Nonlinear optical properties of undoped and doped with Zr and Nb KTiOPO$_4$ crystals

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The structure of the ferroelectric phase of undoped KTiOPO$_4$ and its solid solutions with zirconium and niobium is studied from first principles within the density functional theory. The second-order nonlinear susceptibility tensor and the spontaneous polarization of these materials are obtained. It is shown that an improvement in nonlinear optical properties of KTiOPO$_4$ upon its doping with Zr and Nb cannot be explained by a systematic change in the composition of crystals and is apparently associated with the occurrence of defects. Possible structures of such defects are discussed.

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High nonlinear optical properties of ferroelectrics are widely used in different optical devices, such as parametric amplifiers, frequency mixers and multipliers. Among the materials for nonlinear optics, ferroelectric potassium titanyl phosphate KTiOPO$_4$ (KTP) holds a special place. This material is characterized by high optical nonlinearity and optical damage resistance, weak absorption in the visible and IR spectral regions, and good mechanical properties. The search for ways to improve KTP performance shows that doping it with zirconium and niobium results in considerable enhancement of its nonlinear optical properties. However, the mechanism of the doping effect on these properties remains unclear. In this work, to understand if the improvement in the nonlinear optical properties of KTP is a consequence of systematic changes in the crystal composition, we performed the first-principles calculations of the structure of the ferroelectric phase for undoped KTP and its solid solutions with zirconium and niobium and studied the changes that occur in the second-order nonlinear susceptibility tensor upon doping these crystals.

Calculations were performed within the density functional theory using the ABINIT program on 64-atom unit cells of KTP. Pseudopotentials for the K, Ti, Zr, Nb, and O atoms used in our calculations were taken from Refs. 3 and 4. The nonrelativistic pseudopotential for the P atom (electronic configuration 3s$^2$3p$^1$4s$^3$) was constructed according to the scheme using the OPTIMUM program with the parameters $r_s = r_p = 1.36$, $q_s = q_p = 7.07$, $r_{\text{min}} = 0.01$, $r_{\text{max}} = 1.28$, and $V_{\text{loc}} = 5.0$ a.u. (for explanation of the parameters see Ref. 3). We used the local density approximation (LDA) for the exchange-correlation energy functional. The maximum energy of plane waves was 816 eV and the integration over the Brillouin zone was done on a $4\times6\times4$ Monkhorst–Pack mesh. Optimization of the lattice parameters and the positions of atoms was continued until the residual forces acting on the atoms were less than 0.5 meV/Å. Polarization was calculated using the Berry phase method. The second-order nonlinear susceptibility tensor was calculated within the density functional perturbation theory.

The calculated lattice parameters and the positions of atoms in the ferroelectric $Pnma_{21}$ phase of undoped potassium titanyl phosphate are compared with the experimental data in Table I. It is seen that the calculations reproduce the structure of the polar phase quite well. Calculations of spontaneous polarization for the obtained structure give a value of $P_s = 0.259$ C/m$^2$, which is in good agreement with the experimental data (0.237 C/m$^2$ according to Ref. 10 and 0.200 C/m$^2$ according to Ref. 11). The calculated values of five nonzero independent components of the second-order nonlinear susceptibility tensor $d_{ij}$ (whose values $d_{11}$, $d_{15}$, $d_{33}$, and $d_{24}$ coincide pairwise in the low-frequency limit) for undoped KTP are compared with the experimental data in Table II. It is seen that if one takes into account the spread of the experimental data, the agreement is quite good.

In calculating the properties of doped samples, one of eight titanium atoms in the unit cell was replaced with an impurity atom. The symmetry of the unit cell was thus reduced to $P1$. A comparison of the energies of the structures in which zirconium atom substitutes for titanium atoms at positions Ti(1) and Ti(2) shows that Zr predominantly occupies position Ti(2) (the energy of the 64-atom unit cell with Zr atom at this position is 155 meV lower than that of the structure with Zr atom at position Ti(1)). Our conclusion about the preferential location of Zr at position Ti(2) in KTP is consistent with the experimental data. In calculating the properties of niobium-doped KTP, the potassium atom closest to the Nb atom was additionally removed from the unit cell to ensure the electroneutrality of the crystal. In the lowest-energy structure, the Nb atom occupies position Ti(1) (the energy of the 64-atom unit cell with Nb atom at this position is 115 meV lower than that of the structure with Nb atom at position Ti(2)). The conclusion about the preferential location of Nb at position Ti(1) in KTP is consistent with the experimental data.

