

# Pseudosymmetric Features and Nonlinear Optical Properties of Potassium Titanyl Phosphate Crystals

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## ABSTRACT

A number of publications containing structural data, characteristics of nonlinear optical properties of pure and doped crystals of potassium titanyl phosphate (KTP) family have been reviewed to analyze the structural and symmetry conditionality of nonlinear optical properties of these crystals. The pseudosymmetric features of KTP-type crystals with respect to inversion are investigated. Specifically, pseudoinversion distribution maps are calculated; pseudoinversion extrema and coordinates of pseudoinversion centres are found; and the distributions of pure and doped KTP-type structures and their individual atomic sublattices over the degree of pseudoinversion are analyzed. A correlation between the characteristics of nonlinear optical properties of a number of crystals belonging to the KTP family and the degree of pseudoinversion of their atomic structures is demonstrated.

**Keywords:** Potassium Titanyl Phosphate Family; Pseudosymmetry; Nonlinear Optical Properties

## 1. Introduction

Study of the relationship of structural and symmetric features of crystals with their physical properties is an urgent problem of condensed-matter physics. Point symmetry determines the set of possible physical properties of crystals, primarily, in correspondence with the Neumann principle. The symmetric features of atomic structures of crystals can be characterized more completely taking into account the phenomenon of pseudosymmetry, which makes it possible to establish finer relationships of the structure-property type. Fedorov pseudosymmetry of crystals [1] is the phenomenon of invariance of a considerable part of the crystal atomic structure (part of electron density and (or) subsystem of atomic nuclei) with respect to some group of symmetry operations compatible with the lattice (with respect to some supergroup of the symmetry space group of crystal).

The pseudosymmetry of a specific structure can quantitatively be characterized by the degree of invariance (degree of pseudosymmetry) of its total electron density  $\rho(\mathbf{r})$  with respect to some isometric operation  $\hat{g}$  [1,2]:

$$\eta_g[\rho(\mathbf{r})] = \frac{\int_V \rho(\mathbf{r}) \rho(\hat{g}\mathbf{r}) dV}{\int_V \rho^2(\mathbf{r}) dV}. \quad (1)$$

Integration in Equation (1) is performed over the volume  $V$  of crystal unit cell. If  $\hat{g}$  is not a symmetry operation for the function  $\rho(\mathbf{r})$ , the degree of pseudosymmetry  $\eta_g[\rho(\mathbf{r})] < 1$ ; however, if  $\rho(\mathbf{r})$  is symmetric with respect to the operation  $\hat{g}$ ,  $\eta_g[\rho(\mathbf{r})]$  reaches a maximally possible value: unity.

The second-order susceptibility of crystal determines the intensity of generation of the second optical harmonic and is a structure- and symmetry-sensitive property of crystal. For centrosymmetric crystals, the second-order susceptibility should be zero. One might suggest that reduction of symmetry will lead to some dependence of the second-order susceptibility of crystal on the degree of invariance of crystal structure with respect to inversion.

## 2. Nonlinear Optical Properties of Potassium Titanyl Phosphate Crystals: A Review

The family of crystals with potassium titanyl phosphate (KTP) structure includes more than 100 compounds [3,4]. Their general formula can be written as  $MM'OXO_4$ , where  $M = K, Rb, Na, Cs, Tl, NH_4$ ;  $M' = Ti, Sn, Sb, Zr$ ,

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Ge, Al, Cr, Fe, V, Nb, Ta, Ga;  $X = P, As, Si, Ge$ . Inter-octahedral ( $M-O-M$ ) oxygen atoms can be replaced with OH- and F-; the resulting compounds with the general formula  $MM'(F,OH)XO_4$  also belong to the KTP family. The structure of KTP crystals is described by the space group  $Pna2_1$ .

We considered 118 crystals belonging to the KTP family, including 29 pure and 89 doped ones. Information about the nonlinear optical characteristics of 108 crystals was found in the corresponding publications. All crystals under consideration were separated into three groups with respect to the available data on their structure and nonlinear optical properties; the relationship between these groups is clearly shown in **Figure 1**.

The characteristics of nonlinear optical properties of KTP crystals are listed in **Table 1**, where the parameter  $I/I_{\text{reference}}$  is the ratio of second harmonic intensities from a sample under study studied and a powder sample of reference crystal.

The characteristics of nonlinear optical properties were determined in [8,10,11,24] by the Kurtz-Perry method [26] and in [3,5-7,12,14,19,22] by the method described in [27]. The components of the second-order susceptibility tensor were found in [16,17,20] using the Maker fringe technique [28,29].

With allowance for the results of our analysis of the corresponding publications, we can select crystals whose characteristics of nonlinear optical properties are comparable with those for  $KTiOPO_4$  crystal ( $K_{0.5}Rb_{0.5}TiOPO_4$ , RTA,  $K_{0.966}Ti_{0.966}Nb_{0.034}OPO_4$ ,  $K_{0.921}Ti_{0.921}Nb_{0.079}OPO_4$ , RTP,  $K_{0.99}Ti_{0.99}Sb_{0.01}OPO_4$ ,  $KTi_{0.96}Zr_{0.04}OPO_4$ , TTP,  $KTi_{0.9975}V_{0.0025}OPO_4$ ,  $K_{0.5}Ti_{0.5}Nb_{0.5}OPO_4$ , CTA,  $K_{0.5}Ta_{0.5}Ti_{0.5}OPO_4$ ,  $KTiO(PO_4)_0.5(AsO_4)_0.5$ , TTA,  $KTi_{0.7}Nb_{0.3}OP_{0.7}Si_{0.3}O_4$ ,  $KTi_{0.65}Nb_{0.35}OP_{0.65}Si_{0.35}O_4$ ,  $KTi_{0.6}Nb_{0.4}OP_{0.6}Si_{0.4}O_4$ ,  $RbTi_{0.98}Nb_{0.02}OPO_4$ ,  $Na_{0.87}K_{0.13}TiOAsO_4$ ,  $KTi_{0.7}Nb_{0.3}OAs_{0.7}Si_{0.3}O_4$ ,  $KTi_{0.6}Nb_{0.4}OAs_{0.6}Si_{0.4}O_4$ ,  $RbTi_{0.927}Nb_{0.056}Er_{0.017}OPO_4$ ) and crystals with characteristics of nonlinear optical properties exceeding those of  $KTiOPO_4$  crystal (KTA,  $K_{0.98}Ti_{0.98}Nb_{0.02}OPO_4$ ,  $K_{0.96}Ti_{0.96}Nb_{0.04}OPO_4$ ,  $K_{0.97}Ti_{0.97}Sb_{0.07}OPO_4$ ,  $K_{0.88}Ti_{0.98}Zr_{0.06}OP_{0.99}O_4$ ,  $K_{0.88}Ti_{0.93}Zr_{0.11}OP_{0.99}O_4$ ,  $K_{0.97}Ti_{0.99}OAs_{0.53}P_{0.49}O_4$ ,  $KTi_{0.9}Nb_{0.1}OP_{0.9}Si_{0.1}O_4$ ,  $K_{0.80}Ti_{0.26}Zr_{0.78}OAs_{1.01}O_4$ ,  $KTi_{0.9}Nb_{0.1}OAs_{0.9}Si_{0.1}O_4$ ,  $K_{0.94}Nb_{0.12}Ti_{0.91}OAs_{0.89}Ge_{0.09}O_4$ ,  $KTi_{0.8}Nb_{0.2}OAs_{0.8}Si_{0.2}O_4$ ,  $K_{1.02}Nb_{0.25}Ti_{0.76}OAs_{0.75}Ge_{0.23}O_4$ ,  $K_{0.68}Rb_{0.32}TiOPO_4$ ,  $Cs_{0.5}K_{0.5}TiOAsO_4$ ,  $KTi_{0.97}Zr_{0.03}OPO_4$ ,  $K_{0.54}Li_{0.46}TiOAsO_4$ ,  $K_{1.03}Nb_{0.52}Ti_{0.48}OAs_{0.48}Ge_{0.51}O_4$ ,  $Rb_{0.855}Ti_{0.955}Nb_{0.045}OPO_4$ ,  $KNb_{0.52}Ti_{0.48}OAs_{0.48}Ge_{0.51}O_4$ ,  $RbTi_{0.96}Nb_{0.04}OPO_4$ ,  $K_{0.98}Nb_{0.46}Ti_{0.56}OAs_{0.58}Ge_{0.39}O_4$ ).

