Hydrothermal synthesis and characterization of a new layered compound Li$_2$VGeO$_5$☆

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Abstract

The new compound Li$_2$VGeO$_5$ with a layered structure has been synthesized at 580 °C via the hydrothermal method. The compound crystallizes in the space group $P4/n$ of the tetragonal system with two formula units in a cell of dimensions $a = 6.5187(9)$ Å, $c = 4.5092(9)$ Å ($T = 298$ K), $V = 191.61(5)$ Å^3. The structure is composed of layers made of repeating $[(VO_5)(GeO_4)]^{1-}$ units. Li$^+$ ions reside between the layers. The magnetic susceptibility data show an antiferromagnetic coupling below 5 K with $C = 0.47$ emu K mol^{-1}, and $\theta = -13$ K with $\mu_{eff} = 1.89\mu_B$ for each Li$_2$VGeO$_5$ unit.
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1. Introduction

Layered compounds are of great interest due to their potential applications as ion exchange ionic conductors, batteries and catalysts [1,2]. Synthetic efforts have been directed towards the exchange or insertion of a metal cation into the channels or layers of such compounds. Lithium is the most commonly used cation because of its small size, high mobility and large charge density. Vanadyl(IV) phosphates, especially (VO)$_2$P$_2$O$_7$, have been the subject of recent studies due to their efficiency as catalysts in the production of maleic anhydride from butane and air [3–5]. V(IV)O$_5$ pyramids in (VO)$_2$P$_2$O$_7$ link with diphosphate groups to form a dense-layered structure. Discovery of this compound has encouraged further exploration which has led to the synthesis of several new exotic vanadium compounds. Tetravalent vanadium has a d^1 electronic configuration and occurs in a five (square pyramidal) or a six (octahedral) coordination. The d^1 electron is located in one of the nonbonding orbitals (3d$_{xy}$) and is responsible for the interesting magnetic and optical properties of layered vanadium compounds [6]. In this paper, we describe the hydrothermal synthesis of a new layered vanadium(IV) germanate which has a layered structure with Li$^+$ ions located between the layers.

2. Experimental

2.1. Syntheses

Single crystals of title compounds were synthesized from 0.015 g (1 × 10^{-4} mol) V$_2$O$_3$ and 0.042 g (4 × 10^{-4} mol) GeO$_2$. The starting materials were placed into silver tubes (0.25 cm o.d.) with 0.4 ml of an aqueous 0.5 M solution LiOH. The tubes were then welded shut. Welded tubes were placed into Tuttle "cold sealed" autoclave and heated at 580 °C for 3 days. After the heating process, the autoclave was cooled down under flowing air. The product was washed with water and dark maroon crystals of Li$_2$VGeO$_5$ were obtained in 40% yield along with LiVGe$_2$O$_6$. Based on the vanadium(IV) oxidation state in Li$_2$VGeO$_5$, another reaction was tried to get a better yield of this compound. A mixture of V$_2$O$_3$ (0.075 g, 5 × 10^{-5} mol) and V$_2$O$_5$ (0.090 g, 5 × 10^{-5} mol) were used as starting materials along with the same amount of GeO$_2$ and LiOH, and the reaction mixtures

was heated at 583 °C for 3 days. An approximately 80% yield of Li_2VGeO_5 was obtained from the second reaction.

2.2. Crystallography

A crystal of Li_2VGeO_5, with the approximate dimensions of 0.1 mm × 0.05 mm × 0.03 mm was mounted on a four-circle Rigaku AFC8 diffractometer equipped with a Mercury CCD area detector. Data were collected at room temperature (∼300 K) using graphite monochromated Mo Kα (λ = 0.71073 Å) radiation. The crystal-to-detector distance was approximately 30 mm. A total of 240 frames were recorded as an ω scans of 1° with an X-ray exposure time of 30 s. Tetragonal P4/n, z = 2, a = 6.5187(9) Å, c = 4.5092(9) Å, V = 191.61(5) Å³, D_{cal} = 3.768 g cm⁻³, μ(Mo Kα) = 10.174 mm⁻¹. An empirical absorption correction was applied using a REQABA routine in *Crystal-Clear* software package. The transmission factors ranged from 0.630 to 1.000. The data were merged and averaged in the Laue group 4/m, yielding an internal agreement factor of R_m = 0.001. A total of 256 reflections were used for structure elucidation. Of these, 255 were independent and 242 with $I > 2\sigma(I)$ were used in the refinement. The structure was solved by direct methods with the program SHELXS and refined full-matrix least-squares techniques with the program SHELXL in the SHELXTL suite [7].

