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Coupled Substitution of Niobium and Silicon in $KTiOPO_4$ and $KTiOAsO_4$. Synthesis and Nonlinear Optical Properties of $KTi_{1-x}Nb_xOX_{1-x}Si_xO_4$ (X = P, As)

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Coupled substitution of Nb(V) and Si(IV) for Ti(IV) and P(V)/As(V) in $KTiOPO_4$ (KTP) and $KTiOAsO_4$ (KTA) giving new series of nonlinear optical materials, $KTi_{1-x}Nb_xOX_{1-x}Si_xO_4$ (X = P, As), has been investigated. Substitution up to $x = 0.40$ readily occurs, the members retaining the orthorhombic ($Pna2_1$) structure of KTP. The second harmonic generation (SHG) property of the parent KTP and KTA is not adversely affected by the coupled substitution. SHG intensity of the powder samples of the X = P series shows a slight increase with x up to $x = 0.15$; for $0.15 < x \leq 0.40$, there is a decrease in SHG intensity as compared to that for KTP. A similar trend in SHG intensity is seen for the arsenic analogs.

Introduction

$KTiOPO_4$ (KTP) has attracted considerable attention in recent times[1-3] in view of its unique nonlinear optical properties,[4] which make it particularly suitable for second harmonic generation (SHG) of 1064-nm radiation. KTP crystallizes in an acentric structure[5] (space group $Pna2_1$) consisting of chains of TiO_6 octahedra which are linked by PO_4 tetrahedra. The potassium atoms reside in the open channels along [001] of the framework structure. All the atoms in the structure are on general positions making it specially attractive for isomorphous substitution. Indeed all the atoms in KTP have been replaced partially or completely—K by Na,[6] Rb,[7] Cs,[1] Tl,[8] or NH_4,[9] Ti by V,[10] Zr,[1] Ge,[1] Sn,[11] or (Ga,Nb),[1] P by As[12] or Si,[13] and O by (OH)[1] or F[1]—giving a wide variety of KTP analogs. Interestingly, only a few substitutions, for instance, As substitution for P and Cs/Rb substitution for K, have improved or maintained the SHG response of KTP.[1] All other substitutions seem to adversely affect the SHG response to a greater or lesser extent. Especially significant is the finding that most of the substitutions at the Ti site destroy the SHG response.[1]

Considering that the nonlinear optical properties of KTP arise mainly from the alternating short and long Ti–O bonds in the helical chains of TiO_6 octahedra along the [011] and [0$\bar{1}$1] directions,[1-4] and that the d^0 electronic configuration of Ti(IV) is primarily responsible for the distortion of TiO_6 octahedra,[14] we envisaged that replacement of Ti(IV) by another d^0 cation, e.g. Nb(V), in KTP would result in a new KTP analog probably retaining the nonlinear optical properties. Such a material would be $KNbOSiO_4$, but our attempts to prepare this material are unsuccessful so far. A small quantity of Nb has however been substituted[15] in KTP giving $K_{1-y}Ti_{0.92}Nb_{0.08}OPO_4$, which appears to retain the SHG property of the parent. We have been able to substitute up to about 40 atom % of Nb for Ti in KTP/KTA structures by simultaneously substituting Si for P/As. Accord-

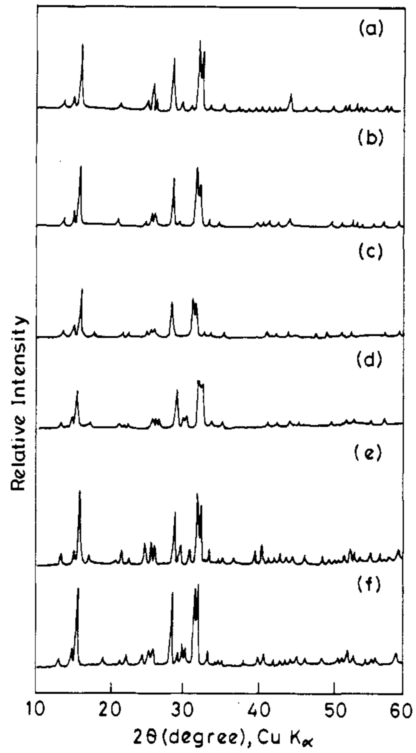

Figure 1. X-ray powder diffraction patterns of $KTi_{1-x}Nb_xOX_{1-x}Si_xO_4$ (X = P, As) members: (a) $KTiOPO_4$, (b) $KTi_{0.8}Nb_{0.2}OP_{0.8}Si_{0.2}O_4$, (c) $KTi_{0.7}Nb_{0.3}OP_{0.7}Si_{0.3}O_4$, (d) $KTi_{0.65}Nb_{0.35}OP_{0.65}Si_{0.35}O_4$, (e) $KTiOAsO_4$, and (f) $KTi_{0.6}Nb_{0.4}OAs_{0.6}Si_{0.4}O_4$.