The calculations of the second-order nonlinear susceptibility tensor show that upon replacing titanium atoms in both positions with zirconium, the three largest components of the tensor are reduced by $\sim 25\%$ (Ta-
TABLE I. Comparison of calculated and experimental lattice parameters and positions of atoms in the ferroelectric $P_{na21}$ phase of potassium titanyl phosphate.

| Atom   | Position | $x$   | $y$   | $z$   | $x$ | $y$   |
|--------|----------|-------|-------|-------|-----|-------|
|        |          | $\text{This work}$ & $\text{Experiment (Ref. 9)}$ |
| $a$    |          | 12.8313 Å | 0.0000 | 0.3729 | 0.5001 | 0.0000 |
| $b$    |          | 6.4155 Å  | 0.24883 | 0.2467 | 0.2692 | 0.2515 |
| $c$    |          | 10.6294 Å | 0.50730 | 0.1808 | 0.5020 | 0.5131 |
| Ti(1)  | 4$a$    | 0.37331 | 0.50212 | 0.0000 | 0.3729 | 0.5001 |
| Ti(2)  | 4$a$    | 0.24443 | 0.26442 | 0.24883 | 0.2467 | 0.2692 |
| P(1)   | 4$a$    | 0.49669 | 0.33802 | 0.25625 | 0.4980 | 0.3364 |
| P(2)   | 4$a$    | 0.18022 | 0.50467 | 0.50730 | 0.1808 | 0.5020 |
| K(1)   | 4$a$    | 0.36995 | 0.77783 | 0.29618 | 0.3780 | 0.7804 |
| K(2)   | 4$a$    | 0.10842 | 0.70554 | 0.1053 | 0.6989 | 0.0669 |
| O(1)   | 4$a$    | 0.27734 | 0.55220 | 0.11732 | 0.2762 | 0.5405 |
| O(2)   | 4$a$    | 0.27739 | 0.46732 | 0.13565 | 0.2753 | 0.4667 |
| O(3)   | 4$a$    | 0.48691 | 0.49776 | 0.14462 | 0.4862 | 0.4865 |
| O(4)   | 4$a$    | 0.50533 | 0.46807 | 0.38368 | 0.5100 | 0.4650 |
| O(5)   | 4$a$    | 0.39749 | 0.19140 | 0.27350 | 0.3999 | 0.1989 |
| O(6)   | 4$a$    | 0.59452 | 0.18859 | 0.23490 | 0.5937 | 0.1925 |
| O(7)   | 4$a$    | 0.10757 | 0.31141 | 0.25629 | 0.5342 | 0.5396 |
| O(8)   | 4$a$    | 0.25505 | 0.46795 | 0.39037 | 0.2530 | 0.4605 |

TABLE II. Components of the second-order nonlinear susceptibility tensor $d_{i\nu}$ in undoped KTP crystals (in pm/V).

| Component | This work | Ref. 12 | Ref. 13 | Ref. 14 | Ref. 15 | Ref. 16 | Ref. 17 |
|-----------|-----------|---------|---------|---------|---------|---------|---------|
| $d_{31}$  | 1.19      | 6.5     | 2.54    | 1.40    | —       | 2.2     | 2.12    |
| $d_{32}$  | 4.51      | 5.0     | 4.35    | 2.65    | —       | 3.7     | 3.75    |
| $d_{33}$  | 15.06     | 13.7    | 16.9    | 10.70   | 17.4    | 14.6    | 15.4    |
| $d_{24}$  | 4.51      | 7.6     | 3.64    | 2.65    | 3.37    | 3.7     | —       |
| $d_{15}$  | 1.19      | 6.1     | 1.91    | 1.40    | 1.78    | 1.9     | 2.02    |

While the spontaneous polarization decreases by only 3–7% (to 0.24 C/m$^2$ for Zr at position Ti(1) and 0.248 C/m$^2$ for Zr at position Ti(2)). The changes in $d_{i\nu}$ thus far exceed the changes in the spontaneous polarization. The appearance of small components of the $d_{i\nu}$ tensor that are missing in the $P_{na21}$ phase is due to the low symmetry of the unit cells containing the impurity (space group $P1$).

