A structural phase transition in the R$_4$Cu$_4$Sn$_4$ compounds (R=Ho, Er and Tm)

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Abstract

Actinide-bearing phosphate compounds can be encountered in mineralogy [1], biochemistry [2] or issued from anthropogenic activities like nuclear fuel reprocessing. They have also been envisioned and investigated as potential host for actinide waste disposal. Because of their numerous oxidation states (e.g. III to VII for neptunium) and corresponding ionic radii, actinides can form various types of isostructural compounds that crystallize in the orthorhombic R$_4$Cu$_4$Ge$_4$ type structure (space group Immm, #71) [1]. The exceptions to this generic orthorhombic crystallography are TmCu$_4$Sn$_4$ and LuCu$_4$Sn$_4$, which have a monoclinic structure (space group C12/m1, #12) at room temperature [2].

In the orthorhombic phase the R atoms occupy two crystallographically distinct sites [3] and these compounds have attracted interest due to the general observation of independent magnetic ordering of these two R sublattices [1].

The present work reveals that a structural phase transition occurs from orthorhombic Immm to monoclinic C12/m1 upon cooling, at 262(2) K and 62(2) K respectively. We also found a structural phase transition at 458(2) K from monoclinic C12/m1 to orthorhombic Immm in TmCu$_4$Sn$_4$ upon heating.

The results show a linear behaviour of the crystallographic transition temperatures with the ionic radii of the R$^{3+}$ ions, and predict no transition for the DyCu$_4$Sn$_4$ compound, in accord with our measurements carried out at low temperatures for this compound.

Here, we present complete structural information from high resolution synchrotron X-ray powder diffraction studies of these R$_4$Cu$_4$Sn$_4$ compounds.

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