	Experiment title: Resolving the crystal-structural enigmas in Na-Super Ionic Conductors (NaSICON) of type $A_3M_2(PO_4)_3$, based on A = Na, Li, M = Cr, Sc, Fe model systems	**Experiment number**: MA-5379
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Report:

Compounds with NaSICON – type structure show a variety of complex phase transitions as a function of temperature (*T*), which are assumed to be due order/ disorder of sodium on the different crystallographic positions of the compounds. From previous studies it is known that twinning might encounter problems with fining correct unit cells. We have selected 4 different compositions (two of them with different synthesis routes) with different sequences of phase transitions, probed by difference scanning calorimetry (DSC) for a detailed study using both powder and single-crystalline material.

Data collection was done using λ = 0.60535 Å and detector distances of mostly 200 mm and 0 mm. By this, high *q*-space resolution data could be acquired. Due to multiple phase transitions in all compounds a narrow temperature increment was chosen not to miss any transitions and pre-ordering phenomena. Data were collected both upon heating from base temperature and upon cooling.

Based on DSC data, the $Na_3Cr_2(PO_4)_3$ compound should show the largest number of phase transitions between 80K and 500 K. Indeed, it was possible to resolve transitions at 270K, 360 K, 420 K and 449 K (Fig 1a) in the powder diffraction data, including the proof of a low *T* transition around 270 K. Towards the room temperature data, some peaks show altered intensity at the low *T* transition but no evident shifts or extinction in Bragg peaks is evident, so this transition might be due to order/ disorder without changing symmetry. Indeed both, the 80 K and the room temperature data can be indexed and refined with a monoclinic cell in $P2_1/n$ and a large unit cell of a = 21.1963(4) Å, b = 8.6655(2), c = 30.5084(6), β = 90.516(8)° at 80 K is determined. The structures of the two intermediate phases need to be clarified, however, it is evident that there are some shifts in peak positions and intensity cancellations, while the structure above 450 K is the well-known, disordered high

temperature $R\bar{3}c$ NaSICON -type structure. Solution of the intermediate structures is not trivial even with the help of the single crystal data and it is ongoing.

The structure of the powder sample of $Na_3Fe_2(PO_4)_3$ shows two clearly detectable phase transitions around 383 K and 445 K (Figure 1*b*). Thereby it transforms from a low temperature *C*2/*c* structure with a large unit cell of a = 15.1439(1) Å, b = 8.7316(1), c = 21.6060(1) and β = 90.174(2)° to trigonal $R\bar{3}c$; the intermediate phase cold not be indexed so far, there are some hints for a incommensurate modulation. Interestingly, the single crystals, prepared from a different approach and measured in a small T interval, do not show such a phase transition sequence and can, at least at room temperature, be indexed on basis of a smaller monoclinic cell, already found in preliminary laboratory X-ray diffraction experiments. Also, at a first glance, no evidence is found for any phase transitions, which appears to be a slight enigma. There is strong evidence now, that material, prepared with different synthesis routes, shows different behaviour as it was found so far only for the Sc^{3+} compound (see below).

For $Na_3Sc_2(PO_4)_3$ it is known that single crystals, grown from the flux, behave different to sintered material. Well developed, flux grown single crystals were analysed both using powder and single crystal diffraction. The single crystals show a 2*a*, 2*b* superstructure with respect to the trigonal $R\bar{3}c$, however, firm evidence is found that this is due to twinning and the correct symmetry is monoclinic, *C*2/*c* with a = 15.4762(3), b = 8.9359(5), c = 22.2544(5), β = 90.012(4)°, this is an unit cell, which is similar to the one found for $Na_3Fe_2(PO_4)_3$ at low temperatures. Around 280 K, an evident change in single crystal diffraction frames hint a phase transition to a structure with a large unit cell with a doubling of the *c* – axis to 44 Å, however, no solution of the structure was possible so far. Powder produced from the single crystal batch unfortunately do not show evident changes with temperature in the range 200 K to 450 K, only sluggish changes in intensities and crossing over of Bragg peaks indicate anisotropic changes in lattice parameters (Figure 1c). For samples, not grown in a Na-phosphate flux, two phase transitions are evident, the first on is sharp and located around 335 K, the second is associated with some discontinuous shifts in peak positions around 440 K (Figure 1d). Both transitions show a distinct hysteresis between heating up and cooling. Unfortunately, single crystals, obtained from long term sintering of these materials, turned out to be not of sufficient qualities, so structures of intermediate phases have to be resolved from powder data. The low temperature structure of these $Na_3Sc_2(PO_4)_3$ samples is monoclinic, *Cc*, with a = 15.3991(2), b = 8.9263(1), c = 9.1024(2) and β = 123.493(7)°.

