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<td><strong>Citation</strong></td>
<td>Zhang, L. Z., Gu, W., Dong, Z., Liu, X., &amp; Li, B. (2008). Phase transformation of a rare-earth Anderson polyoxometalate at low temperature. CrystEngComm, 10(10), 1318-1320.</td>
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<td><strong>Date</strong></td>
<td>2008</td>
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<td><strong>URL</strong></td>
<td><a href="http://hdl.handle.net/10220/9480">http://hdl.handle.net/10220/9480</a></td>
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Phase transformation of a rare-earth Anderson polyoxometalate at low temperature†

Li-Zhi Zhang, a,b Wen Gu, b Zhili Dong, a*Xin Liu a b and Bing Li a

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX
DOI: 10.1039/b000000x

The rare-earth Anderson-type polyoxometalate $\text{[Tm}_2(\text{H}_2\text{O})_{14}\text{CrMo}_6\text{O}_{24}\text{H}_6][\text{CrMo}_6\text{O}_{24}\text{H}_6]\text{-16H}_2\text{O}$ undergoes a temperature-dependent single-crystal-to-single-crystal (SCSC) phase transformation.

It is well known that many materials can undergo solid-state structural phase transformation as a function of temperature, and that different atomic arrangements are stable in different temperature ranges.1 With development of crystal engineering, temperature-dependent single-crystal-to-single-crystal (SCSC) phase transformations have received considerable interest.2-5 However, such SCSC phase transformations are still rare since crystals can hardly retain single crystallinity after the solid-state rearrangement of atoms. Polyoxometalates (POMs) are nano-sized metal–oxygen cluster species with a diverse compositional range and an enormous structural variety.6-11 One of the most important properties of polyoxometalates is their capability to accept large and various numbers of water molecules in their crystal lattice, which makes them very useful in the hydration catalysis.4,5 Since it has been demonstrated that water molecules can play an important role in SCSC phase transformations as a function of temperature,12 polyoxometalates can be good candidates for investigation into temperature-dependent SCSC phase transformations. However, to the best of our knowledge, the temperature-dependent SCSC phase transformation of polyoxometalates has been unknown in the literature.

Herein, we construct the simple but highly hydrophilic polyoxometalate $\text{[Tm}_2(\text{H}_2\text{O})_{14}\text{CrMo}_6\text{O}_{24}\text{H}_6][\text{CrMo}_6\text{O}_{24}\text{H}_6]\text{-16H}_2\text{O}$ by using the Anderson-type anion and the lanthanide cation, and report the temperature-dependent SCSC phase transformation that occurs at surprisingly low temperature (<113 K).

The reaction of $\text{TmCl}_3\text{-6H}_2\text{O}$ (0.2 mmol, 0.055 g) and $\text{Na}_3[\text{CrMo}_6\text{O}_{24}\text{H}_6]\text{-8H}_2\text{O}$ (0.2 mmol, 0.25 g)13 in an aqueous solution (10 mL) at 80 °C for 1 h followed by slow evaporation at room temperature resulted in pink single crystals (0.14 g, yield 48%).14 X-Ray analyses at 294 K reveal that the compound, crystallized as $\text{[Tm}_2(\text{H}_2\text{O})_{14}\text{CrMo}_6\text{O}_{24}\text{H}_6][\text{CrMo}_6\text{O}_{24}\text{H}_6]\text{-16H}_2\text{O}$ (I), belongs to triclinic $\text{P}\overline{1}$ space group with lattice parameters $a = 11.0989(13)$, $b = 11.7203(14)$, $c = 13.9843(16)$ Å; $\alpha = 74.993(2)$, $\beta = 84.548(2)$, $\gamma = 89.545(2)$.15 I exhibits an ionic, asymmetric structure consisting of the $[\text{CrMo}_6\text{O}_{24}\text{H}_6]^3-$ polyoxoanion and the $[\text{Tm}_2(\text{H}_2\text{O})_{14}\text{CrMo}_6\text{O}_{24}\text{H}_6]^-$ polyoxocation (Fig. 1). In this structure, the two Cr atoms lie on independent inversion centres and, as a consequence, the asymmetric unit has one Tm-containing moiety in a general position and two half-Cr-containing moieties. In the polyoxocation, either of Tm$^{III}$ ions is coordinated with 7 water molecules and is bound to the Anderson core by one oxygen atom. The coordination polyhedron of Tm$^{III}$ can be represented as a distorted, bicapped trigonal prism ($\text{Y}_{\text{hex}}$), with the Tm–O bond lengths in the range from 2.293 to 2.390 Å (mean value 2.336 Å). The torsion angle between the top and bottom planes is 18.92°. The distance of strictly symmetrical Tm$^{III}$ ions (Tm–Tm) is 13.768 Å. The angle of Tm⋯Cr⋯Tm is 180°, showing the three atoms are strictly linear. The distance between the polyoxocation and the polyoxoanion is 8.039 Å (defined by the Cr⋯Cr separation).

