

Non-linear optical response of rutile-related oxides, $\text{LiM}^{\text{V}}\text{M}^{\text{VI}}\text{O}_6$, and their derivatives obtained by ion-exchange and intercalation

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Polycrystalline samples of oxides of the general formula $\text{LiM}^{\text{V}}\text{M}^{\text{VI}}\text{O}_6$ ($\text{M}^{\text{V}} = \text{Nb, Ta}; \text{M}^{\text{VI}} = \text{Mo, W}$), crystallizing in a non-centrosymmetric (space group $P4_21m$) rutile structure, exhibit second harmonic generation (SHG) of 1064 nm radiation with efficiencies 15–45 times that of α -quartz; interestingly, the SHG response is retained by the protonated derivatives $\text{HM}^{\text{V}}\text{M}^{\text{VI}}\text{O}_6 \cdot x\text{H}_2\text{O}$, and their *n*-alkylamine intercalates as well.

Transition-metal oxides containing octahedrally coordinated d^0 cations exhibit several novel structural and electronic properties, such as crystallographic shear,¹ ferroelectricity² and non-linear optical (NLO) response^{3,4} (e.g. second harmonic generation), which could be traced to out-of-centre distortions of the metal–oxygen octahedra. These distortions arise from a second-order Jahn–Teller effect^{5,6} that involves mixing of empty cation d orbitals with filled anion p orbitals resulting in removal of degeneracy and consequent spontaneous structural distortion. KTiOPO_4 (KTP) is one such material exhibiting efficient second harmonic generation (SHG) of 1064 nm radiation from an Nd:YAG laser;⁷ the $3d^0$ electronic configuration of Ti^{IV} and the associated distortion of TiO_6 octahedra play a crucial role toward the SHG property of this material.^{8,9} The importance of d^0 electronic configuration is revealed by the synthesis of the Sn^{IV} $4d^{10}$ analogue of KTP, KSnOPO_4 , where the distortion of SnO_6 octahedra as well as the SHG response decrease dramatically.¹⁰ We have recently demonstrated^{11,12} the role of d^0 cations towards the SHG property of this structure by synthesizing several KTP derivatives, $\text{KM}^{\text{V}}_{0.5}\text{Ti}^{\text{IV}}_{0.5}\text{OPO}_4$ and $\text{K}_{0.5}\text{M}^{\text{V}}_{0.5}\text{Ti}^{\text{IV}}_{0.5}\text{OPO}_4$ ($\text{M} = \text{Nb, Ta}$), of which only the latter show SHG response comparable to KTP.

Oxides of the general formula $\text{LiM}^{\text{V}}\text{M}^{\text{VI}}\text{O}_6$ ($\text{M}^{\text{V}} = \text{Nb, Ta}; \text{M}^{\text{VI}} = \text{Mo, W}$), crystallizing in a non-centrosymmetric ($P4_21m$) rutile related structure in which Li, M^{V} and M^{VI} atoms are ordered in layers perpendicular to the c direction, show interesting ion-exchange and intercalation behaviour.^{13–17} The crystal structure of one of the members, LiNbWO_6 , has been determined.¹⁸ The structure (Fig. 1) shows the presence of distorted octahedral environment around the d^0 cations as well as lithium. The lithium atoms in these oxides, $\text{LiM}^{\text{V}}\text{M}^{\text{VI}}\text{O}_6$, are topochemically exchanged with protons in aqueous HNO_3 to yield $\text{HM}^{\text{V}}\text{M}^{\text{VI}}\text{O}_6 \cdot x\text{H}_2\text{O}$.^{15–17} The latter are strong Brønsted acids intercalating readily a wide variety of organic bases including pyridine, aniline and pyrrole. Both the protonated derivatives and their organic intercalates retain the rutile-like $\text{M}^{\text{V}}\text{M}^{\text{VI}}\text{O}_6$ sheets.^{15–17}

Considering that LiNbWO_6 crystallizes in a non-centrosymmetric structure consisting of distorted NbO_6 and WO_6 octahedra, we envisaged that oxides of this family and their derivatives would be potential candidates for SHG. Our investigations, reported here, show that not only the parent materials but also the protonated derivatives as well as their amine intercalates show a distinct SHG response toward 1064 nm radiation. We believe that this is the first report of SHG response of an isostructural series of layered oxides containing d^0 cations, that is not destroyed by ion-exchange and subsequent intercalation of organic molecules.

