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Influence of the Cation Size on the Second Harmonic Generation Response of Chiral $A(VO_2)_2(PO_4)\cdot 3H_2O$ ($A = K^+$, NH_4^+ and Rb^+)

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New insights on the relationships between chirality and nonlinear optical (NLO) properties are of interest for the future design of phases with strong Second Harmonic Generation (SHG) response. The structures of the new $A(VO_2)_2(PO_4)\cdot 3H_2O$ ($A=K^+$ and Rb^+) phases prepared by hydrothermal method were determined by single crystal X-ray diffraction. The SHG properties of these new chiral materials and the previously reported isostructural $NH_4(VO_2)_2(PO_4)\cdot 3H_2O$ were measured. For an incident wavelength of 1064 nm, the SHG responses at 532 nm of Rb, NH_4 and K analogues were respectively 2, 6 and 24 times stronger than quartz. The NLO properties were shown to increase strongly when the structure slightly contracts.

INTRODUCTION

Chiral materials are of interest owing to their physical properties such as dichroism or Second Harmonic Generation (SHG) activity. In the past decades, more attention has been focused on developing new strategies for the design of noncentrosymmetric (NCS) compounds with strong SHG response. In order to develop these strategies, one should firstly be able to identify the characteristics of the material which enhance the response.

In the literature, different features have been reported to play a role in the SHG efficiency. Thus, Ye et al. showed that the SHG response was correlated with the alignment of polar anionic units.[1] They calculated this alignment for different NCS materials and were able to predict the ones exhibiting high response. Then, this optimization of the alignment was a goal for different research groups trying to design new polar materials. Different strategies which enable this design were reported such as the use of Λ shape units or hydrogen bondings.[2-10] Other structural features were shown to play a role in the optimization of NLO properties. Thus, the dimensionality of the crystal structure and the polarizability of alkali metal can influence these properties. For example, Bera *et al.* showed an enhancement of the SHG response when increasing x in $Li_{1-x}Na_xAsS_2$ (Na has a higher polarizability than Li).[11] In $AAsSe_2$ (A = Li, Na,), controlling the dimensionality is presented as a strategy to design better SHG materials.[12] The distortion of a NCS structure from the CS equivalent was also shown to be correlated to the SHG response.[13] This quantification is similar to the previously reported approach to evaluate the chirality degree of a molecule and has been successful to explain the strong SHG response of borate compounds.[14]

In this context, it is important to note that most of the approaches to understand the relationships between crystal structure and SHG response have been focused on inorganic *polar* materials. The inorganic *chiral* materials have been much less studied and the structural parameters influencing the SHG response are not well understood.

In order to provide more insights on the relationships between chirality and nonlinear optical (NLO) properties, we targeted the synthesis of new $A(VO_2)_2(PO_4)\cdot 3H_2O$ (A= alkali metal) isostructural of the previously reported chiral $NH_4(VO_2)_2(PO_4)\cdot 3H_2O$.[15] These materials exhibit different SHG responses and serve to a better understanding of the structural parameters influencing the NLO properties.

EXPERIMENTAL DETAILS

Synthesis

$K(VO_2)_2PO_4\cdot 3H_2O$ and $Rb(VO_2)_2PO_4\cdot 3H_2O$ crystals were prepared by hydrothermal method. The mixture is composed of 1mmol V_2O_5, 2mmol M_2CO_3 (with $M=K^+$ and Rb^+), 1ml H_3PO_4 85% and 4ml H_2O. To prepare samples suitable for single crystal X-ray diffraction, the reactants were loaded in a Teflon-

lined stainless steel autoclave (23ml) and heated at 100°C during 25h and cooled down to room temperature (5°C/h). The crystals were washed with cold water and dried in a dessicator. Layer green crystals of $A_x(VOPO_4)\cdot yH_2O$ were also obtained during hydrothermal synthesis. In order to prepare pure polycrystalline $A(VO_2)_2PO_4\cdot 3H_2O$ samples, the mixture of reactants was refluxed under agitation during 30 min instead of realizing hydrothermal synthesis (Figure S1).

