THE PHYSICAL PROPERTIES OF THE MIXED PYROPHOSPHATES CONTAINING Fe(III), Cr(III) AND ALKALINE METALS IONS

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The paper present the investigation results of the mixed pyrophosphates $NaFeP_2O_7$*,* $KFeP_2O_7$ $NaCrP_2O_7$ *and* $KCrP_2O_7$*. The investigations are performed using the diffuse reflection spectrophotometry and the measurements of the dielectric permittivity, electric resistance and magnetic susceptibility.*

INTRODUCTION

The crystal structure of the $NaFeP_2O_7$ and $KFeP_2O_7$ compounds are known /1/. These compounds have the monoclinic symmetry (space group $P2_1/C$) and are isostructural with the analogue Al(III) compounds. In the structures of the both compounds the Fe(III) ions are surrounded by the six octahedrally arranged O-atoms from the $P_2O_7^{4-}$ ions.

The crystal structure of the corresponding Cr(III) compounds $NaCrP_2O_7$ and $KCrP_2O_7$ are not determined.

The physical properties of these four pyrophosphates until now are not investigated and in this paper the first results of the investigation of theirs properties and presented.

EXPERIMENTAL

The synthesis of these pyrophosphates is accomplished by the mixing of the corresponding aqueous solutions of alkaline metalpyrophosphate ($Na_4P_2O_7$ or $K_4P_2O_7$) and of transition metal chloride ($CrCl_3.6H_2O$ or $FeCl_3.6H_2O$) in the stoichiometric proportion. This procedure is accompanied by the precipitation of the unsoluble mixed pyrophosphate polyhydrate. The heating of this precipitate at the temperatures higher than 300°C cause the complete dehydration.

The compounds obtained on a such manner are examined by the x-ray powder diffractometry. The diffractograms of the Fe(III) compounds confirm the published chrystalographic data /1/. The diffractograms of the Cr(III) compounds show that they are isostructural with the corresponding Fe(III) compounds (in preparation for publication).

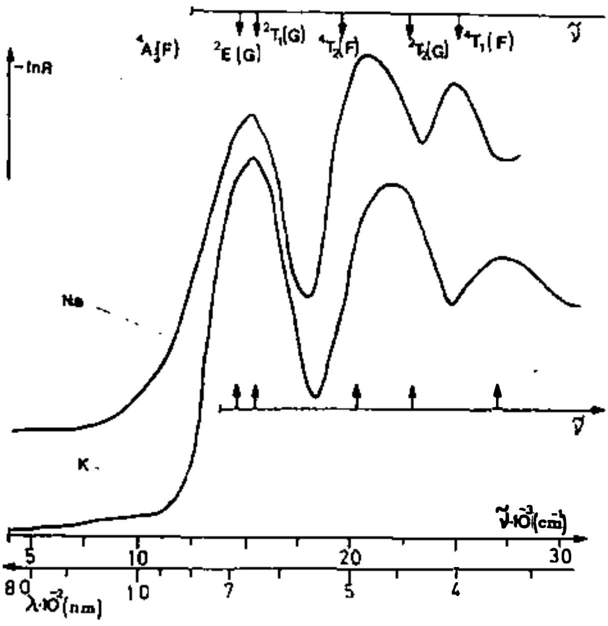

Fig. 1.
The optical spectra of the Cr(III) pyrophosphates

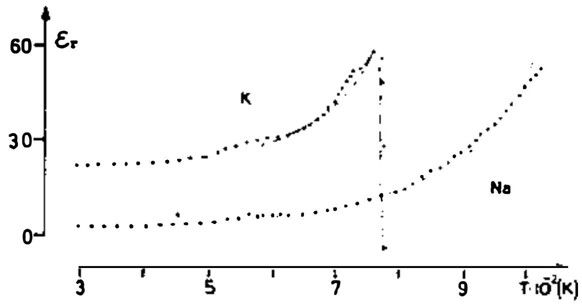

Fig. 2.
The relative dielectric permiltivity of the Fe(III) pyrophosphates

The additonal investigation of the Cr(III) compounds is realised by the use of the diffuse reflection spectrophotometry. The recorded spectra are given in Fig. 1.

The investigation of the physical properties of the four synthetized pyrophosphate consisted of the measurement of the dielectric permitivity, electric resistivity and magnetic susceptibility in the wide temperature region (300 – 1000 K). The more complete description of these measurement is given in /2/.

