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Large scale synthesis, second-harmonic generation, and piezoelectric properties of a noncentrosymmetric vanadium phosphate, Li_2VPO_6

Eun Pyo Lee [a], Dong Woo Lee [a], Yoon-Ho Cho [b], T. Thao Tran [c], P. Shiv Halasyamani [c], Kang Min Ok [a,*]

[a] Department of Chemistry, Chung-Ang University, 221 Heukseok-dong, Dongjak-gu, Seoul 156-756, Republic of Korea
[b] Department of Civil and Environmental Engineering, Chung-Ang University, Seoul 156-756, Republic of Korea
[c] Department of Chemistry, University of Houston, Houston, TX 77204-5003, USA

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ABSTRACT

The phase pure large scale synthesis, second-harmonic generation, and piezoelectric properties of a vanadium phosphate, Li_2VPO_6 are reported. The material has been synthesized by a standard solid-state reaction using Li_2CO_3, V_2O_5, and $NH_4H_2PO_4$ as reagents. The phase purity and crystal structure of the reported material have been confirmed by powder X-ray and neutron diffractions. The material crystallizes in orthorhombic space group $Pna2_1$ (no. 33) with $a=10.32581(7)$ Å, $b=4.63728(3)$ Å, $c=8.56606(5)$ Å, and $Z=4$. The noncentrosymmetric layered structure is composed of distorted VO_6 octahedra and PO_4 tetrahedra. The V^{5+} cations distort either along the approximate [1 0 1] or [−1 0 1] directions attributable to the alignment of distorted VO_6 octahedra, resulting in a polar structure. Powder second-harmonic generating (SHG) measurements on Li_2VPO_6 using 1064 nm radiation, indicate the material has a SHG efficiency of approximately 10 times that of α-SiO_2 and is not phase-matchable (type 1). Converse piezoelectric measurements for the material reveal a piezoelectric coefficient, d_{33}, of 12 pm V^{-1}.

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1. Introduction

Vanadium oxyphosphate materials have shown exceptionally rich structural chemistry attributable to the combination of PO_4 tetrahedra and a variety of structural building blocks found in VO_n polyhedra such as VO_4 tetrahedra, VO_5 square pyramids, and VO_6 octahedra [1–4]. The association of diverse coordination environments containing a great deal of framework flexibilities resulted in various structural topologies, i.e., chains [5,6], layers [7,8], and three-dimensional frameworks [9,10]. In addition, the structurally versatile materials reveal interesting materials characteristics such as catalytic [11,12], electrochemical [13–15], and magnetic properties [16–18]. We are particularly interested in properties observed from a class of materials with noncentrosymmetric (NCS) crystal structures, because the NCS materials can exhibit technologically important functional features such as second-harmonic generation (SHG), piezoelectricity, pyroelectricity, and ferroelectricity [19–24]. With oxide materials, the NCS structures are often observed in compounds containing second-order Jahn–Teller (SOJT) distortive cations, i.e., octahedrally coordinated d^0 transition-metal ions (Ti^{4+}, V^{5+}, W^{6+}, etc.) and lone pair cations (Sb^{3+}, Te^{4+}, I^{5+}, etc.) [25–29]. In fact, several V^{5+}-containing NCS materials exhibiting asymmetric coordination environment through the spontaneous distortion have been reported with their nonlinear optical (NLO) properties [30–40]. With respect to pentavalent vanadium phosphates materials, a number of structurally interesting materials have been also reported [41–45]. Among many, we have been very interested in NCS Li_2VPO_6 that is composed of distorted VO_6 octahedra and PO_4 tetrahedra. In this paper, we describe the large scale pure phase synthesis and the NCS properties such as powder SHG and piezoelectricity of Li_2VPO_6. We also report the structural origin of the NCS properties in the reported material.

2. Experimental section

2.1. Synthesis

Phase pure polycrystalline sample of Li_2VPO_6 was synthesized on the 10 g scale through standard solid-state reaction techniques. Stoichiometric amounts of Li_2CO_3 (Hayashi, 98%), V_2O_5 (Aldrich, 99%), and $NH_4H_2PO_4$ (Aldrich, 98%) were thoroughly mixed with an agate mortar and pestle and pressed into pellets. The pellets were transferred to an alumina crucible and were gradually heated to 580 °C for 36 h with an intermediate regrinding. The pellets were cooled at a rate of 10 °C h^{-1} to room temperature.

