THE PHYSICAL PROPERTIES OF THE MIXED PHOSPHATES OF THE TRANSITION ELEMENTS AND POTASSIUM

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The paper presents the investigation results of some mixed phosphates of a general formula $KM(II)PO_4$, where $M(II)$ = Mn, Co, Ni, Cu. The investigation are performed using the measurements of dielectric permittivity, electric resistance and magnetic susceptibility.

INTRODUCTION

The physical properties of the mixed phosphates of a general formula $KTPO_4$ until now are not investigated. The crystal structures of these compounds are only partially determined. It is known that the $KNiPO_4$ has a crystal modification of the rhombic symmetry /1/ and that $KCuPO_4$ depending on the synthesis method may appear in the two different crystal modification: rhombic /2/ and monoclinic /3/. The analysis of the published data on the crystal structures of the mixed phosphates and pyrophosphates of transition metals (e.g. /4,5/) shows that the other $KTPO_4$ compounds should have the crystal structures of the same type and that it is possible the existence of the polymorphic transitions.

This paper presents the results of the investigation of a group of a four $KM(II)PO_4$ compounds where M(II) = Mn, Co, Ni, Co. The investigations included the crystallographic examination and the studies of the different physical properties.

EXPERIMENTAL

The synthesis of the $KMPO_4$ compounds is accomlished by the method described for the synthesis $NaMPO_4$ compounds /6/. The investigation of the crystal structure of these compounds is performed using the x-ray powder diffractometry. The recorded powder diffractograms shows that Mn, Co and Ni compounds at the room temperature have a rhombic symmetry and that they are isostructural. The diffractogram of the $KCuPO_4$ shows that this compound has probably also rhombic symmetry. (These crystallographic data are in preparation for the publication).

The investigation of the physical properties consisted of the measurement of the dielectric permittivity, the electric resistivity and of the magnetic susceptibility in the wide temperature range (300—1000 K). The relative dielectric permitivity (ϵ_r) is measured at the operating frequency 1 MHz by the use of a capacitor bridge. The electrical resistivity (ρ) is measured by the use of a electrometer circuit. These two measurements on the pellets pressed at the 60 bars are performed. The corresponding results of measurement are represented in Fig. 1. and 2. The magnetic susceptibility is measured by the force method in the magnetic field with maximal induction B = 0,6 T.

RESULTS AND DISCUSSION

The dependence of the dielectric permittivity on the temperature (T) has the same general form for all for compounds (Fig. 1). ϵ_r increas with the temperature increase, pass through the maximum and falls towards zero at very high temperatures. This general feature of the $\epsilon_r(T)$ dependence characteristic for the ionic and polar compounds remains out of the scope of this paper. Our attention is limited to the local deviation of the experimental values $\epsilon_r(T)$ from the monotonus parabolic curve.

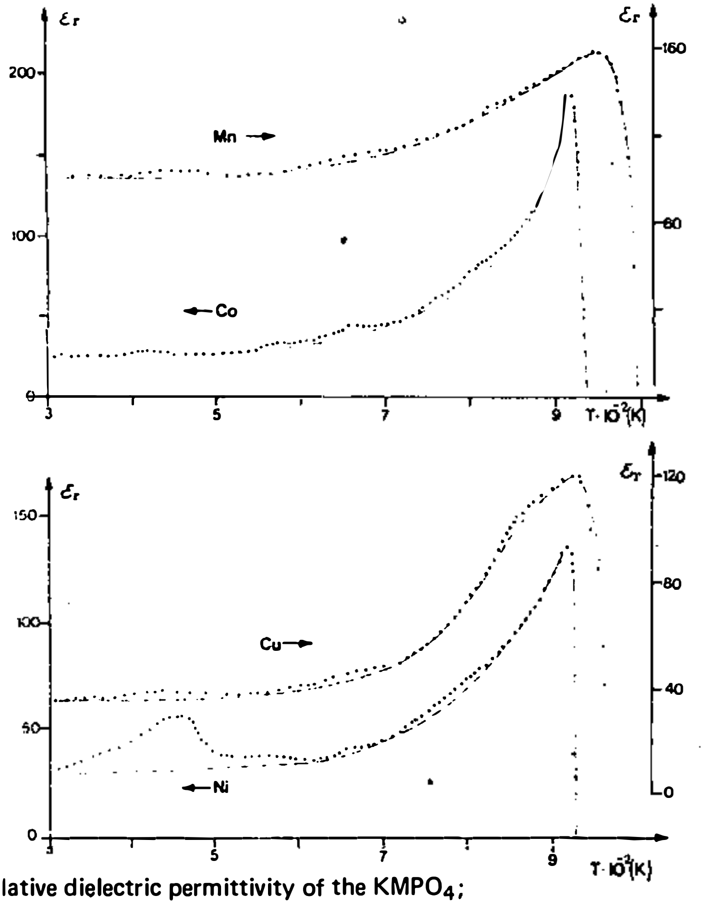

Fig. 1. Relative dielectric permittivity of the $KMPO_4$;