Temperature dependence of the relative dielectric permittivity Cr(T) and of the electric resistivity ρ (T) is given in the Fig. 2–4.

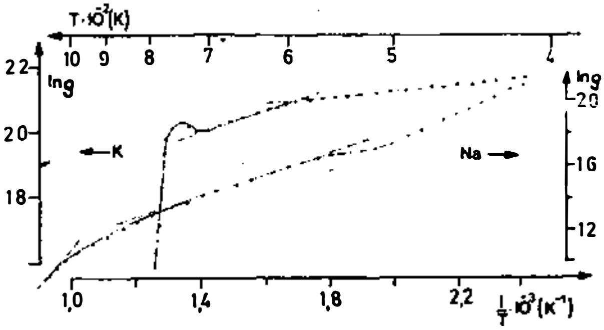

Fig. 3.
The electric resistivity of the Fe(III) pyrophosphates

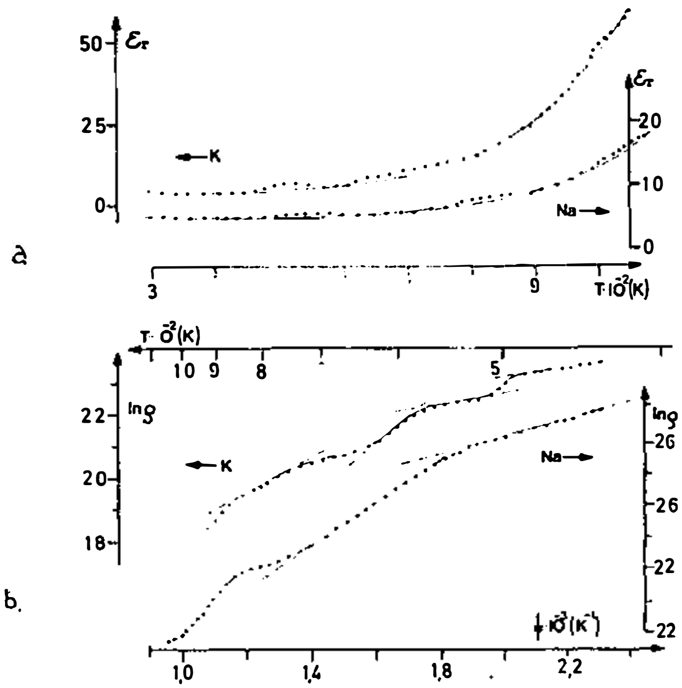

Fig. 4.
The relative dielectric permitivity (a) and the electric resistivity (b) of the Cr(III) pyrophosphates.

RESULTS AND DISCUSSION

The examinations of the recorded optical spectra (Fig. 1) show that they correspond to the Cr(III) ions in the octahedral surroundings /3/, which is in agreement with the results of the our structural examinations. The interpretation of these spectra is effectuated by the use of the graphic method given in /4/. This interpretation showed that the coordination octahedra are probably distorded, which is characteristic for the Cr(III) ion /3/. The arrows in Fig. 1. give the positions of the "centroides" of the electronic transitions in the octahedral field resolved by the weak trigonal distorsion of the octaedra. The realised interpretation enables the determination of the crystal field parameters:

compound	parameter:	10 Dq (cm $^{-1}$)	B (cm^{-1})	β
$NaCrP_2O_7$		19100	810	0,88
$KCrP_2O_7$		19500	710	0,78

The dependence $\epsilon_r(T)$ and the dependence $1n\rho(1/T)$ given in Fig. 2. and 3. for the Fe(III) compounds and in Fig. 4. for the Cr(III) compounds have in general the forms typical for the ionic polar crystal substances. These figures show also that the $\epsilon_r(T)$ curves have in the certain narrow temperature regions the local maxima and that the curves $1n\rho(1/T)$ in the same temperature regions have the "breaks". The such changes in the temperature dependence of the ϵ_r and ρ is caused by the polymorphic phase transition /2/.

The magnetic measurements show that the investigated pyrophosphates are the Curie-Weiss paramagnets. These measurements enables the determinations of the magnetic moments of the Fe(III) and Cr(III) ions. The values of these magnetic moments μ (in Bohr magneton μ_B) are unchanged in the whole examined temperature region:

ion	compound	magnetic moment (μ/μ_B)
Fe	$NaFeP_2O_7$	5,92
	$KFeP_2O_7$	5,87
Cr	$NaCrP_2O_7$	4,68
	$KCrP_2O_7$	3,88

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