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New Transition Metal Phosphates Related to $KTiOPO_4$. Synthesis of $K_{0.5}M_{0.5}M'_{0.5}OPO_4$ (M = Nb, Ta; M' = Ti, V) and $K_{1-x}Ti_{1-x}V_xOPO_4$ Exhibiting Nonlinear Optical Behavior[1]

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IN HONOR OF C. N. R. RAO ON HIS 60TH BIRTHDAY

Several transition metal phosphates of the general formula $KM_{0.5}M'_{0.5}OPO_4$, where $M = Nb^V$ or Ta^V and $M' = Ti^{III}$, V^{III}, Cr^{III}, Fe^{III}, possessing the $KTiOPO_4$ (KTP) structure have been synthesized. Unlike KTP, none of these phosphates exhibit second harmonic generation (SHG) of the 1064-nm radiation. Soft-chemical oxidation of the Ti^{III} and V^{III} phosphates using chlorine in $CHCl_3$, however, restores the SHG property to the oxidized materials, $K_{0.5}M_{0.5}M'_{0.5}OPO_4$ ($M = Nb^V$, Ta^V; $M' = Ti^{IV}$, V^{IV}). $K_{1-x}Ti_{1-x}V_xOPO_4$ ($x \leq 0.25$) prepared similarly from $KTi_{1-x}V_xOPO_4$ also exhibit SHG. The results reveal that exclusive presence of d^0 cations at the Ti^{IV} site preserves the SHG response of KTP derivatives. © 1994 Academic Press, Inc.

INTRODUCTION

$KTiOPO_4$ (KTP) and its arsenic analog (KTA) are important nonlinear optical (NLO) materials specially suited for second harmonic generation (SHG) of 1064-nm radiation (1, 2). Both KTP and KTA crystallize in an acentric structure (space group $Pna2_1$) consisting of one-dimensional chains of $TiO_{6/2}$ octahedra linked by $PO_{4/2}$ ($AsO_{4/2}$) tetrahedra to form a three-dimensional framework (Fig. 1); the potassium ions reside in the intersecting channels formed by the framework (3–5). Several isomorphous substitutions have been made in the KTP structure with the intention of understanding the origin of its NLO behavior (6–8). Interestingly, only a few substitutions have maintained or improved the SHG response of KTP, for instance, As for P and Cs/Rb/Tl for K (6). All other substitutions seem to adversely affect the SHG response of KTP to a greater or lesser extent. We have recently shown that it is possible to substitute up to about 40 atom% of Nb^V at the Ti^{IV} site in both KTP and KTA without destroying the SHG response (9). In an attempt to further understand the role of various transition metal ions on the NLO property of KTP derivatives, we have synthesized a number of KTP analogs of the general formula $KM_{0.5}M'_{0.5}OPO_4$ ($M = Nb^V$, Ta^V; $M' = Ti^{III}$, V^{III}, Cr^{III}, Fe^{III}). We have also synthesized new Ti^{IV} and V^{IV} derivatives, $K_{0.5}M_{0.5}M'_{0.5}OPO_4$ ($M = Nb^V$, Ta^V; $M' = Ti^{IV}$, V^{IV}), by oxidizing the corresponding Ti^{III} and V^{III} phases using chlorine in $CHCl_3$ (10). Our investigations of the structure and properties of these materials, which are reported in this paper, provide new insights into the origin of SHG property of KTP and its derivatives.

EXPERIMENTAL

Phosphates of the formula $KM_{0.5}M'_{0.5}OPO_4$ for $M = Nb^V/Ta^V$ and $M' = Ti^{III}/V^{III}$ were prepared by reacting preheated stoichiometric mixtures of KOH, Nb_2O_5/Ta_2O_5, TiO_2/V_2O_5, and $(NH_4)_2HPO_4$ in a flowing hydrogen atmosphere at 850–950°C for 2 days. Similar phosphates for $M' = Cr^{III}/Fe^{III}$ could be prepared, employing Cr_2O_3/Fe_2O_3, by direct solid state reaction in air at 900°C. $KTi_{1-x}V_xOPO_4$ were prepared by a hydrothermal method as reported in the literature (11). Oxidative deintercalation of potassium from the phosphates was investigated by passing chlorine through a ~2 g suspension of the solid phosphate in 100 ml of $CHCl_3$ (10). Oxidation states of titanium and vanadium in the phosphates were determined by a redox potentiometric titration using Ce(IV) as oxidizing agent.

