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Tuning of physical properties of $Fe_7(PO_4)_6$ by sodium intercalation

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The sodium intercalation of mixed – valence iron phosphate $Fe_3^{2+}Fe_4^{3+}(PO_4)_6$ results in drastic transformation of its physical properties. The parent compound $Fe_7(PO_4)_6$ reaches magnetically ordered state through succession of phase transitions at T_{N1} = 45.5 K and T_{N2} = 16 K marked by sharp singularities in both specific heat C_p and magnetic susceptibility χ. The introduction of sodium suppresses the formation of antiferromagnetic state down to T_N = 33 K in $Na_{0.65}Fe_7(PO_4)_6$. The low temperature phase transition in this compound smears being substituted by broad anomalies in magnetization and specific heat related to the spin/charge disorder effects. The sharp well resolved electron spin resonance spectra in parent material transform into asymmetric broad line in sodium – intercalated substance. The dielectric permittivity ε of $Fe_7(PO_4)_6$ demonstrates a kink at T_{N2}, while no singularity marks T_{N1}. No features accompany magnetic phase transition in dielectric property of $Na_{0.65}Fe_7(PO_4)_6$ but ε reaches the relaxation maxima at high temperatures which can be attributed to the freezing of sodium ions.

Introduction

The iron phosphates with open framework structure are composed of the earth-abundant elements and are of interest due to their catalytic properties in various chemical reactions[1] and gas separation.[2] Besides, these compounds are in the focus in sodium iron batteries research.[3] The intercalation of alkali ions into the pores of crystal structure itself represents a kind of scientific philosophy when the physical properties of a substance can be radically alternated/tuned by an introduction of another material. The guest not only contributes to the overall property but changes the basic features of the host.[4]

Initially, the representatives of this family, i.e. $Fe_5(PO_4)_4O_4H_{10}$,[5] $NaFe_3(PO_4)_3$,[5] $Na_7Fe_4(PO_4)_6$[6] and $NH_4Fe_2(PO_4)_2$,[7] hosted only inorganic constituents. Later, the efforts were applied to enlarge the size of the channels by introduction of organic molecules.[1,2] In addition to the porosity, catalytic activity of substance depends strongly on charge/valence states of transition metal ions in the host. Filling the pores by the foreign ions changes this property also.

The mixed iron (II/III) orthophosphate $Fe_7(PO_4)_6$ was shown to be effective in oxidation of methane to formaldehyde.[8] Its catalytic effectiveness is associated with presence of Fe^{2+} ions in the structure, so that the general formula can be rewritten as $Fe_3^{2+}Fe_4^{3+}(PO_4)_6$. This compound contains the cavities with approximate sizes 5.5 Å ×2.5 Å formed by FeO_x polyhedra and PO_4 groups as shown in Fig. 1.[9] These cavities can be filled with alkali metal ions, e.g. Na^+, which will be accompanied by the change in Fe^{2+}/Fe^{3+} ratio. The synthesis of stoichiometric $NaFe_7(PO_4)_6$ was reported in Ref. 10. The Mössbauer spectroscopy performed in the range 80 K < T < 300 K on