Neutron diffraction study of crystal structure of $K_{1-x}(NH_4)_xCI$ (x=0.2, 0.8) mixed salts

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Abstract

TOF neutron diffraction study shows that at the room temperature $K_{0.2}(NH_4)_{0.8}Cl$ and $K_{0.8}(NH_4)_{0.2}Cl$ compounds form cubic crystal lattices with the corresponding space groups: *Fm3m* and *Pm3m*. It was established considerable distortion of hydrogen atoms in these structures from their initial positions 8g.

I INTRODUCTION

Hydrogen bonded materials are the most attractive systems for investigating phase transition phenomena.

1925, for the first time, R.J.Havingst, E.Marck and F.C.Blake carried out detailed investigations of mitual solubility limits of *KCI* and NH_4CI and dependence of lattice parameters on composition of their mixed solutions by x-ray structure analysis [1]. Then many researchers have been studying low temperature dipolar dynamics and disordered glasslike transition phenomena in $K_{1-x}(NH_4)_xCl$ isomorphous systems [2-5].

At room temperature for x=0 the *KCI* compound crystallizes in NaCl type lattice with the space group Fm3m and NH_4CI in *CsCI* type lattice belonging to Pm3m space group. Mixed salts $K_{1-x}(NH_4)_xCI$ crystallize in one of these two cubic lattices depending on x. In other words, solubility relation between these cubic salts [1].

In our recent work we have studied in detail crystal structures of $K_{1-x}(NH_4)_xCI$ for x=0.1, 0.2, 0.5, 0.6, 0.8 at room temperature by x-ray analysis. As a result, we have established that $K_{0.8}(NH_4)_{0.2}CI$ and $K_{0.9}(NH_4)_{0.1}CI$ compounds form cubic *Fm3m* structure and $K_{0.2}(NH_4)_{0.8}Cl$ compound has cubic *Pm3m* one when $K_{0.5}(NH_4)_{0.5}Cl$ and $K_{0.4}(NH_4)_{0.6}CI$ compounds consist of two phase mixtures: *Fm3m+Pm3m*. By x-ray diffraction method it were determined lattice parameters, coordinates, thermal factors and occupations of *K*, *N* and *CI* atoms, belonging to *Fm3m* and *Pm3m* crystal structures [6].

The purpose of this work is to determine coordinates thermal factors and occupations of hydrogen atoms in $K_{0.8}(NH_4)_{0.2}CI$ and $K_{0.2}(NH_4)_{0.8}CI$ crystalline structure by means of TOF neutron diffraction method.

II EXPERIMENTAL

The TOF neutron diffraction experiments were carried out in Frank Laboratory of Neutron Physics of JINR in Dubna (Russia) by using TOF neutron diffractometer DN-2 at pulsed reactor IBR-2. The neutron flow falling on measured samples is formed by curved mirror neutron transmitter. The distance between sample and decelerator is 24 m and the average flow falling on the sample equals to 10^7 n/cm^2. The scattered neutrons were registered by the single-coordinate helium (^{3}He) detector connected with TOF electronic device, under the angle θ_0=75.5^0. The angle adjustments were made by using NaCl crystal with well studied crystal structure. The resolution of the diffractometer $\Delta d/d \approx 1\%$ for $d_{hkl} = 2$ E.

Samples for experiments were prepared in a powder form by evaporating of water solutions of pure KCl and NH_4CI compounds with the concentrations x=0.2, 0.8: For measurements used powder samples placed into the cylinder container with 7 mm diameter, made of Al foil with thickness 5 mkm

For refining of neutron diffraction spectra used complex program MRIA [8]. The values of coherent scattering of atoms were taken from [9].

III STRUCTURE REFINEMENT AND EXPERIMENTAL RESULTS

The neutron powder diffraction patterns of the both samples are shown on fig.1 and 2. The crystal structure data obtained by refinement are presented in table 1 and 2.

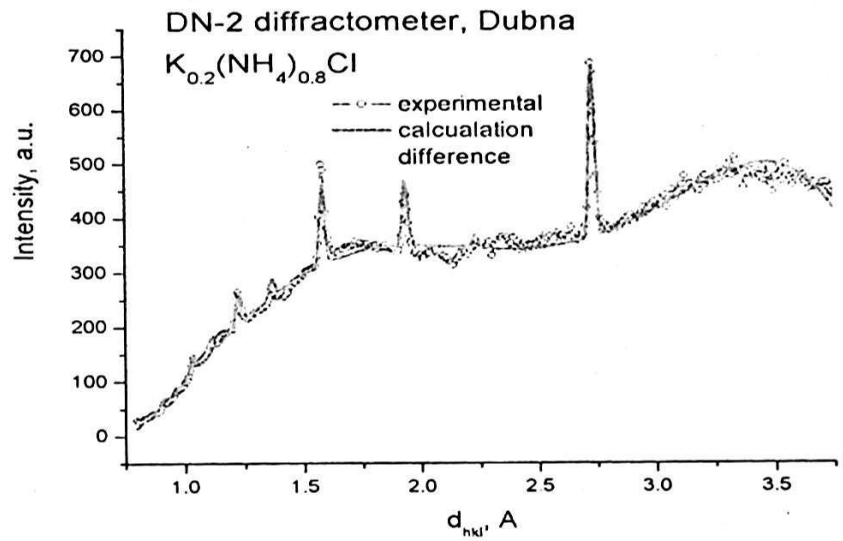

Fig.1. Rietveld refinement patterns for $K_{0.2}(NH_4)_{0.8}Cl$ using neutron powder diffraction data. The observed intensities are shown by dots and the calculated ones by the solid line. The line at the bottom indicates the intensity difference between the experimental and the refined patterns.

