First-principles calculations of nonlinear optical properties of undoped and Zr- and Nb-doped $KTiOPO_4$*

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High nonlinear optical properties of ferroelectrics are widely used in different optical devices—mixers, frequency multipliers, parametric amplifiers, and electro-optic modulators. Among the materials for nonlinear optics, the ferroelectric potassium titanyl phosphate $KTiOPO_4$ (KTP) takes a special place. Doping of KTP with zirconium and niobium was shown to noticeably improve its nonlinear optical properties.[1–3] However, the mechanism of the influence of impurities on these properties remains unclear.

In this work, the structure of the ferroelectric phase in undoped KTP and its solid solutions doped with zirconium and niobium is calculated within the density functional theory, and the second-order nonlinear susceptibility tensor and spontaneous polarization are calculated for these crystals.

The calculations were performed using the `ABINIT` software and pseudopotentials constructed with the `OPIUM` program on the KTP unit cells containing 64 atoms. The local density approximation for the exchange-correlation functional was used. The maximum plane wave energy was 30 Ha, the integration over the Brillouin zone was performed on the 4×4×6 Monkhorst-Pack mesh. The full structure relaxation was stopped when the residual forces acting on the atoms were below 10^{-5} Ha/Bohr. The polarization was calculated by the Berry phase method, the tensor of the second-order nonlinear susceptibility was calculated using the formulas obtained in the density functional perturbation theory.[4] The laboratory computer cluster (24 cores) and "Chebyshev" supercomputer at MSU were used in the calculations.

In undoped KTP (space group $Pna2_1$), the calculated spontaneous polarization is 0.259 C/m^2. The obtained polarization is in a good agreement with experiment (0.237 C/m^2, Ref. 5, and 0.200 C/m^2, Ref. 6). The values of three independent components of the second-order nonlinear susceptibility tensor $d_{i\nu}$ (in the low frequency limit) are given in Table I. They are also in a reasonable agreement with experiment.

When calculating the properties of doped samples, one of 8 titanium atoms in the unit cell was replaced by an impurity atom. The comparison of the energies of the structures in which Zr atom substituted the titanium in *cis*- and *trans*- positions (Ti(1) and Ti(2)), showed that Zr preferably substitutes the Ti(2) position (the energy of a 64-atom unit cell is 155 meV lower than the energy of the structure with Zr at the Ti(1) position). When calculating the properties of Nb-doped KTP, to ensure the electroneutrality of the crystal, the potassium atom closest to the Nb impurity was removed from the unit cell. In this case, the lowest energy of the structure was obtained for Nb atom at the Ti(1) position (it was by 115 meV lower than the energy of the structure with Nb at the Ti(2) position). The conclusions about the preferential Zr(2) and Nb(1) positions in the KTP structure agree with experiment.[1,7]

When substituting both Ti positions with zirconium atoms, all three components of the second-order nonlinear susceptibility tensor are reduced by ∼25% (see Table II, Zr(2) case) whereas the spontaneous polarization is decreased by only 3–7% (0.240 C/m^2 for Zr at the Ti(1) position and 0.248 C/m^2 for Zr at the Ti(2) position). When doping with niobium, the components of the second-order nonlinear susceptibility tensor are decreased much stronger, by 35–40% (Table II, Nb(1) case). The obtained results are in qualitative agreement with experiment, which shows that an enhancement in

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

Component	This work	Ref. 8	Ref. 9	Ref. 10	Ref. 11
d_{33}	15.06	13.7	16.9	10.70	17.4
$d_{24} = d_{32}$	4.51	7.6	3.64	2.65	3.37
$d_{31} = d_{15}$	1.19	6.1	1.91	1.40	1.78

TABLE II. Second-order nonlinear susceptibility tensor $d_{i\nu}$ for two positions of impurities in Zr- and Nb-doped KTP (in pm/V)

Indices	$\nu = 1$	2	3	4	5	6
			KTP: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
			KTP: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
			KTP:Nb(1)			
1	1.273	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	9.767	2.325	1.904	−0.912
			KTP: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

the nonlinear susceptibility of KTP solid solutions is observed only in a limited region of low impurity concentrations.[3] So, we can conclude that an enhancement in the nonlinear optical properties of KTP doped with Zr and Nb is not inherent to the corresponding solid solutions, but apparently results from the appearance of some kind of defects.

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