The dependence 1nρ—1/T (Fig. 2) shows that the electric resistivity for all four compounds become smaller at the higher temperatures, what is well known phenomenon for the dielectrics. But the dependence 1nρ—1/T has not simple monotonus character. At the temperatures which correspond to the temperatures of the local maxima of $\epsilon_r(T)$ the curves 1nρ—1/T have the characteristic shanges, similar for the all investigated compounds.

These "anomalies" can be interpreted as the consequence of the polymorphic phase transitions in the corresponding compounds. This is reliably established in our laboratory durring the investigations of the different compounds. E.G. the such anomalies are established in the case of the $NaMPO_4$ compounds /7/.

The Fig. 1. and 2. show that all examined compounds in the region 300—900 K have four structure phase transitions. According to the same figures is follows that these phase transition hare the diffuse character.

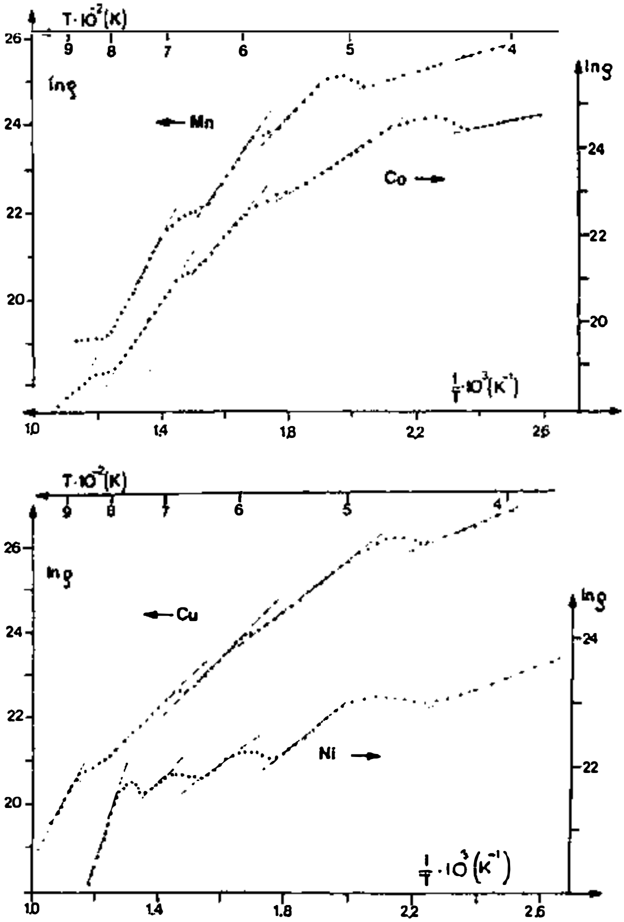

Fig. 2.
Electric resistence of the $KMPO_4$

The measurement of the magnetic susceptibility (χ) shows that the investigated compounds are Curie-Weiss paramagnets. The dependence $1/\chi$–T for all compounds are "broken" straight lines, which breaks correspond to the mentioned polymorphic phase transitions. The measured values of the magnetic susceptibilities after correction for the diamagnetic contribution /8/ enable the calculation of the magnetic moments of the transition metal ions. Table 1. gives the values of the calculated magnetic moments μ (in Bohr magneton μ_B) determined for the region of the room temperature and for the region of the highest measured temperatures. These values show that the increase of the temperature is accompanied by the increase of the orbital contribution to the magnetic moments of d^n ions, i.e. that the quenching of the orbital moment become weaker.

Table 1. The magnetic moments of the transition metal ions

	The magnetic moment μ/μ_B	
ion	the room temperature region	the high temperature region
Mn	5,90	5,92
Co	3,92	5,19
Ni	2,84	3,52
Cu	1,80	2,67

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