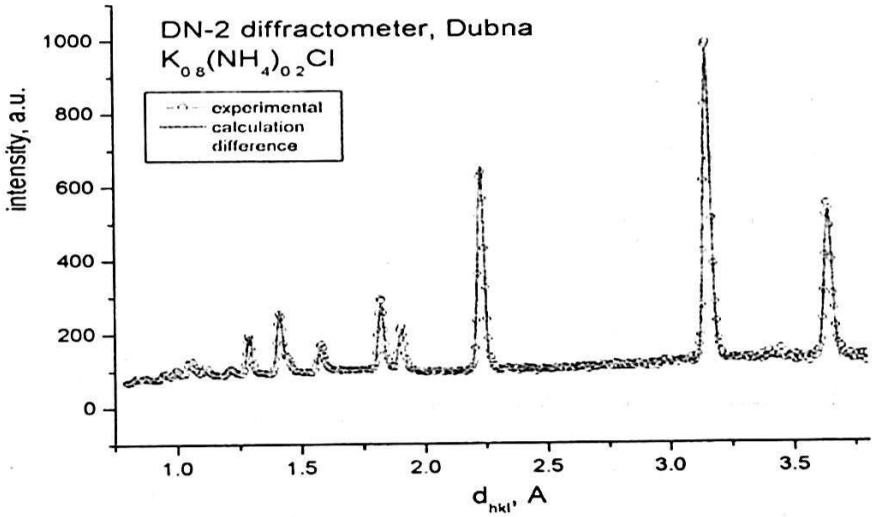

Fig.2. Rietveld refinement patterns for $K_{0.8}(NH_4)_{0.2}Cl$ using neutron powder diffraction data. The observed intensities are shown by dots and the calculated ones by the solid line. The line at the bottom indicates the intensity difference between the experimental and the refined patterns.

Table 1. The crystal structure data for $K_{0.2}(NH_4)_{0.8}Cl$: *x/a, y/b* and *z/c* - fractional atomic co-ordinates, B_{iso}- isotropic temperature factor (E^2) and *n*- atomic occupancy.

Atom	Wyck.	x/a	y/b	z/c	B_{iso}	n
K+1	1a	0.00000	0.00000	0.00000	2.0299(1)	0.200
N-3	1a	0.00000	0.00000	0.00000	2.0299(1)	0.800
Cl-1	1b	0.50000	0.50000	0.50000	2.5478(4)	1.000
H+1	8g	0.19697	0.19697	0.19697	0.2495(3)	0.746
Space group: *P m3m* , Z = 1 Lattice constants: a_0 = 3.87382 E, $\alpha = \beta = \gamma = 90^0$ R-factors: R_p=3.57%, R_{wp}=3.59%, R_e=2.43%						

Table 2. The crystal structure data for $K_{0.8}(NH_4)_{0.2}CI$: *x/a, y/b* and *z/c*- fractional atomic co-ordinates, B_{iso}- isotropic temperature factor (E^2) and n- atomic occupancy.

Atom	Wyck.	x/a	y/b	z/c	B_{iso}	n
K+1	4a	0.00000	0.00000	0.00000	2.8504(4)	0.75
N-3	4a	0.00000	0.00000	0.00000	2.8504(4)	0.25
Cl-1	4b	0.50000	0.50000	0.50000	2.8482(2)	1.000
H+1	32f	0.01309	0.01309	0.01309	15.7258(5)	0.283
Space group: $F\,m3m$, Z = 4 Lattice constants: $a_0 = 6.31459$ E, $\alpha = \beta = \gamma = 90^0$ R-factors: R_p=1.68%, R_{wp}=1.80%, R_e=2.36%						

In the fig.1 and 2 the vertical axes corresponds to scattered neutron intensities, and the horizontal one to distances between atomic planes (*d*, E). In the fig.1 rising of the background level with increasing of *d* is connected with high concentrations of hydrogen atoms.

For refinement of the neutron diffractograms are used our crystal structure data obtained by x-ray structure analysis [7].

For each sample we have determined exactly values of coordinates, thermal factors and occupations of *K, N, H, CI* atoms (see table 1 and 2). In order to calculate hydrogen coordinates, as the preliminary coordinate we took the hydrogen atoms coordinate: $8g(x=y=z=0.146)$ in the cubic lattice of $\alpha-(NH_4)CI$ compound with $Pm3m$ space group symmetry in the international crystallographic database *ICSD*(#20628). The refinement results show that for $K_{0.2}(NH_4)_{0.8}CI$ the coordinate of hydrogen atoms equals to 8g: $(x=y=z=0.19697)$ rising from the preliminary value while for $K_{0.8}(NH_4)_{0.2}CI$ is 8g: $(x=y=z=0.01309)$ lowering from the initial value (see table 1 and 2).

IV CONCLUSIONS

1. At room temperature $K_{0.2}(NH_4)_{0.8}CI$ compound has a $Fm3m$ cubic structure and $K_{0.8}(NH_4)_{0.2}CI$ compound a $Pm3m$ cubic structure. It were determined coordinates, temperature factors and concentrations of atoms.
2. TOF neutron diffraction studies show that the hydrogen atom in $K_{0.2}(NH_4)_{0.8}Cl$ crystal distorts from its preliminary coordinate ($8g$:$x=y=z=0.146$) in growing way having the value $8g$: $x=y=z=0.19697$ and $K_{0.8}(NH_4)_{0.2}CI$ in lowering way having the value $8g$: $x=y=z=0.01309$.

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