Abstract

On the use of supercritical carbon dioxide in Solid State Chemistry and basic structural investigations with chalcogenide halides of the third main group.

One of the tasks of this work was the exploration of the ability of supercritical CO_2 as a solvent and reaction environment in several reactions involving inorganic compounds of different natures. All attempts in this field were not successful. The use of $scCO_2$ as an educt for the permanent fixation of CO_2 (i.e. transformation of oxides or hydroxides in oxide carbonates or carbonates) seems to be a promising field of research.

A second focal point of this work was the preparation, characterisation and the structure determination of new solids in the ternary systems indium – chalcogen – halogen. The syntheses of In_5Ch_5X (Ch = S, Se; X = Cl, Br) and of derivative compounds were performed using the concept of building units. In_5Ch_5X represent four new mixed valence compounds crystallising in two different structure types, namely the chloride type (In_5Ch_5Cl, space group: $P2_1/m$) and the bromide type (In_5Ch_5Br, space group: $Pmn2_1$). In all these compounds indium occurs in three different oxidation states as In^+, covalent $(In\text{-}In)^{4+}$ dumbbells and In^{3+} suggesting the explicit formula $In_5Ch_5X = [In^+]\ [(In_2)^{4+}]\ 2[In^{3+}]\ 5[Ch^{2-}]\ [X^-]$. Beside the similarities remarkable differences were evident not only from the X-ray investigation but mainly from the real structure revealed from HRTEM investigations. The bromide-type compounds revealed ordered crystals. In contrast to that, the chloride-type compounds show several anomalies regarding the real structure, e.g. polylamellar intergrowth of polymorphs, twinning and nanoscale intergrowth of structurally similar compounds (In_5S_5Cl/In_6S_7).

A further topic of interest was the high temperature X-ray investigations of powdered samples $K_2In_{12}Se_{12}Te_7$, $K_2In_{12}Se_{19}$ and In_5Ch_5X (Ch = S, Se; X = Cl, Br). The process of lattice expansion revealed no phase transition for all these compounds within the studied temperature range. The coefficients of thermal expansion for each compound were determined.

Key words: reactions, $scCO_2$, indium chalcogenide halides, crystal structures, real structure, HRTEM, crystal defects, X-ray diffraction, high temperature investigations, expansion coefficient