2.2. Powder X-ray and neutron diffractions

The powder X-ray diffraction (PXRD) data were collected on a Bruker D8-Advance diffractometer using Cu*K*α radiation at room

* Corresponding author. Fax: +82 2 825 4736.
E-mail address: kmok@cau.ac.kr. (K.M. Ok)
URL: http://chem.cau.ac.kr. (K.M. Ok)

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temperature with 40 kV and 40 mA to assess phase purity. The 2θ range was 10–70° with a step size of 0.02°, and a step time of 1 s. Powder neutron diffraction (PND) data were obtained at room temperature using the diffractometer POLARIS at the ISIS Facility, Rutherford Appleton Laboratory, UK. Diffraction patterns were measured by the time-of-flight method using detector banks at scattering angles 2θ of 10.40°, 25.99°, 52.21°, 92.59°, and 146.72° for a total integrated proton current at the production target of 135 μA/h for 8 g of Li_2VPO_6 contained in a 11 mm∅ vanadium cylinder. The PND data were analyzed using the Rietveld method with the GSAS program [46]. The structural refinements of the material were carried out in the space group $Pna2_1$ (no. 33) with a starting model of the reported single-crystal data of Li_2VPO_6 [47]. The experimental, calculated, and difference diffraction plots for Li_2VPO_6 are shown in Fig. 1. The results of the crystallographic data and selected bond distances (Å) for Li_2VPO_6 are summarized in the Supplementary material and Table 1, respectively.

2.3. Infrared spectra

Infrared spectrum of Li_2VPO_6 was recorded on a Varian 1000 Fourier transform IR spectrometer in the 400–4000 cm^{-1}, with the sample embedded in a KBr matrix.

2.4. Powder second-order nonlinear optical measurements

Powder SHG measurements on polycrystalline Li_2VPO_6 were performed on a modified Kurtz-NLO system using 1064 nm radiation [48]. A DAWA Q-switched Nd:YAG laser, operating at 20 Hz, was used for all measurements. Since SHG efficiency has been shown to depend strongly on particle size, polycrystalline samples were ground and sieved (Newark Wire Cloth Co.) into distinct particle size ranges (20–45, 45–63, 63–75, 75–90, 90–125, $>$ 125 μm). In order to make relevant comparisons with known SHG materials, crystalline α-SiO_2 and $LiNbO_3$ were also ground and sieved into the same particle size ranges. Powders with particle size 45–63 μm were used for comparing SHG intensities. All of the powders were placed in separate capillary tubes. No index-matching fluid was used in any of the experiments. The SHG light, i.e., 532 nm green light, was collected in reflection and detected by a photomultiplier tube (Hamamatsu). To detect only the SHG light, a 532 nm narrow band-pass interference filter was attached to the tube. A digital oscilloscope (Tektronix TDS 1032) was used to monitor the SHG signal. A detailed description of the equipment and the methodology used has been published [24].

2.5. Piezoelectric measurements

Converse piezoelectric measurements were performed using a Radiant Technologies RT66A piezoelectric test system with a TREK (model 609E-6) high voltage amplifier, Precision Materials Analyzer, Precision High Voltage Interface, and MTI 2000 Fotonic Sensor. The polycrystalline Li_2VPO_6 was pressed into a 12 mm diameter and ~0.5 mm thick pellet. The pellet was sintered at 580 °C for 6 h. A conducting silver paste was applied to both sides of the pellet surfaces as electrodes and cured at 200 °C for 3 h. A maximum voltage of 900 V was applied to the sample.

Table 1
Selected bond distances (Å) for Li_2VPO_6.

