Chemical Short-Range Order in Hollandite Type Phases for Nuclear Waste Form Applications

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The hierarchical tunnels structure and wide chemical flexibility of Hollandite-type phases offers an interesting opportunity for nuclear waste forms, particularly for ^{137}Cs entrapment, which has limited solubility in current waste form glasses. The nature and extent of structural disorder in these types of materials is still however poorly understood, but clearly has a major impact on the stability of the materials and radioisotope leach rates.

Our PDF and XRD studies, prompted by computational results suggesting cation clustering, show that local structure partial ordering is important in the materials of interest. We present a study of the local tunnel structure of Ba, Cs, Mg, and Na containing Hollandite phases through combined synchrotron X-ray pair distribution function (PDF) and Rietveld analysis of high-resolution synchrotron data. PDF small-box fitting indicates that there are local structural features not described by average structure, and large-box RMC studies are used to capture the nature and extent of cation clustering in $Ba_{0.33}Cs_{1.0}Al_{1.67}Ti_{6.33}O_{16}$. Ti and Al preferentially cluster, thus the tunnel is not a uniformly random Ti/Al host.