The intriguing crystal structure of the rhabdophane mineral $LnPO_4.nH_2O$

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Rare-Earth Phosphates having a general formula of $REEPO_4{\cdot}nH_2O$ (REE = La to Dy, Sc, Y) are widespread minerals such as monazite, xenotime, rhabdophane, and churchite. These minerals represent one of the main sources of rare-earth elements and thorium on Earth. Moreover, because their easy way of preparation, structural flexibility, and high resistance to alteration, phosphate-based ceramics have attracted a variety of interests in different industries such as their use as specific matrices for the sustainable conditioning and disposal of high-level nuclear wastes. Among them, hydrated rhabdophane ($LnPO_4.\ nH_2O$) is considered as a low-temperature precursor for monazite preparation and also could control the potential release of actinides in solution.[1] Hydrated rhabdophane has been considered for more than 50 years to crystallize in a hexagonal structure,[2, 3] until our recent study using synchrotron radiation on a well crystallized samarium based compound. It led to the identification of a low-temperature form with a general formula of $SmPO_4.\ 0.667\ H_2O$[4] crystallizing in the C2 space group of the monoclinic system.[3] The crystal structure consists of infinite chains oriented along the [101] direction and formed by the connection of Sm-polyhedra and P-tetrahedra through the share of O-edges. Therefore, the dehydration of the rhabdophane $SmPO_4.0.667\ H_2O$ goes through two steps The first step was identified around 80°C leading to the formation of $SmPO_4.0.5H_2O$ (Monoclinic, C2) with Z = 12. Then, all the water molecules were evacuated above 220°C yielding to the anhydrous form, which crystallizes in the hexagonal $P3_121$ space group.[5] We found that the confusion about the true crystal structure of the rhabdophane arises from the amount and also distribution of water molecules within the channels.

References

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