There are data in the literature on  $KTiOPO_4$  crystals doped with Nb [30-36], Ge [37], Sn [33,38-40], Zr [41-43], Sb [35,44,45], Ta [35], Fe [46], Hf [47], and Zn [48] and RTP crystals doped with Cs [49] and Zr [50,51]. It was indicated in [39] that an increase in the Sn content

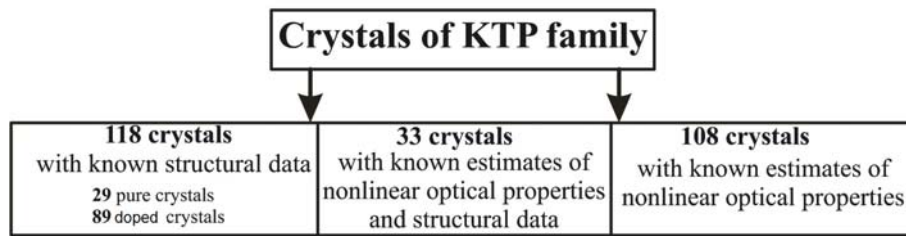
leads to a dramatic decrease in the output second-harmonic intensity to zero. The intensity of second-harmonic generation (SHG) for  $KTi_{1-x}Zr_xOPO_4$  crystals reaches a maximum at  $x = 0.28$ , where it is more than doubled in comparison with the  $KTiOPO_4$  sample [41]. The SHG intensity increases with an increase in the zirconium content in  $RbTi_{1-x}Zr_xOPO_4$  crystals; at  $x = 0.034$ , it rises by 40% [50]. The SHG intensity increases by approximately 35% in comparison with pure  $KTiOPO_4$  samples after replacement of 6% titanium atoms with hafnium [47].  $RbTi_{1-x}Ta_xOPO_4$  and  $RbTi_{1-x}Nb_xOPO_4$  crystals were investigated in [52], as well as Yb-doped  $RbTi_{1-x}Ta_xOPO_4$  crystals and  $RbTi_{1-x}Nb_xOPO_4$  crystals doped with Yb, Ln and Er.  $KTiOPO_4$  crystals doped with transition metals and RTA crystals doped with lanthanides were studied in [53]. A number of compounds ( $RbTi_{0.98}Er_{0.01}Nb_{0.01}OAsO_4$ ,  $RbTi_{0.96}Er_{0.02}Nb_{0.02}OAsO_4$ , and  $KTi_{0.98}Cr_{0.02}O_{0.98}F_{0.02}PO_4$ ,  $KTi_{0.99}Fe_{0.01}O_{0.99}F_{0.01}PO_4$ ,  $RbTi_{0.98}Er_{0.02}O(AsO_4)_{0.98}(SO_4)_{0.02}$ ) exhibited an increase in the SHG intensity in comparison with RTA and KTP crystals, respectively.

### 3. Analysis of the Degree of Invariance of the Structure of KTP Crystals with Respect to Inversion

The complete characteristic of pseudosymmetry of any crystal under study with respect to inversion is a three-dimensional distribution map of the degree of structural invariance (electron density) with respect to this operation (hereinafter, pseudoinversion), calculated for different positions of inversion points within their unit cell. These maps were obtained with scanning steps over the unit-cell axes  $a$ ,  $b$ , and  $c$  chosen to be 0.05 of the corresponding unit-cell parameters. For 118 crystals (**Figure 1**) with known structure, we calculated three-dimensional pseudoinversion maps using Equation (1). The calculations were performed using the computer program and technique described in [54]. Within this approach the electron density function is expanded in a Fourier series in structural amplitudes ([1], see Formulas (5) and (6)).

**Figure 2** presents typical examples of cross sections of three-dimensional distribution maps of the degree of pseudoinversion for the structures of  $KTiOPO_4$ ,  $KSnOPO_4$ ,  $KTiOAsO_4$ ,  $Cs_{0.625}K_{0.375}TiOAsO_4$  crystals (cuts by the plane  $z = 0.25$ ). For the structures presented in **Figure 2**, the origin of coordinates is chosen on the two fold screw axis, and the coordinates of pseudoinversion peaks on the  $x$  and  $y$  axes are 0.25. We chose cuts by the plane  $z = 0.25$  in **Figure 2** because the  $z$  coordinate of the pseudoinversion peaks for the structures of the aforementioned crystals is also 0.25.

This situation is typical of most structures under study; in KTP crystals is accompanied by a phase transition to the centrosymmetric space group  $Pnan$ . Indeed, having



**Figure 1. Groups of KTP crystals under consideration.**

**Table 1. Characteristics of nonlinear optical properties of KTP crystals.**

№	Crystal	Characteristics of nonlinear optical properties	References
		6000 ( $I/I_{SiO_2}$ )	[3,5]
		910 ( $I/I_{SiO_2}$ )	[6,7]
		$4.24 \pm 0.17$ ( $\chi_{2\omega}$ , relative to KDP)	[8]
1	KTiOPO <sub>4</sub> (KTP)	$d_{15}$ (0.852 $\mu\text{m}$ ) = $1.9 \pm 0.1$ pm/V $d_{24}$ (0.852 $\mu\text{m}$ ) = $3.9 \pm 0.2$ pm/V $d_{33}$ (0.852 $\mu\text{m}$ ) = $16.6 \pm 0.8$ pm/V $d_{15}$ (1.064 $\mu\text{m}$ ) = $1.9 \pm 0.1$ pm/V $d_{24}$ (1.064 $\mu\text{m}$ ) = $3.7 \pm 0.2$ pm/V $d_{31}$ (1.064 $\mu\text{m}$ ) = $2.2 \pm 0.1$ pm/V $d_{32}$ (1.064 $\mu\text{m}$ ) = $3.7 \pm 0.2$ pm/V $d_{33}$ (1.064 $\mu\text{m}$ ) = $14.6 \pm 0.7$ pm/V $d_{15}$ (1.313 $\mu\text{m}$ ) = $1.4 \pm 0.1$ pm/V $d_{24}$ (1.313 $\mu\text{m}$ ) = $2.6 \pm 0.1$ pm/V $d_{33}$ (1.313 $\mu\text{m}$ ) = $11.1 \pm 0.6$ pm/V	[9]
		6000 ( $I/I_{SiO_2}$ )	[3,5]
		0.73 ( $I/I_{KTP}$ )	[10]
2	RbTiOPO <sub>4</sub> (RTP), rubidium titanyl phosphate	0.7 ( $I/I_{KTP}$ )	[11]
		$d_{31}$ (1.064 $\mu\text{m}$ ) = $3.3 \pm 0.6$ pm/V $d_{32}$ (1.064 $\mu\text{m}$ ) = $4.1 \pm 0.8$ pm/V $d_{33}$ (1.064 $\mu\text{m}$ ) = $17.1 \pm 3.4$ pm/V	[9]
3	TlTiOPO <sub>4</sub> (TTP), thallium titanyl phosphate	6000 ( $I/I_{SiO_2}$ )	[3,5]
4	NaTiOPO <sub>4</sub>	160 ( $I/I_{SiO_2}$ )	[3]
5	AgTiOPO <sub>4</sub>	5 ( $I/I_{SiO_2}$ )	[3,5,7]
6	(NH <sub>4</sub> )TiOPO <sub>4</sub> (NTP)*, ammonium titanyl phosphate	2400 ( $I/I_{SiO_2}$ )	[5,12]
7	KSnOPO <sub>4</sub>	0.50 ( $I/I_{SiO_2}$ )	[13]
8	KGeOPO <sub>4</sub>	3.3 ( $I/I_{SiO_2}$ )	
9	NaGeOPO <sub>4</sub>	4 ( $I/I_{SiO_2}$ )	[3,5]
10	KVOPO <sub>4</sub>	opaque	
		6000 ( $I/I_{SiO_2}$ )	[3]
		990 ( $I/I_{SiO_2}$ )	[6,7]
		1.09 ( $I/I_{KTP}$ )	[14]
		1.01 ( $I/I_{KTP}$ )	[15]
11	KTiOAsO <sub>4</sub> (KTA), potassium titanyl arsenate	$d_{15}$ (1.064 $\mu\text{m}$ ) = $1.3 \times d_{15}(\text{KTP})$ $d_{24}$ (1.064 $\mu\text{m}$ ) = $(1.8 \pm 0.1) \times d_{15}(\text{KTA})$ $d_{31}$ (1.064 $\mu\text{m}$ ) = $2.8 \pm 0.3$ pm/V $d_{31}$ (1.064 $\mu\text{m}$ ) = $(1.3 \pm 0.1) \times d_{31}(\text{KTP})$ $d_{32}$ (1.064 $\mu\text{m}$ ) = $4.2 \pm 0.4$ pm/V $d_{32}$ (1.064 $\mu\text{m}$ ) = $(1.8 \pm 0.1) \times d_{31}(\text{KTA})$ $d_{33}$ (1.064 $\mu\text{m}$ ) = $16.2 \pm 1.0$ pm/V $d_{15}$ (1.32 $\mu\text{m}$ ) = $1.2 \times d_{15}(\text{KTP})$ $d_{24}$ (1.32 $\mu\text{m}$ ) = $1.7 \times d_{15}(\text{KTP})$	[9,16]