Structure determination

The crystal structures of $K(VO_2)_2PO_4\cdot 3H_2O$ and $Rb(VO_2)_2PO_4\cdot 3H_2O$ were solved using a four-circle Nonius KappaCCD diffractometer with a graphite monochromated Mo Kα radiation (λ=0.71073Å). The intensities were collected through the program COLLECT for the Kappa CCD[16] in the ω-ϕ scanning mode. Using WINGX software,[17] the structures were solved with SIR-97[18] and refined with SHELXL-97.[19]

Chemical formula	$K(VO_2)_2(PO_4)\cdot 3H_2O$	$Rb(VO_2)_2(PO_4)\cdot 3H_2O$
Chemical formula weight (g.mol^{-1})	353.95	400.32
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
Z	4	4
a (Å)	7.1203(1)	7.1884(2)
b (Å)	10.1782(2)	10.3290(3)
c (Å)	12.3477(3)	12.3618(4)
V (Å^3)	894.86(3)	917.85(5)
T (K)	293(2)	293(2)
Maximum 2θ	64°	55°
λ(Mo Kα) (Å)	0.71073	0.71073
Unique data after merging	3096	2103
Observed data (>2.0σ(F^2)).	2950	1815
Free parameters	136	137
Data collected	h : -10, 10 k : -14, 15 l : -18, 16	h : -9, 8 k : -13, 13 l : -16, 15
$\rho_{calc.}$ (g.cm^{-3})	2.458	2.820
Absorption coefficient	2.208 cm^{-1}	8.183 cm^{-1}
Rint	0.024	0.071
R_1	0.026	0.039
wR_2	0.069	0.075
Goodness-of-fit	1.22	1.16
Min, Max (e/ Å^3)	-0.55, 0.63	-0.70, 1.01

Table 1. Crystal data for $K(VO_2)_2(PO_4)\cdot 3H_2O$ and $Rb(VO_2)_2(PO_4)\cdot 3H_2O$

Thermal analysis

Thermogravimetric and Differential Scanning Calorimetry (DSC) measurements were monitored on a SETARAM TG-DSC111 instrument under pure argon from room temperature to 800°C with an heating rate of 5°C/min.

Particle-size distribution analysis

The analysis of the particle-size distribution was performed by laser diffraction. The samples of $A(VO_2)_2(PO_4)\cdot 3H_2O$ ($A=K^+$, NH_4^+ and Rb^+) were dispersed in ethanol solution. A Beckman-Coulter LS-230 apparatus equipped with a 750 nm laser beam was used to measure the diameter of the particles with sizes ranging from 0.4 µm to 2000 µm.

UV-Visible diffuse reflectance

Diffuse reflectance spectra were collected from 350 nm to 1000 nm for compounds $A(VO_2)_2(PO_4)\cdot 3H_2O$ ($A=K^+$, NH_4^+ and Rb^+) on a Varian Cary 5G spectrophotometer equipped with a 60 mm integrating sphere. The samples were prepared by finely grinding the materials in a mortar. The absorption data (a/S) were calculated from the reflectance data with the use of the Kubelka-Munk function (a/S = $(1\text{-}R)^2/2R$) where a is the absorption coefficient, S is the scattering coefficient, and R is the reflectance.

Second Harmonic Generation measurements

Figure 1 shows the experimental setup used for the TR-SHG measurements. A Nd:YAG Q-switched laser (Quantel) operating at 1.06 µm was used to deliver up to 360 mJ pulses of 5 ns duration with a repetition rate of 10 Hz. An energy adjustment device made up of two polarizers (P) and a half-wave plate (λ/2) allowed the incident energy to vary from 10 to ca. 312 mJ per pulse. A RG1000 filter was used after the energy adjustment device to remove light from laser flash lamps. The samples (few mg of powder in a crucible) were placed in a computer controlled Heating-Cooling stage (Linkam THMS-600) and were irradiated with a beam (4 mm in diameter).
The signal generated by the sample (diffused light) was collected into an optical fiber (500 µm of core diameter) and directed onto the entrance slit of a spectrometer (Ocean Optics). A boxcar integrator allowed an average spectrum (spectral range 490-590 nm) with a resolution of 0.1 nm to be recorded over 3 s (30 pulses).

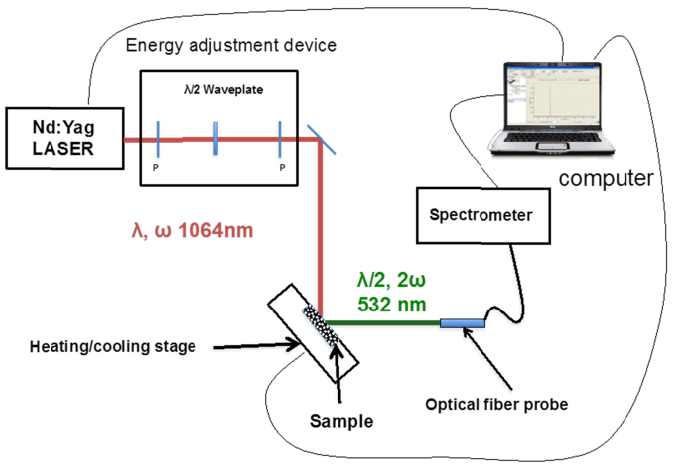

Figure 1. Experimental setup Second Harmonic Generation Apparatus constituted of Nd:YAG Q-switched laser operating at 1064 nm.

