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Keywords: phase transitions, spontaneous strain, benchtop XRD

MS14- Combined approaches for structure characterization of modulated and complex structures

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MS14-P01

Structure elucidation of a zeolite with multi-dimensional disorder by combining HRTEM and XRPD analyses

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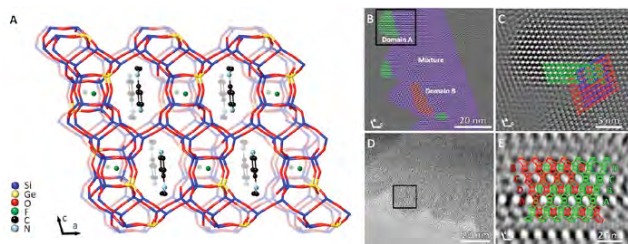
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We present a detailed structure analysis of zeolite IM-18 with a complex disordered framework structure that was unknown for more than 10 years.^[1,2] IM-18 has a novel framework topology and a three-dimensional 8x8x10-ring channel system, making it ideal for the shape selective catalysis of small molecules. The unique disorder in the structure makes the structure analysis complicated, so we combined three complementary techniques, including single-crystal electron diffraction (SCED), high resolution transmission electron microscopy (HRTEM) and synchrotron X-ray powder diffraction (XRPD) to reveal the details of the disorder.

Solving the structure of a polycrystalline material that is also disordered can be very challenging as there are no standard procedures to follow. Rotation electron diffraction (RED) allowed us to solve the average structure of the material, the local ordering was observed from the HRTEM images (Fig. 1B-E), but the fine details of the structure and location of the OSDA and Ge could only be derived from XRPD data (Fig. 1A). We found that IM-18 contains two different types of stacking faults along two directions, which were difficult to observe using HRTEM because of the beam sensitivity of the material. We could describe the structure as 1D long-range ordered and 2D disordered, which culminates in a mixture of four types of domains.

By using such an approach, we not only demonstrated the general procedures for *ab initio* structure elucidation of disordered nanocrystals, but also the potential that the combination of SCED, HRTEM and XRPD offers.



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MS14-P02

NMR crystallography of beryl minerals at 9.4 T and 19.6 T

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The available description of the aluminosilicate beryl group of minerals suggests $RX_3Al_2(Si_6O_{18}) \cdot H_2O$ as general formula, with beryl $Be_3Al_2Si_6O_{18}$ (*P6/mcc*) and pezzottaite $Cs(Be_2Li)Al_2Si_6O_{18}$ (*R-3c* or *R3c*) as end-members. It involves a wide diversity of intermediate chemical compositions because the structure can incorporate different alkali atoms in solid solution, located at channel R site and tetrahedral X sites, and H_2O molecules in the structural channel. Reciprocal-space techniques have resolved only average structures in the intermediate members, related to one of the two the ideal crystal structure of the end-members, and have difficulties in the study of water molecules. Here, high-resolution multinuclear NMR spectroscopy, leading to ^{29}Si , ^{27}Al , 9Be , ^{133}Cs , 7Li , ^{23}Na and 1H spectra at 9.4 T as well as ^{27}Al and 9Be spectra at 19.6 T, has been used to investigate the short- and medium-range structures in nine specimens along the solid solution of this group. The 1H NMR SP and CP experiments suggest that hydrogen atoms are actually as OH groups for compensation of local charge, instead of water molecules which were detected in very low concentration. The structural description by reciprocal-space techniques and NMR coincides only in the alkali-free perfectly long-range ordered *P6/mcc* beryl end-member, which in fact is extremely rare in Nature, having one tetrahedral site for Si atoms, one octahedral site for Al atoms, and one tetrahedral site for Be atoms. However a tectosilicate description seems more appropriated that a cyclosilicate classification from the values of the ^{29}Si chemical shifts, as Be and Si atoms form a Q^4 configuration. The most common mineral is alkali-rich beryl having a crystal structure with lower local symmetry than the ideal average hexagonal structure, with at least two sites for Si atoms, four sites for Be atoms, two R sites and two X sites for Li atoms, two R sites for Na atoms, one R site Cs atoms, and two types of OH groups. The NMR data of pezzottaite indicate six tetrahedral sites for Si atoms, two octahedral sites for Al atoms, one tetrahedral site for Be atoms, two R sites and two X sites for Li atoms, three R sites for Cs atoms, and two types of OH groups with one of them different from that of beryl. The lack of resolving power of diffraction techniques to resolve the structural detail of non stoichiometric beryl is similar to that found in order-disorder series of K-feldspars (Sánchez-Muñoz et al. 2013).