

Thermal behavior of borax, $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 8\text{H}_2\text{O}$

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ABSTRACT

Globally, borax is one of the most important borate minerals, both industrially and from a technological viewpoint. Despite its importance, there have been only a few reports on the structural changes of borax upon heating. In this study, we have investigated the thermal behavior and structural characteristics of borax using thermal analysis, in situ high-temperature synchrotron X-ray diffraction, in situ variable-temperature single-crystal X-ray diffraction, and quantum chemical calculations. Differential scanning calorimetry (DSC) curve showed a large endothermic peak at 349 K corresponding to the dehydration reaction of borax. X-ray diffraction (XRD) pattern remained almost unchanged up to 353 K. Above 363 K, the XRD peaks gradually became less intense until they disappeared at 403 K. The unit-cell volume continuously increased with increasing temperature and became constant just before its phase transition to tinalconite. The volumetric thermal expansion coefficient between 113 and 323 K was $7.84 \times 10^{-5} \text{ K}^{-1}$. The *a* and *c* lattice parameters exhibited a slight increase trend with increasing temperature, whereas the *b* lattice parameter increased significantly. Therefore, the thermal expansibilities followed the order $b/b_0 \gg c/c_0 > a/a_0$. The increasing *b* lattice parameter was closely related to the elongation of the O4···H7B hydrogen-bond interaction along the *b*-axis. Na-O bond lengths were isotropically expanded with increasing temperature, whereas the B-O bond lengths and angles remained unchanged even after the phase transition to tinalconite. Molecular orbital calculations revealed that an electron cloud shared by two borate tetrahedra led to the formation of a large electron cloud distribution over the $\text{B}_4\text{O}_5(\text{OH})_4$ cluster. The intramolecular interactions with substantial covalent character made the cluster quite rigid. The existence of borate minerals containing the $\text{B}_4\text{O}_5(\text{OH})_4$ clusters in their structure evidenced the presence of moderately acidic or alkaline water, wherein the borate minerals grew via the incorporation of $\text{B}_4\text{O}_5(\text{OH})_4$ clusters. Our results indicate that the connection geometry of the fundamental building block consisting of $\text{B}\phi_3$ triangles and $\text{B}\phi_4$ tetrahedra (ϕ : O^{2-} , OH^-) can potentially be used as a palaeoenvironmental indicator.

Keywords: Borax, sodium tetraborate decahydrate, dehydration, single-crystal X-ray diffraction, powder X-ray diffraction, quantum chemical calculation