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Table I. Lattice Parameters and SHG Intensity of $KTi_{1-x}Nb_xOX_{1-x}Si_xO_4$ (X = P, As) Members

compd	lattice parameters (Å) *a*	*b*	*c*	*V* (Å^3)	SHG intensity[a]
$KTiOPO_4$	12.815(8)	6.402(4)	10.589(6)	868.7	1.00
$KTi_{0.9}Nb_{0.1}OP_{0.9}Si_{0.1}O_4$	12.852(6)	6.410(3)	10.598(5)	873.1	1.05
$KTi_{0.8}Nb_{0.2}OP_{0.8}Si_{0.2}O_4$	12.897(9)	6.420(6)	10.603(9)	877.9	0.96
$KTi_{0.7}Nb_{0.3}OP_{0.7}Si_{0.3}O_4$	12.929(9)	6.439(4)	10.623(7)	884.4	0.84
$KTi_{0.65}Nb_{0.35}OP_{0.65}Si_{0.35}O_4$	12.947(6)	6.444(3)	10.633(8)	887.1	0.81
$KTi_{0.6}Nb_{0.4}OP_{0.6}Si_{0.4}O_4$	12.970(5)	6.462(4)	10.640(7)	891.7	0.72
$KTiOAsO_4$	13.102(9)	6.561(8)	10.759(9)	924.9	1.01
$KTi_{0.9}Nb_{0.1}OAs_{0.9}Si_{0.1}O_4$	13.125(8)	6.572(4)	10.777(7)	929.7	1.04
$KTi_{0.8}Nb_{0.2}OAs_{0.8}Si_{0.2}O_4$	13.130(9)	6.575(6)	10.773(9)	930.0	1.03
$KTi_{0.7}Nb_{0.3}OAs_{0.7}Si_{0.3}O_4$	13.142(8)	6.571(7)	10.782(9)	931.0	0.98
$KTi_{0.6}Nb_{0.4}OAs_{0.6}Si_{0.4}O_4$	13.149(5)	6.573(4)	10.790(6)	932.6	0.90

[a] Normalized with respect to KTP.

ingly, we have synthesized two new solid-solution series, $KTi_{1-x}Nb_xOX_{1-x}Si_xO_4$ (X = P, As), which exist for $0 \leq x \leq 0.40$, and examined their structures and SHG properties. Both the series of solid-solutions, which are reported in this paper, retain the SHG response toward doubling of 1064-nm radiation frequency, indicating that substitution of Nb(V) for Ti(IV) does not adversely affect the nonlinear optical properties of KTP and KTA, unlike, for example, the substitution of Sb(V) for Ti(IV).[13]

Experimental Section

Polycrystalline samples of the composition $KTi_{1-x}Nb_xOX_{1-x}Si_xO_4$ (X = P, As), were prepared by the ceramic method using K_2CO_3/KNO_3, TiO_2, Nb_2O_5, SiO_2, and $(NH_4)H_2PO_4/(NH_4)H_2AsO_4$ as starting materials. Stoichiometric quantitities of the starting materials corresponding to various x values were thoroughly mixed and reacted, first at 500 °C for 12 h and later at 900 °C for 24 h with a grinding in between. Lower temperatures (750–800 °C) and longer durations of reaction were required for the formation of desired phases with $x > 0.30$. Formation of single-phase products was checked by X-ray powder diffraction (JEOL JDX-8P X-ray diffractometer, Cu Kα radiation). Lattice parameters were derived by least-squares refinement of the powder diffraction data from single-phase materials. Infrared spectra were recorded with a Perkin-Elmer spectrometer, Model 580, using KBr pellets.

SHG intensities were measured on polycrystalline samples sieved to uniform grain size (150–200 μm). A pulsed Q-switched Nd:YAG laser (Quanta Ray DCR-2A) with a pulse duration of 8 ns at 1.06 μm was used to generate a second harmonic signal from the samples. The forward scattered SHG light was collected using a lens and passed through a filter which transmits only the 532-nm radiation. The intensities of the incident laser beam and SHG radiation were measured using an energy ratio meter equipped with pyroelectric and silicon detectors. Measured SHG intensities of samples were normalized with respect to that of KTP.

