Synthesis, Structure, and Characterization of a Layered Mixed Metal Oxychloride, $PbVO_3Cl$

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Until now, layered materials have drawn an enormous attention, because they have exhibited rich structural variations as well as demonstrated extremely important functional characteristics such as intercalation behavior, ion-exchanging property, superconductivity, optical property, and storage of radioactive cations.[1-8] Thus, designing new layered compounds still remains a continuing challenge. Among them, layered materials consisting of asymmetric units are of particular interest attributable to their potential applications to the frequency doubling and waveguiding materials, piezoelectric sensors, and memory materials.[9-11] One very important and fundamental requirement for obtaining these types of materials is crystallographic non-centrosymmetry (NCS).[9] From the theoretical studies and synthetic approaches, it has been known that combining second-order Jahn-Teller (SOJT) cations would be one of the most effective methods to increase the incidence of NCS materials.[12-16] With oxides, two representative SOJT cations include octahedrally coordinated d^0 transition metals (Ti^{4+}, V^{5+}, W^{6+}, *etc.*) and lone pair cations (Pb^{2+}, Sb^{3+}, Te^{4+}, *etc.*). With this in mind, we have been investigating to develop any new materials in the Pb−V−oxychloride system. With respect to vanadium oxychloride materials, a few examples such as $A_5(VO_4)_3Cl$ (A = Ca, Sr, or Ba),[17] A_2VO_4Cl (A = Ca or Sr),[18,19] and AVO_3Cl (A = Sr, Ba, or Cd)[20] have been reported. They reveal the 1D-chain and/or 2D-layered framework structures. And also, there are several reports showing lead vanadium oxychlorides minerals such as $Pb_5(VO_4)_3Cl$,[21] $Pb_{14}(VO_4)_2O_9Cl_4$,[22] and $PbCu_3(VO_4)_2Cl_2$.[23] Most of the materials were synthesized by standard solid-state reactions, hydroxide flux methods, or hydrothermal techniques. A brief structural description of $PbVO_3Cl$ has been reported recently.[24] However, in this paper, we report the phase pure solid-state synthesis, crystal growing, complete structural analysis, bond valence calculations, and full characterization of $PbVO_3Cl$ along with dipole moment calculations for VO_5 square pyramids. Although centrosymmetric, the two-dimensional lead vanadium oxychloride has an interesting layered structure containing both of the SOJT cations, i.e., V^{5+} and Pb^{2+}, in its framework.

Experimental Section

Synthesis. $Pb(NO_3)_2$ (Junsei, 99.5%), PbO (Kanto, 98.5%), $PbCl_2$ (Hayashi, 99%), V_2O_5 (Junsei, 99.0%), and NaCl (Duksan, 99.0%) were used as received. Crystals of $PbVO_3Cl$ were prepared by a hydrothermal reaction method. 1.449 g (4.38 mmol) of $Pb(NO_3)_2$, 0.106 g (1.82 mmol) of NaCl, 0.113 g (0.63 mmol) of V_2O_5, and 5 mL of deionized water were placed in a 23-mL Teflon-lined stainless steel autoclave that was subsequently sealed. The autoclave was gradually heated to 230 °C, held for 3 days, and cooled slowly to room temperature at a rate of 1 °C min^{-1}. The products were recovered by filtration and washed with water. Powder X-ray diffraction patterns on the manually separated colorless needles, colorless blocks, and yellow rods were determined to be $PbCl_2$, $Pb(NO_3)_2$, and $PbVO_3Cl$, respectively. A yield of 48% based on lead was observed from the manually separated yellow rods of $PbVO_3Cl$. Pure polycrystalline $PbVO_3Cl$ was synthesized through a standard solid-state reaction technique. A stoichiometric mixture of PbO (0.653 g, 2.93 mmol), $PbCl_2$ (0.814 g, 2.93 mmol), and V_2O_5 (0.532 g, 2.93 mmol) was thoroughly ground and pressed into a pellet. The pellet was introduced into a fused silica tube that was evacuated and sealed. The tube was gradually heated to 450 °C, held for 12 h, and cooled down to room temperature. The powder X-ray diffraction pattern on the resultant yellow powder indicated the material was single-phase and in a good agreement with the generated pattern from the single-crystal data.