Finally, $Li_3Fe_2(PO_4)_3$ was investigated between 200K and 650 K and the powder data give evidence for a structural phase transition at 520 K. The second and less well-developed transition, observed in DSC data, could not be resolved clearly, only minor, discontinuous changes in intensities are found.

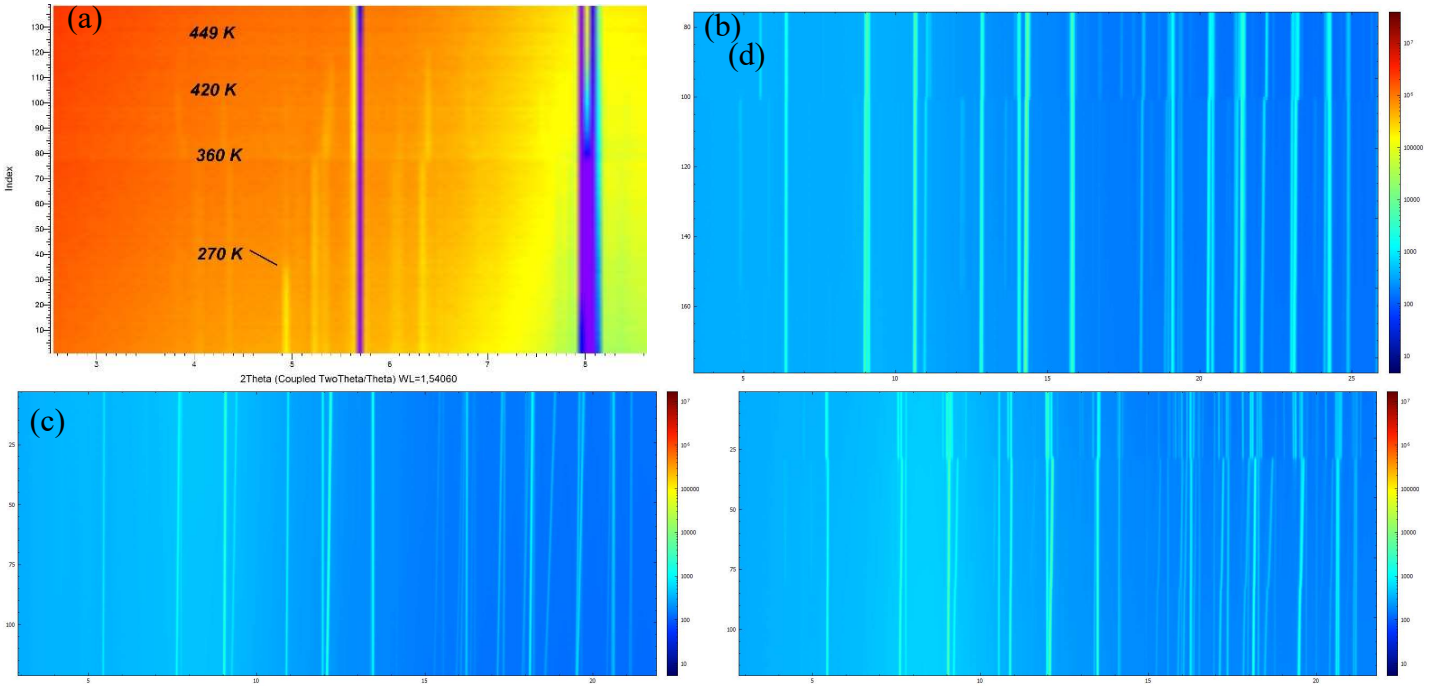

Figure 1: (a) 2D plot of powder diffraction data of $Na_3Cr_2(PO_4)_3$ between 80 K and 480K, revealing 4 structural phase transitions; (b) 2D plot of powder diffraction data of $Na_3Fe_2(PO_4)_3$, revealing the nature of the two observed phase transitions, (c) and (d) 2D plots of the powder diffraction data showing Na3Sc2(PO4)3. Prepared by flux growth (c) with no evident phase transition and (d) by solid state sintering with at least 2 evident structural phase transitions.