CRYSTALLOGRAPHY AS A VERSATILE RESEARCH TOOL

Philipp Hans[a,b], Berthold Stöger [a]

[a]E057D - X-ray Center XRC

[b]CEST Competence center for Electrochemical Surface Technology, Wr. Neustadt, Austria

INTRODUCTION

In order to exemplify methods of contemporary crystallography, two cases are discussed in the present contribution: the results of a research publication of the redetermination of a crystal structure and the results of ongoing investigations of catalytically active, amorphous networks. This contribution is intended to give insights into the physical theory applied as well as refinement strategies on a basic level.

ALLOTWINNIG IN THE MIXED CARBONATE $KAgCO_3$

In the first example, the redetermination of the crystal structure of $KAgCO_3$ is discussed [1]. It is based on crystals made up of two different polytypes with *Pccb* and *Ibca* symmetry, respectively. Motivation was given because in one of the reported structural characterizations of $KAgCO_3$, violations of the systematic absences of the *Ibca* space group were noted.

Crystals of $KAgCO_3$ belong to an order-disorder (OD) family of structures composed of layers of two kinds. Sharp diffraction spots and the absence of diffuse scattering indicate highly ordered macroscopic domains. There are two polytypes with a maximum degree of order [MDO_1: *Pccb*; MDO_2: Ibca, doubled a-axis compared with MDO_1], which are both realised to a different extent in two crystals under investigation. In the case at hand, different structures can be generated by stacking differently orientated layers. An allotwin model (addition of the intensities of both domains) was used for simultaneous refinement of the structure of $KAgCO_3$ against all reflections.

Figure 1 shows a sub-division of the structure into different layers and the unit cell doubling in the second polytype.

DETECTION OF NANO-PRECIPITATES IN AN AMORPHOUS MATRIX

The second example is delicate. Investigation of a material with alleged catalytic properties ([3]) by pair-distribution-function (PDF) analysis ([2]) was performed. Rutile (TiO_2) nano-particles could be modeled together with an amorphous-matrix (a-SiO_2)

Strictly speaking, it is forbidden to apply established practices for data treatment in the PDF-methodology here, as the material is constituted by multiple phases. It is an interesting finding that it was possible however, to satisfactorily describe the measured PDFs by means of the PDFs of crystalline rutile, fused quartz and a modulation wave. While this might be an indication for a restructuring of the amorphous matrix around the particles as is known from colloid studies, further methodological research must be performed to elucidate the reliability of the results. The refinements are shown in figure 2.

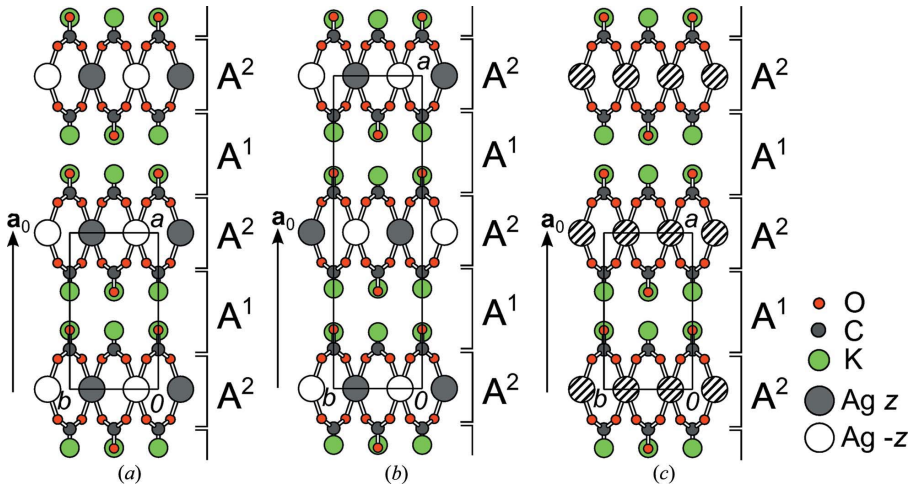

Figure 1: The (a) MDO_1 (*Pccb*) and (b) MDO_2 (*Ibca*) polytypes, and (c) the family structure of $KAgCO_3$ viewed down [001]. Ag atoms at (x, y, z) and (x, y, -z) by large grey and white spheres or, if both positions are occupied, by hatched spheres. Other color codes are given in the legend. Layer types are indicated to the right.

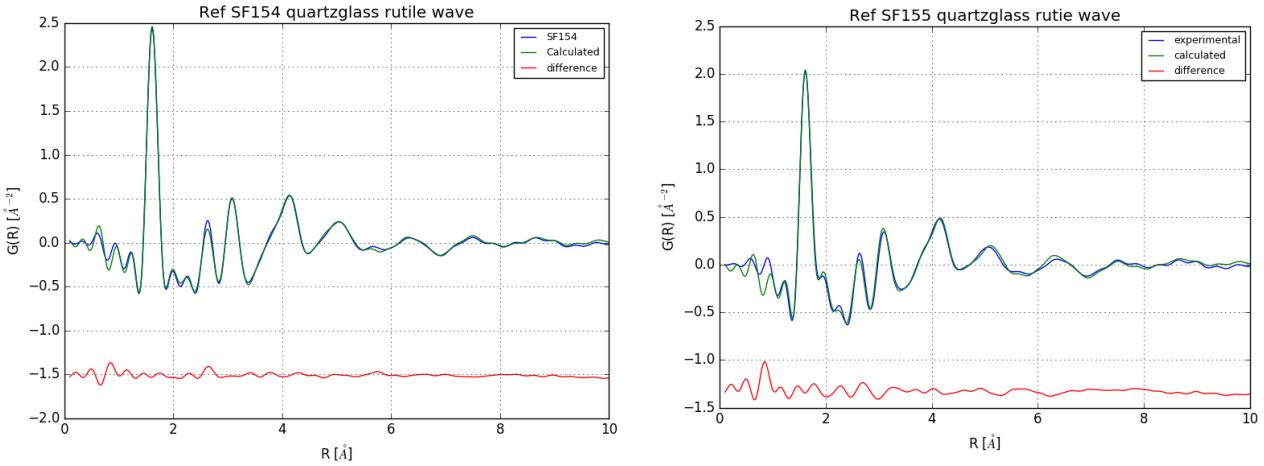

Figure 2: For two similar materials, rutile-particles with extensions of only a few unit cells, could be incorporated into a model that satisfactorily described the measured PDFs G(r). This is interesting as in the theoretical framework, a considerable error is expected for polyphasic materials.

CONCLUSION

Properly applied, the tools of crystallography exhibit great capabilities to structural solution complex materials. In this contribution, research results are to be discussed and analysed in terms of their trustworthiness.

REFERENCES

[1] Hans, P., Stöger, B., Weil, M. & Zobetz, E.: *"Structure of the mixed-metal carbonate KAgCO3revisited: order–disorder (OD) polytypism and allotwinning"*. Acta Crystallographica Section B Structural Science, Crystal Engineering and Materials, 71 (2), p. 194-202, 2015.

[2] Neder, RB and Proffen, T: *"DISCUS: A program for diffuse scattering and defect-structure simulation"*. Journal of applied crystallography, 30 (2), p. 171-175, 1997.

[3] Taramasso, M, Perego, G, Notari, B & others: *"Preparation of porous crystalline synthetic material comprised of silicon and titanium oxides"*. US patent, 4410501, 1983.