The solid phosphates were characterized by X-ray powder diffraction, magnetic susceptibility measurement, diffuse reflectance spectroscopy, and infrared absorption spectroscopy. Lattice parameters were derived from least-squares refinement of the powder diffraction data. SHG intensities were measured on polycrystalline samples using a pulsed Nd:YAG laser.

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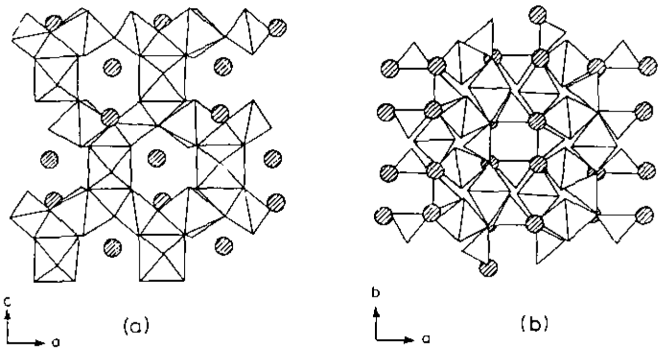

FIG. 1. Crystal structure of $KTiOPO_4$ (KTP) viewed along the (a) [0 1 0] and (b) [0 0 1] directions (adapted from Ref. (1)).

RESULTS AND DISCUSSION

We have been able to prepare a number of KTP derivatives of the formula $KM_{0.5}M'_{0.5}OPO_4$ for M = Nb or Ta and M' = Ti, V, Cr, or Fe by direct solid state reaction of the constituents. Powder X-ray diffraction patterns (Fig. 2) show that all these phosphates are isostructural, crystallizing with the orthorhombic KTP structure. In Table 1, we list the lattice parameters and other characteristics of the phosphates synthesized. Chemical analysis of the oxidation states of titanium and vanadium in the phosphates (Table 1) as well as the effective magnetic moments, obtained from Curie–Weiss plots of inverse molar susceptibility, χ_M^{-1}, versus temperature, T (Table 1 and Fig. 3), are consistent with the formulation $KM^{V}_{0.5}M'^{III}_{0.5}OPO_4$. Among the phosphates synthesized, $KNb_{0.5}Fe_{0.5}$

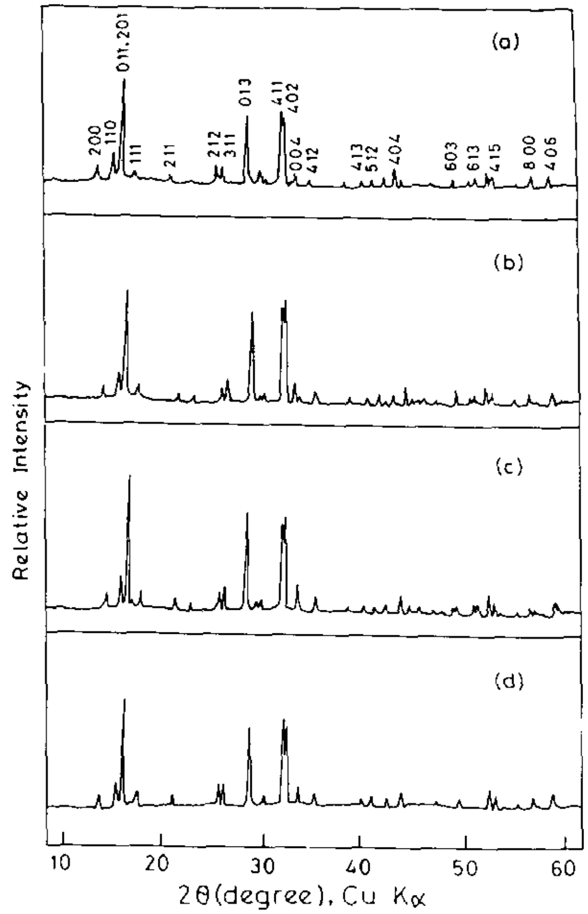

FIG. 2. X-ray powder diffraction patterns of $KNb_{0.5}M'_{0.5}OPO_4$. (a) M' = Ti; (b) M' = V; (c) M' = Cr, and (d) M' = Fe.