Crystallographic determination. The structure of $PbVO_3Cl$ was determined by standard crystallographic methods. A yellow plate crystal (0.02 × 0.05 × 0.22 mm^3) was used for single crystal X-ray diffraction. The data were collected using a Bruker SMART APEX CCD X-ray diffractometer at room

Table 1. Crystal data for $PbVO_3Cl$

formula	$PbVO_3Cl$
fw	341.58
space group	*Pnma* (No. 62)
Z	4
a (Å)	10.0580(12)
b (Å)	5.2888(6)
c (Å)	7.1871(9)
V (Å^3)	382.32(8)
T (K)	298.0(2)
ρ_{calc} (g cm^{-3})	5.934
μ (mm^{-1})	46.951
λ (Å)	0.71073
$R(F)^a$	0.0311
$R_w(F_o^2)^b$	0.0818

$^aR(F) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. $^bR_w(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond distances (Å) and bond angles (°) for $PbVO_3Cl$

Bond distances		Bond valence	Bond angles	
Pb(1)–O(1) × 2	2.489(5)	0.361 × 2	O(1)–Pb(1)–O(1)	62.3(3)
Pb(1)–O(2)	2.797(7)	0.157	O(1)–Pb(1)–Cl(1)	77.81(13)
Pb(1)–Cl(1)	2.806(2)	0.474	O(1)–Pb(1)–Cl(1)	78.28(12)
Pb(1)–Cl(1) × 2	2.9846(11)	0.292 × 2	O(1)–Pb(1)–Cl(1)	134.87(13)
Bond valence sum of Pb(1)		1.937	Cl(1)–Pb(1)–Cl(1)	73.51(5)
			Cl(1)–Pb(1)–Cl(1)	124.76(8)
V(1)–O(1) × 2	1.824(6)	0.945 × 2	O(1)–V(1)–O(1)	79.9(2)
V(1)–O(1) × 2	1.920(5)	0.729 × 2	O(1)–V(1)–O(1)	84.2(3)
V(1)–O(2)	1.599(7)	1.736	O(1)–V(1)–O(1)	96.1(3)
Bond valence sum of V(1)		5.084	O(1)–V(1)–O(1)	145.36(11)
			O(1)–V(1)–O(2)	105.4(3)
			O(1)–V(1)–O(2)	108.4(2)

temperature using graphite-monochromated Mo Kα radiation at the Korea Basic Science Institute. A hemisphere of data was collected using a narrow-frame method with scan widths of 0.30° in omega, and an exposure time of 5 s per frame. The first 50 frames were remeasured at the end of the data collection to monitor instrument and crystal stability. The maximum correction applied to the intensities was < 1%. The data were integrated using the Bruker SAINT program,[25] with the intensities corrected for Lorentz, polarization, air absorption, and absorption attributable to the variation in the path length through the detector faceplate. Ψ-scans were used for the absorption correction on the hemisphere of data. The data were solved and refined using SHELXS-97[26] and SHELXL-97,[27] respectively. All of the atoms were refined with anisotropic displacement parameters and converged for $I > 2\sigma(I)$. All calculations were performed using the WinGX-98 crystallographic software package.[28] The final Fourier difference map revealed minimum and maximum peaks of −3.162 and 3.687 e Å^{-3}, respectively. Crystallographic data and selected bond distances and angles for $PbVO_3Cl$ are given in Tables 1 and 2.

Table 3. Powder XRD Data for the $PbVO_3Cl$. Refined Unit Cell: a = 10.030(2) Å, b = 5.2732(16) Å, c = 7.1729(19) Å, and Space Group *Pnma* (No. 62)

h	k	l	d_{obs}	d_{calc}	I_{obs}
1	0	1	5.822	5.834	9
2	0	0	5.008	5.015	11
0	1	1	4.247	4.249	9
2	0	1	4.106	4.110	45
1	1	1	3.911	3.912	11
2	1	0	3.634	3.634	19
0	0	2	3.583	3.586	10
1	0	2	3.375	3.377	49
2	1	1	3.242	3.242	10
3	0	1	3.030	3.030	100
2	0	2	2.917	2.917	5
1	1	2	2.843	2.844	19
0	2	0	2.634	2.637	10
4	0	0	2.508	2.507	18
3	0	2	2.445	2.445	5
4	0	1	2.367	2.367	19
4	1	0	2.265	2.264	11
2	2	1	2.220	2.219	17
0	1	3	2.179	2.178	8
4	1	1	2.159	2.159	13
1	1	3	2.129	2.128	7
1	2	2	2.079	2.078	8