Continued

		6000 ( $I/I_{\text{SiO}_2}$ )	[3]
12	RbTiOAsO <sub>4</sub> (RTA), rubidium titanyl arsenate	$d_{31}$ (1.064 $\mu\text{m}$ ) = 2.3 $\pm$ 0.5 pm/V $d_{31}$ (1.064 $\mu\text{m}$ ) = 3.55 $\times$ $d_{36}$ (KDP) $d_{32}$ (1.064 $\mu\text{m}$ ) = 3.8 $\pm$ 0.7 pm/V $d_{32}$ (1.064 $\mu\text{m}$ ) = 11.71 $\times$ $d_{36}$ (KDP) $d_{33}$ (1.064 $\mu\text{m}$ ) = 15.8 $\pm$ 1.6 pm/V $d_{33}$ (1.064 $\mu\text{m}$ ) = 31.05 $\times$ $d_{36}$ (KDP)	[9]
13	CsTiOAsO <sub>4</sub> (CTA), cesium titanyl arsenate	$d_{31}$ (1.064 $\mu\text{m}$ ) = 2.1 $\pm$ 0.4 pm/V $d_{32}$ (1.064 $\mu\text{m}$ ) = 3.4 $\pm$ 0.7 pm/V $d_{33}$ (1.064 $\mu\text{m}$ ) = 18.1 $\pm$ 1.8 pm/V $d_{31}$ (1.32 $\mu\text{m}$ ) = 1.1 $\pm$ 0.1 pm/V $d_{32}$ (1.32 $\mu\text{m}$ ) = 1.7 $\pm$ 0.6 pm/V	[9,17]
14	TiTiOAsO <sub>4</sub> (TTA), thallium titanyl arsenate	6000 ( $I/I_{\text{SiO}_2}$ )	
15	NH <sub>4</sub> TiOAsO <sub>4</sub>	100 ( $I/I_{\text{SiO}_2}$ )	
16	KGeOAsO <sub>4</sub>	0.03 ( $I/I_{\text{SiO}_2}$ )	
17	KSnOAsO <sub>4</sub>	0.53 ( $I/I_{\text{SiO}_2}$ )	[3]
18	RbZrOAsO <sub>4</sub>	3 ( $I/I_{\text{SiO}_2}$ )	
19	CsZrOAsO <sub>4</sub>	2 ( $I/I_{\text{SiO}_2}$ )	
20	NH <sub>4</sub> ZrOAsO <sub>4</sub>	1 ( $I/I_{\text{SiO}_2}$ )	
21	KSbOSiO <sub>4</sub>	0.5 ( $I/I_{\text{SiO}_2}$ )	[18]
22	NaSbOSiO <sub>4</sub>	0.4 ( $I/I_{\text{SiO}_2}$ )	
23	AgSbOSiO <sub>4</sub>	1.1 ( $I/I_{\text{SiO}_2}$ )	[18]
24	KSbOGeO <sub>4</sub>	0.95 ( $I/I_{\text{SiO}_2}$ )	
25	NaSbOGeO <sub>4</sub>	0.8 ( $I/I_{\text{SiO}_2}$ )	
26	AgSbOGeO <sub>4</sub>	1.5 ( $I/I_{\text{SiO}_2}$ )	
27	KFePO <sub>4</sub> F	2.66 ( $I/I_{\text{SiO}_2}$ )	[3,5]
28	KGaAsO <sub>4</sub> F	0.02 ( $I/I_{\text{SiO}_2}$ )	[3]
29	KFeAsO <sub>4</sub> F	1 ( $I/I_{\text{SiO}_2}$ )	
30	K <sub>2</sub> FeNb(PO <sub>3</sub> ) <sub>2</sub>	1 ( $I/I_{\text{SiO}_2}$ )	[5]
31	RbScFAsO <sub>4</sub>	0.5 ( $I/I_{\text{SiO}_2}$ )	[19]
32	CsScFAsO <sub>4</sub>	1.2 ( $I/I_{\text{SiO}_2}$ )	
33	Ag <sub>0.5</sub> K <sub>0.5</sub> TiOPO <sub>4</sub>	130 ( $I/I_{\text{SiO}_2}$ ) 135 ( $I/I_{\text{SiO}_2}$ )	[3] [7]
34	Ag <sub>0.85</sub> K <sub>0.15</sub> TiOPO <sub>4</sub>	7 ( $I/I_{\text{SiO}_2}$ ) 0.01 ( $I/I_{\text{KTP}}$ ) ***	[3,6,7] [14]
35	(NH <sub>4</sub> ) <sub>0.5</sub> K <sub>0.5</sub> TiOPO <sub>4</sub>	1100 ( $I/I_{\text{SiO}_2}$ )	[3,5]
36	K <sub>0.5</sub> Rb <sub>0.5</sub> TiOPO <sub>4</sub>	6000 ( $I/I_{\text{SiO}_2}$ )	[3]
37	K <sub>0.68</sub> Rb <sub>0.32</sub> TiOPO <sub>4</sub>	$d_{31}$ (1.06 $\mu\text{m}$ ) = 6.5 pm/V $d_{32}$ (1.06 $\mu\text{m}$ ) = 5.0 pm/V $d_{33}$ (1.06 $\mu\text{m}$ ) = 13.7 pm/V $d_{24}$ (1.06 $\mu\text{m}$ ) = 7.6 pm/V $d_{15}$ (1.06 $\mu\text{m}$ ) = 6.1 pm/V	[20]
38	Na <sub>0.2</sub> K <sub>0.8</sub> TiOPO <sub>4</sub>	675 ( $I/I_{\text{SiO}_2}$ )	[7]
39	Na <sub>0.4</sub> K <sub>0.6</sub> TiOPO <sub>4</sub>	620 ( $I/I_{\text{SiO}_2}$ )	
40	Na <sub>0.55</sub> K <sub>0.45</sub> TiOPO <sub>4</sub>	570 ( $I/I_{\text{SiO}_2}$ )	
41	Na <sub>0.65</sub> K <sub>0.35</sub> TiOPO <sub>4</sub>	590 ( $I/I_{\text{SiO}_2}$ ) 100 ( $I/I_{\text{SiO}_2}$ )	[6]
42	Na <sub>0.95</sub> K <sub>0.05</sub> TiOPO <sub>4</sub>	90 ( $I/I_{\text{SiO}_2}$ ) 0.11 ( $I/I_{\text{KTP}}$ ) ***	[7] [14]
43	K <sub>0.55</sub> Li <sub>0.45</sub> TiOPO <sub>4</sub>	620 ( $I/I_{\text{SiO}_2}$ ) 0.68 ( $I/I_{\text{KTP}}$ ) ***	[6] [14]