3. Results and discussion

The compound was originally isolated as a by-product of our effort to prepare the spin-Peierls V(III) compound $LiVGe_2O_6$ [8,9]. It was subsequently prepared with good yield by the following designed synthesis.

$$V_2O_3 + V_2O_5 + 2GeO_2 \xrightarrow[580\,°C]{LiOH(aq)} Li_2VGeO_5$$
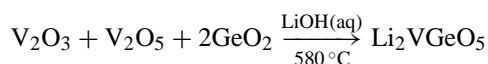
The structure of Li_2VGeO_5 was determined by single crystal X-ray diffraction. The title compound has been obtained as maroon polyhedra and has a layered structure with square pyramidal vanadyl groups connected by tetrahedral germanates. The unit cell view of this compound is shown in Fig. 1. In Fig. 2, corner sharing VO_5 and GeO_4 units can be seen. The layers, VO_5/GeO_4, lie along the *ab* plane, and the lithium atoms reside between the layers. There are two crystallographically inequivalent oxygen atoms. Vanadium has four equal bonds to O2 atoms in the square plane with a bond distance of 1.959(3) Å. In addition, there is a fifth short bond to the O1 atom of 1.643(7) Å, typical of a V=O group. The O1–V–O1 angle in the square plane ranges from 84.40(5)° to 143.59(16)° and the O1–V–O2 angle is 108.21(8)°. Schindler et al. found that vanadyl bond distances range from 1.48 to 1.66 Å with a maximum at 1.59 Å, while equatorial V–O bonds are in the range of 1.8–2.12 Å with a maximum at 1.97 Å [10]. The angles between the vanadyl bond and the four equatorial bonds are
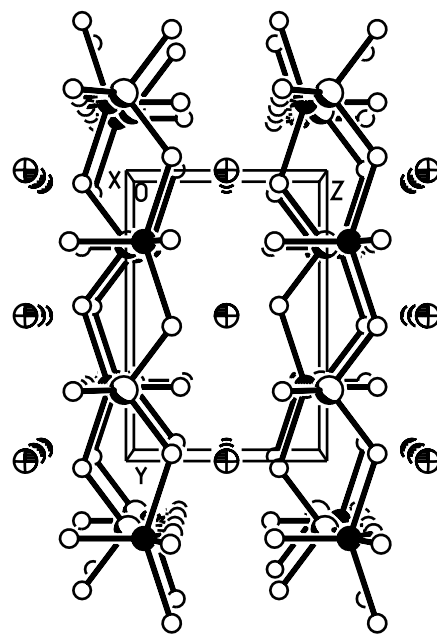

Fig. 1. A projection of the unit cell as viewed down the *a*-axis. Li_2VGeO_5, where Ge atoms are shaded circles, V atoms are solid circles, O atoms are open circles and Li is full thermal ellipsoids with 70% probability. Selected bond distances and angles are as follows: V1=O2 = 1.637(4) Å; V1–O1 = 1.959(2) × 4 Å; Ge1–O1 = 1.748(2) × 4 Å. O1–V1–O2 = 108.17(5)° × 4; O1–V1–O1 = 84.42(3)° × 4; O1–V1–O1 = 143.66(10)° × 4. O1–Ge1–O1 = 111.11(6)° × 4; O1–Ge1–O1 = 106.25(11)° × 2.

in the range 100–110°. Our results for V–O bond distances and angles are in complete agreement with their study. The germanium atom has four equal Ge–O bonds forming a tetrahedron (1.750(3) Å). The lithium atoms between the layers have four short bonds to the O2 atom and four longer bonds to the O1 atom with bond distances of 2.039(2) and 2.533(2) Å, respectively.
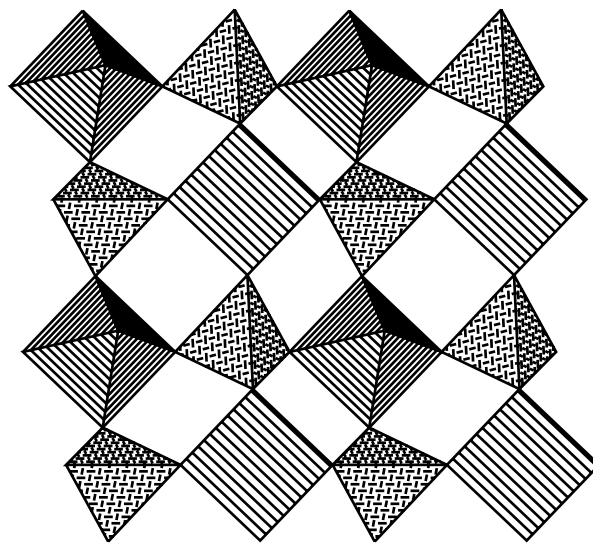

