A structurally elusive phase transition with significant physicochemical consequences – the case of the $[C(NH_2)_3]_3[Dy(EDTA)(CO_3)]\cdot H_2O$ crystal

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Streszczenie

The phase transition of the $[C(NH_2)_3]_3[Dy(EDTA)(CO_3)]\cdot H_2O$ crystal was studied in the context of its structural, spectroscopic, dielectric and magnetic properties. The observed phase transition (at about 110 K) is accompanied by the partial rotation of the guanidinium cation and minute variations of the geometry of the $[Dy(EDTA)(CO_3)]^{3-}$ complex anions leading to three slightly different sites of the Dy(III) ion. As a result, the formal unit cell dimension increases, with triplication along the *b* crystallographic axis being observed. The enthalpy of this process is found to be ΔH = 1092 J mol^{-1}. Although there are no significant changes in the X-ray powder diffraction patterns of both phases, important variations of the f–f transitions in the Dy(III) cation, as well as the overtone transitions ascribed to the ligand, are observed. It was established that the oscillator strengths of the $^6H_{15/2} \rightarrow {}^6F_{3/2}$ transition and the quantum yield Φ decrease nonmonotonically when the temperature drops down, with the most pronounced jumps in the curves observed in the temperature range where the phase transition occurs. Magnetic measurements were also performed. It was found that the estimated value of the effective energy barrier to the reversal of the magnetisation is U_{eff} = 36.3 cm^{-1}. *Ab initio* calculations performed within the present work allowed the correlation of observed spectra recorded below 100 K with different sites of the Dy(III) cation. Furthermore, the theoretical results indicate that diminishing U_{eff} is probably due to quantum tunneling of the magnetisation.

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