

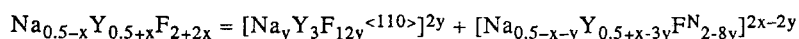
RELATIONS BETWEEN THE STRUCTURE AND THE PROPERTIES OF ANIONIC CONDUCTIVITY OF THE Na_{0.5-x}Y_{0.5+x}F_{2+2x} SOLID SOLUTIONS

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The local structure of the anionic conductors Na_{0.5-x}Y_{0.5+x}F_{2+2x} having a fluorite disordered structure stabilized by doping has been described by a tridimensional arrangement of ordered microdomains in which the interstitial fluorine atoms (F_{<100>} 48i : TMuu) are associated in [NaY₃F₁₂^{<110>}]²⁻ clusters diluted in a fluorite matrix (1).

The fluorine arrangement obtained from structural refinements (2x = 0.02 ; 0.04 ; 0.08 ; 0.18 and 0.28) agrees completely with the number of fluorine atoms used by the model in the different anionic sublattices :



Na _{0,49} ^Y _{0,59} ^F _{2,02}	[(Na _{0,04} ^Y _{0,13} ^F _{0,53} □ _{0,35}] ^{0,08-}	[Na _{0,45} ^Y _{0,38} ^F _{1,51} □ _{0,15}] ^{0,08+}
Na _{0,48} ^Y _{0,52} ^F _{2,04}	[(Na _{0,04} ^Y _{0,13} ^F _{0,53} □ _{0,35}] ^{0,08-}	[Na _{0,44} ^Y _{0,39} ^F _{1,53} □ _{0,13}] ^{0,08+}
Na _{0,46} ^Y _{0,54} ^F _{2,08}	[(Na _{0,01} ^Y _{0,04} ^F _{0,14} □ _{0,09}] ^{0,02-}	[Na _{0,45} ^Y _{0,50} ^F _{1,87} ^{0,03}] ^{0,02+}
Na _{0,41} ^Y _{0,59} ^F _{2,18}	[(Na _{0,03} ^Y _{0,09} ^F _{0,35} □ _{0,23}] ^{0,06-}	[Na _{0,38} ^Y _{0,50} ^F _{1,70} ^{0,06}] ^{0,06+}
Na _{0,36} ^Y _{0,64} ^F _{2,28}	[(Na _{0,05} ^Y _{0,15} ^F _{0,58} □ _{0,39}] ^{0,10-}	[Na _{0,31} ^Y _{0,49} ^F _{1,52} ^{0,08}] ^{0,10+}

Such a model shows that the metastable fluorite structure of the Na_{0.5-x}Y_{0.5+x}F_{2+2x} solid solutions is stabilized by the substitution of 2 or 3 % of the normal fluorine atoms (F_N 8c : $\frac{1}{4}\frac{1}{4}\frac{1}{4}$) by oxygen. The number of substituted oxygen atoms corresponds with that measured by γ activation (2).

We have observed that the anionic conductivity of the Na_{0.5-x}Y_{0.5+x}F_{2+2x} solid solutions is quite independent of the anion excess (3). This behaviour is different to that generally observed with the doped fluorite structures as CaF₂ or β PbF₂ (4,5).

In the proposed structural description all the interstitial fluorine atoms are trapped in $[\text{NaY}_3\text{F}_{12}^{<110>}]^{2-}$ clusters, the stability of which is steadied by the yttrium atoms. Almost all the anionic vacancies induced in the normal fluorine sublattice of the fluorite structure are also trapped in the fluorine cuboctahedra ($12\text{F}_{<110>}$).

So, it seems that the anionic conductivity could be connected with the motion of the normal fluorine atoms, enhanced by their anharmonic vibrations (related to the 60 % of inelastic contribution at the neutron diffuse scattering measured at room temperature).

NMR measurements and neutron diffraction studies performed at various temperatures indicate exchange between the normal and interstitial fluorine atoms. At 760 C the diffusion paths may be observed on the neutron Fourier difference maps (2).

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