TABLE 1

Composition, Color, Lattice Parameters, and SHG Intensity of $KM_{0.5}M'_{0.5}OPO_4$ and $K_{0.5}M_{0.5}M'_{0.5}OPO_4$

Composition	Color	Reducing power		Lattice parameters (Å)			μ_{eff} BM[b]	SHG intensity[c]
		Found	Expected[a]	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(7)	1.71	—
$KNb_{0.5}V_{0.5}OPO_4$	Brown	1.02	1.00	12.949(6)	6.431(8)	10.686(4)	2.85	—
$KNb_{0.5}Cr_{0.5}OPO_4$	Green	—	—	12.894(7)	6.435(6)	10.629(6)	3.82	—
$KNb_{0.5}Fe_{0.5}OPO_4$	Orange	—	—	12.956(9)	6.467(5)	10.698(8)	5.70	—
$KTa_{0.5}Ti_{0.5}OPO_4$	Black	0.47	0.50	12.981(8)	6.484(7)	10.763(8)		—
$KTa_{0.5}V_{0.5}OPO_4$	Grey	0.98	1.00	12.985(4)	6.442(3)	10.696(4)		—
$KTa_{0.5}Cr_{0.5}OPO_4$	Green	—	—	12.914(5)	6.433(3)	10.670(6)		—
$KTa_{0.5}Fe_{0.5}OPO_4$	Orange	—	—	13.045(7)	6.450(8)	10.662(6)		—
$K_{0.5}Nb_{0.5}Ti_{0.5}OPO_4$	White	—	—	12.879(9)	6.402(7)	10.659(4)	Diamag.	0.90
$K_{0.5}Nb_{0.5}V_{0.5}OPO_4$	Yellowish green	0.52	0.50	12.801(6)	6.357(4)	10.569(5)	1.72	0.50
$K_{0.5}Ta_{0.5}Ti_{0.5}OPO_4$	White	—	—	12.852(9)	6.409(8)	10.663(6)	Diamag.	0.80
$K_{0.5}Ta_{0.5}V_{0.5}OPO_4$	Yellow	0.54	0.50	12.819(7)	6.367(4)	10.615(5)	1.75	0.40

[a] Corresponds to the number of electrons per formula unit required for the oxidation of titanium/vanadium.

[b] Per mole of Ti, V, Cr, or Fe.

[c] Normalized with respect to that of $KTiOPO_4$ which is taken as unity.

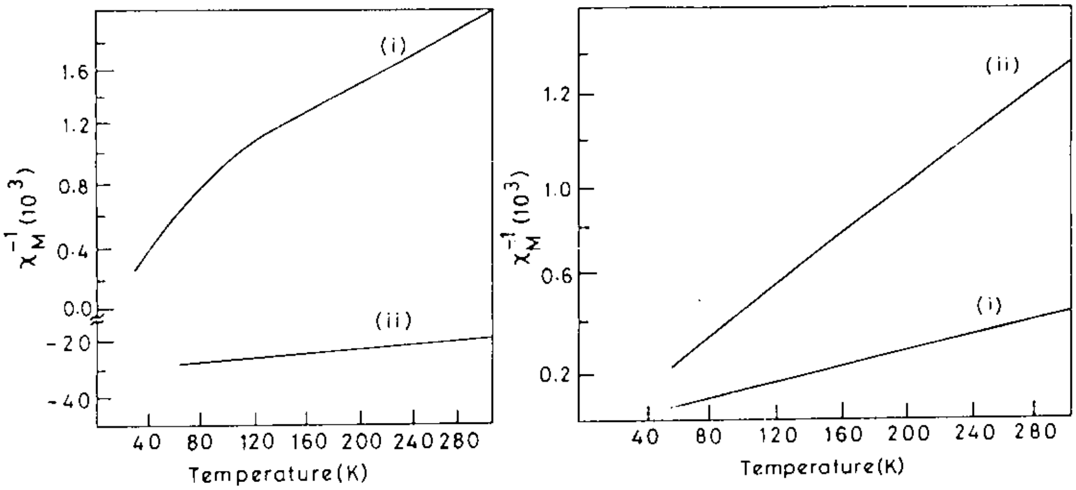

FIG. 3. Plots of inverse molar magnetic susceptibility, χ_M^{-1}, versus temperature, T, for (a) $KNb_{0.5}Ti_{0.5}OPO_4$ (i) and $K_{0.5}Nb_{0.5}Ti_{0.5}OPO_4$ (ii) and (b) $KNb_{0.5}V_{0.5}OPO_4$ (i) and $K_{0.5}Nb_{0.5}V_{0.5}OPO_4$ (ii).

OPO_4 has already been reported in the literature (6). Formation of these phosphates together with the report (6) of similar phosphates for M' = Ga and Mn reveals that the KTP structure is indeed versatile, accommodating readily a number of pentavalent and trivalent cations (that are stable in octahedral oxygen coordination) at the Ti^{IV} site, without change of structure. All these phosphates absorb strongly in the visible region, mainly due to the presence of trivalent transition metal cations. Accordingly, none of these materials show a SHG response toward 1064-nm radiation.