Upon doping with niobium, the components of the second-order nonlinear susceptibility tensor decrease more considerably, by as much as 35–40% (Table III). Unfortunately, we are unable to correlate this effect with the change of polarization in niobium-doped samples, since a crystal with polarized defects such as Nb$_{Ti-V_K}$ has no paraelectric phase.

In several earlier works discussing the nature of the strong optical nonlinearity of KTP, the high values of the nonlinear optical susceptibility were associated with strong distortion of the oxygen octahedra surrounding titanium atoms. Our calculations of the structure of the ferroelectric phase in doped crystals show that the distortions, which are usually characterized by a difference between the maximum and minimum Ti–O distances in the oxygen octahedra, are $\Delta R(Ti(1)–O) = 0.337$ Å and $\Delta R(Ti(2)–O) = 0.214$ Å in undoped KTP. When Zr occupies position Ti(1), the average values of the distortions of the TiO$_6$ octahedra are slightly lower (0.332 and 0.207 Å, respectively), whereas for Zr occupying position Ti(2) they are slightly higher (0.342 and 0.216 Å, respectively). The local environment of the Zr impurity is characterized by substantially less distortion, $\Delta R(Zr(1)–O) = 0.221$ Å and $\Delta R(Zr(2)–O) = 0.147$ Å.

As follows from our calculations, the substitution of titanium with zirconium results in small changes in distortions of the TiO$_6$ octahedra. This contradicts the results of X-ray measurements, which showed a marked de-
improvement in the nonlinear optical properties of KTP with the results of calculations). This means that the optical nonlinearity of crystals decreases in agreement with the results of calculations. A decrease in the second-order nonlinear susceptibility at small niobium concentrations. Our results indicating a decrease in the distortions. We believe that the reason for this discrepancy is that the X-ray data were analyzed by assuming that the coordinates of the oxygen atoms surrounding Ti and Zr were the same; i.e., the difference in the local environment of these atoms was ignored.

When doping with niobium, the average values of the distortions of the TiO_6 octahedra are reduced to 0.305 and 0.197 Å, respectively, when Nb occupies position Ti(1); and to 0.312 and 0.215 Å when Nb occupies position Ti(2). The local environment of niobium atoms is characterized by distortions of $R$(Nb(1)−O) = 0.272 Å and $R$(Nb(2)−O) = 0.140 Å. The significant reduction of all distortions in niobium-doped sample correlates with the strong decrease of the Curie temperature that is observed experimentally.

The above data show that for zirconium doping, the changes in the octahedra distortions are too small to explain the observed changes in the nonlinear susceptibility of doped crystals (tens of percent). For niobium doping, we see a notable reduction in distortions of the oxygen octahedra, which also does not explain the experimentally observed increase in the nonlinear response of KTP at small niobium concentrations. Our results indicating a decrease in the second-order nonlinear susceptibility when KTP is doped with zirconium and niobium thus provide no explanation for the enhancement of the optical nonlinearity of KTP-based solid solutions at low impurity concentrations (at high impurity concentration, the optical nonlinearity of crystals decreases in agreement with the results of calculations). This means that the improvement in the nonlinear optical properties of KTP upon its doping with Zr and Nb is not a consequence of a systematic change in the composition of corresponding solid solutions and is likely associated with the presence of some defects in doped samples. Such defects could be impurity atoms substituting for other atoms besides Ti.

