Soft-chemical Synthesis of New Non-linear Optical Materials, $\mathrm{K_{0.5}M_{0.5}Ti_{0.5}OPO_4}$ (M = Nb, Ta), Related to $\mathrm{KTiOPO_4}$†

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Soft-chemical oxidation of $\mathrm{KTiOPO_4}$-like $\mathrm{KM^{V}_{0.5}Ti^{III}_{0.5}OPO_4}$ (M = Nb, Ta) using chlorine in $\mathrm{CHCl_3}$ is accompanied by partial deintercalation of potassium, yielding $\mathrm{K_{0.5}M^{V}_{0.5}Ti^{IV}_{0.5}OPO_4}$ compounds which are new non-linear optical materials that exhibit efficient second-harmonic generation of 1064 nm radiation, as does $\mathrm{KTiOPO_4}$.

Potassium titanyl phosphate, $\mathrm{KTiOPO_4}$ (KTP), is a unique non-linear optical (NLO) material[1] that combines several useful optical properties, the most prominent among them being second-harmonic generation (SHG) of the 1064 nm radiation from Nd lasers. Since its introduction as an SHG material, considerable effort has been made to understand and modify the optical properties of this material.[2,3] This effort has resulted in a large number of isomorphously substituted derivatives, whose powder SHG intensity value‡ varies from 6000 for KTP to nearly zero for many substituted materials.[2a] The only substitutions that retain or enhance the SHG response of KTP are those of arsenic for phosphorus and caesium/rubidium for potassium.[2a] It is particularly interesting that most of the substitutions at the titanium site adversely affect the SHG response.[2,4,5]

Considering that the NLO property of KTP is intimately related to the $\mathrm{Ti^{IV}}$ $\mathrm{d^0}$ electronic configuration, which results in distorted $\mathrm{TiO_6}$ octahedra in the KTP structure and the associated hyperpolarizability,[6] we believed that substitution of other $\mathrm{d^0}$ cations such as $\mathrm{Nb^V/Ta^V}$ in KTP would be of special significance. Previous work[7] has shown that it is possible to substitute only *ca.* 8 atom% of $\mathrm{Nb^V}$ in KTP, giving $\mathrm{K_{1-y}Ti_{0.92}Nb_{0.08}OPO_4}$. Substitution of larger quantities of $\mathrm{Nb^V/Ta^V}$ in KTP by direct synthetic methods has not been possible. Here, we report the synthesis of $\mathrm{K_{0.5}M^{V}_{0.5}Ti^{IV}_{0.5}OPO_4}$ (M = Nb, Ta) by a soft-chemical route[8] involving oxidative deintercalation of potassium from the parent $\mathrm{KM^{V}_{0.5}Ti^{III}_{0.5}OPO_4}$ by using chlorine in $\mathrm{CHCl_3}$. The SHG response of the new KTP analogues, $\mathrm{K_{0.5}M^{V}_{0.5}Ti^{IV}_{0.5}OPO_4}$ (M = Nb, Ta), towards 1064 nm radiation is nearly as intense as the parent KTP. That the SHG is not adversely affected by substitution of as much as 50 atom% of $\mathrm{Nb^V/Ta^V}$ for $\mathrm{Ti^{IV}}$ in KTP, unlike, for example, the substitution of $\mathrm{Sb^V}$ or $\mathrm{Sn^{IV}}$,[4,9,10] reveals the importance of the $\mathrm{d^0}$ electronic configuration of the transition metal in determining the NLO properties of the KTP family of oxides. The present work, together with the recent work of McCarron *et al.*,[11] who reported that simultaneous substitution of $\mathrm{Mg^{II}}$ and $\mathrm{Nb^V}$ for $\mathrm{Ti^{IV}}$ in KTP destroys the SHG property, reveals that exclusive presence of $\mathrm{d^0}$ cations at the $\mathrm{Ti^{IV}}$ sites is essential to preserve the non-linear optical property of substituted KTP analogues.