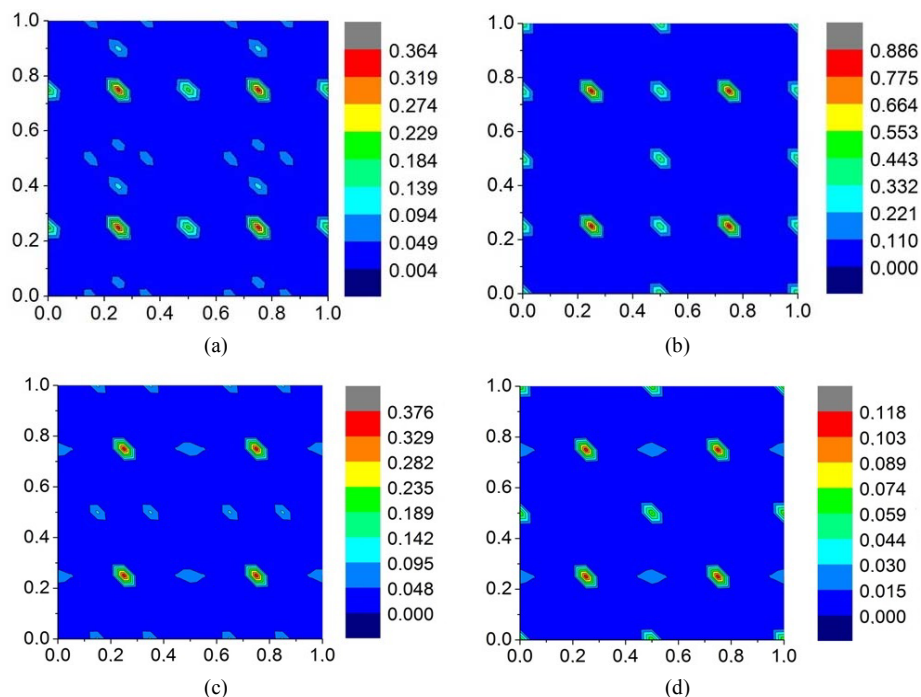
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44	$K_{0.966}Ti_{0.966}Nb_{0.034}OPO_4$	$d_{15} (1.064 \mu m) = (0.8 \pm 0.1) \times d_{15}(KTP)$ $d_{24} (1.064 \mu m) = (2.2 \pm 0.1) \times d_{15}(Nb: KTP)$	[9]
45	$K_{0.921}Ti_{0.921}Nb_{0.079}OPO_4$	$d_{15} (1.064 \mu m) = 0.75 \times d_{15}(KTP) \pm 10\%$ $d_{24} (1.064 \mu m) = 1.13 \times d_{24}(KTP) \pm 10\%$ $d_{33} (1.064 \mu m) = 0.9 \times d_{33}(KTP) \pm 10\%$	
46	$K_{0.98}Ti_{0.98}Nb_{0.02}OPO_4$	$4.56 \pm 0.18$	
47	$K_{0.96}Ti_{0.96}Nb_{0.04}OPO_4$	$4.97 \pm 0.18$	
48	$K_{0.89}Ti_{0.89}Nb_{0.11}OPO_4$	$2.39 \pm 0.25$	
49	$K_{0.99}Ti_{0.99}Sb_{0.01}OPO_4$	$4.18 \pm 0.22$	
50	$K_{0.97}Ti_{0.97}Sb_{0.07}OPO_4$	$4.50 \pm 0.18$	( $\chi_{2\omega}$ (relative to KDP)) [8]
51	$K_{0.83}Ti_{0.83}Sb_{0.17}OPO_4$	$1.02 \pm 0.05$	
52	$KTi_{0.97}Zr_{0.03}OPO_4$	$4.58 \pm 0.21$	
53	$KTi_{0.96}Zr_{0.04}OPO_4$	$4.33 \pm 0.2$	
54	$K_{0.88}Ti_{0.98}Zr_{0.06}OP_{0.99}O_4$	$1.8 (I/I_{KTA})$	[21]
55	$K_{0.88}Ti_{0.93}Zr_{0.11}OP_{0.99}O_4$	$1.7 (I/I_{KTA})$	
56	$KTi_{0.5}V_{0.5}OPO_4$	$0.0008 (I/I_{KTP})$	[22]
57	$KTi_{0.75}V_{0.25}OPO_4$	$0.05 (I/I_{KTP})$	[5]
58	$KTi_{0.85}V_{0.15}OPO_4$	$0.1 (I/I_{KTP})$	
59	$KTi_{0.95}V_{0.05}OPO_4$	$0.13 (I/I_{KTP})$	[22]
60	$KTi_{0.9975}V_{0.0025}OPO_4$	$1 (I/I_{KTP})$	
61	$K_{0.67}Ti_{0.5}V_{0.5}OPO_4$	$0.20 (I/I_{KTP})$	[5]
62	$K_{0.75}Ti_{0.75}V_{0.25}OPO_4$	$0.24 (I/I_{KTP})$	
63	$K_{0.85}Ti_{0.85}V_{0.15}OPO_4$	$0.36 (I/I_{KTP})$	
64	$K_{0.5}Ti_{0.5}Nb_{0.5}OPO_4$	$0.9 (I/I_{KTP})$	[23]
65	$K_{0.5}Ta_{0.5}Ti_{0.5}OPO_4$	$0.8 (I/I_{KTP})$	
66	$KGa_{0.5}Nb_{0.5}OPO_4$	$1 (I/I_{SiO_2})$	[3]
67	$KFe_{0.5}Nb_{0.5}OPO_4$	$2.7 (I/I_{SiO_2})$	
68	$K_{0.5}Nb_{0.5}V_{0.5}OPO_4$	$0.5 (I/I_{KTP})$	[23]
69	$K_{0.5}Ta_{0.5}V_{0.5}OPO_4$	$0.4 (I/I_{KTP})$	
70	$KTiO(PO_4)_{0.5}(AsO_4)_{0.5}$	$6000 (I/I_{SiO_2})$	[3]
71	$K_{0.97}Ti_{0.99}OAs_{0.53}P_{0.49}O_4$	$1.6 (I/I_{KTA})$	[21]
72	$KTi_{0.9}Nb_{0.1}OP_{0.9}Si_{0.1}O_4$	$1.05 (I/I_{KTP})$	[15]
73	$KTi_{0.8}Nb_{0.2}OP_{0.8}Si_{0.2}O_4$	$0.96 (I/I_{KTP})$	
74	$KTi_{0.7}Nb_{0.3}OP_{0.7}Si_{0.3}O_4$	$0.84 (I/I_{KTP})$	
75	$KTi_{0.65}Nb_{0.35}OP_{0.65}Si_{0.35}O_4$	$0.81 (I/I_{KTP})$	
76	$KTi_{0.6}Nb_{0.4}OP_{0.6}Si_{0.4}O_4$	$0.72 (I/I_{KTP})$	
77	$K_2GaGeP_2O_9(F, OH)$	$10 (I/I_{SiO_2})$	[5]
78	$KTi_{0.5}Ga_{0.5}O_{0.5}PO_4F_{0.35}(OH)_{0.15}$	$200 (I/I_{SiO_2})$	[3]
79	$KGaPO_4F_{0.7}(OH)_{0.3}$	$0.72 (I/I_{SiO_2})$	[3, 5]
80	$RbTi_{0.98}Nb_{0.02}OPO_4$	$0.97 (I/I_{KTP})$	[10]
81	$RbTi_{0.96}Nb_{0.04}OPO_4$	$1.23 (I/I_{KTP})$	
82	$RbTi_{0.93}Nb_{0.07}OPO_4$	$0.73 (I/I_{KTP})$	
83	$Rb_{0.855}Ti_{0.955}Nb_{0.045}OPO_4$	$1.2 (I/I_{KTP})$	[11]
84	$RbTi_{0.927}Nb_{0.056}Er_{0.017}OPO_4$	$0.7 (I/I_{KTP})$	
85	$Rb_{0.855}Ti_{0.95}Ta_{0.04}OPO_4$	$0.95 (I/I_{KTP})$	[24]
86	$RbTi_{0.95}Ta_{0.03}Y_{0.02}OPO_4$	$0.80 (I/I_{KTP})$	
87	$RbGa_{0.5}Nb_{0.5}OPO_4$	$1 (I/I_{SiO_2})$	[3]
88	$(NH_4)_{0.5}H_{0.5}TiOPO_4^{**}$	$60 (I/I_{SiO_2})$	[5]
		$40 (I/I_{SiO_2})$	[12]

