Investigation of structural phase transitions and superionic property of a Vanthoffite mineral, $Na_6Co(SO_4)_4$

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There are several naturally occurring minerals that show temperature induced phase transitions, leading to a variety of materials which display specific properties such as superionic conductivity and ferroic behaviour.[1-5] Some of the minerals crystallize with different hydration levels and show phase transitions at elevated temperature.[2,3] It is important to note that superionic conductors exhibit high ionic conductivity ($\approx 10^{-3}$ to 10^{-1} S/cm) at modest temperatures (400-600 °C) and are playing a major role to design next generation solid state batteries.[1,4] The ionic conductivity of a material and its crystal structure are highly correlated with each other. In this context, the phase behaviour of compound belongs to the Vanthoffite family, $Na_6Co(SO_4)_4.xH_2O$ (x = 2, 4) with temperature has been investigated. Single crystals of di-and tetra-hydrates of the mineral $Na_6Co(SO_4)_4$ grow concomitantly from aqueous solution containing stoichiometric molar ratio of starting materials. Both of this hydrated forms have similar morphology and crystallize in $P\ \bar{1}$ with Z=1. In fact, the elusive anhydrous crystal ($Na_6Co(SO_4)_4$) [inset Fig. 1a] could be produced *in situ* from the tetra-hydrate/di-hydrate crystal and the transition pathway has been characterized via variable temperature single crystal X-ray diffraction analysis. Further, we have also examined the phase transitions displayed by the anhydrous phase using *in situ* powder X-ray diffraction and *in situ* Raman spectroscopy with respect to temperature [Fig. 1b]. The structural features are shown to correlate with the conductivity measurements with the super ionic behaviour (σ =1.1× 10^{-2} S/cm) appearing at 570 ˚C [Fig. 1a]. These observations are significant for the development and understanding of mineral based solid electrolytes.

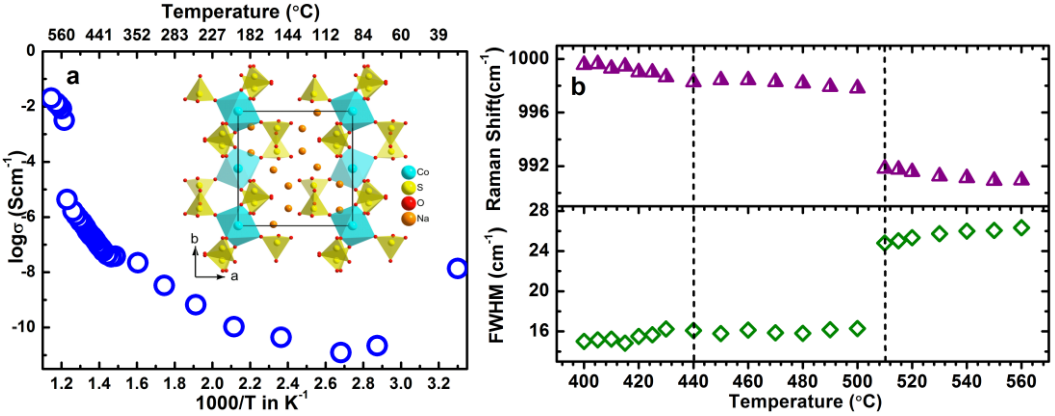

Figure 1 (a) Temperature dependent Conductivity plot of $Na_6Co(SO_4)_4$, the inset shows crystal structure of $Na_6Co(SO_4)$= and, (b) Temperature evolution of Raman shift and FWHM of symmetric stretching mode of the SO4 ion

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