$\text{LiM}^{\text{V}}\text{M}^{\text{VI}}\text{O}_6$ ($\text{M}^{\text{V}} = \text{Nb, Ta}; \text{M}^{\text{VI}} = \text{Mo, W}$) were prepared by reacting Li_2CO_3 , $\text{M}^{\text{V}}\text{O}_5$ and $\text{M}^{\text{VI}}\text{O}_3$ (at 750 °C for $\text{M}^{\text{VI}} = \text{W}$ ^{13,14} and around 600 °C for $\text{M}^{\text{VI}} = \text{Mo}$ ¹⁷) for 2 days with one intermittent grinding. Proton-exchanged derivatives, $\text{HM}^{\text{V}}\text{M}^{\text{VI}}\text{O}_6 \cdot x\text{H}_2\text{O}$, were prepared, as reported earlier,^{15–17} by treating 1 g portions of the parent oxides in 100 ml aliquots of 2 mol l^{-1} HNO_3 at room temperature with stirring for 2 days. Amine intercalates of $\text{HM}^{\text{V}}\text{M}^{\text{VI}}\text{O}_6 \cdot x\text{H}_2\text{O}$ were prepared by refluxing the solid with a 10% solution of the amine in *n*-heptane for 2 days. Powder X-ray diffraction patterns showed formation of single-phase materials in all the cases and their lattice parameters (Table 1) were in agreement with the values reported earlier.^{13–17}

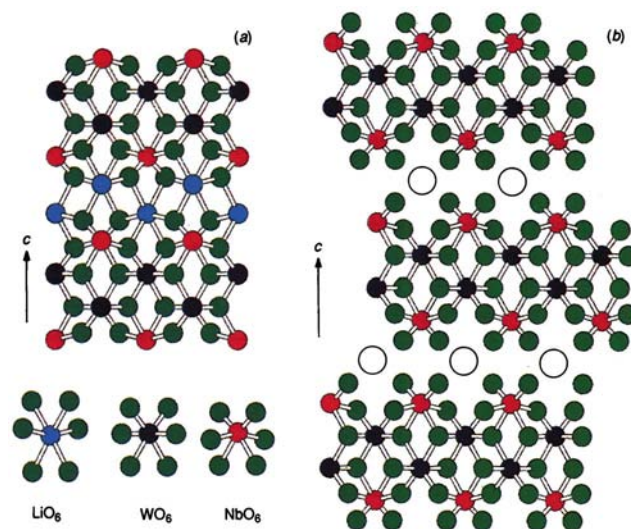


Fig. 1 (a) Structure of LiNbWO_6 viewed down the b -axis. (b) Schematic structure of $\text{HNbWO}_6 \cdot 1.5\text{H}_2\text{O}$, showing rutile-like NbWO_6 slabs separated by water molecules. The possible sites for water molecules are indicated by large open circles.

Table 1 Composition, lattice parameters and SHG intensity of $\text{LiM}^{\text{V}}\text{M}^{\text{VI}}\text{O}_6$ and their derivatives^a

Composition	Lattice parameters/Å		SHG intensity ^b
	<i>a</i>	<i>c</i>	
LiNbMoO_6	4.685	9.25	20
LiTaMoO_6	4.674	9.23	16
LiNbWO_6	4.681	9.28	26
LiTaWO_6	4.669	9.30	28
$\text{HNbMoO}_6 \cdot \text{H}_2\text{O}$	4.690	26.75	22
$\text{HNbWO}_6 \cdot 1.5\text{H}_2\text{O}$	4.71	25.70	33
$(\text{NH}_2\text{C}_6\text{H}_{13})_{0.51}\text{HNbMoO}_6$	4.70	24.50	32
$(\text{NH}_2\text{C}_8\text{H}_{17})_{0.53}\text{HNbMoO}_6$	4.72	29.40	16
$(\text{NH}_2\text{C}_6\text{H}_{13})_{0.76}\text{HNbWO}_6$	4.71	23.90	40
$(\text{NH}_2\text{C}_7\text{H}_{15})_{0.74}\text{HNbWO}_6$	4.73	27.20	36
$(\text{NH}_2\text{C}_8\text{H}_{17})_{0.92}\text{HNbWO}_6$	4.72	29.40	45

^a The amine intercalates retain water of hydration. ^b The values, which are relative to quartz, are accurate within ± 2 units.

SHG intensities were measured on polycrystalline samples sieved to uniform grain size (25–45 μm) by the method of Kurtz and Perry.¹⁹ A pulsed Q-switched Nd:YAG laser (Quanta Ray DCR-2A) with a pulse duration of 8 ns at 1064 nm was used to generate SHG signal from the samples. The backward scattered SHG light was collected using a spherical concave mirror and passed through a filter which transmits only 532 nm radiation. Measured SHG intensities of $\text{LiM}^{\text{V}}\text{M}^{\text{VI}}\text{O}_6$ and their derivatives (Table 1) are 15–45 times that of α -quartz, measured under similar conditions. The SHG intensity of $\text{LiM}^{\text{V}}\text{M}^{\text{VI}}\text{O}_6$ and their derivatives are in the same order of magnitude as that of β - BaB_2O_4 , which is 82 times that of α -quartz.²⁰

