MS13-1-17 New high-entropy oxides in a mullite-type structure
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Abstract
Engineering compositional disorder into materials have attracted immense interest since the introduction of the high-entropy concept in 2004 [1]. High-entropy materials represent a class of compounds containing a high number of metal cations in ca. equal amounts statistically mixed in a single-phase solid solution. Only in 2015, the first high-entropy oxide (HEO) was synthesized [2]. Until now, it has been assumed that they crystallize in simple crystal structures [3] and mainly HEOs in a rock-salt, fluorite, spinel, perovskite and pyrochlore structure have been reported.
Yet, with this study we demonstrate the feasibility to synthesize HEOs possessing a complex connectivity of polyhedral units in a mullite-type structure (Figure 1). 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) show a variety of attractive properties including multiferroicity. To map out the synthesizability in this system, we produced 5 HEOs with compositions of $Bi_2(Al_{0.25}Ga_{0.25}Fe_{0.25}Mn_{0.25})_4O_9$, $(Eu_{0.2}HE)_2Mn_4O_{10}$ (HE = $Nd_{0.2}Sm_{0.2}Y_{0.2}Bi_{0.2}$), $(Er_{0.2}HE)_2Mn_4O_{10}$, $(Ce_{0.2}HE)_2Mn_4O_{10}$ and $(Nd_{0.2}Sm_{0.2}Y_{0.2}Er_{0.2}Eu_{0.2})_2Mn_4O_{10}$. We show that the materials represent statistically mixed solid solutions using a combination of neutron and X-ray powder diffraction (XRD) 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 XRD. Surprisingly, all of them directly form out of an amorphous precursor without the formation of any other binary or ternary oxides.
On one hand, the targeted introduction of disorder into such a complex host lattice offers a great degree of freedom to fine-tune the material's properties. On the other hand, the feasibility to crystallize structurally complex HEOs is intriguing and encourages to search for additional structure-types to extend the landscape of high-entropy materials.

References
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Crystal structures of the parent compounds.