The X-ray powder diffraction data were collected on a SCINTAG XDS2000 diffractometer using Cu Kα radiation at room temperature with 35 kV and 30 mA in the 2θ range 5 ~ 70° with a step size of 0.02°, and a step time of 1 s. The unit-cell parameters taken from the powder X-ray diffraction on the polycrystalline product were refined by using the program CHEKCELL.[29] The refined unit-cell, d_{obs}, d_{calc}, and I_{obs} for $PbVO_3Cl$ are given in Table 3.

Characterization. Thermogravimetric analysis was performed on a Setaram LABSYS TG-DTA/DSC Thermogravimetric Analyzer. The polycrystalline $PbVO_3Cl$ sample was contained within an alumina crucible and heated to 1000 °C at a rate of 10 °C min^{-1} under flowing air. Infrared spectrum was recorded on a Varian 1000 FT-IR spectrometer in the 400 ~ 4000 cm^{-1} range, with the sample intimately pressed between two KBr pellets. SEM/EDX analyses have been performed using a Hitachi S-3400N/Horiba Energy EX-250 instruments. EDX analysis for $PbVO_3Cl$ provided a Pb : V : Cl ratio of 1 : 1 : 1.

Results and Discussion

$PbVO_3Cl$ is a new mixed metal oxychloride material crystallizing in a centrosymmetric orthorhombic space group *Pnma* (No. 62) with a structure similar to that of $CdVO_3Cl$.[20] The crystal structure consists of VO_5 square pyramids and PbO_3Cl_3 polyhedra (see Figure 1). Each V^{5+} cation is bonded to five oxygen atoms in a distorted square pyramidal environment with one "short" (1.599(7) Å) and four "normal" bonds (1.824(6) - 1.920(5) Å). The O−V−O bond angles range from 79.9(2) to 145.36(11)°. The distorted VO_5 square pyramid in the $PbVO_3Cl$ structure suggests the short apical V−O bond has a double bond character (V=O). Infrared spectral data for $PbVO_3Cl$ confirm the presence of the apical V=O double bond. The Pb^{2+} cations are bonded to three oxygen atoms and three chlorine atoms, which generate PbO_3Cl_3 polyhedral coor-