Continued

89	$(\text{NH}_4)_{0.5}(\text{H}_3\text{O})_{0.5}\text{TiOPO}_4$	700 ( $I/I_{\text{SiO}_2}$ )	[3,5]
		650 ( $I/I_{\text{SiO}_2}$ )	[5,12]
90	$\text{Cs}_{0.5}\text{K}_{0.5}\text{TiOAsO}_4$	6700 ( $I/I_{\text{SiO}_2}$ )	[3]
91	$\text{Na}_{0.87}\text{K}_{0.13}\text{TiOAsO}_4$	790 ( $I/I_{\text{SiO}_2}$ )	[5,6]
		0.87 ( $I/I_{\text{KTP}}$ ) <sup>***</sup>	[14]
92	$\text{Na}_{0.98}\text{K}_{0.02}\text{TiOAsO}_4$	0.01 ( $I/I_{\text{KTP}}$ )	
93	$\text{K}_{0.54}\text{Li}_{0.46}\text{TiOAsO}_4$	970 ( $I/I_{\text{SiO}_2}$ )	[6]
		1.07 ( $I/I_{\text{KTP}}$ ) <sup>***</sup>	[14]
94	$\text{Ag}_{0.98}\text{K}_{0.02}\text{TiOAsO}_4$	10 ( $I/I_{\text{SiO}_2}$ )	[6]
95	$(\text{NH}_4)_{0.5}\text{K}_{0.5}\text{TiOAsO}_4$	100 ( $I/I_{\text{SiO}_2}$ )	[3]
96	Sc: KTA (0.22 % dopant)	$d_{24} (1.32 \mu\text{m}) = 1.4 \times d_{15}(\text{KTP})$	[16]
97	$\text{K}_{0.80}\text{Ti}_{0.26}\text{Zr}_{0.78}\text{OAs}_{1.01}\text{O}_4$	1.2 ( $I/I_{\text{KTA}}$ )	[21]
98	$\text{KTi}_{0.9}\text{Nb}_{0.1}\text{OAs}_{0.9}\text{Si}_{0.1}\text{O}_4$	1.04 ( $I/I_{\text{KTP}}$ )	[15]
99	$\text{KTi}_{0.8}\text{Nb}_{0.2}\text{OAs}_{0.8}\text{Si}_{0.2}\text{O}_4$	1.03 ( $I/I_{\text{KTP}}$ )	
100	$\text{KTi}_{0.7}\text{Nb}_{0.3}\text{OAs}_{0.7}\text{Si}_{0.3}\text{O}_4$	0.98 ( $I/I_{\text{KTP}}$ )	
101	$\text{KTi}_{0.6}\text{Nb}_{0.4}\text{OAs}_{0.6}\text{Si}_{0.4}\text{O}_4$	0.90 ( $I/I_{\text{KTP}}$ )	
102	$\text{K}_{0.94}\text{Nb}_{0.12}\text{Ti}_{0.91}\text{OAs}_{0.89}\text{Ge}_{0.09}\text{O}_4$	1.3 ( $I/I_{\text{KTA}}$ )	[21]
103	$\text{K}_{1.02}\text{Nb}_{0.25}\text{Ti}_{0.76}\text{OAs}_{0.75}\text{Ge}_{0.23}\text{O}_4$	1.1 ( $I/I_{\text{KTA}}$ )	
104	$\text{K}_{1.03}\text{Nb}_{0.52}\text{Ti}_{0.48}\text{OAs}_{0.48}\text{Ge}_{0.51}\text{O}_4$	1.1 ( $I/I_{\text{KTA}}$ )	
105	$\text{KNb}_{0.52}\text{Ti}_{0.48}\text{OAs}_{0.48}\text{Ge}_{0.51}\text{O}_4$	1.3 ( $I/I_{\text{KTA}}$ )	
106	$\text{K}_{0.98}\text{Nb}_{0.46}\text{Ti}_{0.56}\text{OAs}_{0.58}\text{Ge}_{0.39}\text{O}_4$	1.2 ( $I/I_{\text{KTA}}$ )	
107	$\text{KGa}_{0.5}\text{Nb}_{0.5}\text{OAsO}_4$	1 ( $I/I_{\text{SiO}_2}$ )	[3]
108	$\text{RbGa}_{0.5}\text{Nb}_{0.5}\text{OAsO}_4$	5.5 ( $I/I_{\text{SiO}_2}$ )	

\*A value of 1100 was indicated in [3], with reference to [5], where a value of 2400 was reported. \*\*A value of 140 was indicated in [25], with reference to [12], where a value of 40 was reported, and a value of 6 was indicated in [3], with reference to [5], where the corresponding value was found to be 60. \*\*\*Values of second-harmonic generation intensity for  $\text{KTiOPO}_4$  crystal were reported in [14] with reference to [6], where the corresponding values were given for quartz crystal. The values of [14] correspond to those of [6], when divided by  $I/I_{\text{SiO}_2}$  value for  $\text{KTiOPO}_4$  crystal (also taken from [6]).



**Figure 2.** Cut of three-dimensional distribution maps of the degree of pseudoinversion of crystal structure by the plane  $z = 0.25$ : (a)  $\text{KTiOPO}_4$  (CSD-No 20970); (b)  $\text{KSnOPO}_4$  (CSD-No 68706); (c)  $\text{KTiOAsO}_4$  (CSD-No 202158); and (d)  $\text{Cs}_{0.625}\text{K}_{0.375}\text{TiOAsO}_4$  (CSD-No 74595).

added inversion to the set of symmetry operations of the space group  $Pna2_1$ , which describes the structure of KTP crystals at room temperature, we obtain the group  $Pnan$ , where the inversion centre with respect to the twofold screw axis has coordinates (0.25, 0.25).

Thus, in the polar phase of KTP structures, the pseudoinversion peaks are located specifically at inversion centres of these crystals in their high-symmetry nonpolar phase. With allowance for this circumstance, we will characterize the pseudosymmetry of the electron density in each crystal with a known structure by the maximum value of pseudoinversion  $\eta_{\max}$  in the three-dimensional map, and the point with the coordinates corresponding to the found  $\eta_{\max}$  values will be referred to as pseudoinversion centres.

Since the origin of coordinates is arbitrarily chosen in X-ray diffraction analysis, the coordinates of the pseudoinversion centres may differ from 0.25. In the  $Pna2_1$  group [55], the origin of coordinates on the  $z$  axis can be chosen at any point, while in the directions of the  $x$  and  $y$  axes it may lie either on the twofold axis or at the intersection of mirror planes; therefore, the  $x$  and  $y$  coordinates of pseudoinversion centres can be either (0.25, 0.25) or (0, 0).

To refine the coordinates of pseudoinversion centres and  $\eta_{\max}$  values, we additionally calculated the distribution of the degree of pseudoinversion with a relative scanning step of 0.025 over the unit cell axes. Fixed refined  $x$  and  $y$  coordinates of pseudoinversion centres were used for repeated calculation of pseudoinversion distribution along the  $z$  axis with a relative scanning step of 0.001.

**Table 2** contains the maximum pseudoinversion values  $\eta_{\max}$  and coordinates of pseudoinversion centres  $z(\eta_{\max})$  for a number of KTP structures.

**Figures 3(a)** and **3(b)** show the distribution histograms for the degree of pseudoinversion  $\eta_{\max}$  for pure and doped KTP crystals.

The distribution of pure KTP crystals over pseudoinversion is fairly uniform. As is indicated in **Table 2**, the mean value  $\langle \eta_{\max} \rangle$  for them is 0.606. The situation for doped crystals is different: the pronounced maximum in the histogram in **Figure 3(b)**, which amounts to 31%, lies in the range of pseudoinversion values of 0.4 - 0.5, which is followed by a sharp falloff. Therefore, the fraction of pseudo-centrosymmetric structures among doped KTP crystals is very small. The mean value  $\langle \eta_{\max} \rangle$  for doped crystals is 0.490. Thus, doped KTP crystals are "less symmetric" with respect to inversion than pure compositions.

For the crystals listed in **Table 2**, along with the calculations of the pseudoinversion of their structures as a whole, pseudoinversion extrema for sublattices of individual types of atoms ( $\eta_{\max}(\text{sublattices})$ ) were also cal-

culated. Pseudoinversion was calculated for the pure sublattices of all 118 crystals in **Table 2**; the distribution histogram of the corresponding extrema is shown in **Figure 3(c)**. For 89 doped crystals in **Table 2**, the results of similar calculations for  $M$ - and  $M'$ -type sublattices containing doped atoms are presented as histograms in **Figure 3(d)**. The histograms in **Figure 3(c)** indicate that the sublattices of  $X$ ,  $O$ , and  $F$  atoms are most pseudo-centrosymmetric, sublattices of  $M$ -type atoms are least pseudo-centrosymmetric, and the pseudoinversion of the  $M'$  sublattice is intermediate ( $\langle \eta_{\max}(X) \rangle \geq 0.857$ ,  $\langle \eta_{\max}(O) \rangle \geq 0.720$ ,  $\langle \eta_{\max}(F) \rangle \geq 0.870$ ,  $\langle \eta_{\max}(M) \rangle \geq 0.395$ ,  $\langle \eta_{\max}(M') \rangle \geq 0.661$ ).

In the presence of impurities, the general view of the histogram for the  $M'$  sublattice (**Figure 3(d)**) barely differs from that in **Figure 3(c)**; its characteristic maximum shifts to higher pseudoinversion values and the mean value  $\langle \eta_{\max}(M') \rangle$  becomes 0.700.

The pseudoinversion histogram for the  $M$ -type sublattice changes more radically: the pronounced peak in the range of 0.3 - 0.4 in **Figure 3(c)** disappears in **Figure 3(d)**, and the distribution becomes more uniform in a wider pseudoinversion range; the fraction of crystals with ultimately acentric  $M$  sublattices increases. The mean pseudo inversion  $\langle \eta_{\max}(M) \rangle$  becomes 0.384; *i.e.*, it barely changes in comparison with  $\langle \eta_{\max}(M) \rangle$  for  $M$  sublattices without impurities. Thus, the analysis of the pseudo inversion of individual sublattices suggests that the reductions of pseudoinversion of structures as a whole at a transition to doped KTP compositions, which is noted in **Table 2** and **Figure 3(b)**, is related to a great extent to the higher sensitivity of the pseudoinversion of  $M$ -type sublattice to the presence of doped atoms. Note that pseudosymmetry was previously studied [58] by the atomic displacement method [1] for 11 KTP-type structures. In particular, it was established that the potassium sublattice is less centrosymmetric in comparison with the  $\text{TiO}_6\text{-PO}_4$  subsystem, and its pseudosymmetry relative to inversion is more sensitive to introduction of impurities.

