ON THE PHASE TRANSITIONS OF NASICON-TYPE $Na_3Sc_2(PO_4)_3$

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NASICON-type materials belong to the group of hetero-polyhedral framework compounds exhibiting ionic conductivity. These 'NAtrium Super Ionic CONductors' were first reported by GOODENOUGH et al. (1976) in consequence of a systematic exploration of cubic skeleton structures like pyrochlore and cristobalite-type carnegieite leading to the type material $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$. Nowadays, NASICONs are classified with the general formula $A_xM_2(XO_4)_3$ (A = Li, Na, K, Mg, Ca; M = Al, Sc, Y, Ti, Zr, V, Nb, Cr, Mn, Fe, Ga, In; X = Si, P, As, S). Due to their physical properties they gained interests as a solid electrolyte over decades, followed up by investigations as a potential insertion host for energy storage applications (JIAN et al., 2017).

The ionic conductivity is strongly symmetry correlated. Based on the pseudo-cubic, trigonal framework (ideally *R3c*) of the corner-linked MO_6 and XO_4 polyhedra three polymorphs are known for $Na_3Sc_2(PO_4)_3$, which exhibit up to now the highest sodium ion conductivity. The reversible states are (i) ionic insulator: monoclinic, low temperature α-phase below ~65 °C, (ii) ionic conductor: average rhombohedral, intermediate β-phase, and (iii) 'superionic' phase: rhombohedral, high temperature γ-phase above ~165 °C. All phase changes are induced by sodium ion order / disorder (COLLIN et al., 1986).

DSC measurements, Fig.1, show two distinct and smooth phase transitions (ΔT ~40 °C) at ~10 °C (α→β) and ~160 °C (β→γ) during heating. On cooling the β→α transition is faint, moreover, the unsteady signal from 65 to -20 °C indicates a second β'-type phase. On dT-PXRD patterns, Fig. 2, this temperature range is characterized by the presence of sharp and diffuse incommensurate reflections. The β→γ transition is evident by a discontinuous increase of the ***c***-axis and a small positive anomaly in the basal plane of the trigonal substructure. The general thermal expansion of $Na_3Sc_2(PO_4)_3$ is strongly anisotropic.

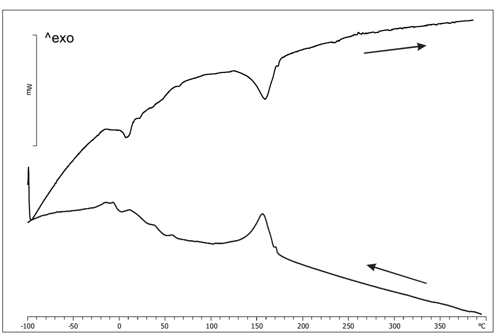

Figure 1. DSC curves of $Na_3Sc_2(PO_4)_3$, (-100 to 400 °C), heating (upper curve), cooling (lower curve).

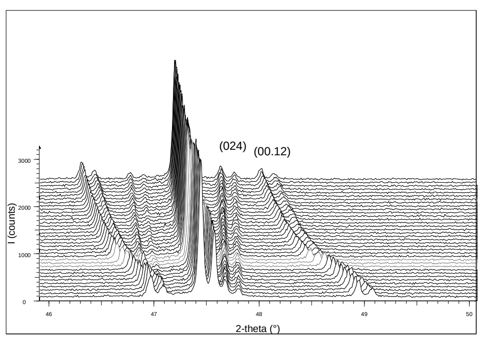

Figure 2. dT-PXRD of $Na_3Sc_2(PO_4)_3$, (50-400 °C), β→γ phase transition (gray patterns).

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GOODENOUGH, J.B., HONG, H.Y.-P., KAFALAS, J.A. (1976): Mater. Res. Bull., 11, 203-220.
JIAN, Z., HU, Y.-S., JI, X., CHEN, W. (2017): Adv. Mater., 29, 1601925.