Poster Presentations

[MS18-P07] **Structural examinations of synthetic and natural single crystals of mullite.**
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Czochralski-grown single crystals of mullite (by S. Uecker, IKZ, Berlin-Adlershof, Germany, after [1]) were examined to revisit its average and modulated crystal structure. Furthermore, single crystals of naturally grown mullite from the Bellerberg in the Eifel area, Germany, were examined for comparison. X-ray diffraction data of the synthetic variant were collected for a 0.15x0.26x0.31 mm³ crystal on a Bruker diffractometer (APEX II area detector, Mo-Kα) and neutron diffraction data for a ~4x4x4 mm³ crystal at FRM II (RESI with MAR345 detector), both from the same specimen. For data collection on the natural variant a four-circle Bruker diffractometer with Photon area detector was used.

The melt-grown synthetic crystals have the usual 2 Al2O3/1 SiO2 composition ("2/1 mullite") and average structure with space group P b a m (see, e.g., Angel & Prewitt [2,3]). The observed diffuse scattering matches well that observed by Welberry & Withers [4,5] and Freimann & Rahmann [6] and satellite reflections are observed with q = (0.3137(3) 0 ½), similar to that given by Angel & Prewitt [2,3]. Refinements of average structure

parameters versus X-ray and neutron diffraction data confirm the results of Angel & Prewitt with respect to distances and angles as well as to site occupancies (Robs = 2.14 %). The refinement of the 1D-modulated structure was successfully performed in superspace group Pbam(a01/2)0ss (Robs(sat) = 10.9%). Two more q-vectors, q2 & q3 = (0 0.4021(5) ±0.1834(2)), were observed, pointing at two further sets of regularly arranged but rather diffuse maxima in the overall diffuse scattering. The analysis of the corresponding higher-dimensionally modulated structure is in progress. Surprisingly, the diffraction data on natural mullite single crystals display pronounced differences to the synthetic variant. Essentially no diffuse scattering is observed as well as there are no satellites indicative for a modulated structure. Instead, we observed solely a doubling of lattice parameter c, indicated by rather weak, yet significant superstructure reflections in ½ c* with respect to the mullite lattice. This is similar for natural sillimanite and thus it has to be established whether the crystal is simply a sillimanite (Al2SiO5 or 1 Al2O3/1 SiO2). However, the reflection conditions of sillimanite's space group P b n m are not obeyed (210 violations with I/σ(I)-values of 3 to 15, out of 1218 reflections affected by the rules). Instead, the observations rather seem to comply with space group P n a m (like P b n m a different setting of space group P n m a, but with different axes orientations, both with c' = 2c a klassengleiche subgroup to P b a m [7], the space group of mullite) or – indistinguishably with respect to reflection conditions – P n a 21, as was found with JANA2006 [8]. For these space groups in their settings only 8 reflections (out of 1222 affected ones) violate the conditions, and even those possess I/σ(I)-values smaller than 4! As the rules implied by these space groups are so much better obeyed than those for setting P b n m we expect that the violations for the latter should not result from Umweganregung or λ/2 effects – considering that these effects should also affect other space groups to a similar extent. These findings still have to be verified for other

natural crystals. Accordingly, we also observed lattice parameters (a=7.5127(4), b=7.6822(4), c=5.7849(3) Å) which do not comply with neither sillimanite nor with the well-known series of mullites, as reported in Fischer et al. [9] and Fischer and Schneider [10], but rather seem to fall into the gap between these two. The structure analysis is in progress.

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Keywords: synthetic and natural mullite single crystals, diffuse scattering, average and modulated structure.