According to Kurtz and Perry SHG powder method, SHG signal intensities were compared to the signal of a reference compound (α-quartz powder- 45 µm average size).[20] As the synthesized materials undergo slight degradation, the SHG measurements were performed at 80K and the incident energy was set at the minimum intensity.

RESULTS AND DISCUSSION

Structure description

The isostructural $A(VO_2)_2(PO_4)\cdot 3H_2O$ (A=K^+, NH_4^+ and Rb^+) materials crystallize in the chiral space-group $P2_12_12_1$. The structure is built of vanadium oxide chains running along the *a* axis and connected by phosphate groups (Figure 2). The alkali metals and free water molecules are localized inside of the channels. In the chains, $V(1)O_6$ and $V(2)O_6$ corner-sharing octahedra form trimer fragments. The V-O bond lengths in $V(1)O_6$ octahedra range from 1.6068(21) Å/ 1.5968(43) Å to 2.2490(21) Å/ 2.2675(44) Å for A=K/Rb, respectively. The two shortest V=O bonds are terminal. In $V(2)O_6$ octahedra, the bond distances range from 1.6524(43) Å/ 1.6519 (11) Å to 2.2045(20) Å/ 2.2220(42) Å for A=K/Rb, respectively. One of the two shortest bonds corresponds to a terminal oxide ligand whereas the other one alternates with a long V-O bond along the chains. The volume of the unit cells increase with the size of the cations such as $K^+ < NH_4^+ < Rb^+$ (V/Z = 223.71 $Å^3$, 228.5 $Å^3$ and 229.46 $Å^3$, respectively).

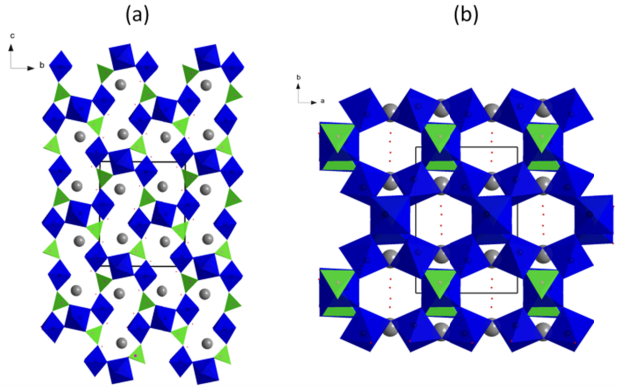

Figure 2. Crystal structures of $A(VO_2)_2(PO_4)\cdot 3H_2O$ (A=K^+, NH_4^+ and Rb^+) compounds viewed (a) along *a* and (b) along *c*. Phosphates and vanadium oxides groups are represented in green and blue color, respectively.

Thermal behaviour of $A(VO_2)_2(PO_4)\cdot 3H_2O$ (A=K^+, NH_4^+ and Rb^+)

The thermogravimetric analysis and Differential Scanning Calorimetry performed on $A(VO_2)_2(PO_4)\cdot 3H_2O$ (A=K^+, NH_4^+ and Rb^+) phases show a weight loss between room temperature and 170°C accompanied by an endothermic peak in the DSC curve corresponding to the dehydration of the materials (loss of three water molecules) (Figure 3). The melting process of the anhydrous phases is identified by another endothermic peak for potassium and rubidium vanadium phosphate phases at 520°C. For $NH_4(VO_2)_2(PO_4)\cdot 3H_2O$, a second weight variation corresponding to the loss of NH_3 and ½ H_2O is observed at 330°C. This weight loss is in agreement with the previous transformation of $NH_4(VO_2)_2(PO_4)\cdot 3H_2O$ into $(VO)_2P_2O_7$ and amorphous phase at about 400°C under ammoxidation conditions.[15]