V(1)–O(1)	1.975(13)	P(1)–O(1)	1.548(2)
V(1)–O(2)	1.992(13)	P(1)–O(2)	1.5570(18)
V(1)–O(3)	2.297(13)	P(1)–O(3)	1.5127(17)
V(1)–O(4)	2.186(15)	P(1)–O(4)	1.543(2)
V(1)–O(5)	1.636(16)		
V(1)–O(6)	1.666(14)		
Li(1)–O(1)	2.495(5)	Li(2)–O(1)	2.189(5)
Li(1)–O(2)	2.118(5)	Li(2)–O(2)	2.234(5)
Li(1)–O(3)	2.312(5)	Li(2)–O(3)	2.120(5)
Li(1)–O(4)	2.083(5)	Li(2)–O(4)	1.960(5)
Li(1)–O(5)	1.997(5)	Li(2)–O(5)	2.120(5)
Li(1)–O(6)	2.067(6)	Li(2)–O(6)	2.147(5)

3. Results and discussion

3.1. Structure

The crystal structure of Li_2VPO_6 has been reported [47]; thus, only a brief structural description will be given here in order to explain the structure–property relationships. Li_2VPO_6 crystallizes in a polar noncentrosymmetric space group $Pna2_1$ (No. 33). The material exhibits a layered structure that is composed of VO_6 octahedra and PO_4 tetrahedra (see Fig. 2). The unique V^{5+} cation is in distorted octahedral coordination environment with six oxygen atoms. Specifically, the V^{5+} cation distorts toward an edge of the VO_6 octahedron (local C_2 direction), which results in two short (1.636(16) and 1.666(14) Å), two intermediate (1.975(13) and 1.992 (13) Å), and two long (2.186(15) and 2.297(13) Å) V–O bond distances. The P^{5+} cation is in slightly distorted tetrahedral geometry, linked to four oxygen atoms with bond lengths ranging from 1.5127(17) to 1.5570(18) Å. The two unique Li^+ cations are in six-fold pseudo-octahedral environment with Li–O contact distances in the range 1.960(5)–2.495(5) Å. A list of the selected bond distances for Li_2VPO_6 is given in Table 1. The bond distances are consistent with those previously reported [43,44,49]. Within the layer, VO_6 octahedra and PO_4 tetrahedra share their corners and edges, which generate six-membered rings (6MRs) in the *bc*-plane (see Fig. 3). In connectivity terms, the layer can be described as $\{[VO_{2/1}O_{4/2}]^{3-}\ [PO_{4/2}]^{+}\}^{2-}$ anionic sheets. The anionic layers are separated by two Li^+ cations and the overall charge balance is maintained. Bond valence sum calculations [50,51] for the V^{5+}, P^{5+}, Li^+, and O^{2-} result in values of 4.87, 4.81, and 1.02–1.08, and 1.66–2.16, respectively.

3.2. Infrared spectroscopy

The infrared spectrum of Li_2VPO_6 revealed V–O and P–O vibrations. V–O vibrations are observed at around 570–620 cm^{-1}. P–O vibrations occur at about 880–1110 cm^{-1}. Bands occurring around 420–470 cm^{-1} are attributable to superimposed vibrations of O–V–O and O–P–O. The assignments are consistent with those

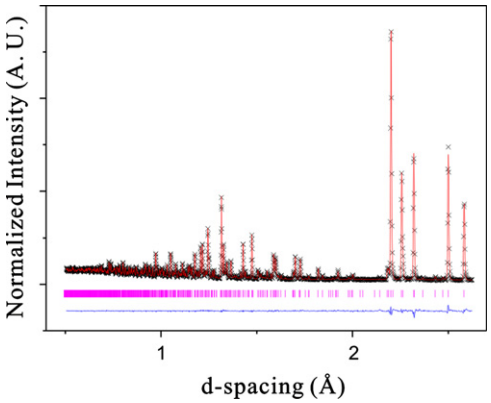

Fig. 1. Experimental, calculated, and difference neutron diffraction plots for Li_2VPO_6. The diffraction pattern collected by the highest resolution 146.72° detector bank is shown. The calculated pattern (red solid line) is compared with observed data (×). The locations of reflections are indicated by the magenta vertical bars. The difference between the observed and calculated profiles is shown at the bottom (blue solid line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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