Polymorphism of Tl[*Ch*CN] (*Ch*=O, S, Se)

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In this work, we present our studies on temperature dependent behaviour of three different binary thallium cyanates with the general formula Tl[*Ch*CN] (*Ch*=O, S, Se). Whereas the crystal structure of Tl[SCN] has been reported, data on Tl[OCN] and Tl[SeCN] is absent in literature. At 298 K Tl[SCN] crystallizes in the orthorhombic space group *Pbcm* (№ 57, *a*=6.783(1), *b*=6.816(1), *c*=7.606(1) Å, *V*=351.65 Å^3). The S and N atoms of the almost linear [SCN]$^-$-anion can be differentiated from each other without any apparent disorder. By increasing of the temperature to 400 K, Tl[SCN] undergoes an order-disorder transition from *Pbcm* into the higher symmetric tetragonal space group *I*4/*mcm* (№ 140). Due to the head-to-tail disorder of the [SCN]$^-$-anion, S and N atoms occupy the same atomic position.[1,2] Both space groups are related by symmetry, which is described with the aid of the Bärnighausen formalism (Fig. 1, left).

Tl[SeCN] shows similar behaviour. At 298 K it crystallizes isotypically with Tl[SCN] in the space group *Pbcm* (*a*=7.038)1), *b*=6.906(1), *c*=7.724(1) Å, *V*=375.45(9) Å^3). At 400 K, the considerable mass disparity between the Se and N atoms results in merely partial orientational disorder of the [SeCN]$^-$ anion. Se and N atom positions are occupied in the ratio of 0.1 to 0.9 and *vice versa*. It still crystallizes in the space group *Pbcm* (*a*=6.9596(8), *b*=7.0376(8), *c*=7.8570(6) Å, *V*=384.83(7) Å^3). Phase transition to the fully disordered *I4/mcm* phase was studied by high-temperature PXRD.

From single-crystal X-Rray diffraction data, the lightest homologue Tl[OCN] is disordered at 298 K. It crystallizes isotopically with ht-Tl[SCN] in the space group *I*4/*mcm* (*a*=6.2437(3), *c*=7.1742(3) Å, *V*=279.68(3) Å^3). However, due to a low scattering contrast of O and N atoms, the atomic occupancies cannot be determined exactly. To check if ordering occurs at 298 K or at lower temperatures, we used time-of-flight powder neutron diffraction (Fig. 1, right). Additionally, we studied luminescence and thermal properties, and performed quantum chemical calculations for all three compounds.

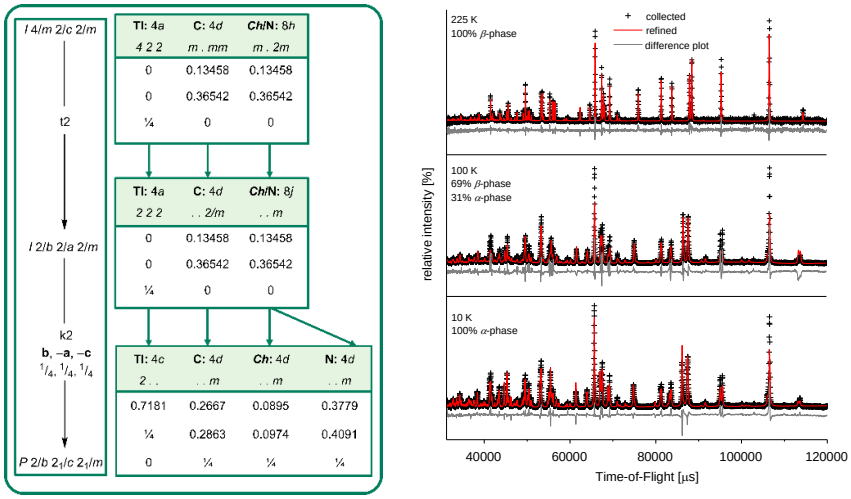


***Figure 1**. Left: Bärnighausen tree of the transition of Tl[ChCN] from the space group I4/mcm (№ 140, ß-phase) to the space group Pbcm (№ 140, α-phase). Right: phase transition of Tl[OCN] as followed by ToF-NPD.*

[1] R. Lippman, R. Rudman, *Acta Crystallogr. A.* **1981**, *37*, C106–C106.

[2] R. Lippman, R. Rudman, *J. Chem. Phys.* **1983**, *79*, 3457–3461.