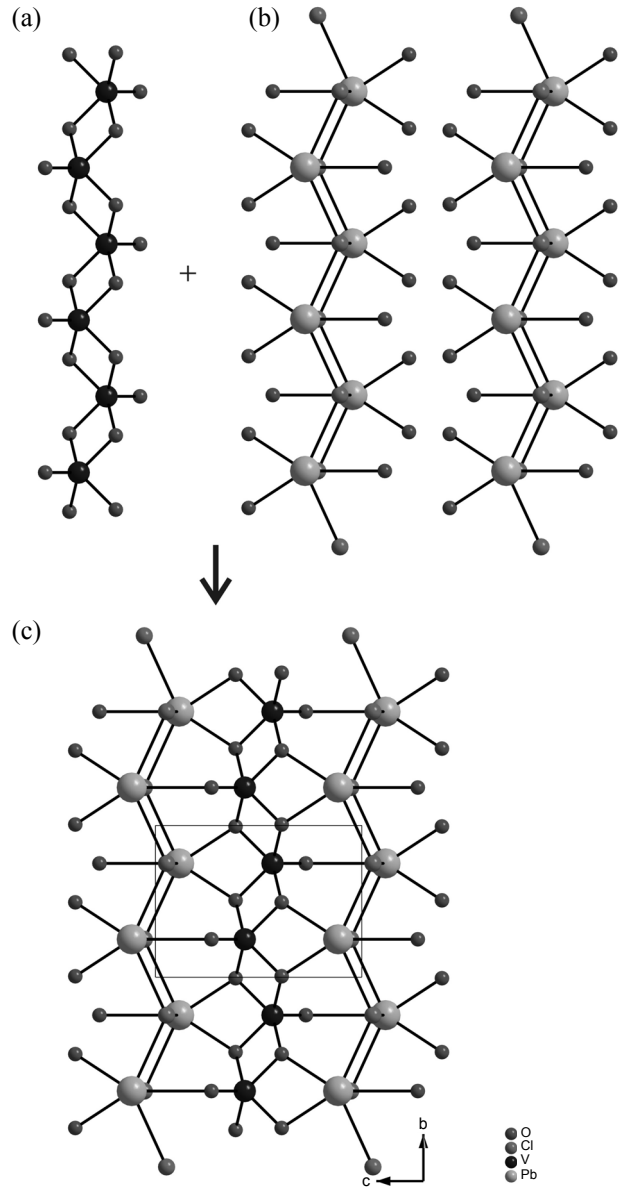

Figure 1. Ball-and-stick diagram of (a) VO_5 square pyramidal bands, (b) PbO_3Cl_3 polyhedral bands, and (c) linking of the bands to form a two-dimensional layer in the *bc*-plane.

dination environment. The Pb−O and Pb−Cl bond distances range 2.489(5) - 2.797(7) Å and 2.806(2) - 2.9846(11) Å, respectively. There are also two long Pb(1)−O(1) (3.213(5) Å) contacts and one long Pb(1)−Cl(1) (3.280(2) Å) interaction. These longer contacts may be attributable to the lone pair electrons on the Pb^{2+} cation. Thus, the Pb^{2+} is in asymmetric coordination environment due to the nonbonded electron pair. Each oxygen atom is bonded to two or three metals: while the O(1) is bonded to two V^{5+} cations and one Pb^{2+} cation, the O(2) is connected to one V^{5+} and one Pb^{2+} cation. However, each chlorine atom is bonded to three Pb^{2+} cations. Thus, in connectivity terms, the VO_5 and PbO_3Cl_3 moieties could be formulated as cationic $[VO_{1/2}O_{4/3}]^{1.3333+}$ square pyramids and anionic $[PbO_{1/2}O_{2/3}Cl_{3/3}]^{1.3333-}$ polyhedra. Bond valence calculations[30,31] on $PbVO_3Cl$ resulted in values of 1.94 and 5.08 for Pb^{2+} and V^{5+}, respectively. The VO_5 square

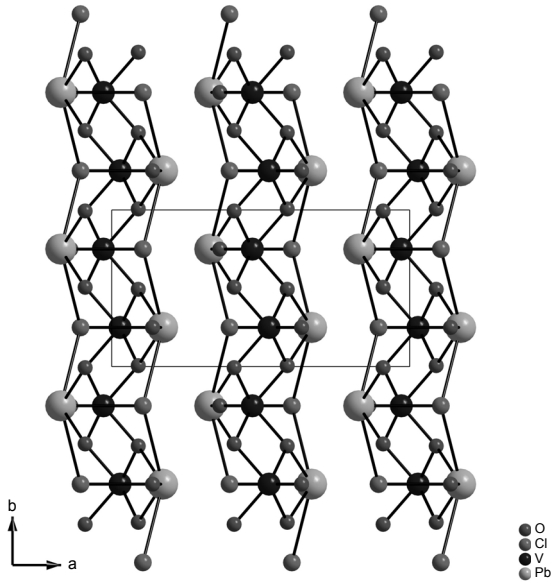

Figure 2. Ball-and-stick diagram of $PbVO_3Cl$ revealing the 2D-layered structure. Note the lone pair on the Pb^{2+} point to the [100] and [-100] directions.

