ON THE IDENTIFICATION OF OXYGEN AND FLUORINE ATOMS IN DISORDERED INORGANIC OXYFLUORIDE COMPOUNDS

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It is considered practically impossible to differentiate between oxygen and fluorine atoms by X-ray diffraction in disordered structures of oxyfluoride compounds due to the similarity of their ionic radii and diffusion factors. Indeed, many transition metal oxyfluoride compounds containing polar pseudo-octahedral MO_xF_{6-x} (x = 1-3) anions form crystal structures without any fluorine-oxygen (F/O) ordering owing to a large number of local anion configurations. Because of this static disorder, it is impossible to determine the positions of O and F atoms and find the real geometry of the polyhedron. However, this becomes possible in the case of dynamic disorder of oxyfluoride anions when the central atom is displaced from the center of the octahedron toward a vertex, edge, or face (depending on the number of oxygen atoms in the polyhedron), which enables the identification of O and F atoms owing to inherent differences between M–O and M–F bonding. On cooling, such compounds undergo phase transitions of the order–disorder type with substantial changes in the entropy. The examples of static and dynamic orientational disorder in oxyfluoride compounds of d^0 transition metals are given.

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