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Stacking faults in a layered cobalt tellurium phosphate oxochloride

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ABSTRACT

The new compound $Co_2Te_3(PO_4)O_6Cl$ was synthesized by chemical reactions in a sealed and evacuated silica tube. The crystal structure was solved from single crystal diffraction data and is made up by charge neutral layers. Within the layers two types of chains are made up by edge sharing $[CoO_6]$ and $[CoO_5Cl]$ polyhedra respectively. The chains are separated by tellurium oxide and phosphate building blocks. There are only weak Van der Waals interactions in between the layers and severe diffuse scattering is observed due to faulted stacking of the layers. Structure solutions in a P-1 triclinic cell and a larger monoclinic cell in $P2_1/c$ are discussed and compared to a computer generated model. The reasons for the stacking faults may be due to that there are two positions available for each layer that results in similar connectivity to the next layer in addition to the relatively wide channels in between the layers that reduce the Van der Waals interactions in between them.

1. Introduction

Incorporating p-element cations having a stereochemically active lone pair such as *e.g.* As^{3+}, Se^{4+}, Sb^{3+} or Te^{4+} into transition metal oxohalides has proven to be an efficient synthetic approach for finding compounds having specific structural and physical properties. The presence of lone pairs and halide ions, that both act as terminal ligands, have shown to result in a high probability of forming low-dimensional arrangements of the structural building blocks. Most commonly layered crystal structures are found from which the halide ions and the lone pairs are protruding. Weak Van der Waals interactions are responsible for the coherence in between layers. Transition metal ions within the covalently bonded layers are therefore well separated along the stacking direction, but can interact within the layers to form topologies may can lead to *e.g.* frustrated magnetism as in $Ni_5(TeO_3)_4X_2$ and $FeTe_2O_5X$ ($X = Cl$, Br) [1,2]. To further separate structural building blocks and to extend the chemical system, the inclusion of tetrahedral building blocks is investigated. Phosphate groups are well defined tetrahedral building units, which are known for the formation of open framework structures due to their predominantly corner sharing coordination behavior. So far the recently synthesized compounds $Fe_7(PO_4)_3Sb_3O_6X_3$ ($X = Cl$, Br) are two of few examples [3] of transition metal phosphate oxohalides having also a lone pair element present. Strong one dimensional diffuse scattering is often observed in faulted layered structures. Stacking faults are fairly common among metals or simple binary compounds which are built from close packing of hexagonal layers such as in *e.g.* Si [4], SiC [5] or GaN [6] where the energy needed for a layer dislocation is low. Different kinds of stacking disorder can occur *e.g.* in $Gd_5Si_{4-x}Bi_x$ [7] by changing the stoichiometry. Among oxide materials a faulted layer stacking can for example occur from intercalating species such as water molecules in $MnH_2P_3O_{10}\cdot 2H_2O$ [8] or β-$Ni(OH)_2$ [9]. Stacking faults are also present in many open framework structures or minerals such as zeolites where the faulted layers are covalently linked together [10] or in *e.g.* layered brownmillerites [11]. Faulted stacking of layers will lead to one-dimensional diffuse scattering affecting the diffraction lines along the stacking direction. Diffuse diffraction lines often make the structure solution and its refinement difficult. In this work we report the structure and synthesis of a new layered cobalt tellurium phosphate oxochloride having irregular stacking of layers.

2. Experimental section

Purple plate like single crystals of $Co_2Te_3(PO_4)O_6Cl$ were prepared by chemical reactions in evacuated and sealed silica tubes in a yield of 20%. For the synthesis a 1:1:1:1 ratio of starting materials $CoCl_2$ (Sigma–Aldrich), CoO (ABCR), TeO_2 (Sigma–Aldrich) and $(NH_4)H_2PO_4$ (STREM chemicals) was used. The starting powder was

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ground in an agate mortar and heated to 250 °C in air to decompose the ammonium salt before sealing in a silica tube under vacuum. The reaction took place at 550 °C for ~70 h. Crystals of the title compound for single crystal diffraction experiments were isolated manually from blue powder and unreacted starting materials. EDS analysis of the blue powder revealed that it is an oxide phase and the percentage of the heavy elements were 29.6 at% Co, 46.0 at% Te and 24.5 at% P.

Single crystal X-ray diffraction experiments on $Co_2Te_3(PO_4)O_6Cl$ were carried out on an Oxford Diffraction Xcalibur3 diffractometer equipped with a graphite monochromator. Data collection was carried out at 293 K using MoKα radiation, $\lambda = 0.71073$ Å. Absorption correction and data reduction were made with the software CrysAlis RED that was also employed for the analytical absorption correction [12]. The structure solution was carried out with SHELXS-97 and the refinement with SHELXL-97 [13] in the WINGX environment [14]. All atomic positions were refined isotropically as the anisotropic refinement did not give positive temperature parameters for all atoms, which is mainly due to the fact that the intensities from the diffuse scattering streaks could not be integrated properly. The diffuse scattering originating from stacking faults was simulated using the program DIFFaX [15] and results were compared qualitatively. EDS measurements were carried out on a JEOL 7000F scanning electron microscope. Crystal data are reported in Table 1, atomic coordinates and isotropic temperature parameters for all atoms, tables with bond distances and elemental composition from EDS are given in the Supplementary material. The structural drawings are made with the program DIAMOND [16].

Table 1
Crystal data and structure refinement parameters for $Co_2Te_3(PO_4)O_6Cl$ in two different unit cell settings.