With the hope of restoring the SHG property, we investigated soft-chemical oxidation of Ti^{III} and V^{III} phosphates in the above series. As expected, we could oxidize the Ti^{III} phosphates quantitatively by passing chlorine gas through a suspension of the phosphate in $CHCl_3$ (10), according to the reaction

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

X-ray diffraction patterns (Fig. 4) show that the deintercalated materials retain the parent KTP structure, albeit with a decrease in the lattice parameters (Table 1), the decrease being consistent with the oxidation of Ti^{III} to Ti^{IV}. Energy dispersive X-ray emission analysis also shows that potassium is indeed deintercalated according to the reaction [1]. Interestingly, unlike the parent materials, the deintercalated materials show a positive SHG response toward 1064-nm radiation, the intensity of the SHG radiation from powder samples, measured at 532 nm, being about 90% (Nb) and 80% (Ta) of the parent KTP (Table 1). The restoration of the SHG property to

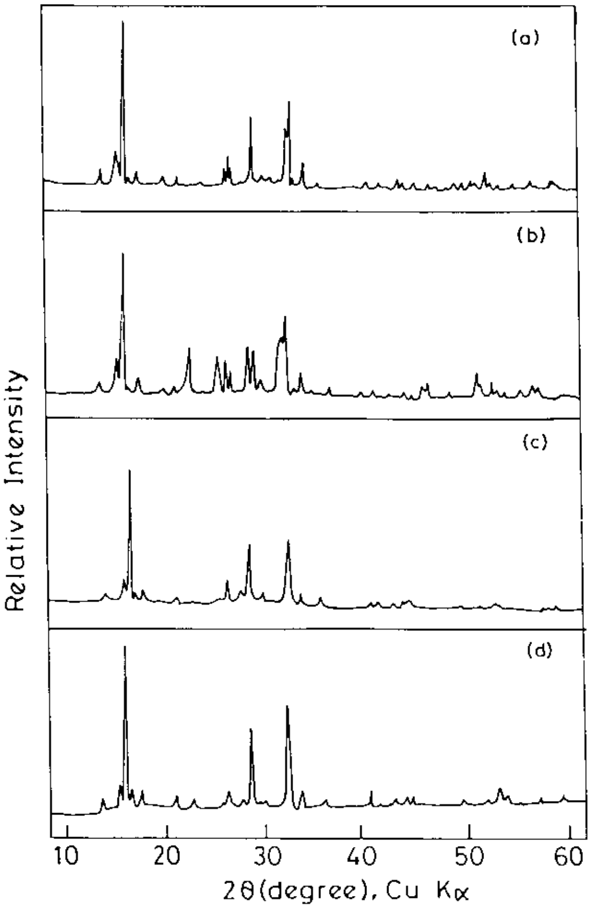

FIG. 4. X-ray powder diffraction patterns of (a) $K_{0.5}Nb_{0.5}Ti_{0.5}OPO_4$, (b) $K_{0.5}Ta_{0.5}Ti_{0.5}OPO_4$, (c) $K_{0.5}Nb_{0.5}V_{0.5}OPO_4$, and (d) $K_{0.5}Ta_{0.5}V_{0.5}OPO_4$.

the KTP derivatives, $K_{0.5}M^{V}_{0.5}Ti^{IV}_{0.5}OPO_4$ (M = Nb, Ta), is indeed remarkable, revealing that substitution of as much as 50 at.% of pentavalent Nb and Ta for Ti in KTP does not destroy the SHG property. Previous work (12) on Nb^{V} substitution by direct synthetic methods has shown that it is possible to substitute about 8 at.% of Nb in KTP without affecting the SHG property.

We could similarly oxidize the V^{III} phosphates, $KM_{0.5}V^{III}_{0.5}OPO_4$ (M = Nb, Ta), by passing chlorine through a suspension of the solid in $CHCl_3$ to give $K_{0.5}M_{0.5}V^{IV}_{0.5}OPO_4$. Oxidation state analysis (Table 1) and magnetic susceptibility measurement (Fig. 3) reveal that the vanadium is oxidized to the IV state in the deintercalated phosphates. X-ray powder diffraction patterns (Fig. 4) show that the KTP structure is retained by the deintercalated phosphates. As representative examples, we give in Table 2 an indexing of the powder diffraction data for both $KNb_{0.5}V_{0.5}OPO_4$ and $K_{0.5}Nb_{0.5}V_{0.5}OPO_4$. Calculation of powder diffraction intensities for the KTP structure (Table 2) suggests that the K(2) atoms at 9-coordinated sites are most likely deintercalated in preference to the K(1) atoms.