#### 4. Comparison of the Nonlinear Optical Characteristics of KTP Crystals and the Pseudoinversion of Their Structures

A model was proposed in [8], according to which the second-order susceptibility of crystals is related to the symmetry of KTP-type structures and their pseudoinversion as follows:

$$\chi_{2\omega} \sim \sqrt{1 - \eta} \quad (2)$$

As can be seen in **Table 1**, the SHG data with respect to the reference sample (powder of pure  $\text{SiO}_2$  crystal) differ by an order of magnitude in different studies for KTP [3,5-7], and KTA [3,6,7] crystals. Based on this fact, we illustrated Equation (2) by selecting a group of com-

**Table 2. Maximum pseudoinversion values  $\eta_{\max}$  and  $z$  coordinates of pseudoinversion centres  $z(\eta_{\max})$  for a number of KTP structures.**

№	Crystal	CSD-№ [56]	$\eta_{\max} \pm 0.005$	$z(\eta_{\max})$
1	KTiOPO <sub>4</sub>	20970	0.363	0.254
2	RbTiOPO <sub>4</sub>	281379	0.350	0.451
3	TiTiOPO <sub>4</sub>	81436	0.534	0.205
4	KSnOPO <sub>4</sub>	68706	0.886	0.250
5	KGeOPO <sub>4</sub>	39735	0.812	0.251
6	KVOPO <sub>4</sub>	79651	0.314	0.254
7	KTiOAsO <sub>4</sub>	202158	0.375	0.258
8	RbTiOAsO <sub>4</sub>	71907	0.276	0.243
9	CsTiOAsO <sub>4</sub>	280315	0.539	0.252
10	KSnOAsO <sub>4</sub>	80976	0.846	0.247
11	RbSnOAsO <sub>4</sub>	80977	0.714	0.234
12	KSbOSiO <sub>4</sub>	69429	0.884	0.250
13	NaSbOSiO <sub>4</sub>	66354	0.474	0.250
14	KSbOGeO <sub>4</sub>	39463	0.634	0.252
15	RbSbOGeO <sub>4</sub>	71933	0.557	0.248
16	NaSbOGeO <sub>4</sub>	39788	0.408	0.251
17	TiSbOGeO <sub>4</sub>	84128	0.449	0.252
18	KTaOGeO <sub>4</sub>	39585	0.686	0.250
19	AgSbOSiO <sub>4</sub>	39789	0.644	0.250
20	BiCdOVO <sub>4</sub>	91474	0.580	0.133
21	KFeFPO <sub>4</sub>	39560	0.702	0.250
22	NH <sub>4</sub> FeAsO <sub>4</sub> F	170672	0.880	0.208
23	NH <sub>4</sub> FePO <sub>4</sub> F	75110	0.826	0.251
24	NH <sub>4</sub> GaPO <sub>4</sub> F	89953	0.920	0.251
25	CsScFAsO <sub>4</sub>	87817	0.355	0.309
26	KAlFPO <sub>4</sub>	39445	0.612	0.250
27	KCrPO <sub>4</sub> F	39440	0.687	0.498
28	KGaFPO <sub>4</sub>	80893	0.771	0.264
29	RbScFAsO <sub>4</sub>	87816	0.485	0.233
30	Ag <sub>0.85</sub> K <sub>0.15</sub> TiOPO <sub>4</sub>	67540	0.442	0.053
31	Ba <sub>0.06</sub> K <sub>0.88</sub> TiOPO <sub>4</sub>	280413	0.426	0.254
32	K <sub>0.981</sub> Cr <sub>0.019</sub> TiOPO <sub>4</sub>	98245	0.410	0.245
33	K <sub>0.565</sub> Li <sub>0.34</sub> TiOPO <sub>4</sub> *	83482	0.755	0.259
34	Na <sub>0.95</sub> K <sub>0.05</sub> TiOPO <sub>4</sub>	67539	0.371	0.260
35	K <sub>0.845</sub> Na <sub>0.155</sub> TiOPO <sub>4</sub>	85092	0.406	0.254
36	Na <sub>0.114</sub> K <sub>0.886</sub> K(TiO) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub>	281363	0.400	0.246
37	Na <sub>0.48</sub> K <sub>0.52</sub> TiOPO <sub>4</sub>	71239	0.378	0.255
38	K <sub>0.42</sub> Na <sub>0.58</sub> TiOPO <sub>4</sub>	71928	0.407	0.265
39	K <sub>0.433</sub> Na <sub>0.567</sub> TiOPO <sub>4</sub>	71929	0.406	0.252
40	Na <sub>0.992</sub> K <sub>0.008</sub> TiOPO <sub>4</sub>	59284	0.377	0.251
41	K <sub>0.5</sub> Rb <sub>0.5</sub> TiOPO <sub>4</sub>	71243	0.363	0.325
42	K <sub>0.84</sub> Rb <sub>0.16</sub> TiOPO <sub>4</sub>	81251	0.378	0.244
43	K <sub>0.88</sub> Rb <sub>0.12</sub> TiOPO <sub>4</sub>	88030	0.377	0.255
44	K <sub>1.14</sub> Rb <sub>0.86</sub> TiOPO <sub>4</sub>	400849	0.271	0.257
45	K <sub>0.535</sub> Rb <sub>0.465</sub> TiOPO <sub>4</sub>	71905	0.270	0.246
46	K <sub>0.857</sub> Rb <sub>0.143</sub> TiOPO <sub>4</sub>	81250	0.365	0.245
47	Sr <sub>0.06</sub> Cr <sub>0.05</sub> K <sub>0.87</sub> Ti <sub>0.95</sub> OPO <sub>4</sub>	280412	0.514	0.248