Results and Discussion

We first attempted to synthesize the $x = 1$ member of the series, $KTi_{1-x}Nb_xOP_{1-x}Si_xO_4$, with the hope of preparing a new analog of KTP, namely $KNbOSiO_4$. Our attempts employing the ceramic method as well as the hydrothermal method using $NbCl_5$, SiO_2, and KOH as starting materials failed to yield the desired phase. In the ceramic preparations, $K_6Nb_6Si_4O_{26}$ was the major phase.[16] We have, however, been able to prepare members of the solid-solution series $KTi_{1-x}Nb_xOP_{1-x}Si_xO_4$ for $0 < x \leq 0.40$ by the ceramic method. Members up to $x = 0.40$ possess the orthorhombic structure of KTP (Figure 1), while the $x = 0.50$ member shows additional reflections, possibly due to impurity phase(s), in the X-ray pattern (Figure 1). We could also prepare arsenic analogs $KTi_{1-x}Nb_xOAs_{1-x}Si_xO_4$, for x up to 0.40 (Figure 1). The lattice parameters of all the members are listed in Table I, and indexed powder diffraction data for a representative member, $x = 0.40$ in the KTA series, are given in Table II. The variation of the cell parameters with x for the X = P series is shown in Figure 2. The a parameter as well as the cell volume show a marked increase with x, probably reflecting the replacement of smaller Ti(IV)/P(V) by the larger Nb(V)/Si(IV) ions.[17] Formation of the solid solutions $KTi_{1-x}Nb_xOX_{1-x}Si_xO_4$, for x up to 0.40, shows that it is possible to replace a considerable amount of Ti(IV) by Nb(V) in the KTP structure, provided Si(IV) is simultaneously substituted for P/As.

Table II. X-ray Powder Diffraction Data for $KTi_{0.6}Nb_{0.4}OAs_{0.6}Si_{0.4}O_4$

hkl	d_{obs} (Å)	d_{cal} (Å)	I_{obs}	*hkl*	d_{obs} (Å)	d_{cal} (Å)	I_{obs}
200	6.583	6.574	8	223	2.270	2.276	9
110	5.887	5.879	23	512	2.224	2.224	14
011	5.627	5.617	100	130	2.159	2.161	7
210	4.635	4.648	3	323	2.125	2.123	6
202	4.162	4.170	8	404 024	2.085	2.085	7
112	3.986	3.979	14				
310	3.655	3.647	14	205 015	2.049	2.050	7
212	3.534	3.521	20				
311	3.460	3.455	22	132	2.006	2.006	10
203 013	3.153	3.155	84	330	1.961	1.960	9
121	3.063	3.058	19	603 033	1.871	1.871	8
312	3.013	3.021	24	621 431	1.796	1.798	8
220	2.949	2.940	23				
411 221	2.836	2.836	94	523 711	1.783	1.783	9
402 022	2.805	2.807	98	424	1.762	1.761	19
				225	1.740	1.740	14
004	2.694	2.697	17	530	1.683	1.687	8
320	2.622	2.629	7	531	1.663	1.663	8
222	2.581	2.581	9	234 800	1.647	1.647 1.644	11
313	2.564	2.561	6				
511	2.383	2.381	6	026	1.576	1.578	15

We have recorded the infrared spectra of the members of the $KTi_{1-x}Nb_xOX_{1-x}Si_xO_4$ series in order to provide further support to the formation of phases with the KTP structure. KTP shows a characteristic infrared absorption spectrum in the 200–1200-cm^{-1} region with as many as 15 absorption bands, which are due to the two crystallographically distinct PO_4 and distorted TiO_6 groups.[18] The spectra of the Nb-substituted phases are similar to the spectrum of KTP (Figure 3) showing most of the characteristic absorption bands. Particularly significant is the shift in the TiO_6 absorption frequencies in the 600–820-cm^{-1} region toward lower frequencies in the Nb-substituted KTP analogs.

Measurement of the SHG intensity of powder samples of the $KTi_{1-x}Nb_xOX_{1-x}Si_xO_4$ series using pulsed Nd:YAG laser shows the frequency-doubling characteristic of KTP. The green (532 nm) light due to the SHG effect could be observed visually. Quantitative SHG intensities of the X = P series normalized to that of KTP show a slight enhancement up to $x = 0.15$, followed by a decrease in the region $0.15 < x \leq 0.40$. The arsenic analogs show a similar but less drastic variation of SHG intensity (Table I). It must be pointed out that the variation in intensity especially the increase for $0.00 < x \leq 0.15$ may not be significant, given