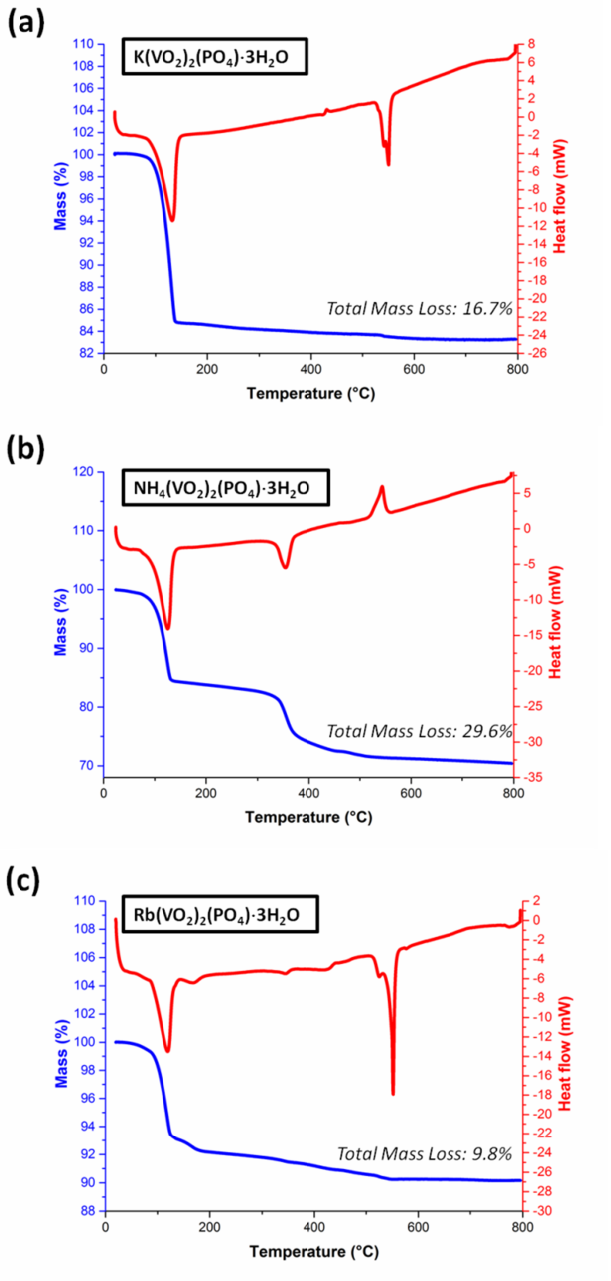

Figure 3. Thermogravimetric analysis and Differential Scanning Calorimetry of (a) $K(VO_2)_2(PO_4)\cdot 3H_2O$ (6.6 mg) (Expected weight loss: 15.2%), (b) $NH_4(VO_2)_2(PO_4)\cdot 3H_2O$ (8 mg) (Expected weight loss: 24.02%) and (c) $Rb(VO_2)_2(PO_4)\cdot 3H_2O$ (Expected weight loss: 13.48%) (12.7 mg) compounds under Argon.

Influence of the cation size on the SHG properties

As the $A(VO_2)_2(PO_4)\cdot 3H_2O$ ($A=K^+$, NH_4^+ and Rb^+) materials crystallize in the space-group $P2_12_12_1$, these phases are potentially SHG active (every chiral compounds except the ones in the point-group 432 can be active).[21] The crystal size distributions are similar for every compounds. Thus, the average size is about 18 µm, 25 µm and 32 µm for the K, Rb and NH_4 analogues, respectively (Figure S2). Moreover, UV-Vis diffuse reflectance spectra show that the compounds have similar absorption at the frequency of the second harmonic (532 nm) (Figure 4) and the three samples show similar crystallinity. These results allow a fair comparison between the SHG responses of the $A(VO_2)_2(PO_4)\cdot 3H_2O$ ($A=K^+$, NH_4^+ and Rb^+) materials. The SHG measurements were performed at 80K in order to higher the laser damage thresholds. A little degradation occurred even by using a low incident energy (fundamental energy = 28 mJ). Even if a decrease of the signal was observed after the first measurements, it was possible to compare the SHG responses: At 532 nm, the response of K, NH_4 and Rb analogues are about 24, 6 and 2 times stronger than that of quartz (Figure 5). The evolution of the SHG response for different cations in our chiral inorganic structures cannot be compared with the one of previously reported polar inorganic structures. Firstly, the polarizability of the cations in our structures plays no role on the SHG response since the intensity is lower when the alkali metal is more polarizable. Moreover, the dimensionality which is identical in the three materials cannot be a factor influencing the NLO properties. In addition, the Cheng's theory cannot be used because the materials are not polar (the net dipole moments cancel each other in chiral $P2_12_12_1$,space group). All these features which are specific of polar materials can also not be used to understand the relationships between the chirality and the SHG performances. Moreover, the NLO property cannot be related to the distortion from the centrosymmetry. Hence, the distortion of the $A(VO_2)_2(PO_4)\cdot 3H_2O$ ($A=K^+$, NH_4^+ and Rb^+) structures from one to the other is negligible in comparison of the distortion of this chiral structure from its pseudosymmetric centric structure.

