, nonlinear optical; OA, optical active; EM, enantiomorphic; Σ, all acentric properties; NCS, non-centrosymmetric; CS, centrosymmetric; 1-a, optical uniaxial crystals; 2-a, optical biaxial crystals.

$M_nE_mPO_t$ or $E_nE_mP_pO_t$ in which cation types E and M are defined by the relation $L(\text{E–O}) \leq 198\,\text{nm} < L(\text{M–O})$.

Fig. 1 shows our version for scheme of interrelationships between crystal classes and symmetry dependent material properties [13]. In this diagram wide left part with triangle top represents noncentrosymmetric crystals. This part is divided into vertical strips I–VI and rhomb VII depicting the symmetry class divisions different in combination of possible material properties [13]. The groups I–VI contain all piezoelectric crystals dividing into polar (ferro- or pyro-electric I–III) and non-polar crystals (pure piezoelectric IV–VI). Only the crystals of group III have all acentric properties. The rectangular region in the right part of the scheme contains centrosymmetric crystal classes. All point symmetry groups are also arranged into seven horizontal levels giving seven crystal symmetry systems.

It is interesting to see the statistical distribution of the noncentrosymmetric phosphates over 21 point symmetry classes. The results of the calculations for our collection are shown in Fig. 2. As it is seen, the plentiful sets of simple and binary phosphate crystals related to crystallographic classes C_{2v} (69), D_2 (51), C_s (38) and C_2 (30). From the other side, the noncentrosymmetric phosphates relating to classes C_{3h} (0), C_{6v} (1), C_4 (1), D_6 (2), D_4 (2) and D_{3h} (2) are uncommon in nature. The comparison of the distribution for phosphates with that for more numerous set of noncentrosymmetric binary oxides (∼600 [19,20]), encompassing arbitrary combinations of cations, exhibits same specific features of phosphate compounds. The most numerous sets for phosphates (∼25.4%) as well as for binary oxides (∼32%) are related to C_{2v} class. At the same time unexpectedly high is the part of phosphates with D_2 symmetry (20.6%). For binary oxides the part of compounds from class D_2 is only 2.8%. Evidently, this effect is a specific feature of phosphate crystals confirming a suggestion that the distribution of the inorganic crystals on the symmetry classes is appreciably stipulated by the crystal composition and the nature of chemical bonds.

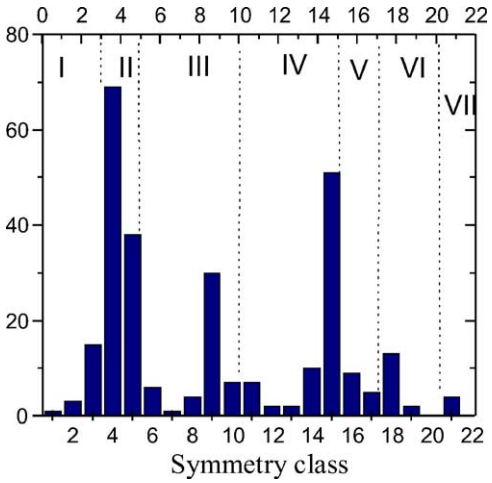

Fig. 2. Distribution of noncentrosymmetric phosphate crystals among point symmetry classes: (1) C_{6v}; (2) C_{4v}; (3) C_{3v}; (4) C_{2v}; (5) C_s; (6) C_6; (7) C_4; (8) C_3; (9) C_2; (10) C_1; (11) T; (12) D_6; (13) D_4; (14) D_3; (15) D_2; (16) D_{2d}; (17) S_4; (18) T_d; (19) D_{3h}; (20) C_{3h}; (21) O.

3. Optical nonlinearity and chemical bond lengths

In Fig. 3 the noncentrosymmetric phosphates are shown as points on the plane of the shortest chemical bonds. In

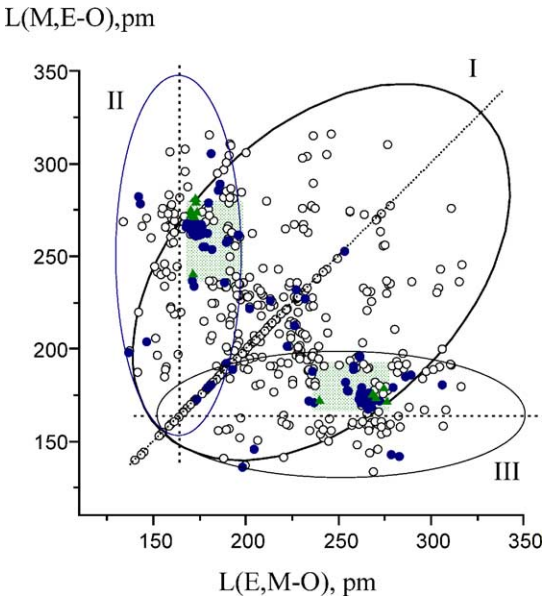

Fig. 3. The plane of the shortest chemical bonds for noncentrosymmetric simple and binary phosphates. The crystals with high nonlinear optical susceptibility $\chi^{(2)} \geq 4\,\text{pm/V}$ are shown by (▲), phosphates with $0.05 < \chi^{(2)} < 4\,\text{pm/V}$ by (●) and these with negligible or unknown acentric properties, $\chi^{(2)} \leq 0.05\,\text{pm/V}$ by (○).

