MS14-P04

Atomic displacements in yttrium-manganese-oxide with and without fe-substitution, revealed by resonant X-ray diffraction

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Yttrium-Manganese-Oxide YMn_2O_5 (YMO) is studied since 1973 due to its remarkable magnetic properties, e. g. different modulation phenomena and several respective phase transitions. The ambient temperature phase of YMO is paraelectric and paramagnetic. The lattice has the orthorhombic space group *Pbam* (55) and its building units are [MnO_5] pyramides and [MnO_6] octahedra, the latter forming chains along the *c* direction. At 45 K, 40 K, 39 K and 19 K, the structure changes between several magnetic modulations [1]. Here, we are interested in the commensurate modulated phase between 39 K and 19 K. Presumably within space group $Pb2_1m$ (26), the respective lattice modulation vector is 0 0 ½, whereas the polarization points along *b*. However, crystal structure refinements in a non-centrosymmetric space group showing polar displacements have not yet been successful. Moreover, there is still disagreement about the interplay of magnetic superstructure and a polar displacement pattern. To analyze possible displacements of the commensurate phase in detail, we apply the newly developed and highly sensitive Resonant X-ray Diffraction (RXD) Method *REXSuppress* that uses destructive interference of the intensity at carefully chosen Bragg reflections [2]. For this structure analysis, we determined atomic displacement parameters (ADP) of the high and low temperature phase with the same method and surveyed the appearance of superstructure reflections that would accompany the transition to space group $Pb2_1m$ (26).

Additionally, we examined the distribution of Fe in Yttrium-Manganese-Iron-Oxide ($YMnFeO_5$), which results from the substitution of 50% Mn. The element- and site-selectivity of RXD is capable of separating the two distinct Mn Wyckoff sites (pyramide and octahedron), in particular with the octahedral site possessing forbidden reflections (reflection condition hkl with $h + k = 2n$). Thus, the question of occupation is easily accessible and will be treated similar as by [3].

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Keywords: refinement, mullite, commensurate

MS15- Crystallography in Earth and space

Chairs: Dr. Anna Pakhomova, Prof. JuanMa García-Ruiz

MS15-P01

Evidence of screw dislocation on gypsum crystals as principal mechanism of growth at low supersaturation

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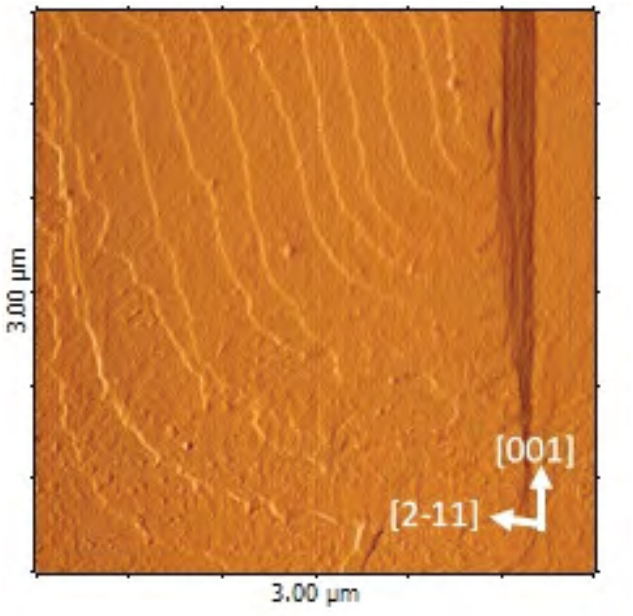
Gypsum mineral mainly occurs on evaporitic environment around the world [1, 2]. It has also been reported as a relevant phase in Mars [3-5]. The growth conditions during the growth of gypsum crystals influences the surface growth mechanisms and the habit. Many authors suggest that the growth mechanisms of gypsum crystals at low supersaturation is due to dislocation growth, these studies are based on kinetic data fitted to theoretical equations[6, 7]. However, the observation of hillocks on the surface gypsum crystals has been challenging. A couple of studies on the cleavage face (010) of gypsum by Atomic Force Microscopy (AFM) and Differential Interface Contrast Microscopy (DICM) shown some hillock but only one of them could be clearly identified as a screw dislocation, so the authors conclude that the main growth mechanism at low supersturation on this face is by 2D nucleation[8, 9]. Equivalent studies on the (120) face are missing, mainly due to the roughness of these faces. In a preliminary study of the gypsum (120) face using crystals growing by evaporation, we observed that hillocks spread on (120) at low supersaturation. Those hillocks are made by monolayers with a height of 4.30 Å corresponding to the d-spacing. These hillocks show an asymmetric morphology (figure 1).



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Keywords: Gypsum, Growth Mechanism, Screw Dislocation

MS15-P02

Synthesis and crystallographic study of laflammeite ($Pd_3Pb_2S_2$) and thalhammerite ($Pd_9Ag_2Bi_2S_4$)

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Mineral laflammeite ($Pd_3Pb_2S_2$) was firstly described by Barkov et al. (2002) from the Kirakkajuppura platinum-deposit, Penikat layered complex, Finland. Barkov et al. (2002) provided chemical and physical characterisation of this mineral, however its detailed crystal structural analysis has been lacking. Thalhammerite ($Pd_9Ag_2Bi_2S_4$) was discovered in millerite-pyrite-chalcopyrite vein-disseminated ore from the Komsomolsky mine in the Talnakh deposit, Russia (Sluzhenikin and Mokhov, 2015). Crystal structures of both minerals and relevant crystal-chemical implications will be presented.

Laflammeite occurs as subhedral platelets up to 150 µm, however the crystals are finely twinned and consequently unsuitable for a direct crystal structure study (Barkov et al. 2002). Thalhammerite occurs as tiny inclusions (from few µm up to about 40-50 µm) in sulphide ore where it forms intergrowns with other Pd-bearing minerals. Therefore, both minerals were synthetized by silica glass tube technique by heating at 400 ºC from stoichiometric mixture of elements. The prepared synthetic analogues of laflammeite and thalhammerite were used for a crystal structure study. The structural identity between natural and synthetic materials was subsequently confirmed by an electron-backscattered diffraction.

Laflammeite, $Pd_3Pb_2S_2$, crystalizes in *Pmmn* space group (a = 5.78, b = 8.18, c = 5.96 Å) and Z = 2. Its crystal structure show many similarities with structures of shandite ($Ni_3Pb_2S_2$, $R\bar{3}m$), parkerite ($Ni_3Bi_2S_2$, $C2/m$) and vymazálovaite ($Pd_3Bi_2S_2$, $I213$). All these minerals show a common structure motive: a pseudocubic subcell of the CsCl-type composed of Bi(Pb) and S atoms. A half of available octahedral voids is occupied by Ni(Pd) atoms. The distribution of Ni(Pd) atoms (i.e. the ordering scheme) determines the structure type (Weihrich et al. 2007). Laflammeite can be considered as antiperovskites superstructures.

Thalhammerite, $Pd_9Ag_2Bi_2S_4$ shows $I4/mmm$ symmetry (a = 8.02, c = 9.15 Å) and Z = 2. Its unique crystal structure is based on a three-dimensional framework which consists of two types of blocks of polyhedra that interpenetrate and support each other. The first type consists of corner-sharing [PdS_4] and [$PdBi_2S_2$] squares. The second is formed by flattened tetrahedra [$PdBi_2S_2$]. Silver atoms occupy channels running along the c direction. Thalhammerite crystal structure merges metallic building blocks with structure motives typical for polar sulphides.