The intensities of parent $\text{LiM}^{\text{V}}\text{M}^{\text{VI}}\text{O}_6$ are in the range 16–28 times that of α -quartz. The optical absorption edge of these materials, recorded using a Pye-Unicam UV–VIS spectrometer, shows a systematic shift towards shorter wavelengths in the order: LiNbMoO_6 (370 nm) > LiTaMoO_6 (350 nm) > LiNbWO_6 (340 nm) > LiTaWO_6 (330 nm) (Fig. 2). We do not however see a correlation between the optical absorption edge and the SHG intensity of this series. One would have expected an inverse relationship between the SHG intensity and the square of the mean band gap and, hence the optical absorption edge, on the basis of bond-orbital theory.⁴

According to the bond polarizability model of Bergman and Crane,²¹ the NLO response of a solid is a summation of the polarizabilities of the contributing cation–anion bonds. In the presence of highly polarizable $\text{M}^{\text{V}}\text{–O}$ ($\text{M}^{\text{V}} = \text{Nb}^{\text{V}}, \text{Ta}^{\text{V}}$) and $\text{M}^{\text{VI}}\text{–O}$ ($\text{M}^{\text{VI}} = \text{Mo}^{\text{VI}}, \text{W}^{\text{VI}}$) bonds in an oxide, one would expect a strong SHG response provided other factors are favourable. Wiegel *et al.*²² have recently shown that the SHG response of LiNbO_3 and LiTaO_3 increases considerably by substitution of W for Nb/Ta, presumably because the polarizability of W–O bonds is much higher than those of $\text{Nb–O}/\text{Ta–O}$ bonds. The fact that the SHG intensities of rutile-like $\text{LiM}^{\text{V}}\text{M}^{\text{VI}}\text{O}_6$ reported here are only about 25 times that of α -quartz is most likely due to a cancellation of the polarizabilities of the individual $\text{M}^{\text{V}}\text{–O}$ and $\text{M}^{\text{VI}}\text{–O}$ bonds in this structure. This could be seen from the orientation of the $\text{M}^{\text{V}}\text{O}_6$ and $\text{M}^{\text{VI}}\text{O}_6$ octahedra in the *c*-direction, wherein the off-centre displacements of the M^{V} and M^{VI} atoms are in the opposite direction (Fig. 1). If, in such a structure, the M^{V} and M^{VI} atoms are randomly distributed, the net polarizability would be small. The crystal structure of

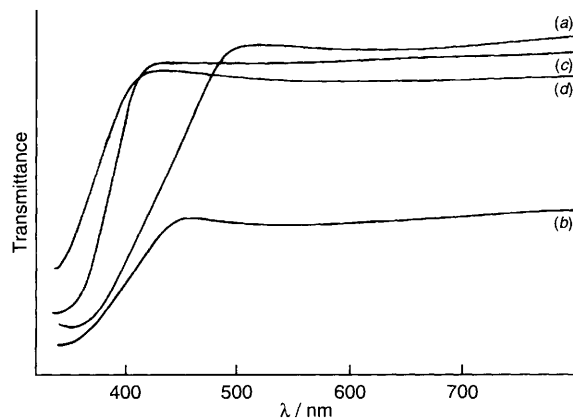


Fig. 2 Diffuse reflectance spectra of (a) LiNbMoO_6 , (b) LiTaMoO_6 , (c) LiNbWO_6 and (d) LiTaWO_6 .

LiNbWO_6 indeed reveals considerable disorder of Nb/W atoms.¹⁸

A significant new result from the present work is that the protonated derivatives, $\text{HM}^{\text{V}}\text{M}^{\text{VI}}\text{O}_6 \cdot x\text{H}_2\text{O}$, and their alkylamine intercalates retain the SHG response of the parent oxides (Table 1). This result suggests that the SHG response of these materials is a two-dimensional property arising from the net hyperpolarizability of $\text{M}^{\text{V}}\text{M}^{\text{VI}}\text{O}_6$ slabs (Fig. 1). Accordingly, the Li–O bonds linking the $\text{M}^{\text{V}}\text{M}^{\text{VI}}\text{O}_6$ slabs in the third dimension do not seem to make an appreciable contribution to the net polarizability of $\text{LiM}^{\text{V}}\text{M}^{\text{VI}}\text{O}_6$.

In summary, rutile-related $\text{LiM}^{\text{V}}\text{M}^{\text{VI}}\text{O}_6$ oxides ($\text{M}^{\text{V}} = \text{Nb}, \text{Ta}$; $\text{M}^{\text{VI}} = \text{Mo}, \text{W}$) show a distinct SHG response towards 1064 nm radiation that is not destroyed in the protonated derivatives, $\text{HM}^{\text{V}}\text{M}^{\text{VI}}\text{O}_6 \cdot x\text{H}_2\text{O}$, and their alkylamine intercalates.

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