In niobium-doped samples, possible positions for the impurity atoms are the sites of phosphorus atoms. Calculations of the defect formation energy according the reaction

$$\text{KTiOPO}_4 + x\text{Nb}_2\text{O}_5 \rightarrow \text{KTiO(P}_1–2x\text{Nb}_2x\text{)O}_4 + x\text{P}_2\text{O}_5$$

yield a value of 2.440 eV per impurity atom for substitution of sites P(1) and 2.368 eV for substitution of sites P(2). Interestingly, these energies are even lower than the energies of defect formation when Nb occupies sites Ti(1) and Ti(2) (2.490 and 2.605 eV, respectively). This means that upon doping with niobium, a substantial part of Nb atoms can migrate to phosphorus sites, mainly sites P(2).

In zirconium-doped samples, such defects can be Zr atoms at the positions of potassium atoms, whose coordination by oxygen atoms is 8 and 9. The existence of such defects could explain a decrease in ionic conductivity associated with the migration of potassium ions, which was experimentally observed in zirconium-doped KTP. Estimates of the formation energy of such defects according the reaction

$$\text{KTiOPO}_4 + x\text{ZrO}_2 \rightarrow (\text{Zr}_x\text{K}_{1–4x})\text{TiOPO}_4 + 2x\text{K}_2\text{O}$$

for the impurity at site K(1) yield a value of ~13 eV per impurity atom. This energy far exceeds that of defect formation when Zr occupies sites Ti(1) and Ti(2) (0.639 and 0.484 eV, respectively) and is so high that the thermodynamic formation of such defects is hardly possible even near the melting temperature. However, as was established in Ref. [20], the maps of the differential electron density distribution in zirconium-doped KTP show an additional peak of the electron density near the potassium sites. In Ref. [20], this peak was explained by these sites being populated by K atoms, but it could result from the existence of the above defects. If this is true, the obtained data could indicate that these defects are formed at the stage of the sample growth. At high growth rate from a viscous solution, microinclusions of the liquid phase could be trapped within a crystal, resulting in the formation of such nonequilibrium defects.

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**TABLE III.** Components of the second-order nonlinear susceptibility tensor $d_{i\nu}$ in KTP crystals doped with Zr and Nb for two possible dopant sites (in pm/V).

| Index | $\nu$ = 1 | 2 | 3 | 4 | 5 | 6 |
|-------|---------|---|---|---|---|---|
|       | $K$TP : Zr(1) |       |       |       |       |       |
| $i$ = 1 | $-0.691$ | $-0.548$ | $-0.805$ | $0.246$ | $0.693$ | $0.215$ |
| 2 | $0.215$ | $0.937$ | $1.652$ | $3.076$ | $0.246$ | $-0.548$ |
| 3 | $0.693$ | $3.076$ | $11.099$ | $1.652$ | $-0.805$ | $0.246$ |
| $K$TP : Zr(2) |       |       |       |       |       |       |
| 1 | $0.015$ | $0.243$ | $0.200$ | $-0.316$ | $0.658$ | $0.404$ |
| 2 | $0.404$ | $1.143$ | $1.754$ | $3.424$ | $-0.316$ | $0.243$ |
| 3 | $0.658$ | $3.424$ | $11.712$ | $1.754$ | $0.200$ | $-0.316$ |
| $K$TP : Nb(1) |       |       |       |       |       |       |
| 1 | $1.723$ | $0.824$ | $1.904$ | $-0.912$ | $0.741$ | $0.436$ |
| 2 | $0.436$ | $1.123$ | $2.325$ | $2.702$ | $-0.912$ | $0.824$ |
| 3 | $0.741$ | $2.702$ | $0.767$ | $2.325$ | $1.904$ | $-0.912$ |
| $K$TP : Nb(2) |       |       |       |       |       |       |
| 1 | $0.475$ | $0.104$ | $0.117$ | $0.064$ | $1.158$ | $0.237$ |
| 2 | $0.237$ | $0.237$ | $0.362$ | $4.205$ | $0.064$ | $0.104$ |
| 3 | $1.158$ | $4.205$ | $13.936$ | $0.362$ | $0.117$ | $0.064$ |
In this work, we do not show tables with the coordinates of all 64 atoms and the lattice parameters for the obtained unit cells because of their large size.

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