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Theoretical polytypism and practical twinning of aragonite crystalsPavel Gavryushkin¹, Alexander Rečnik², Nina Daneu²

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In the present work, we show the results of investigation of aragonite (CaCO₃) microstructure with transmission electron microscopy (TEM) under ambient and elevated temperature, complemented by density functional theory calculations. As objects of investigation we choose crystals from Tazouta (Marocco), Cuenca (Spain), and Koge-Dava (Russia) localities. All crystals were well faceted, 1-3 centimetres length. Different localities were chosen to cover different genesis, morphology and chemistry.

The ubiquitous twinning by {110} down to unit cell size was found on all studied crystals. In some areas twinning is so dense, that these areas can be considered as disordered polytype of aragonite. The super-structural reflections (0.5 0.5 0) were found on [1-10] projection. We suggest that these reflections arise from the diffraction on numerous twinning planes, locally doubling d(110). Also strong reflections prohibited for aragonite symmetry was found in [1-10] projection. Appearance of prohibited reflections can be explained by the presence of flattened domains with decreased symmetry.

Calculated enthalpies of polytypes, produced by ordered twinning by {110}, shows that at 0 K enthalpies of O4-O16 polytypes are even lower than the enthalpy of aragonite. This is consistent with ubiquitous twinning by {110} in both organic and inorganic samples and characterise this twinning as the fundamental feature of aragonite structure. Calculated Gibbs energies indicate that temperature energetically stabilise aragonite relative to other polytypes, which explains absence of ordered polytypes in real crystals.

On heating of powder sample above 350C, satellites reflections appear in [1-10] zone axis. One of the possible explanations of such changes is the generation and ordering of {110} twin boundaries. It was theoretically shown [1] that mechanical twinning taking place during aragonite grinding [2] is realised by the shift of {110} layers of aragonite structure. In our work, we suggest another mechanism of {110} twin boundaries generation, more appropriate for high-temperature conditions.

References:

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MS13-P10

Solid-state synthesis and structural characterization of novel geo-inspired sulfate, Na₂CuM₂(SO₄)₄ (M=Mg, Zn)Oleg Siidra¹, Diana Nekrasova^{1,2}, Zhuici Chen¹, Vadim Kovrugin^{1,2}, Olivier Mentre², Marie Colmont²

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Sulfates attract considerable attention due to their wide distribution in nature. A large group of anhydrous sulfate minerals is formed in high-temperature exhalative processes in fumaroles of volcanoes. Many of the exhalative minerals demonstrate unique structure types and may be of interest from the view point of materials science.

Itelmenite, Na₂CuMg₂(SO₄)₄, was recently found in a fumarole of the Naboko scoria cone of the Fissure Tolbachik volcano eruption (2012-2013), Kamchatka Peninsula, Russia [1]. [M²⁺₃(SO₄)₄]²⁻ sulphate framework in itelmenite is unique and has not been described before in minerals or synthetic compounds. Sulphate tetrahedra are packed into pseudolayered arrangements perpendicular to the *a* axis. Structure topology of itelmenite is rather simple. Each MO₅ or MO₆ polyhedron shares all common corners with sulphate tetrahedra thus forming heteropolyhedral framework with voids filled by Na⁺ cations.

Single crystals of Mg- and Zn-dominant synthetic analogues of itelmenite were grown by the solid-state reaction from the mixture containing equimolar quantities of anhydrous CuSO₄, Na₂SO₄, MgSO₄ or ZnSO₄. Na₂CuMg₂(SO₄)₄ (**1**) and Na₂CuZn₂(SO₄)₄ (**2**) are orthorhombic, *Pbca*. **1**: *a* = 9.531(6) Å, *b* = 8.745(6) Å, *c* = 28.72(2) Å, *V* = 2393.3(3) Å³. **2**: *a* = 9.458(5) Å, *b* = 8.811(4) Å, *c* = 28.850(15) Å, *V* = 2404(2) Å³. Mixed cationic character of M1, M2 and M3 sites is similar to that observed in natural sample. Symmetrical M3 octahedral site is occupied exclusively by Mg and Zn in the structures of **1** and **2**, respectively.

Obtained materials were investigated using powder X-ray diffraction, high-temperature powder X-ray diffraction, IR spectroscopy and DSC-TGA.

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