this figure, because of arbitrariness in the choice of the first cation in chemical formula for binary phosphates, any compound containing two cations E or M is displayed by two points positioned symmetrically in reference to the bisectrix of the coordinate angle. The points related to simple phosphates lie on the bisectrix. As it is evident, near all points may be covered by a rossete of three partly crossing ellipses, with central tilted ellipse I containing dominant part of the crystals of type $M^1_nM^2_mP_pO_t$ and symmetrical II and III ellipses, generated by the crystals of $M_nE_mP_pO_t$ and $E^1_nE^2_mP_pO_t$ types. All phosphates lying away the rosette are characterized by the presence of center of inversion. Thus, a rossette shows us the ranges of the shortest bonds between cations and oxygen under which the formation of noncentrosymmetric phosphates is possible. All the phosphate compounds with known optical nonlinearity lie inside the ellipses and these are shown by special points depending on $\chi^{(2)}$ level (Fig. 3). Peculiar feature of the present situation in observation of physical properties of phosphates is that high levels of $\chi^{(2)}$ have been found only for the compounds from one crystal family, namely $KTiOPO_4$ (KTP), and these are having the same structure type (C_{2v}). For comparison the complete region of KTP family (233.8/275.7) × (170.5/179.1) pm^2, is displayed by hatching. Nevertheless, in Fig. 3 the crystals from KTP family with relatively high $\chi^{(2)}$ are presented by close group of points positioned in proximity to the long axes of ellipses II–III. Earlier the tendency of positioning of the compounds with high $\chi^{(2)}$ nearly long axis of ellipses was also detected in molybdates and tungstates [18]. The phosphates with comparatively low optical nonlinearity are scattered over ellipses II–III and central part of ellipse I without any essential agglomeration. It is interesting to point that external part of ellipse I at (L(M–O) > 253 pm) is free of the compounds with detectable $\chi^{(2)}$. This and adjacent regions contain binary phosphates composed by one or two cations both of which are characterized by comparatively long chemical bonds to oxygen 200 < (L(M–O) < 310 pm), for example, $CsNdP_4O_{12}$. The compounds of this type ($KNdP_4O_{12}$, $NaYP_2O_7$, $Ca_9In(PO_4)_7$, InP_3O_9, LaP_3O_9, CeP_5O_{14} and others) are interesting for creation of self-frequency doubling laser media [21]. Such compounds are generated by alkali, alkali-earth or rare-earth elements and relate to $M^1_nM^2_mP_pO_t$ type. So, it is reasonable future task for experimentators to test optical nonlinearity of the phosphates.

In Fig. 4 the dependence of $\chi^{(2)}$ on L(E–O) is presented for the compounds listed in Table 1. Sharp maximum is evident at $L \sim$ 171–175 pm that is typical range for the shortest bond length Ti–O for phosphate compounds of KTP type. For binary oxides the highest $\chi^{(2)}$ value is observed for $PbTiO_3$ (42 pm/V, C_{4v}) with L(Ti–O) = 178 pm [22]. For binary molybdates the maximum $\chi^{(2)}$ value (~23 pm/V) reported in literature was measured by powder method in $CsMoO_3(IO_3)$ and $RbMoO_3(IO_3)$, (C_{2v}) [23]. In these compounds also the cation is present with the shortest oxide bond length

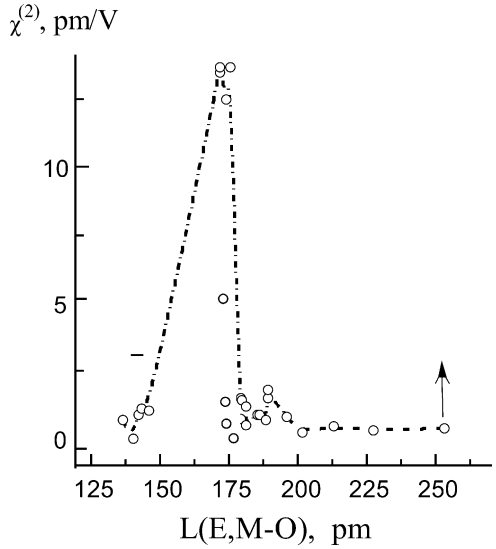

Fig. 4. Nonlinear optical susceptibility $\chi^{(2)}$ as a function of the shortest oxide bond length L(E, M–O) in phosphates.

L(I–O) = 179.8–181.1 pm and L(Mo–O) = 171 pm. Further, for binary tungstates the highest $\chi^{(2)}$ > 70 pm/V was reported for β-$LiNbWO_6$ (C_{3v}), with L(W–O) = 173.6 pm [8,24]. Another binary tungstate, $Na_2TeW_2O_9$, possesses $\chi^{(2)} \approx$ 8.9 pm/V and averaged L(Te–O) ≈ 188 pm [25]. All these examples confirm the common tendency that high $\chi^{(2)}$ is most probable for oxides containing the combination of alkali ion and any ion from the set E = Ti, Nb, Ta, I, W, Mo having L(E–O) ≈ 170–190 pm.

4. Conclusions

The criterion of the shortest chemical bond length is used for definition of the field of noncentrosymmetric phosphate crystals. This approach yields the estimations of bond length characteristics promising for high optical nonlinearity. As to phosphate crystals, the compounds including any alkali ion and an ion from the set Ti, Nb, I and, possibly, Ta are the most promising for high optical nonlinearity.

Acknowledgements

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