Since it was not possible to substitute large quantities of $\mathrm{Nb^V}$ or $\mathrm{Ta^V}$ in KTP by direct synthetic methods, we adopted the following indirect route for the synthesis of $\mathrm{K_{0.5}M_{0.5}Ti_{0.5}OPO_4}$ (M = Nb, Ta). We first prepared $\mathrm{KM_{0.5}Ti_{0.5}OPO_4}$ by reducing a pre-heated mixture of appropriate constituents in flowing hydrogen at 850–900 °C for 48 h. Powder X-ray diffraction patterns (Fig. 1) showed the formation of single-phase KTP-like materials, while oxidation-state analysis by potentiometric titration using $\mathrm{Ce^{IV}}$ as oxidant (Table 1) and magnetic susceptibility measurements were consistent with the formula $\mathrm{KM^{V}_{0.5}Ti^{III}_{0.5}OPO_4}$. The dark-coloured samples, absorbing over the entire visible region, did not show any SHG activity towards 1064 nm radiation. $\mathrm{KM^{V}_{0.5}Ti^{III}_{0.5}OPO_4}$ was then oxidised by passing $\mathrm{Cl_2}$ gas through a suspension of *ca.* 2 g of the solid in 100 ml of $\mathrm{CHCl_3}$. The white powders, obtained after several days of oxidation followed by washing§ and drying the samples at 300 °C in air, were found to be $\mathrm{K_{0.5}M^{V}_{0.5}Ti^{IV}_{0.5}OPO_4}$ (M = Nb, Ta), the oxidation of $\mathrm{Ti^{III}}$ to $\mathrm{Ti^{IV}}$ being accompanied by deintercalation of an equivalent quantity of potassium according to the reaction

$$\mathrm{KM^{V}_{0.5}Ti^{III}_{0.5}OPO_4} + 1/4\ \mathrm{Cl_2} \rightarrow \mathrm{K_{0.5}M^{V}_{0.5}Ti^{IV}_{0.5}OPO_4} + 1/2\ \mathrm{KCl} \quad (1)$$

X-Ray diffraction patterns (Fig. 1) showed that the deintercalated phosphates retained the present structure, albeit with a decrease in the lattice parameters (Table 1), the decrease being consistent with the oxidation of $\mathrm{Ti^{III}}$ to $\mathrm{Ti^{IV}}$. Energy-dispersive X-ray emission (EDX) analysis showed that potassium was indeed deintercalated according to reaction (1).

The SHG response of the deintercalated materials, $\mathrm{K_{0.5}M^{V}_{0.5}Ti^{IV}_{0.5}OPO_4}$ (M = Nb, Ta), towards 1064 nm radiation was dramatic, being almost as intense as that of KTP measured under similar conditions (Table 1). Although it is known[7] that powder intensity data are affected by a number of experimental variables such as particle size, the alignment of