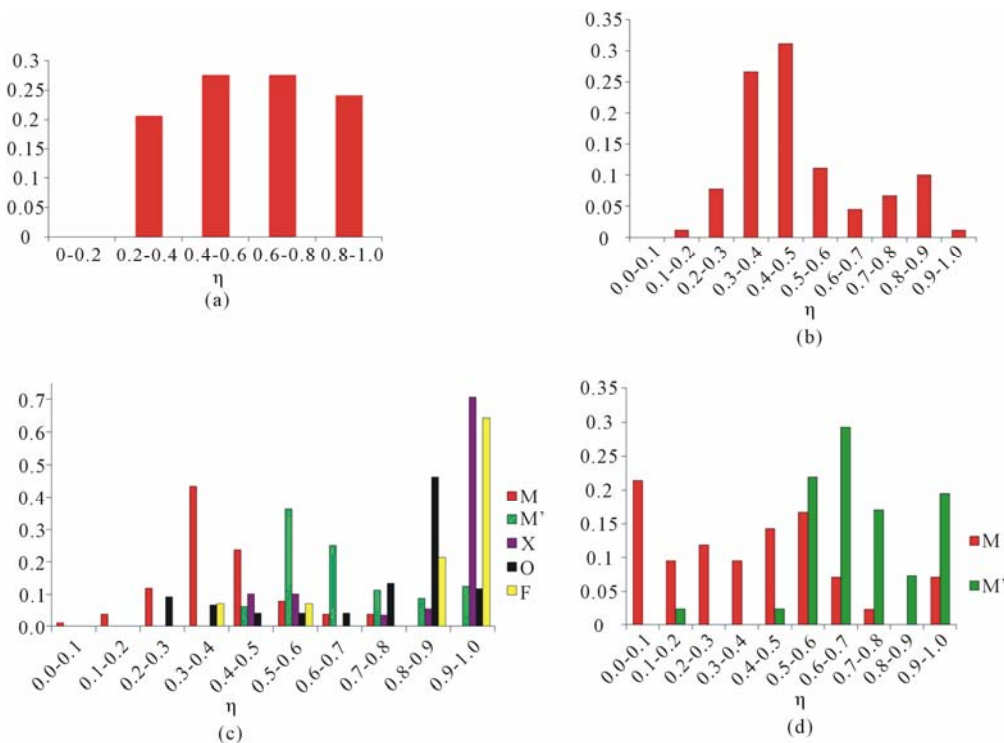
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48	$K_{0.59}Ti_{0.41}TiOPO_4$	39777	0.190	0.199
49	$K_{0.812}Ti_{0.188}TiOPO_4$	85099	0.217	0.255
50	$KGe_{0.042}Ti_{0.958}OPO_4$	39950	0.439	0.254
51	$KGe_{0.063}Ti_{0.937}OPO_4$	39882	0.467	0.253
52	$KGe_{0.184}Ti_{0.816}OPO_4$	39951	0.568	0.252
53	$K_{0.84}Ti_{0.92}Nb_{0.08}OPO_4$	67120	0.546	0.254
54	$K_{0.89}Nb_{0.11}Ti_{0.89}OPO_4$	250046	0.822	0.252
55	$K_{0.93}Nb_{0.07}Ti_{0.93}OPO_4$	250016	0.593	0.252
56	$K_{0.96}Nb_{0.04}Ti_{0.96}OPO_4$	91556	0.480	0.253
57	$K_{0.97}Nb_{0.03}Ti_{0.97}OPO_4$	54149	0.439	0.253
58	$K_{0.99}Ti_{0.988}Sb_{0.0125}OPO_4^*$	250298	0.430	0.254
59	$K_{0.874}Ti_{0.927}Sb_{0.074}OPO_4^*$	250299	0.587	0.254
60	$K_{0.893}Ti_{0.833}Sb_{0.166}OPO_4^*$	250300	0.956	0.250
61	$KSn_{0.53}Ti_{0.47}OPO_4$	250087	0.705	0.249
62	$KSn_{0.064}Ti_{0.934}OPO_4$	91534	0.461	0.253
63	$KSn_{0.75}Ti_{0.25}OPO_4$	250088	0.840	0.250
64	$KSn_{0.504}Ti_{0.496}OPO_4$	72720	0.769	0.241
65	$K_{0.998}Ti_{0.998}W_{0.002}OPO_4$	82601	0.394	0.254
66	$KTi_{0.99}Zr_{0.01}OPO_4$	418713	0.408	0.068
67	$KTi_{0.975}Zr_{0.025}OPO_4$	418715	0.415	0.068
68	$KTi_{0.981}Zr_{0.019}OPO_4$	418714	0.425	0.068
69	$KTi_{0.97}Zr_{0.03}OPO_4$	173235	0.404	0.254
70	$KTi_{0.96}Zr_{0.04}OPO_4$	173233	0.414	0.254
71	$KTi_{0.88}Hf_{0.12}OPO_4$	421394	0.473	0.001
72	$KTi_{0.97}Hf_{0.03}OPO_4$	421393	0.432	0.253
73	$KTi_{0.99}Hf_{0.01}OPO_4$	421392	0.410	0.254
74	$KTiOP_{0.5}As_{0.5}O_4$	72051	0.585	0.255
75	$KTiOP_{0.38}As_{0.62}O_4$	80024	0.546	0.259
76	$KTiOP_{0.56}As_{0.44}O_4$	80023	0.473	0.259
77	$KTiOP_{0.58}As_{0.42}O_4$	71904	0.485	0.242
78	$KTiOP_{0.75}As_{0.25}O_4$	80022	0.440	0.257
79	$KTiOP_{0.57}As_{0.43}O_4$	400850	0.520	0.261
80	$K_{0.5}Na_{0.5}Sn_{0.5}Ti_{0.5}OPO_4$	67585	0.695	0.269
81	$K_{0.5}Rb_{0.5}Sn_{0.5}Ti_{0.5}OPO_4$	67587	0.648	0.257
82	$K_2(Cr_{0.63}Ti_{0.37})(Cr_{0.43}Ti_{0.57})(PO_4)_2(F_{0.65}O_{0.35})(F_{0.41}O_{0.59})$	87835	0.776	0.257
83	$Na_{0.505}Rb_{0.495}TiOPO_4$	71240	0.505	0.325
84	$Tl_{0.23}Rb_{0.77}TiOPO_4$	81438	0.362	0.201
85	$Rb_{0.766}Tl_{0.234}TiOPO_4$	85100	0.363	0.201
86	$RbTi_{0.927}Nb_{0.056}Er_{0.017}OPO_4$	96408	0.335	0.015
87	$Rb_{0.98}Ti_{0.99}Nb_{0.01}OPO_4$	250274	0.303	0.198
88	$Rb_{0.855}Ti_{0.955}Nb_{0.045}OPO_4$	[11]	0.261	0.197
89	$RbTi_{0.97}Zr_{0.03}OPO_4$	417985	0.311	0.200
90	$RbTi_{0.98}Zr_{0.02}OPO_4$	418599	0.254	0.197
91	$RbTi_{0.98}Zr_{0.016}OPO_4$	418598	0.317	0.201
92	$Rb_2TiGe_{0.121}Ti_{0.879}O_2(PO_4)_2$	281380	0.342	0.198
93	$Na_{0.5}Rb_{0.5}Sn_{0.5}Ti_{0.5}OPO_4$	67586	0.452	0.495
94	$KNb_{0.5}V_{0.5}OPO_4$	86787	0.730	0.250
95	$KGa_{0.5}Ge_{0.5}F_{0.5}O_{0.5}PO_4$	80894	0.881	0.262
96	$K_{0.5}Rb_{0.5}SnOPO_4$	67584	0.638	0.253
97	$Cs_{0.6}K_{0.4}TiOAsO_4$	74597	0.389	0.263

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98	$\text{Cs}_{0.61}\text{K}_{0.39}\text{TiOAsO}_4$	74596	0.464	0.151
99	$\text{Cs}_{0.595}\text{K}_{0.405}\text{TiOAsO}_4$	74598	0.638	0.253
100	$\text{Cs}_{0.625}\text{K}_{0.375}\text{TiOAsO}_4$	74595	0.265	0.239
<b>101</b>	$\text{K}_{0.534}\text{Li}_{0.34}\text{TiOAsO}_4$ *	83483	0.385	0.263
<b>102</b>	$\text{Na}_{0.87}\text{K}_{0.13}\text{TiOAsO}_4$	67541	0.436	0.259
103	$\text{K}_{1.65}\text{V}(\text{V}_{0.78}\text{W}_{0.22})\text{O}_2(\text{AsO}_4)_2$	260558	0.807	0.253
104	$\text{KAlNbO}_2((\text{As}_{0.8}\text{Nb}_{0.2})\text{O}_4)_2$	[57]	0.881	0.251
105	$\text{Cs}_{0.068}\text{Rb}_{0.95}\text{TiOAsO}_4$	280501	0.376	0.243
106	$\text{Cs}_{0.62}\text{Rb}_{1.38}\text{TiO}_2(\text{AsO}_4)_2$	280502	0.331	0.255
107	$\text{Cs}_{1.12}\text{Rb}_{0.85}(\text{TiO})_2(\text{AsO}_4)_2$	280503	0.286	0.252
108	$\text{Cs}_{1.43}\text{Rb}_{0.57}(\text{TiO})_2(\text{AsO}_4)_2$	280504	0.372	0.344
109	$\text{Cs}_{1.73}\text{Rb}_{0.27}(\text{TiO})_2(\text{AsO}_4)_2$	280505	0.371	0.345
110	$\text{Cs}_{1.4}\text{Rb}_{0.6}(\text{TiO})_2(\text{AsO}_4)_2$	280506	0.369	0.159
111	$\text{Cs}_{1.72}\text{Rb}_{0.28}(\text{TiO})_2(\text{AsO}_4)_2$	280507	0.373	0.340
112	$\text{Cs}_{0.9}\text{Rb}_{0.1}\text{TiOAsO}_4$	280508	0.330	0.109
113	$\text{NH}_4\text{Fe}(\text{AsO}_4)_{0.19}(\text{PO}_4)_{0.81}\text{F}$	420019	0.877	0.208
114	$\text{NH}_4\text{Fe}(\text{AsO}_4)_{0.37}(\text{PO}_4)_{0.63}\text{F}$	420020	0.865	0.207
115	$\text{NH}_4\text{Fe}(\text{AsO}_4)_{0.74}(\text{PO}_4)_{0.26}\text{F}$	420021	0.898	0.207
116	$\text{NH}_4\text{VAsO}_4\text{F}_{0.8}\text{O}_{0.2}$	419640	0.852	0.207
117	$(\text{NH}_4)_2\text{Ga}_2(\text{PO}_4)(\text{HPO}_4)\text{F}_3$	89952	0.429	0.418
118	$(\text{NH}_4)_{0.875}\text{K}_{0.125}\text{FePO}_4\text{F}$	260152	0.772	0.167
Mean value $\langle \eta_{\max} \rangle$ for pure crystals (29 structures)				0.606
Mean value $\langle \eta_{\max} \rangle$ for doped crystals (89 structures)				0.490

For crystals with numbers 2, 13, 16, 20, 25, 30, 34, 40, 41, 71, 83, 86, 92, 93, 98, 101, 102, 108-112, and 117, the (x, y) coordinates of pseudo-inversion centres are (0, 0); for other crystals they are (0.25, 0.25). The numbers of crystals with known estimated characteristics of nonlinear optical properties are bolded. \*The chemical composition of the crystals is given in correspondence with the CIF files indicated here; it somewhat differs from the corresponding chemical formulas in **Table 1**, which are given in correspondence with the references to original studies.



