Crystal structure, complex phase diagram and re-entrant phase transition in $NaSrPO_4$

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The crystal chemistry of $A^IB^{II}XO_4$ (A^I = Alkali ion, B^{II} = alkali-earth ion, X = P, V, As) is very rich and has been widely investigated [1]. We have been investigated the crystal structures [2,3] and magnetic properties of several compositions within the $A^IB^{II}XO_4$ series [4]. The research activity related to this series of materials is driven mainly due to their ferroelectric, ferroelastic properties and possible applications for LEDs [1, 5]. Within the rich $A^IB^{II}VO_4$ sub-family (X = V), we have recently found a new structural type: the larnite structure with the composition $NaSrVO_4$ [3]. In this contribution, we are investigating its counter phosphate composition.

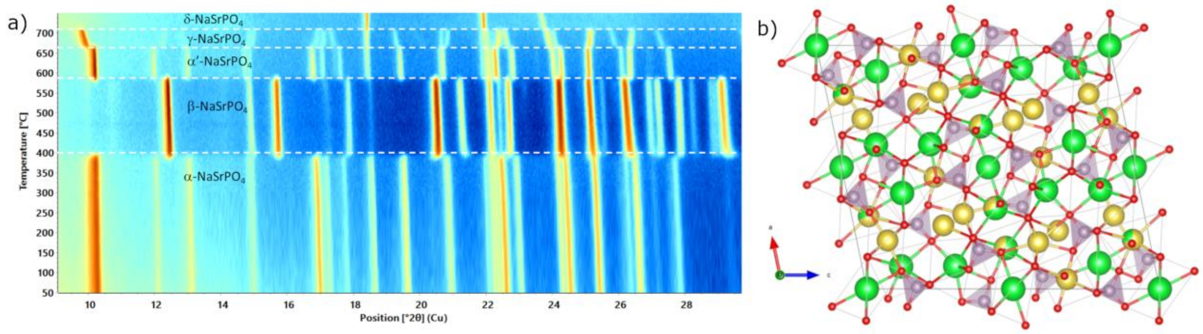

Figure 1: a) Temperature phase diagram of $NaSrPO_4$ and b) crystal structure of the α re-entrant polymorph

Despite its simple chemistry, $NaSrPO_4$ has never been reported so far. We present the synthesis, crystal structure and its polymorphism. Surprisingly, this material exhibits a complex structure (31 atoms in the asymmetric unit-cell, Z = 10) at room temperature (RT) 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 (see Fig. 1). $NaSrPO_4$ exhibits 4 phase transitions between RT and 750°C. Additionally, $NaSrPO_4$ exhibits a re-entrant phase transition slightly below 600°C before to reach a trigonal paraelastic phase at high temperature. We show that the sequence of phase transitions is strongly driven by the history of the sample and several phases can be quenched at RT. Finally, the co-existence of Na channels within the structure with weakly bounded Na atoms makes this material a likely candidate for ionic conductivity.

[1] Isupov V A, Phase transitions in anhydrous phosphates, vanadates and arsenates of monovalent and bivalent elements. Ferroelectrics, 274, 203-283 (2002)

[2] Nénert G, O'Meara P, Degen T, Crystal structure and polymorphism of $NaSrVO_4$: the first $A^IB^{II}X^VO_4$ larnite-related structure from X-ray powder diffraction data. Physics and Chemistry of Minerals, 44, 455-463 (2017)

[3] Nénert G, Synthesis and crystal structure of the new vanadate AgCaVO4: comparison with the arcanite structure. 232, 669-674 (2017)

[4] Nénert G, Bettis J, Kremer R, Ben Yahia H, Ritter C, Gaudin E, Isnard O, Whangbo M H Magnetic properties of the $RbMnPO_4$ zeolite-ABW- type material: A frustrated zigzag spin chain. Inorganic Chemistry 52, 9627-9635 (2013)

[5] Choi S, Yun Y J, Kim S J, Jung H-K, Thermally stable white-emitting single composition $Na(Sr,Ba)PO_4:Eu^{2+}$, Mn^{2+} phosphor for near-ultraviolet-pumped light-emitting diodes. Optics Letters 38, 1346-1348 (2013)