A structural phase transition in the intermetallic compound \( \text{Tm}_3\text{Cu}_4\text{Sn}_4 \)

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Abstract. The ternary intermetallic system \( \text{R}_3\text{T}_4\text{X}_4 \) (where \( \text{R} = \) rare earth; \( \text{T} = \) Mn, Cu, Ag, Au, Pd; \( \text{X} = \) Si, Ge, Sn) comprises an extensive series of isostructural compounds that form in the orthorhombic \( \text{Gd}_3\text{Cu}_4\text{Ge}_4 \)-type structure (space group \( \text{Immm} \#, \#71 \)). The exceptions to this generic structure are \( \text{Tm}_3\text{Cu}_4\text{Sn}_4 \) and \( \text{Lu}_3\text{Cu}_4\text{Sn}_4 \) which have a monoclinic structure (space group \( \text{C}12/m1 \#, \#12 \)) at room temperature. Here, we report a structural phase transition in \( \text{Tm}_3\text{Cu}_4\text{Sn}_4 \) from monoclinic \( \text{C}12/m1 \) to orthorhombic \( \text{Immm} \) upon heating above room temperature. We have carried out X-ray powder diffraction and differential scanning calorimetry on \( \text{Tm}_3\text{Cu}_4\text{Sn}_4 \) and we observe the structural transition at 458(2) K.

1. Introduction
The orthorhombic \( \text{R}_3\text{Cu}_4\text{Sn}_4 \) (\( \text{R} = \) rare earth; \( \text{T} = \) Mn, Cu, Ag, Au, Pd; \( \text{X} = \) Si, Ge, Sn) compounds exhibit a rich variety of magnetic ordering behaviour of the R sublattices [1]. The space group of this generic orthorhombic structure is \( \text{Immm} \) (\#71) and the R atoms occupy two crystallographically inequivalent sites [2, 3]. The magnetic moments observed at the two R sites usually exhibit quite different magnetic ordering temperatures and ordering modes.

The exceptions to this generic orthorhombic crystallography are \( \text{Tm}_3\text{Cu}_4\text{Sn}_4 \) and \( \text{Lu}_3\text{Cu}_4\text{Sn}_4 \) which form in a monoclinic \( \text{C}12/m1 \) (\#12) cell at room temperature (RT). With regard to \( \text{Tm}_3\text{Cu}_4\text{Sn}_4 \) it was shown that a single-crystal sample formed with the monoclinic \( \text{C}12/m1 \) cell [4] whereas a polycrystalline sample annealed at 670 K formed in the orthorhombic \( \text{Immm} \) cell [5]. In this paper we show that the monoclinic structure of \( \text{Tm}_3\text{Cu}_4\text{Sn}_4 \) transforms to the generic orthorhombic structure at 458(2) K. To the best of our knowledge, this is the first clear determination of such a crystallographic transformation in this intermetallic family.

2. Experimental Methods
The \( \text{Tm}_3\text{Cu}_4\text{Sn}_4 \) sample was prepared in an argon-arc furnace. Stoichiometric amounts of the pure elements [Tm (99.9%), Cu (99.999%), Sn (99.998%)] were melted several times under pure (less than 1-ppm impurity) argon to ensure homogeneity. The resulting ingot was annealed \textit{in vacuo} at 800º C for two weeks and water-quenched. X-ray powder diffraction measurements were made at room temperature using Cu-K\( \alpha \) radiation on a PANalytical X’Pert Pro diffractometer equipped with a high-temperature stage. Diffraction patterns were obtained over the temperature range 295 K – 495 K and all patterns were refined using the Rietveld method and the FullProf/WinPlotr suite [6, 7]. Differential Scanning Calorimetry (DSC) was carried out on a Perkin-Elmer DSC-4 system at a constant heating rate of 2 K/minute.
3. Results
In figure 1 we show the refined XRD pattern of Tm₃Cu₄Sn₄ obtained at 295 K and in table 1 we give the structural data determined from this refinement. The space group at 295 K is monoclinic C12/m1. The conventional R-factors for this refinement are $R_F = 2.9$, $R_{\text{struct}} = 3.9$ and GoF = 2.6.

![Cu-Kα X-ray powder diffraction pattern of Tm₃Cu₄Sn₄ (at 295 K) and refined in the C12/m1 monoclinic space group.](image)

**Table 1.** Crystallographic data (at 295 K) for Tm₃Cu₄Sn₄ in the monoclinic phase

| Atom | Site | x   | y   | z   | x   | y   | z   |
|------|------|-----|-----|-----|-----|-----|-----|
| Tm (1) | 2a  | 0   | 0   | 0   | 0   | 0   | 0   |
| Tm (2) | 4i  | 0.1298(1) | 0 | 0.6373(4) | 0.8702(1) | 0 | 0.5075(4) |
| Cu (1) | 4i  | 0.3358(4) | 0 | 0.0233(8) | 0.6642(3) | 0 | 0.6875(7) |
| Cu (2) | 4i  | 0.3208(4) | 0 | 0.6297(8) | 0.6791(4) | 0 | 0.3088(7) |
| Sn (1) | 4i  | 0.2157(2) | 0 | 0.2056(5) | 0.7843(2) | 0 | 0.9899(5) |
| Sn (2) | 4i  | 0.5055(2) | 0 | 0.2997(4) | 0.4944(2) | 0 | 0.7941(4) |