TABLE 2

X-Ray Powder Diffraction Data for $KNb_{0.5}V_{0.5}OPO_4$ and $K_{0.5}Nb_{0.5}V_{0.5}OPO_4$

	$KNb_{0.5}V_{0.5}OPO_4$				$K_{0.5}Nb_{0.5}V_{0.5}OPO_4$			
$h\ k\ l$	d_{obs} (Å)	d_{cal} (Å)	I_{obs}	I_{cal}[a]	d_{obs} (Å)	d_{cal} (Å)	I_{obs}	I_{cal}[b]
2 0 0	6.463	6.476	14	13	6.394	6.401	9	10
1 1 0	5.754	5.760	38	48	5.698	5.693	28	34
2 0 1	5.505	5.537	100	100	5.471	5.475	100	100
0 1 1		5.510	[c]	44		5.448	[c]	32
0 0 2	—	5.343	—	5	5.292	5.285	3	2
1 1 1	5.068	5.070	15	19	5.011	5.013	11	7
2 1 1	4.201	4.197	8	7	4.152	4.148	6	2
1 1 2	3.917	3.917	6	6	—	3.873	—	4
2 1 2	3.480	3.470	20	25	—	3.431	—	3
3 1 1	3.401	3.398	30	35	3.369	3.359	19	14
0 1 3	3.121	3.116	84	92	3.095	3.081	45	43
1 2 1	3.008	2.996	8	6	—	2.961	—	2
3 1 2	2.983	2.976	11	11	2.950	2.943	8	6
4 1 1	2.797	2.791	89	42	2.751	2.759	65	18
2 2 1		2.781		61		2.749		23
4 0 2	2.776	2.769	96	44		2.737		18
0 2 2		2.755		53		2.724		35
0 0 4	2.675	2.672	20	21	2.652	2.642	10	10
2 2 2	2.535	2.535	11	9	2.507	2.506	8	4
5 1 1	2.341	2.344	6	5	—	2.317	—	3
4 1 3	2.243	2.245	7	3	2.222	2.220	6	2
2 2 3		2.240		7		2.214		2
5 1 2	2.191	2.191	9	14	2.170	2.166	6	8
3 1 4	2.151	2.142	4	2	—	2.118	—	—
1 3 0	2.117	2.115	10	11	—	2.091	—	4
4 0 4	2.062	2.061	19	16	2.040	2.038	8	7
0 2 4		2.055		6		2.032		2
2 0 5	2.029	2.029	8	5	2.006	2.007	6	2
0 1 5		2.028		3		2.006		2
1 3 2	1.977	1.966	7	7	—	1.959	—	2
4 2 3	1.920	1.921	6	2	—	1.899	—	1
3 3 0		1.920		5		1.898		2
6 0 3	1.845	1.846	15	10	1.825	1.825	2	5
6 2 0	1.792	1.792	8	4	1.771	1.771	2	2
5 1 4		1.786		7				4
6 1 3	1.774	1.774	11	11	—	1.754	—	—
4 2 4	1.735	1.735	19	25	1.715	1.715	6	13
4 1 5	1.719	1.719	15	6	—	1.700	—	2
2 2 5		1.716		11				7
1 3 4	1.656	1.658	6	1	—	1.639	—	—
5 3 0		1.651		7		1.632		2
8 0 0	1.619	1.619	13	9	1.600	1.600	2	4
4 0 6	1.560	1.560	14	7	1.543	1.543	4	5
3 3 4		1.559		4				2
0 2 6	1.558	1.558	7	8	—	1.535	—	3

[a] Calculated using LAZY PULVERIX assuming that Nb occupies the Ti(1) site and V the Ti(2) site in the KTP structure (Ref. (3)).

[b] Calculated assuming that K atoms at the K(2) site are deintercalated.

[c] Merges with (201) reflection.

We have recorded the infrared absorption spectra of $KNb_{0.5}V^{III}_{0.5}OPO_4$ and its deintercalation product to characterize the structural changes. While the spectra of both compounds (Fig. 5) are in general similar to that of KTP (13), we see distinct changes in the bands associated with the metal-oxygen octahedra. The two bands at 710 and 808 cm^{-1} in the parent compound, which are due to the distorted MO_6 octahedra, shift to 775 and 860 cm^{-1} in the deintercalated material, the shift being consistent with the oxidation of V^{III} to V^{IV} on deintercalation. For comparison, we have also recorded the spectra of $KVOPO_4$ (Fig. 5). The two bands associated with $V^{IV}O_6$ octahedra occur at 835 and 895 cm^{-1} in this material.