Fig. 2. The VO_5/GeO_4 layer, VO_5 are shown as lined polyhedra, and GeO_4 tetrahedra are herringbone polyhedra.
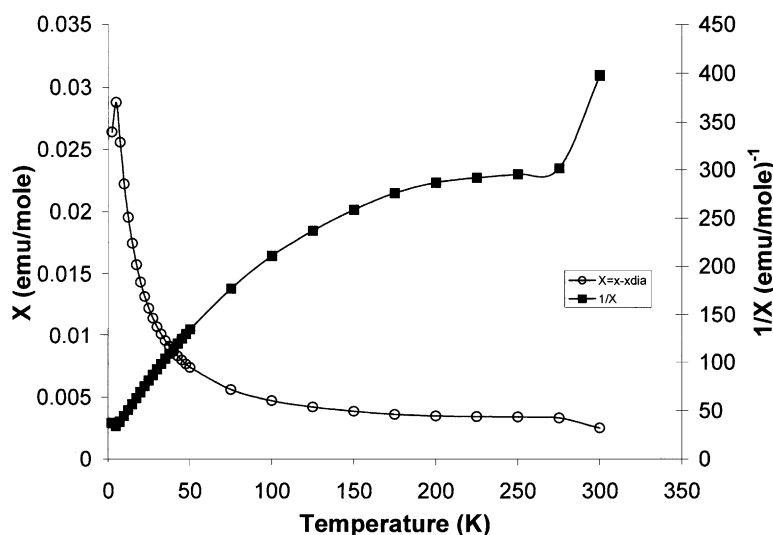
Fig. 3. Plot of magnetic susceptibility (solid squares) and reciprocal susceptibility (open circles) as a function of temperature for Li_2VGeO_5.

Li_2VGeO_5 has a structure very similar to α-$VOPO_4$ [11,12]. The layered units are isostructural except that the two interlayer Li^+ ions charge compensate for the V(IV) in our title compound. The layered compound vanadyl phosphate is a good host for intercalation reactions and it is isostructural with a number of other compounds containing pentavalent metals including, $NbOPO_4$ [13], $TaOPO_4$ [14], $VOMoO_4$ [15], $MoOPO_4$ [16] and α-$VOSO_4$ [17]. In α-$VOPO_4$, six oxygen atoms surround the vanadium to form a very distorted octahedron with one long bond (2.85 Å) and one short bond (1.58 Å) along the *c*-axis. Without this long bond, the coordination of vanadium can be considered a square pyramid. In contrast, in the title compound the Li atom separates the layers by over 4 Å, thus making the vanadium an ideal square pyramid. This very weak bond in α-$VOPO_4$ can be replaced with other ligands leading to its extensive intercalation chemistry. As many as two water molecules can fit between the layers [18]. It should be noted that there is a known lithium vanadyl phosphate, β-$LiVOPO_4$ [19], but it has a structure very different from α-$VOPO_4$ [20].

The bond valence sums for crystallographically unique atoms in the title compound were calculated in order to help determine their approximate oxidation states. The vanadium has a +4 charge as expected from its crystal structure and all the other atoms have values close to their expected oxidation states.[1]

Fig. 3 shows the temperature dependence of the magnetic susceptibility and reciprocal magnetic susceptibility for Li_2VGeO_5. Li_2VGeO_5 does not display Curie–Weiss behavior over the temperature range considered here. A Néel point, T_N, for the transition from paramagnetic to antiferromagnetic behavior was observed at 4.62 K.

The IR absorption spectra of Li_2VGeO_5 were consistent with the X-ray structure. There are three bands centered at 810, 820, 755 cm^{-1} which could be associated with the GeO_4 group. The absence of a broad band above 3000 cm^{-1} suggests that the compound does not contain the OH^- ion. A stretch observed at 960 cm^{-1} is characteristic of V=O stretching typically seen at 985 ± 50 cm^{-1} [21]. The diffuse reflectance spectrum of Li_2VGeO_5 at room temperature reveals the presence of an electronic transition centered at 575 nm, as expected by its dark maroon color. The optical band gap was approximately 1 eV (1000 nm).

In summary, we have successfully synthesized hydrothermally well formed single crystals. Li_2VGeO_5 has a very interesting layered structure built of V(IV)O_5 square pyramids and GeO_4 tetrahedra with Li^+ ions between the layers. We feel that with the careful choice of base mineralizers and transition metals, a wide variety of new transition metal germanates will be discovered using hydrothermal techniques.

Acknowledgements

Supporting information available: X-ray crystallographic files in CIF format for Li_2VGeO_5.

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[1] Bond valence sums for Li_2VGeO_5: V(1) = 3.96(5), Ge(2) = 3.98(4), Li(3) = 0.91(6), O(1) = 1.67(3), O(2) = 1.83(2).

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