This monoclinic C-centred cell is not a conventional cell and we identified the body-centred conventional cell using the SETSTRU program on the Bilbao Crystallographic Server [8]. The space group of the conventional cell is I12/m1 (12). The lattice parameters and atomic positions in this conventional cell are given in table 1. We refer the reader to the work of Mighell [9] for a detailed discussion of the conventional and reduced cells in monoclinic systems.

In figure 2 we show the temperature dependence of a section of the XRD pattern of Tm₃Cu₄Sn₄. The structural transformation from the RT monoclinic phase to the higher-temperature orthorhombic phase is clearly seen as the monoclinic peaks merge due to the formation of the higher-symmetry orthorhombic structure.
Figure 2. Thermal evolution of a section of the X-ray powder diffraction pattern of Tm$_3$Cu$_4$Sn$_4$

In figure 3 we show the angular positions of the (511) and (311) monoclinic peaks as they merge to form the (114) orthorhombic peak, as a function of temperature. These data indicate the completion of the transformation to the orthorhombic structure occurring at 458(2) K. We can also follow the crystallographic transformation by monitoring the peak width upon heating and in figure 4 we show the temperature dependence of the full-width at half-maximum intensity for the peaks monitored in figure 3. Once again, the formation of the orthorhombic structure is observed at 458(2) K.

Figure 3. Temperature dependence of the (511) and (311) peak positions of Tm$_3$Cu$_4$Sn$_4$.

Figure 4. Temperature dependence of the width of the (511) and (311) peaks of Tm$_3$Cu$_4$Sn$_4$.

An independent determination of the structural transition temperature can be found in the DSC data shown in figure 5 where the onset of the transformation is clearly observed at 457(3) K.

In table 2 we give the structural data determined from the refined XRD pattern of Tm$_3$Cu$_4$Sn$_4$ in its orthorhombic Immm phase, obtained at 473 K. The conventional R-factors for this refinement are $R_F = 4.3$, $R_{struct} = 5.9$ and GoF = 2.2.
Figure 5. Differential scanning calorimetry trace of Tm$_3$Cu$_4$Sn$_4$ obtained at a heating rate of 2 K/minute.

Table 2. Crystallographic data (at 473 K) for Tm$_3$Cu$_4$Sn$_4$ in the orthorhombic Immm cell, $a = 4.4028(1)$ Å, $b = 6.9139(2)$ Å, $c = 14.5261(4)$ Å.

| Atom  | Site  | x   | y   | z   |
|-------|-------|-----|-----|-----|
| Tm (1)| 2a    | 0   | 0   | 0   |
| Tm (2)| 4j    | 0.5 | 0   | 0.3718(2) |
| Cu    | 8l    | 0   | 0.3149(5) | 0.3249(2) |
| Sn (1)| 4i    | 0   | 0   | 0.2175(2) |
| Sn (2)| 4h    | 0   | 0.2018(3) | 0.5   |

Figure 6. Relationship between the monoclinic (left and centre) and orthorhombic (right) forms of Tm$_3$Cu$_4$Sn$_4$ shown as projections onto the ac plane and bc plane, respectively.

The relationship between the monoclinic (C 12/m1 & I 12/m1) and orthorhombic (Immm) forms of Tm$_3$Cu$_4$Sn$_4$ is shown in figure 6. The most significant difference is in the atomic positions of the Cu(2) sites whose relative displacement is nearly three times those of the other sites. In the orthorhombic Immm structure, the Cu atoms occupy a single crystallographic site (8l) with the point group $m$. In the monoclinic cells, the Cu atoms split into two 4i sites. Finally, the fact that only the Tm and Lu
R₃Cu₄Sn₄ compounds form the monoclinic phase suggests that the size of the R ion might play a major role in determining the crystallography in the R₃T₄X₄ intermetallic series.

4. Conclusions
We have used X-ray powder diffraction, complemented by differential scanning calorimetry, to show that the room temperature monoclinic crystal structure of Tm₃Cu₄Sn₄ transforms to the generic orthorhombic structure of the R₃T₄X₄ intermetallic family at 458(2) K.

Acknowledgments
We are grateful for financial support from the Natural Sciences and Engineering Research Council of Canada and the Canada Foundation for Innovation. We also thank Dr M. Bieringer (Chemistry, U. Manitoba) for giving us access to his diffractometer. Finally, JMC acknowledges support from the Canada Research Chairs programme.

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