Mullite-type materials: Introducing a new structure-type for the design of high-entropy oxides

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High-entropy oxides (HEO) present a new class of materials containing 5 or more metal cations in close to equal amounts in a single-phase solid solution. The high-entropy concept was first introduced in 2004 in the form of alloys [1], whereas the first HEO was presented in 2015 [2]. Until now, it has been assumed that HEOs have a strong tendency to crystallize in simple crystal structures e.g. rock salt, fluorite, perovskite and pyrochlore [3]. However, our study challenges this assumption by the first successful synthesis of a HEO possessing a complex connectivity of polyhedral units in a mullite-type structure. The parent compounds $Bi_2M_4O_9$ (M = Al^{3+}, Ga^{3+} and Fe^{3+}) and $REMn_4O_{10}$ (RE = rare earth elements, Y and Bi) (Figure 1) show a variety of attractive properties such as multiferroicity and catalytic activity. The crystal structure is built up from edge-sharing MO_6 octahedral chains which are interconnected by double tetrahedral M_2O_7 units ($Bi_2M_4O_9$) or Mn_2O_8 double pyramids ($REMn_4O_{10}$).

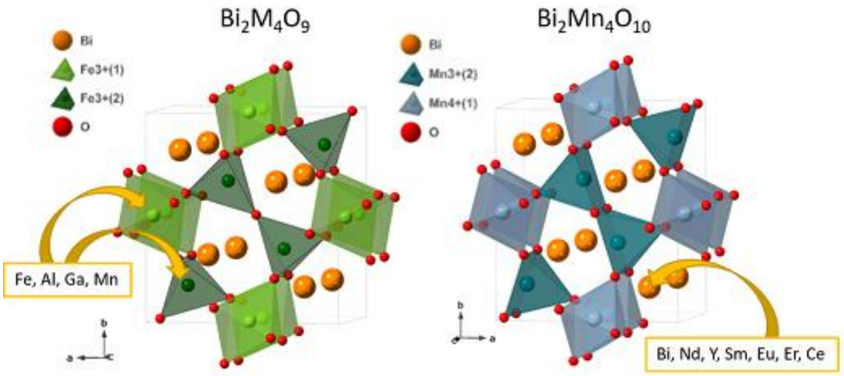

Fig.1 Crystal structures of the parent compounds $Bi_2M_4O_9$ and $Bi_2Mn_4O_{10}$

In this work, we introduce 5 new HEOs with mullite-type structure $Bi_2(AlGaFeMn)O_9$, $(EuHE)_2Mn_4O_{10}$, $(ErHE)_2Mn_4O_{10}$, $(CeHE)_2Mn_4O_{10}$ (HE = Nd,Sm,Y,Bi) and $(Nd,Sm,Y,Er,Eu)_2Mn_4O_{10}$. We show that the materials represent statistically mixed solid solutions using a combination of Neutron and X-ray powder diffraction with subsequent Rietveld analysis, X-ray total scattering and Pair distribution Function analysis, transmission electron microscopy, infrared and Raman spectroscopy. In addition, we follow their formation *in situ* by X-ray diffraction with a second scale time resolution. Surprisingly, all of them directly form out of an amorphous precursor without the formation of any other binary or ternary oxides. From a chemical point of view, the feasibility to crystallize structurally complex HEOs is fundamentally interesting and the targeted introduction of disorder into such a complex host lattice certainly bears great potential for the discovery of new physical phenomena.

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