The lanthanoids form various metal-rich halides. With few exceptions, such as \( \text{Gd}_2 \text{X}_3 \), \( \text{Tb}_2 \text{X}_3 \), \( \text{X} = \text{Cl}, \text{Se} \), they are most commonly found as ternary compounds with nonmetals like \( \text{N}, \text{B}, \text{C} \), and \( \text{N} \). Especially large is the number of carbide-halides, of which those compounds containing gadolinium were examined in more detail.

The structurally characterized phases are listed in Table 1 according to their condensation. In this classification scheme, the structures are constructed from edge-sharing \( \text{Gd}_6 \text{X}_{12} \) clusters, in which their centers are occupied by c atoms or \( \text{Gd}^3+ \) ions. The structurally characterized phases are interrupted by structural disorder in the clusters. \( \text{In}_n \text{Mo}_{3n} \text{O}_{4n+2} \) is the first compound, \( \text{In}_8 \text{Mo}_{32} \text{O}_{52} \), where discrete cluster anions with four and five condensed \( \text{Mo}_6 \)-octahedra are arranged in layers, which are stacked in an alternating sequence (fig. 1a). A single oligomeric cluster of five condensed octahedra is shown in figure 1b. All free edges are bridged by \( \text{O} \) atoms. The channels between the clusters are occupied by linear \( \text{N-M}-\text{bonded poly­}

cations \( \text{In}_8 \text{Si}^+ \) and \( \text{In}_8 \text{Si}^- \). The layers seen in fig. 1a have the general composition \( \text{In}_n \text{Mo}_{3n} \text{O}_{4n+2} \), where \( \text{n} \) indicates the number of \( \text{Mo}_6 \)-octahedra in the oligomeric cluster. The number of \( \text{Mo-Mo}\)-bonding states can be estimated by suitable fragmentation of the oligomeric cluster into \( \text{Mo}_2\text{O}_{4n+2}^- \text{(n-l)}\text{Mo}_6 \text{O}_{4n} \) units (A. Simon in A. K. Cheetham and F. Day (Eds.) Inorganic Solids, Oxford University Press, in print).

Accordingly, one expects, besides "homogeneous structures" (i.e. structures with a single type of layers), also structures with clusters of other length. A first confirmation of their existence was provided by high resolution transmission electron microscopy (A. Simon, W. Mertin, Hj. Mattausch, H. Gruehn, Angew. Chem. 1986, 28, 831). An electron microscopic photograph of an \( \text{In}_n \text{Mo}_{3n} \text{O}_{4n+2} \) crystal fragment shows the alternating sequence of the \( \text{Mo}_14 \) and \( \text{Mo}_9 \)-layers. Such alternating layer segments occur in ordered regions of 10\( \text{pm} \) extension. In the same sample regions are found in which stacking disorder is recognizable: two consecutive \( \text{In}_n \text{Mo}_{3n} \text{O}_{4n+2} \) layers are followed by two immediately adjacent \( \text{In}_n \text{Mo}_{3n} \text{O}_{4n+2} \) layers. Another part of the same sample is exclusively made up of identical \( \text{In}_n \text{Mo}_{3n} \text{O}_{4n+2} \) layers over distances of 10\( \text{pm} \). In the meantime, the respective new compound \( \text{In}_n \text{Mo}_{3n} \text{O}_{4n+2} \) has been isolated as a homogeneous phase and has been characterized by X-ray crystallography (\( a = 3160.6, b = 948.9, c = 983.9 \text{pm} \)).

Fig. 1: a: Projection of the crystal structure of \( \text{In}_n \text{Mo}_{3n} \text{O}_{4n+2} \) on [010]. The oligomeric clusters \( \text{Mo}_{14} \) and \( \text{Mo}_9 \) are arranged in layers (small circles Mo-atoms; large circles with crosses O-atoms). b: Oligomeric cluster with five edge-linked \( \text{Mo}_6 \) octahedra in \( \text{In}_n \text{Mo}_{3n} \text{O}_{4n+2} \).