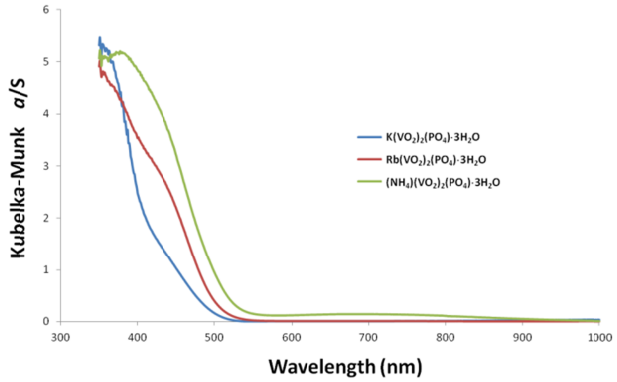

Figure 4. Diffuse reflectance spectra of compounds $A(VO_2)_2(PO_4)\cdot 3H_2O$ ($A=K^+$, NH_4^+ and Rb^+). The reflectance is converted with use of the Kubelka-Munk equation.

The main difference between the structures of $K(VO_2)_2(PO_4)\cdot 3H_2O$, $NH_4(VO_2)_2(PO_4)\cdot 3H_2O$ and $Rb(VO_2)_2(PO_4)\cdot 3H_2O$ is the volume of the unit-cells. The contraction of the structure would be at the origin of the different SHG responses. For the materials reported in this article, the more the crystal structure is contracted, the stronger the SHG response is. Thus, the SHG intensities which are 2, 6 and 24 times stronger than quartz correspond to unit-cells with V/Z of 229.46 $Å^3$ (for A=Rb), 228.5 $Å^3$ (for $A=NH_4$) and 223.71 $Å^3$ (for A=K) respectively (Figure S3). This slight contraction of the structure would also be at the origin of this strong increase of the SHG response.

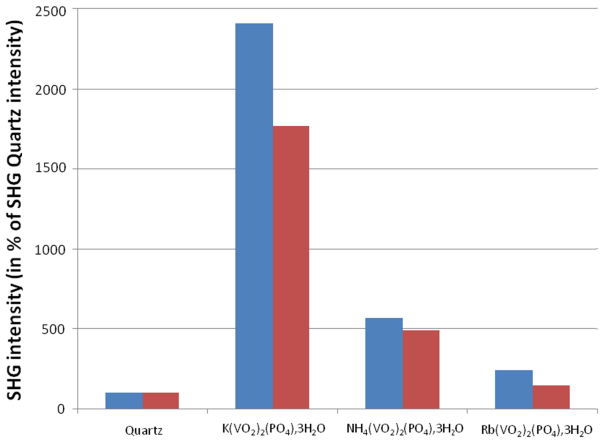

Figure 5. SHG measurements of $A(VO_2)_2(PO_4)\cdot 3H_2O$ ($A=K^+$, NH_4^+ and Rb^+) materials (First and second measurement in blue and red, respectively).

CONCLUSIONS

SHG was firstly demonstrated in 1961 in a quartz crystal.[22] Since then, little effort has been realized to understand the relationships between *chiral* inorganic materials and SHG response. Thus, most of the attention has been focused on the *polar* inorganic materials but the relationships between polar structure and the NLO properties are different than for the ones of chiral structures. The determination of the crystal structure of new chiral $A(VO_2)_2(PO_4)\cdot 3H_2O$ ($A=K^+$ and Rb^+) and the SHG measurements showed that the response depends on the contraction of the structure. This observation could also be of interest for the future design and enhancement of SHG properties from chiral inorganic materials.

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Notes and references

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Electronic Supplementary Information (ESI) available: Powder X-ray diffraction patterns (Figure S1), Particle-size distribution analysis (Figure S2), SHG Intensity vs. Unit-cell volume (Figure S3) and Crystallographic data of compounds $A(VO_2)_2(PO_4)\cdot 3H_2O$ ($A=K^+$ and Rb^+) (CSD-427070 and CSD-427071, respectively).

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