**Figure 3.** Distribution histogram of the degree of pseudo-inversion for (a) pure KTP crystals (29 structures), (b) doped KTP crystals (89 structures), (c) pure atomic sublattices of individual types for 118 KTP crystals from Table 2, and (d) doped sublattices of individual types of atoms for 89 KTP crystals from Table 2.

positions (from the aforementioned set of crystals) for which experimental SHG data were obtained either by the powder method [26], or directly with respect to a powder of pure  $\text{KTiOPO}_4$  crystal, or the data can be recalculated with respect to it based on a specific publication. In addition, since most sources yield data on the ratio of second-harmonic intensities for the studied and reference samples ( $I/I_{\text{KTP}} = I_{2\omega}/I_{2\omega}(\text{KTP})$ ), they were additionally recalculated into estimated values of the relative effective second-order susceptibility (it will be denoted as  $\chi_{2\omega}/\chi_{2\omega}(\text{KTP})$ ). In the first approximation, one can assume that

$$I_{2\omega} \sim I_{\omega}^2 \cdot \chi_{2\omega}^2,$$

where  $I_{2\omega}$  is the second harmonic intensity and  $I_{\omega}$  is the primary radiation intensity. Therefore, the desired ratio  $\chi_{2\omega}/\chi_{2\omega}(\text{KTP})$  was estimated to be

$$\chi_{2\omega}/\chi_{2\omega}(\text{KTP}) \sim I_{2\omega}/I_{2\omega}(\text{KTP}).$$

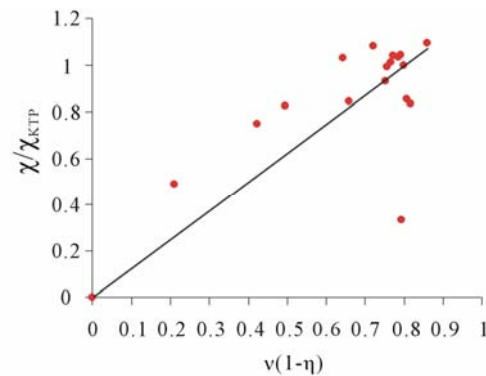
**Figure 4** shows the dependence of the set of  $\chi_{2\omega}/\chi_{2\omega}(\text{KTP})$  values for  $\text{KTiOPO}_4$  (CSD-№ 20970),  $\text{RbTiOPO}_4$  (CSD-№ 281379, [10, 11]),  $\text{KTiOAsO}_4$  (CSD-№ 202158, [14, 15]),  $\text{K}_{0.565}\text{Li}_{0.34}\text{TiOPO}_4$  (CSD-№ 83482, [14]),  $\text{RbTi}_{0.927}\text{Nb}_{0.056}\text{Er}_{0.017}\text{OPO}_4$  (CSD-№ 96408, [11]),  $\text{Rb}_{0.855}\text{Ti}_{0.955}\text{Nb}_{0.045}\text{OPO}_4$  ([11]),  $\text{K}_{0.534}\text{Li}_{0.34}\text{TiOAsO}_4$  (CSD-№ 83483, [14]),  $\text{Na}_{0.87}\text{K}_{0.13}\text{TiOAsO}_4$  (CSD-№ 67541, [14]),  $\text{K}_{0.89}\text{Nb}_{0.11}\text{Ti}_{0.89}\text{OPO}_4$  (CSD-№ 250046, [8]),  $\text{K}_{0.96}\text{Nb}_{0.04}\text{Ti}_{0.96}\text{OPO}_4$  (CSD-№ 91556, [8]),  $\text{K}_{0.99}\text{Ti}_{0.988}\text{Sb}_{0.0125}\text{OPO}_4$  (CSD-№ 250298, [8]),  $\text{K}_{0.874}\text{Ti}_{0.927}\text{Sb}_{0.074}\text{OPO}_4$  (CSD-№ 250299, [8]),  $\text{K}_{0.893}\text{Ti}_{0.833}\text{Sb}_{0.166}\text{OPO}_4$  (CSD-№ 250300, [8]),  $\text{KTi}_{0.97}\text{Zr}_{0.03}\text{OPO}_4$  (CSD-№ 173235, [8]), and  $\text{KTi}_{0.96}\text{Zr}_{0.04}\text{OPO}_4$  (CSD-№ 173233, [8]) crystals on the pseudoinversion  $\eta = \eta_{\text{max}}$  of their atomic structures in the

$$\left(\sqrt{1-\eta}, \chi_{2\omega}/\chi_{2\omega}(\text{KTP})\right)$$

coordinates. The linear approximation of the dependence presented in **Figure 4** within the model described in [8], is characterized by a correlation coefficient of 0.91, and the confidence interval boundaries are (0.76, 0.97) at a confidence probability of 0.95.

Equation (2) can be more pronounced within the concentration series of samples of the same qualitative composition. For example, the SHG intensity decreases with an increase in the tin fraction in the  $\text{KTi}_{1-x}\text{Sn}_x\text{OPO}_4$  series, and the calculation of pseudoinversion for a series of known structures of this composition indicates a monotonic increase in the latter (**Figure 5**).

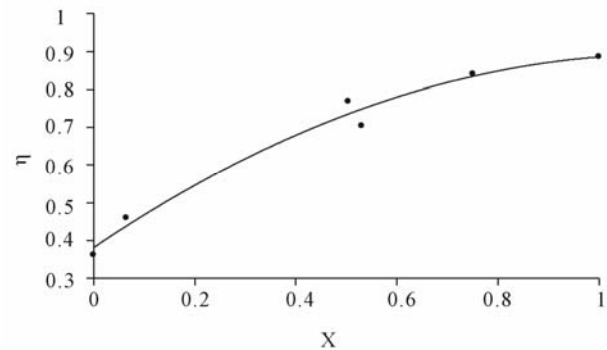
The boundary-composition crystal  $\text{KSnOPO}_4$  has almost zero SHG intensity and the largest (in the  $\text{KTi}_{1-x}\text{Sn}_x\text{OPO}_4$  series) pseudoinversion: 0.886 (**Table 1**, no. 7; **Table 2**, no. 4). This fact is in agreement with the



**Figure 4.** Correlation between the relative effective second-order susceptibility  $\chi_{2\omega}/\chi_{2\omega}(\text{KTP})$  for a number of KTP crystals and their pseudoinversion in the

$$\left(\sqrt{1-\eta}, \chi_{2\omega}/\chi_{2\omega}(\text{KTP})\right)$$

coordinates (see [8] for the approximation model).



**Figure 5.** Dependence of the pseudoinversion on the tin content in  $\text{KTi}_{1-x}\text{Sn}_x\text{OPO}_4$  crystals (calculation based on the structural data CSD-№ 20970, 91534, 72720, 250087, 250088, 68706).

data of Godfrey *et al.* [58], who established that the  $\text{KSnOPO}_4$  structure can be partially described (in good approximation) by the  $Pnan$  group; exact description is obtained within the  $Pna2_1$  group.

## 5. Conclusions

To date, despite the numerous publications on the structure and properties of KTP crystals, the question of the structural conditionality of the behavior of their nonlinear optical properties has not been completely clarified.

In this paper, we reported the results of studying the pseudosymmetric features of known structures of KTP crystals with respect to inversion and tried to analyze the entire set of known nonlinear optical parameters of these crystals in view of the obtained pseudosymmetric characteristics. In particular, it was shown that doped structures of KTP crystals have on average a lower degree of pseudoinversion than “pure” compositions; in some cases this feature adequately correlates with the increase in the

relative intensity of the second optical harmonic. This correlation may manifest itself within the concentration series samples of the same qualitative composition.

We believe that, in order to establish the fundamental correlations between the structural and symmetric features of crystals (in particular, those belonging to the KTP family) and their nonlinear optical properties, for example, having the degree of pseudoinversion as a symmetric characteristic, it is necessary to primarily calculate this characteristic for the entire structure. This thesis is justified by the fundamental principles of symmetry in physical crystallography. The Neumann principle, which sets a relationship between the symmetry of a medium (crystal) and the set of physical properties that are forbidden or allowed in this medium, deals with specifically the symmetry of the medium as a whole rather than the symmetry of its individual structural fragments within the unit cell. This approach was applied both in [8] and in this study. However, this does not depreciate the validity of the analysis of the characteristics of sublattices of individual types of atoms. Due to this analysis one can find sublattices with pseudosymmetric characteristics exhibiting a more significant sensitivity, for example, at a transition to doped compositions, and therefore, can determine to greater extent the behavior of the pseudosymmetric characteristics of crystal structures, as whole and physical properties of crystals.

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