pyramids share their edges through oxygen atoms and form infinite uni-dimensional bands along the [010] direction (see Figure 1(a)). As can be seen in Figure 1(a), the axial oxygen ligands of VO_5 point alternately along the [001] and [00-1] directions. On the other hand, the PbO_3Cl_3 polyhedra share their edges through chlorine atoms and construct another infinite uni-dimensional bands along the [010] direction (see Figure 1(b)). In fact, infinite chains are first made by anionic $[PbO_{1/2}O_{2/3}Cl_{3/3}]^{1.3333-}$ polyhedra. The linkage occurs by the corner-sharing of the PbO_3Cl_3 polyhedra through Cl(1) along the [010] direction. In addition, further inter-chain connection is made through the chlorine atoms along the [100] direction to generate infinite bands. The PbO_3Cl_3 polyhedra reveal a local asymmetric coordination environment attributable to the lone pairs. The two infinite uni-dimensional bands are now connected through O(1) and O(2) in an inter-chain manner, which results in a two-dimensional layers in the *bc*-plane (see Figures 1(c) and 2). As can be seen in Figure 2, the lone pair on the Pb^{2+} point to the [100] and [-100] directions. Thus, the lone pair polarizations associated with Pb^{2+} cancel and the overall symmetry is centrosymmetric. The entire structure can be described as neutral layers of $\{[VO_{1/2}O_{4/3}]^{1.3333+}[PbO_{1/2}O_{2/3}Cl_{3/3}]^{1.3333-}\}^0$.

The infrared spectrum of $PbVO_3Cl$ revealed the presence of V=O vibrations in the region *ca.* 918 - 962 cm^{-1} and V–O vibrations in the region *ca.* 730 cm^{-1}. The stretches 510 - 590 cm^{-1} can be attributed to Pb−O vibrations. The assignments are consistent with those previously reported.[32,33]

The thermal behavior of $PbVO_3Cl$ was investigated using thermogravimetric analysis (TGA). $PbVO_3Cl$ is not stable at high temperature, above 470 °C, and decomposes to a corresponding oxide. Powder XRD measurement on the calcined material revealed $PbVO_3Cl$ decomposed to $Pb_2V_2O_7$[34] in static air. The decomposition is consistent with the following reaction:

Table 4. Calculation of dipole moments for VO_5 square pyramids. D = Debyes

Compound	Species	Dipole moments (D)
$AgVSeO_5$[38]	$V(1)O_5$	29.42
$Cs_{0.3}V_2O_5$[39]	$V(1)O_5$	17.85
	$V(2)O_5$	4.18
$Cs_{0.35}V_3O_7$[40]	$V(1)O_5$	18.12
$K_3(VO_2)_2PO_4(PO_3OH)\cdot H_2O$[41]	$V(1)O_5$	11.93
	$V(2)O_5$	5.22
$Li_xV_2O_5$[42]	$V(1)O_5$	17.00
$MnV_2O_6\cdot 4H_2O$[43]	$V(1)O_5$	6.83
V_2O_5[44]	$V(1)O_5$	13.79
$PbVO_3Cl$[a]	$V(1)O_5$	8.70
VO_5 square pyramids	(average)	13.30
10 examples	(range)	4.18 − 29.42

[a]This work

$$2\ PbVO_3Cl + \tfrac{1}{2}\ O_2\ (g) \rightarrow Pb_2V_2O_7 + \tfrac{1}{2}\ Cl_2\ (g)$$

The local dipole moment calculations on $PbVO_3Cl$ were performed in order to better understand the asymmetric coordination environment of V^{5+} in the VO_5 square pyramids. This approach has been described earlier with respect to metal oxy-fluoride octahedra.[35,36] We recently reported the dipole moments for $BiCl_6$ octahedra as well using the similar method.[37] Using this methodology, we found that the local dipole moment for the $V(1)O_5$ square pyramid is about 8.7 D (D = Debyes). For comparison, an examination of 10 examples of VO_5 polyhedra with V^{5+} cation reveals that the dipole moments range from 4.18 to 29.42 D and average value of 13.30 D (see Table 4) depending on the degree of distortions.

Single crystals and pure polycrystalline phase of a new layered mixed metal oxychloride, $PbVO_3Cl$ containing both the d^0 transition metal cation and lone pair cation were successfully synthesized by the hydrothermal and standard solid-state reaction techniques. The synthesized oxychloride crystallizes in the orthorhombic (*Pnma*) crystal structure. The structure reveals a 2-D layered framework consisting of infinite bands of VO_5 square pyramids and PbO_3Cl_3 polyhedra. Full characterization including powder XRD, bond valence calculations, Infrared spectroscopy, thermogravimetric analysis, and local dipole moment calculations have been successfully demonstrated.

Supplementary Material. Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (49) 7247-808-666; E-mail: crystdata@fiz-karlsruhe.de) on quoting the depository number CSD-420548. Detailed experimental data can be obtained from the authors upon request.

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