Diffuse reflectance spectra of $KM_{0.5}V_{0.5}OPO_4$ (Fig. 6) show two absorption bands centered around 700 and 400–500 nm. On oxidation, the 400- to 500-nm band nearly disappears in the deintercalated materials, $K_{0.5}M^{V}_{0.5}V^{IV}_{0.5}OPO_4$. Accordingly, the latter phases show a positive SHG response toward the 1064-nm radiation, the intensity of the SHG light being about 40–50% of KTP (Table

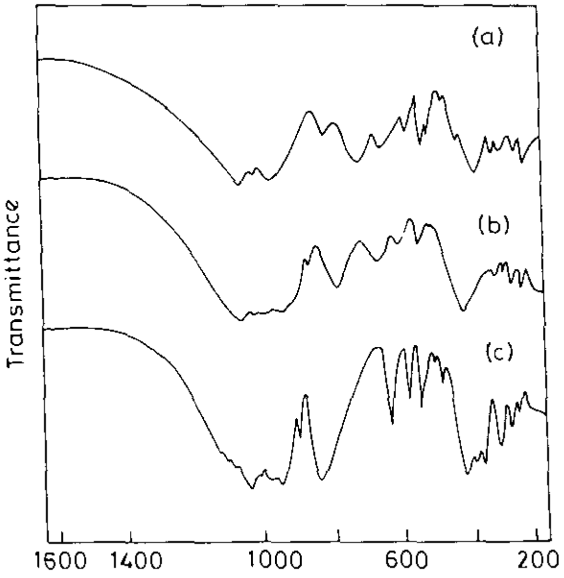

FIG. 5. Infrared absorption spectra of (a) $KNb_{0.5}V_{0.5}OPO_4$, (b) $K_{0.5}Nb_{0.5}V_{0.5}OPO_4$, and (c) $KVOPO_4$.

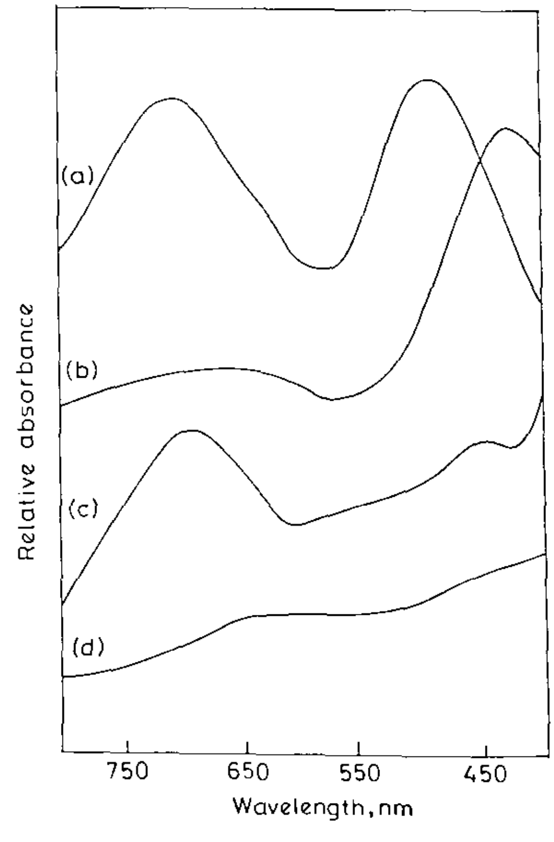

FIG. 6. Diffuse reflectance spectra of (a) $KNb_{0.5}V_{0.5}OPO_4$, (b) $K_{0.5}Nb_{0.5}V_{0.5}OPO_4$, (c) $KTa_{0.5}V_{0.5}OPO_4$, and (d) $K_{0.5}Ta_{0.5}V_{0.5}OPO_4$.

1). This result is specially significant in view of the literature report (11) that the SHG intensity of $KTi_{0.5}V_{0.5}OPO_4$ is almost zero. Since the charge-transfer energy for Nb^V/Ta^V–O–V^{IV} is higher than that for the combination Ti^{IV}–O–V^{IV}, the absorption in the region 500–600 nm is much less for $K_{0.5}M^V_{0.5}V^{IV}_{0.5}OPO_4$ (M = Nb, Ta) than for $KTi_{0.5}V_{0.5}OPO_4$. As a result, we see a fairly strong SHG response from $K_{0.5}M_{0.5}V_{0.5}OPO_4$, providing experimental support to the theoretical contention (11) that the d^1 electronic configuration of V^{IV} (t_{2g} occupancy) does not affect optical nonlinearity of KTP derivatives.

