

Crystal structure, complex phase diagram and re-entrant phase transition in NaSrPO₄

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The crystal chemistry of A^IB^{II}XO₄ (A^I = Alkali ion, B^{II} = alkali-earth ion, X = P, V, As) is very rich and has been widely investigated, particularly the phosphate family [1]. In recent years, we have been investigating the crystal structures [2,3] and magnetic properties of some compositions within the A^IB^{II}XO₄ series [4]. Besides the pure interest from a crystal chemistry point of view, the research activity related to this series of materials is driven mainly due to their ferroelectric, ferroelastic properties and possible applications as phosphors for LEDs [1, 5]. Within the rich A^IB^{II}VO₄ sub-family (X = V), we have recently found a new structural type: the larnite structure with the composition NaSrVO₄ [3]. In this contribution, we are investigating its counter phosphate composition.

Despite its simple chemistry NaSrPO₄ has never been reported so far. Here, we present the synthesis, crystal structure and phase transitions of this phosphate. Surprisingly, this material exhibits a complex structure (31 atoms in the asymmetric unit-cell, Z = 10) at room temperature characterized by a strongly under bonded Na atom. This under-bonded atom is responsible for the complex and rich phase diagram as function of temperature as illustrated in Fig. 1. NaSrPO₄ exhibits 4 phase transitions between room temperature and 750°C. Besides its rich phase diagram, NaSrPO₄ exhibits a re-entrant phase transition slightly below 600°C before to reach a hexagonal paraelastic phase at high temperature. In addition, we show that the sequence of phase transitions is strongly driven by the history of the sample and several phases can be quenched at room temperature. Finally, the co-existence of Na channels within the structure with weakly bounded Na atoms makes this material a likely candidate for ionic conductivity.

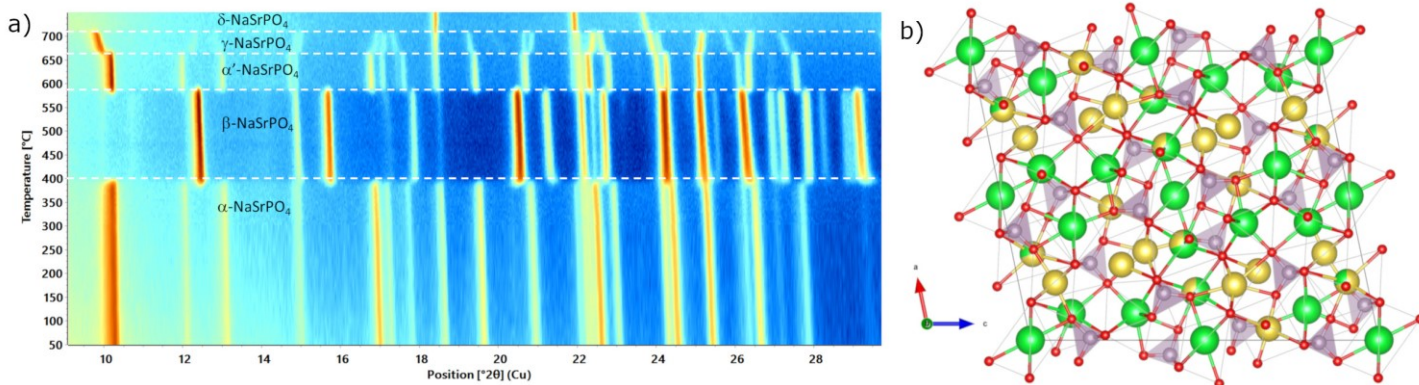


Figure 1. a) Temperature phase diagram of NaSrPO₄ and b) crystal structure of the α re-entrant polymorph.

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