In the X-ray analyses, when the crystal of I was cooled from 294 K to temperatures below ca. 113 K, a change in the lattice parameters was observed. Phase I’, crystallized as $[\text{Tm}_2(\text{H}_2\text{O})_{14}\text{CrMo}_6\text{O}_{24}\text{H}_6][\text{CrMo}_6\text{O}_{24}\text{H}_6]\text{-16H}_2\text{O}$, belongs to triclinic $\text{P}\overline{1}$ space group with the lattice parameters $a = 15.607(4)$, $b = 15.934(5)$, $c = 16.088(5)$ Å; $\alpha = 86.667(12)$, $\beta = 72.242(9)$, $\gamma = 64.394(9)$.16 I’ exhibits a very similar ionic, asymmetric structure to I, consisting of the $[\text{CrMo}_6\text{O}_{24}\text{H}_6]^+$ polyoxoanion and the $[\text{Tm}_2(\text{H}_2\text{O})_{14}\text{CrMo}_6\text{O}_{24}\text{H}_6]^-$ polyoxocation with a distance of 8.040 Å (Fig. 1).

![Fig. 1](https://www.rsc.org/xxxxxx) Process of the temperature-induced SCSC transformation. (Left) Ball and stick representations of I; (right) ball and stick representations of I’. The color code is as follows: thulium (purple), molybdenum (yellow), chromium (blue), and oxygen (red).
However, unlike that of 1, in this structure, the asymmetric unit has the two Tm-containing and two Cr-containing moieties all in general positions. In the polyoxocation of 1, the two TmIII ions are not strictly symmetrical. The Tm–O bond lengths of the two TmIII ions are within the range of 2.282–2.387 Å (mean value 2.342 Å) and of 2.272–2.429 Å (mean value 2.343 Å), respectively. The torsion angles between the top and bottom planes in their distorted, bicapped trigonal prisms (Fig. 3) are 19.05 and 15.38°, respectively. The arrangement of Tm...Cr...Tm (strictly linear in 1) is slightly distorted with an angle of 178.20°. By comparison of the ionic structures shown in Fig. 1 and the packing frameworks shown in Fig. 4, the significant difference between 1 and 1' was found as the relative conformation of polyoxocations ([Tm_2(H_2O)_{14}CrMo_6O_{24}H_6]^{3+}) and polyoxoanions ([CrMo_6O_{24}H_6]^{3-}), which resulted in the final phase transformation. X-Ray analyses of different single crystals of 1 at 113 K indicated that the phase 1' could be quickly detected. When 1' was warmed above 113 K, it quickly transformed back to 1. The results further demonstrate that the transformation between phase 1 and phase 1' was fast and reversible. Although the phase transformation can be directly observed by the changes of lattice parameters and packing frameworks, it is difficult to explain the detailed mechanism because the guest water molecules are all disordered and the hydrogen bonds in this system are very complex. We can speculate that there should be cooperative movement between clusters and guest water molecules in the crystal lattice. It would be a challenge to study the mechanism of temperature-dependent SCSC phase transformations in polyoxometalates systems.

To examine the thermal stability of compound 1, thermal gravimetric analysis (TGA) was carried out in the range of 25–900 °C (Fig. 5). The crystalline samples collapsed from 40 °C, indicating that polyoxometalates are not suitable for calefactive investigation into SCSC phase transformations. There were two major water-loss steps. The first step between 40 and 170 °C by the weight loss of 10.11%, corresponded to the loss of all uncoordinated water molecules (calcd 9.88% for 16H_2O). At the second step, the compound lost coordinated water molecules (the weight loss of 8.95%) between 170 and 300 °C (calcd 8.65% for 14H_2O) but did not decompose until 700 °C. Our preliminary data indicate that compound 1 can undergo a few desorption and adsorption cycles. When the resulted sample at the

![Fig. 5](Thermal gravimetric analysis data of 1.)