Since it has been reported (11) that the absence of an obvious SHG response for $KTi_{1-x}V_xOPO_4$ for $x > 0.05$ is due to the charge-transfer absorption extending into the visible, we considered it interesting to oxidize V^{IV} in these materials to V^V without destroying the structure and find out what effect it has on the SHG property. We investigated soft-chemical oxidation of three different compositions in the $KTi_{1-x}V_xOPO_4$ system for $x = 0.15$, 0.25, and 0.50. We find that oxidation occurs readily for the $x = 0.15$ and 0.25 compositions according to the reaction

$$KTi_{1-x}V_xOPO_4 + x/2\ Cl_2 \rightarrow K_{1-x}Ti_{1-x}V_xOPO_4 + x\ KCl, \quad [2]$$

giving $K_{1-x}Ti_{1-x}V_xOPO_4$ derivatives, where all the vanadium is now present in the V state (Table 3). The deintercalated materials, which retain the parent KTP structure (Fig. 7), show a positive SHG response of about 25–35% of KTP intensity. Chlorine oxidation of the $x = 0.5$ member does not, however, proceed to completion. The partially oxidized material, $K_{0.67}Ti_{0.5}OPO_4$, which is green in color, shows a weak SHG response (Table 3).

The present work, together with the previous work on KTP and its derivatives (6, 7, 11, 14, 15), provides some new insight into the origin of SHG property and its relation to the electronic configuration of the transition metal ions substituted in the KTP structure. It is known (7, 15) that the NLO behavior of KTP is a solid state property arising from extended (cooperative) interaction of the distorted TiO_6 octahedra, giving rise to a charge-transfer excited state that is delocalized along the Ti–O–Ti chains. It is this delocalized state that seems to result in a high degree of polarization with unusually large excited state contribution and the associated hyperpolarizability. Presumably, any substitution that disrupts the extended Ti–O–Ti interaction would be detrimental to the NLO property. The present work as well as the previous work (9, 12) show that substitution of d^0 cations such as Nb^V and Ta^V, which support ferroelectric distortion of metal-oxygen octahedra (16, 17) just as Ti(IV), does not seem to adversely affect the SHG property of KTP. Substitution of V^V ($3d^0$) also does not seem to be very detrimental to

TABLE 3

Composition, Color, Lattice Parameters, and SHG Intensity of $K_{1-y}Ti_{1-x}V_xOPO_4$ and Their Parents

Composition	Color	Reducing power		Lattice parameters (Å)			SHG intensity[b]
		Found	Expected[a]	*a*	*b*	*c*	
$KTi_{0.85}V_{0.15}OPO_4$	Yellow	0.15	0.15	12.808(5)	6.400(6)	10.578(6)	0.10
$K_{0.85}Ti_{0.85}V_{0.15}OPO_4$	Yellow	0.01	0.00	12.800(6)	6.364(3)	10.572(8)	0.36
$KTi_{0.75}V_{0.25}OPO_4$	Brown	0.26	0.25	12.812(6)	6.401(6)	10.569(8)	0.05
$K_{0.75}Ti_{0.75}V_{0.25}OPO_4$	Yellowish green	0.02	0.00	12.723(8)	6.340(5)	10.561(8)	0.24
$KTi_{0.50}V_{0.50}OPO_4$	Brown	0.48	0.50	12.799(7)	6.390(6)	10.560(4)	—
$K_{0.67}Ti_{0.50}V_{0.50}OPO_4$	Green	0.17	0.00	12.716(4)	6.363(3)	10.529(5)	0.20

[a] Expected for complete oxidation of vanadium.

[b] Normalized with respect to that of $KTiOPO_4$ (hydrothermally synthesized) which is taken as unity.

the SHG property of KTP, but for its oxygen-metal charge-transfer absorption occurring at longer wavelengths than those with Nb^V and Ta^V. Similarly the substitution of V^{IV} ($3d^1$) with its short V=O bonds does not seem to destroy the SHG property, but for a charge-transfer absorption of a different kind, probably of the type Ti^{IV}–O–$V^{IV} \rightarrow Ti^{III}$–O–$V^V$ (18), which extends into the visible (11). Since this charge-transfer energy is higher for the combinations Nb^V–O–V^{IV} and Ta^V–O–V^{IV} than for Ti^{IV}–O–V^{IV}, we find that the phases $K_{0.5}Nb^V_{0.5}V^{IV}_{0.5}OPO_4$ and $K_{0.5}Ta^V_{0.5}V^{IV}_{0.5}OPO_4$ show a clear SHG response, unlike $KTi^{IV}_{0.5}V^{IV}_{0.5}OPO_4$ (Table 1).