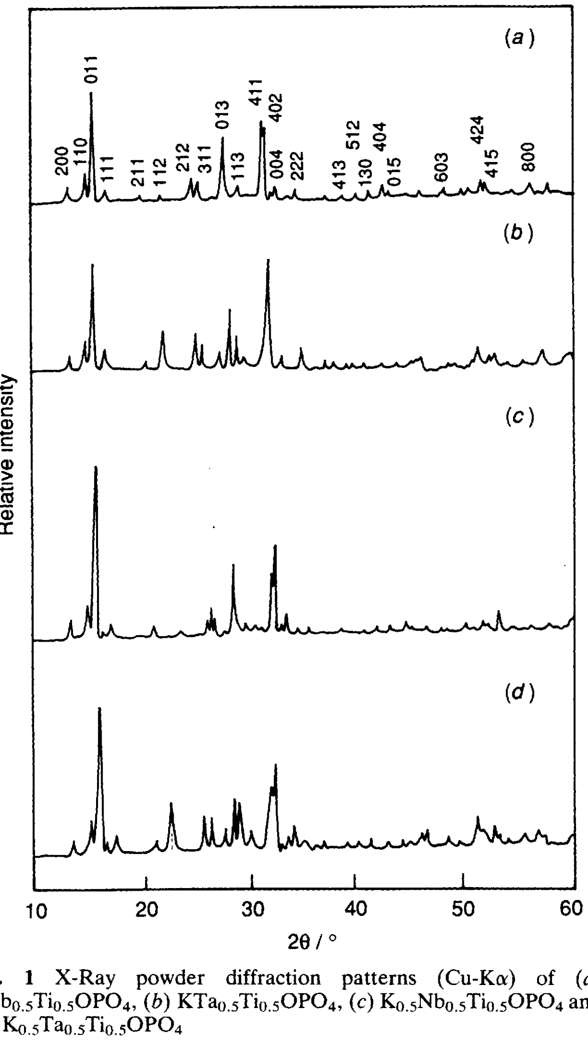

Fig. 1 X-Ray powder diffraction patterns (Cu-Kα) of (*a*) $\mathrm{KNb_{0.5}Ti_{0.5}OPO_4}$, (*b*) $\mathrm{KTa_{0.5}Ti_{0.5}OPO_4}$, (*c*) $\mathrm{K_{0.5}Nb_{0.5}Ti_{0.5}OPO_4}$ and (*d*) $\mathrm{K_{0.5}Ta_{0.5}Ti_{0.5}OPO_4}$

Table 1 Composition, colour, lattice parameters and SHG intensity of KTP-like phosphates

Composition	Colour	Reducing power[a]		Lattice parameters/Å			SHG intensity[b]
		Found	Calcd.	*a*	*b*	*c*	
$KNb_{0.5}Ti_{0.5}OPO_4$	dark blue	0.48	0.50	12.976(5)	6.488(4)	10.773(6)	—
$K_{0.5}Nb_{0.5}Ti_{0.5}OPO_4$	white	—	—	12.879(9)	6.402(7)	10.659(4)	0.90
$KTa_{0.5}Ti_{0.5}OPO_4$	black	0.47	0.50	12.981(7)	6.484(5)	10.763(8)	—
$K_{0.5}Ta_{0.5}Ti_{0.5}OPO_4$	white	—	—	12.882(6)	6.409(8)	10.663(8)	0.80

[a] Determined by titration with Ce^{IV}. [b] Normalized with respect to that of $KTiOPO_4$ which is taken as unity.

the beam and the preferred orientation of the crystallites, the comparable SHG intensities from both $K_{0.5}M_{0.5}Ti_{0.5}OPO_4$ and KTP, measured under the same conditions, were striking.

The significance of the present work lies not only in the synthesis of new derivatives of KTP showing SHG activity, but, more importantly, in revealing the role of d^0 cations towards the NLO properties of KTP and its derivatives. Unlike d^{10} cation (Sn^{IV}, Sb^V) substitution, which destroys the SHG activity of KTP,[4,9,10] the present work as well as the previous work[7,12] show that substitution of d^0 cations (Nb^V, Ta^V) for Ti^{IV} in KTP does not destroy the SHG activity. The difference is most likely due to a difference in the nature of bonding and the associated distortions of metal–oxygen octahedra.[13] With a filled d-shell, the π-interaction in the metal–oxygen octahedra is essentially antibonding, the distortion merely bending the metal–oxygen–metal bonds, without displacing the metal atom from the centre of its octahedron. On the other hand, the distortions of d^0 metal–oxygen octahedra involve displacement of the metal away from the centre, creating long and short metal–oxygen bonds.[13] The presence of such distorted octahedra is known[6] to be an essential feature for hyperpolarizability of KTP. Accordingly, d^0 cation substitutions do not destroy the SHG response of the KTP structure. What seems to be specially significant is that, while the coupled substitution[11] of Nb^V and Mg^{II} at the Ti^{IV} sites dramatically destroys the SHG activity of KTP, considerable substitution of Nb^V/Ta^V has not destroyed it. Since SHG of KTP is a cooperative property arising from extended metal–oxygen–metal interaction in the solid state,[6b] the present work together with the results of Mg^{II} and Nb^V substitution[11] in KTP suggests that exclusive presence of d^0 cations at the Ti^{IV} sites is essential for preserving the NLO properties of KTP derivatives; even a small percentage of substitution of an alien cation such as Mg^{II} at the Ti^{IV} sites, which presumably destroys the connectivity of d^0 cation octahedra, is detrimental to the NLO properties of KTP derivatives.

In summary, we have synthesized two new KTP derivatives, $K_{0.5}M_{0.5}Ti_{0.5}OPO_4$ (M = Nb, Ta), by a soft-chemical route. The SHG response of both the materials towards doubling of 1064 nm radiation frequency is nearly the same as the parent KTP, revealing that d^0 cation substitution at the Ti^{IV} site is not detrimental to the SHG activity of the KTP structure.

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Footnotes

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‡ The intensity values quoted are relative to that of quartz.

§ KCl present in the deintercalated products was removed by repeated washing with acetonitrile.

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