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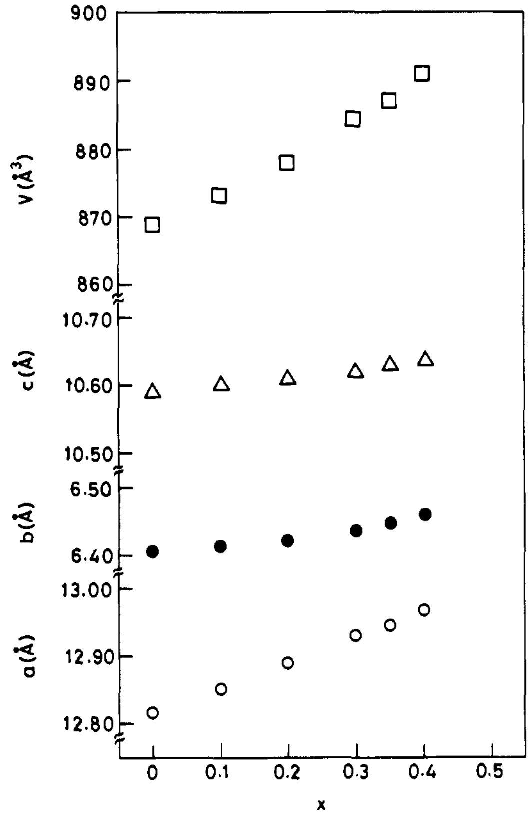

Figure 2. Variation of lattice parameters with x for the $KTi_{1-x}Nb_xOP_{1-x}Si_xO_4$ series.

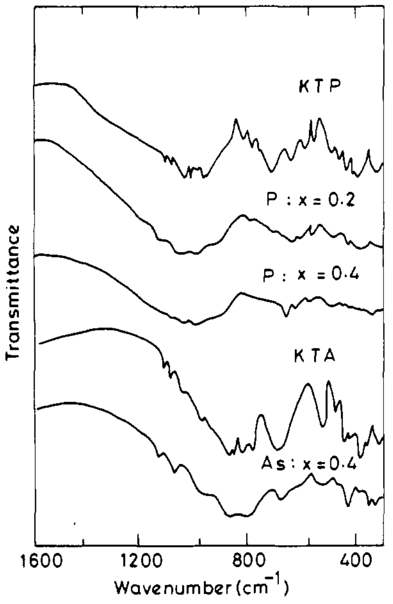

Figure 3. Infrared absorption spectra of $KTi_{1-x}Nb_xOX_{1-x}Si_xO_4$ ($X = P$, As) members.

the large number of variables (particle size, alignment of the beam, sample packing and positioning, and preferred orientation) that affect the measured intensities. It is however striking that both the $X = P$ and $X = As$ series show a similar trend in SHG intensity.

While it is difficult to attribute significance to the finer variation of SHG intensities of the Nb-substituted KTP analogs, what seems to be important is that considerable substitution of Nb(V) for Ti(IV) in KTP and KTA has not destroyed the SHG response. This result stands in contrast to that of Sn(IV) and Sb(V) substitution in KTP. Thus, both $KSnOPO_4$[19] and $KSbOSiO_4$[20] crystallize with the same KTP structure; nevertheless, their SHG response is nearly zero. Similarly, the SHG response of the series $KTi_{1-x}Sb_xOP_{1-x}Si_xO_4$ rapidly decreases[13] with x, becoming nearly zero for values of $x > 0.2$. The effect of Sn(IV) and Sb(V) substitutions on the nonlinear optical properties of KTP has been attributed to the presence of more symmetric SnO_6/SbO_6 octahedra than their TiO_6 counterparts in the KTP structure. The symmetric octahedra in turn arise from the d^{10} electronic configuration of these cations; with a filled d-shell, the bonding between metal and oxygen is such that it leaves the metal at the center of its octahedron.[21] Nb(V), on the other hand, possessing a d^0 electronic configuration, is similar to Ti(IV) in its crystal chemistry of oxides,[14,22] exhibiting a ferroelectric distortion of metal–oxygen octahedra. The distortion is characteristic of oxides of d^0 cations where a strong π bonding between metal and oxygen is possible.[14,21] Accordingly, Nb(V) substitution in KTP and KTA seems to preserve the distorted octahedral environment around the metal atom and the alternating long and short metal–oxygen bonds in the octahedral chains and therefore does not destroy the nonlinear optical property of the material. Further work employing single crystals is necessary to fully characterize the structure and nonlinear optical properties of these materials.

The recent work of McCarron et al.[23] on the substitution of Nb(V) and Mg(II) for Ti(IV) in KTP is relevant to the present work. Even a 10 atom % substitution of Nb(V) and Mg(II) at Ti(IV) sites in KTP results in a dramatic loss of SHG, unlike the coupled substitution reported here. The result seems to suggest that exclusive presence of d^0 cations at the Ti(IV) sites is essential to preserve the nonlinear optical property of KTP analogs.

In summary, we have shown that it is possible to substitute up to about 40 atom % of Nb(V) for Ti(IV) in both KTP and KTA by coupled substitution of Si(IV) for P/As. Significantly, the Nb substitution in KTP and KTA does not destroy the SHG response, indicating the importance of the d^0 electronic configuration of the transition metal ion in determining the nonlinear optical property of KTP and related materials. Further work is in progress to substitute other d^0 metal ions in the KTP structure by similar techniques.

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