MS15-P9 Cell Dimensions of Titanium from 10 K to 290 K

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We have measured the unit cell of Ti from 10 K to 290 K, using a Bruker area detector diffratometer. The three lowest temperatures were 10, 28 and 45 K. Form 90 K to 290 K we used a Cryoindustries of America nitrogen cooler. Below 90 K we used a helium cooler from the same company. The sus for our measurements are about 0.00007 Å for *a* and 0.00017 Å for *c*. 290 K values are 2.95151 Å for *a* and 4.68483 Å for *c*. Corresponding 10 K values are 2.94650 and 4.67977 Å.

From 290 K to 45 K we see no unusual behavior, but at 28 K we measure the *c* axis to be longer than at 10 and 45 K. The *a* axis did not show any unusual behavior. This is at variance with earlier published measured and computed values, which showed negative thermal expansion for *c* below 170 K. Our crystal was of high purity, and the temperatures are reliable to better than 1 K. The measurements we have for comparison were performed with a capacitance dilatometer.

Keywords: Titanium, thermal expansion, 10 K to 290 K

MS15-P10 Structure Determination of Synthetic Shlykovite by Using Rotation Electron Diffraction

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Electron crystallography has attracted rapidly attention in recent years for structure solution of unknown crystals that are too small to be studied by single crystal X-ray diffraction. We developed rotation electron diffraction (RED) for collection and processing of 3-dimensional (3D) electron diffraction (ED) data. It combines fine electron beam tilt and coarse goniometer tilt to collect ED patterns semi-automatically with a large tilt range (~±70°) [1, 2]. The RED method has been used for structural analysis of polycrystalline materials including complex zeolites [3], and would be useful for studying structures of rare and new minerals. For TEM investigations, the crystals are observed in high vacuum. It was found that crystal structures could be changed under such conditions due to the removal of water and organic molecules in the crystal. This problem could be solved if the samples are studied under cryogenic conditions, i.e. at liquid nitrogen temperature.

Recently, we are succeeded for the first time in synthesis of a mineral analogue to shlykovite ($KCaSi_4O_9(OH)\bullet 3H_2O$) [4], which is one type of phyllosilicates and belongs to the mountainite family. The synthetic shlykovite crystals show a 2D nanosheet-like morphology. Therefore, the water molecule and organic molecules in the interlayer space are easily removed in high vacuum, which results in a different unit cell with that in the air. Hence, the structure of shlykovite was determined by using cryo-TEM, in which water molecules remained in the structure. By analyzing the reconstructed 3D reciprocal lattice, the space group and unit cell parameters of the synthetic shlykovite were determined as $P2_1/c$ and a=6.59 Å, b=7.03 Å, c=26.99 Å, β=95.1°. The structure could be solved from the RED data. The combination of cryo-TEM and RED technique shows the capability for the analysis of crystals with flexible structures. It is complement to X-ray crystallography for studying crystals which have small sizes and unique morphology. The synthesis of shlykovite reveals a new route to synthesize natural minerals and can improve strategies toward the synthesis of new crystal structures.

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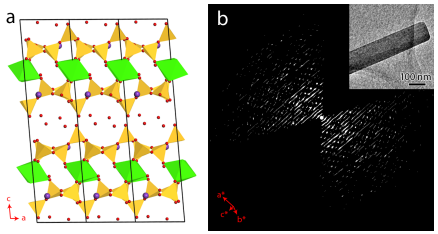

Figure 1. (a) Crystal structure of shlykovite viewed along the *b*-axis. Si: yellow tetrahedral; Ca: green octahedral; K: purple sphere; O: red sphere. (b) 3D reciprocal lattice of the synthetic shlykovite reconstructed from the RED data. Insert is the crystal from which the RED data was collected.

Keywords: electron crystallography, cryo-electron microscopy, electron diffraction, crystal structure, phyllosilicates, shlykovite.

MS15-P11 Cronstedtite-6T_2, a non-MDO polytype

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The new 6T_2 polytype of cronstedtite was identified, together with known 2H_1, 2H_2, 3T, 1M and probably 2M_1 polytypes in the mineral assemblage of an ore veinlet in the active quarry near Pohled, Czech Republic. The GPS co-ordinates of the locality are 49°35'50.326"N, 15°39'49.730"E [1].

Lattice parameters are a=5.4976(3), c=42.601(1) Å, Z=6, space group $P3_1$, composition $(Fe^{2+}_{2.515}\ Fe^{3+}_{0.485})(Si_{1.515}\ Fe^{3+}_{0.485})\ O_5\ (OH)_4$. The refinement converged to R_{obs} = 4.13% for 3244 independent reflections [2]. The polytype belongs to the subfamily (Bailey's group) A.

The structure is built of edge-sharing octahedral (*Oc*), and corner-sharing tetrahedral (*Tet*) sheets forming the 1:1 layers (corresponding to OD packets) by sharing apical corners of *Tet* sheet. There are two independent 1:1 layers, where the odd one is shifted with respect of the even one by $-(\mathbf{a}_1+\mathbf{a}_2)/3$ and raised by **c**/6 of the hexagonal cell. The sextuple multiplicity is achieved by mapping this pair of layers by 3_1 axis repeatedly to two other equivalent positions raised by **c**/3, 2**c**/3 There are two tetrahedral and three octahedral sites per each 1:1 layer (*T*1, *T*2, *M*1, *M*2, *M*3 in even layers, *T*11, *T*12, *M*11, *M*12, *M*13 in odd layers), all in general positions. The *M*3, *M*13 octahedra are smaller than *M*1, *M*2, *M*11, *M*12, thus *Oc* sheets in both layers are *meso-octahedral*. In even layers, however, the *M*2 octahedron is somewhat smaller than *M*1, so the *Oc* sheet is "transitional" to a *hetero-octahedral* character. The occupancies of Si:Fe in *T* positions were refined to: *T*1: 0.96:0.04(1), *T*2: 0.63:0.37(1), *T*11: 0.55:0.45(1), *T*12: 0.89:0.11(1). Ditrigonalization angles α are +11.4(5)°, and +10.9(5)°, in even and odd layers, respectively. Hydrogen positions were localized and geometries of hydrogen bonds linking the 1:1 layers were described. The structure is an example of OD structure of more than one kind of layers with a very low degree of desymmetrization. Cronstedtite-6T_2 is a non-MDO polytype, because more than one kind of packet triplets can be distinguished in the stacking sequence.

Another, quite different sextuple non-MDO polytype 6T_1 of the isostructural mineral lizardite [3] belongs to the group D.

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