

Title: Single-crystal X-ray diffraction study of mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) from 213 to 303 K

*Ryutaro Ikeda¹

1. University of tsukuba

Introduction

Renewable energy is of increasing importance in modern society due to its low environmental impact, ubiquity and sustainability. Since some renewable energy resources (e.g. sunlight, wind and tides) have variable outputs, storage technologies have great potential for affording the supply from these resources. In recent years, much attention has been paid to phase change materials (PCMs) due to its high energy storage capacity. PCMs are substances with a heat of fusion which can store and releasing large amounts of energy. Mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) is known as one of the PCMs. With increasing temperature, mirabilite transforms to thenardite (Na_2SO_4) at a dehydration temperature of 306 K. On the contrary, thenardite is rehydrated back to mirabilite at 283 K. The reversible reaction involves large exothermic and endothermic heats. To date, however, there is little information on temperature dependence of crystal structure in mirabilite. The structure of mirabilite contains ribbons consisting of edge-sharing $\text{Na}(\text{H}_2\text{O})_6$ octahedra along the *c*-axis. These ribbons alternate with chains of the SO_4 tetrahedra and the two H_2O molecules. Levy and Lisensky (1978) identified disorder over two orientations of the SO_4 tetrahedra by single-crystal neutron diffraction measurement at room temperature. The characteristic two orientations, related by a rotation of about 30° about the $S \times \times \times O5$ vector, generate pairs of partially occupied sulfate oxygen sites ($O4' / O4''$, $O6' / O6''$, and $O7' / O7''$). Levy and Lisensky (1978) found that the primed sites are about 25% occupied, and the double-primed sites are about 75% occupied. Recently, Brand et al. (2008) performed powder neutron diffraction measurements on mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{D}_2\text{O}$) in the temperature range from 10 to 300 K. They reported that the unit cell of mirabilite is isotopically expanded up to 300 K. The authors however couldn't observe the two orientations for the SO_4 tetrahedra in the structure, which was previously identified by Levy and Lisensky (1978). In the study, we performed temperature-dependent single-crystal X-ray diffraction measurement of mirabilite in the temperature range between 213 and 303 K. Here, we report the crystal structure change of mirabilite associated with the characteristic exothermic and endothermic heats.

Methods

Single crystals of mirabilite were obtained by slow cooling of a saturated solution of Na_2SO_4 . After the synthesis, a single crystal was stored in a 0.7 mm Lindemann glass capillary to avoid dehydration. Temperature dependent single-crystal X-ray diffraction study on mirabilite was performed using a single-crystal diffractometer (APEXII ULTRA, Bruker AXS Inc., Germany) equipped with a liquid nitrogen cryostat, a CCD detector, multilayer optics, and graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) generated by a rotating anode. The measurements were conducted at temperature ranges between 213 and 303 K with 10 K step in both heating and cooling processes.

Results and Discussion

The *a* and *c* lattice parameters and unit cell volume were monotonously changed with temperature, whereas the *b* lattice parameter remained almost unchanged. The result is entirely consistent with the

previous report that thermal expansivities of the *a*- and *c*-axes are of similar magnitude, while the *b*-axis shows a much smaller thermal expansion (Brand et al. 2008). The disorder over two orientations of the SO₄ tetrahedra was observed in the present study. At room temperature, the primed and double-primed sites are about 25% and 75% occupied, respectively, which is completely consistent with the result by single-crystal neutron diffraction study (Levy and Lisensky 1978). A clear temperature dependence of the disorder over two orientations was, however, unobserved in the study. It is noteworthy that the SO₄ tetrahedral volume coordinated by primed oxygen atoms showed a pronounced temperature dependence. In the vicinity of dehydration temperature of mirabilite, it approached to that of thenardite (Na₂SO₄), which would be a trigger initiating the dehydration of mirabilite.

Keywords: sodium sulfate, Single crystal XRD, mirabilite, Phase change