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**Fig. 2** Coordination polyhedron around Tm in 1. Bond lengths (Å): Tm(1)–O(12), 2.390(5); Tm(1)–O(13), 2.377(5); Tm(1)–O(14), 2.293(6); Tm(1)–O(15), 2.317(8); Tm(1)–O(16), 2.386(6); Tm(1)–O(17), 2.327(6); Tm(1)–O(18), 2.301(6); Tm(1)–O(19), 2.294(6).

**Fig. 3** Coordination polyhedron around (a) Tm1 and (b) Tm2 in 1’. Bond lengths (Å): Tm(1)–O(1), 2.282(5); Tm(1)–O(2), 2.330(6); Tm(1)–O(3), 2.360(6); Tm(1)–O(4), 2.357(5); Tm(1)–O(5), 2.309(5); Tm(1)–O(6), 2.330(6); Tm(1)–O(7), 2.384(5); Tm(1)–O(8), 2.387(6); Tm(2)–O(14), 2.407(6); Tm(2)–O(32), 2.382(5); Tm(2)–O(33), 2.340(6); Tm(2)–O(34), 2.316(5); Tm(2)–O(35), 2.429(5); Tm(2)–O(36), 2.310(5); Tm(2)–O(37), 2.287(5); Tm(2)–O(38), 2.272(6).

**Fig. 4** View of three-dimensional structures running to the a axis for (a) 1 and (b) 1’.
second step was exposed to atmospheric humidity at room temperature overnight, water was readsorbed, as shown by the recovery of the 17.48% weight loss below 300 °C upon a second thermal treatment (Fig. 6). Interestingly, rehydration did not render the sample amorphous and a clear XRD pattern was observed (Fig. 7a). The XRD comparison (Fig. 7) showed that the original ionic hydration structure was potentially recovered on rehydration (with some loss of crystallinity). It appears that the water is necessary to hold the clusters in place and maintain the structure of the whole compound. These results indicate that this adsorption system may provide some reversible coordination bonds and hydrogen bonds. The sorption feature is slightly different from that in those well-reported porous metal–organic frameworks, in which adsorption properties are connected with holes or channels.

In conclusion, the rare-earth Anderson-type polyoxometalate [Tm(H₂O)₆CrMo₆O₂₄H₂][CrMo₆O₂₄H₂]·16H₂O undergoes single-crystal-to-single-crystal phase transformation at low temperature. The results indicate that polyoxometalates can be good candidates for investigation into temperature-dependent SCSC phase transformations. We expect that this example can provide some useful information for the studies of SCSC phase transformations of polyoxometalates.

We are thankful for financial support from the NTU Research Scholarship, the National Natural Science Foundation of China (Grants 20371027 and 20071020) and the Tianjin Science Foundation (Grant 0336092111). We thank Mei-Ling Liu and Dr Yongxin Li for their good suggestions.

Notes and references

14. Anal. Calcd (Found) (%): Cr 3.6 (3.4), Mo 39.5 (39.2), Tm 11.6 (11.3).
15. Crystal data for 1: H₃₂Cr₂Mo₁₂O₇₈Tm₂, Mᵣ = 2913.72, triclinic, P1, a = 11.0889(13) Å, b = 11.7203(14) Å, c = 13.9843(16) Å, α = 74.993(2)°, β = 84.548(2)°, γ = 89.545(2)°, V = 1748.9(4) Å³, Z = 1, μ(Cu) = 5.2 Å⁻¹, μ(Mo) = 5.8 Å⁻¹, μ(Tm) = 6.1 Å⁻¹, μ(max) = 8.0 Å⁻¹ (10 ≤ k ≤ 12, 11 ≤ l ≤ 17, T = 294(2) K, F(000) = 1386, 36 restraints used in the refinement, GOF = 1.012, R1 = 0.0476, wR2 = 0.1339. CSD no. 417007.
16. Crystal data for 1': H₃₄Cr₂Mo₁₂O₇₈Tm₂, Mᵣ = 2913.72, triclinic, P1, a = 15.607(4) Å, b = 15.934(5) Å, c = 16.088(5) Å, α = 86.667(12)°, β = 72.242(9)°, γ = 64.394(9)°, V = 2323.3(17) Å³, Z = 2, μ(Cu) = 2.8 Å⁻¹, μ(Mo) = 5.5 Å⁻¹, μ(Tm) = 5.2 Å⁻¹ (10 ≤ l ≤ 21), T = 113(2) K, F(000) = 2772, 162 restraints used in the refinement, GOF = 1.065, R1 = 0.0434, wR2 = 0.1265. CSD no. 417560.