Unit cell setting	1	2
Empirical formula	$Co_2Te_3(PO_4)O_6Cl$	$Co_2Te_3(PO_4)O_6Cl$
Formula weight (g/mol)	1454.16	1454.16
Temperature (K)	293	293
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	P-1	$P2_1/c$
a (Å)	5.1671(3)	5.1783(3)
b (Å)	11.0523(8)	11.0826(7)
c (Å)	19.1695(17)	38.088(5)
α (°)	98.337(7)	90
β (°)	92.823(6)	94.875(8)
γ (°)	90.029(5)	90
Volume (Å^3)	1081.82(14)	2177.9(3)
Z	4	8
Density$_{calc.}$ (g cm^{-3})	4.464	4.464
Absorption coefficient (mm^{-1})	11.43	11.43
F(000)	1288	2576
Crystal color	Pink	pink
Crystal habit	Plate	plate
Crystal size (mm^3)	0.075 × 0.047 × 0.0150	
Theta range for data collection (°)	4.14–32.25	4.14–32.25
Index ranges	$-7 \leq h \leq 7$ $-16 \leq k \leq 15$ $-28 \leq l \leq 18$	$-7 \leq h \leq 7$ $-15 \leq k \leq 16$ $-57 \leq l \leq 43$
Reflections collected –unique	10,292–6647 (2557–2452)[a]	19,868–7095
Data/restraints/parameters	6647/0/137	7095/0/137
Internal R value	Rint = 0.099 Rint = 0.054b	Rint = 0.177
Goodness-of-fit on F^2	1.019/0.865[a]	1.076
Final *R* indices[a] [$I > 2\text{sigma}(I)$]	R1 = 0.1654 R1 = 0.0759[a] wR2 = 0.3611 wR2 = 0.1456[a]	R1 = 0.1599 wR2 = 0.3448
R indices (all data)	R1 = 0.2468 R1 = 0.1584[a] $wR_2 = 0.3917$ $wR_2 = 0.1634$[a]	R1 = 0.2807 $wR_2 = 0.3886$
Largest diff. peak and hole (eÅ^{-3})	32.346 and –4.648 (2.351 and –1.838)[a]	9.428 and –8.797

[a] Refinement without reflections lying within the diffuse scattering streaks with $k = 2n+1$.

3. Results and discussion

3.1. Modeling the diffuse scattering

Inspecting the reconstructed diffraction pattern of the (0kl) layer one can observe that diffraction lines along *l* give sharp Bragg peaks for $k = 2n$ and diffuse streaks for $k = 2n + 1$, which indicates disorder in the crystal structure along [001], see Fig. 1. The crystal structure was initially solved assuming a triclinic unit cell in the space group $P{-}1$. As expected the structural model fitted the experimental data poorly ($R_1 = 16.5\%$ for 2855 reflections), due to the diffuse streaks which cannot be properly integrated by the data reduction software. The refinement could be significantly improved by omitting the reflections originating from the diffuse lines to $R_1 = 7.6\%$ for 1170 reflections. The structure could also be solved in a monoclinic unit cell with the space group $P2_1/c$. This choice is consistent with the systematic absences found in the (h0l) layer. Absent lines with $h = 2n + 1$ confirm the *c*-glide. There are two layers in the monoclinic cell, which are related to each other by the *c*-glide operation, which leads to the conclusion that the diffuse scattering arises due to irregular stacking of the layers. There are two possibilities for the layers to stack: i) by a glide operation, where the next layer is a mirror image (mirror plane perpendicular to [010]) of the initial layer or ii) by a layer shift, where the next layer is the same as the initial layer shifted along [010]. The two stacking possibilities occur randomly in the structure with equal probabilities. To confirm this theory a computer simulation was set up using the program DIFFaX. To match the input criteria in DIFFaX the monoclinic unit cell was divided into half along [001], giving a

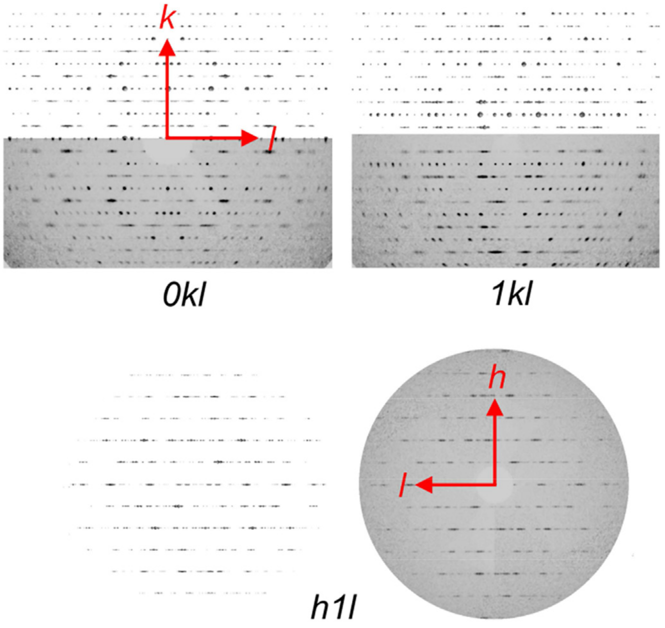

Fig. 1. Comparison of calculated and experimental diffraction intensities of the (0kl), (1kl) and (h1l) planes. Patterns with white background are calculated, the ones with grey background are experimental.