It is known that the SHG property and the ferroelectric, piezoelectric, and pyroelectric properties of KTP have the same origin, namely the local structural distortions which give rise to the noncentrosymmetric structure (6, 19). The structural distortions in turn depend on the electronic configuration (oxidation state) of the transition metal and on the nature of atoms filling the K tunnels in the structure (6). Among the various derivatives of KTP synthesized in the present work, we find that only those containing exclusively d^0 cations at the Ti^{IV} site, viz. $K_{0.5}M_{0.5}Ti^{IV}_{0.5}OPO_4$ (M = Nb^V, Ta^V), show an SHG response that is comparable to that of KTP (Table 1). Derivatives containing both d^0 and d^1 cations such as $K_{0.5}M_{0.5}V^{IV}_{0.5}OPO_4$ (M = Nb^V, Ta^V), on the other hand, show a weaker SHG response (Table 1). This decrease in SHG intensity of V^{IV} containing KTP derivatives occurs despite the fact that $V^{IV}O_6$ octahedra are strongly distorted with short V=O bonds (11). The weak SHG response of V^{IV} containing KTP derivatives is presumably due to the optical absorption in the visible region.

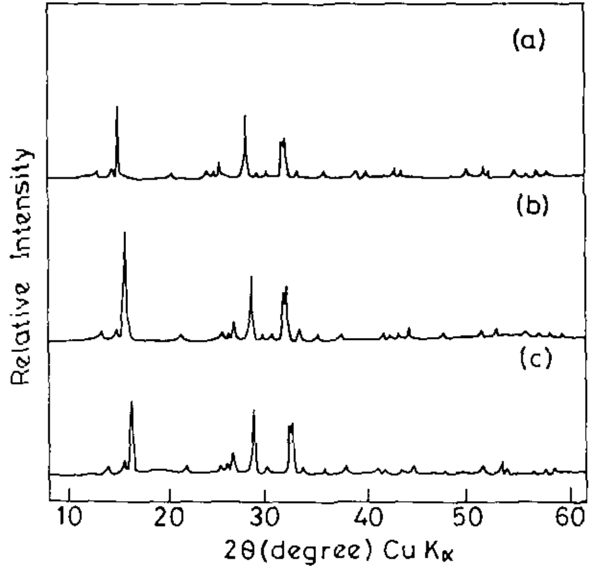

FIG. 7. X-ray powder diffraction patterns of (a) $K_{0.85}Ti_{0.85}V_{0.15}OPO_4$, (b) $K_{0.75}Ti_{0.75}V_{0.25}OPO_4$, and (c) $K_{0.67}Ti_{0.5}V_{0.5}OPO_4$.

All other substitutions of transition metal ions (Ti^{III}, V^{III}, Cr^{III}, Fe^{III}), which absorb in the visible and do not support a ferroelectric distortion of the octahedra, destroy the SHG property of KTP. Even a nontransition metal ion such as Ga(III), which does not absorb in the visible, destroys the SHG property of KTP (6), probably because this cation does not lend itself to distorted metal-oxygen octahedra and disrupts the extended M–O–M interaction in the octahedral chains. Determination of the structures as well as the ferroelectric/piezoelectric properties is essential to establish quantitative structure–property relationships of the new KTP derivatives reported in this paper.

In conclusion, we have prepared several transition metal phosphates of the formulas $KM_{0.5}M'_{0.5}OPO_4$ (M = Nb^V, Ta^V; M' = Ti^{III}, V^{III}, Cr^{III}, Fe^{III}) and $K_{0.5}M_{0.5}M'_{0.5}OPO_4$ (M' = Ti^{IV}, V^{IV}) which are isostructural with $KTiOPO_4$ (KTP). Among these phosphates, only the latter exhibit a positive SHG response to 1064-nm radiation. The results reveal that the SHG response of KTP is a sensitive property that is retained only by a very few substitutions at the Ti^{IV} site, such as Nb^V and Ta^V. The present work together with the recent work of McCarron *et al.* (20) on coupled substitution of Mg^{II} and Nb^V in KTP suggest that exclusive presence of d^0 cations at the Ti^{IV} sites is essential for preserving the NLO properties of KTP derivatives.

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