

PHYSICAL PROPERTIES OF MIXED PYROPHOSPHATES
OF COBALT AND NICKEL WITH BARIUM

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INTRODUCTION

Mixed pyrophosphates of cobalt and nickel with barium $BaMP_2O_7$, where $M=Co(II)$ and $Ni(II)$, are synthesized and then a series of investigations is performed. These compounds have not been described in literature so far. There are literature data of some tests realised on mixed pyrophosphates with the same formula but where $M=Mg$ and Zn /1/.

SYNTHESIS

Synthesis of these compounds is made by applying the procedure which is, in principle, described in literature (for example /2/). This method gives homogeneous polycrystalline specimens applied in research described here below.

CRYSTALLOGRAPHIC DATA

The synthesized samples are investigated by x-ray diffractometry. This experiment shows that the investigated compounds have the monoclinic symmetry and enables the determination of the unit cell parameters; the corresponding data are stated in Table 1.

Table 1.

compound	unit cell parameters			
	a(nm)	b(nm)	c(nm)	β (°)
$BaCoP_2O_7$	1,1410	1,320	0,7877	111,8
$BaNiP_2O_7$	1,2268	1,586	0,8030	113,3

We would mention here that the interplanar spacings (d) for the strongest lines of examined diffraction patterns correspond to the interplanar spacings of Mg and Zn -compounds /1/ pointing out to possible isostructurality of all four pyrophosphates.

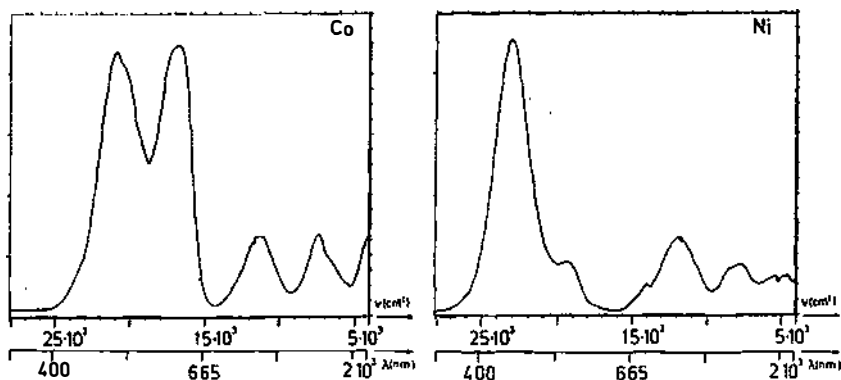


Fig.1.

OPTICAL SPECTRA

Synthesized compounds are investigated by diffuse reflectance spectroscopy. Spectra are recorded in the range $357\text{nm} + 2500\text{nm}$ (i.e. $2,8 \cdot 10^4 \text{cm}^{-1} + 4 \cdot 10^3 \text{cm}^{-1}$) at a room temperature and in respect to BaSO_4 as reference sample. The spectra recorded are plotted in Fig.1. When these spectra are compared to optical spectra (crystal i.e. ligand field spectra) of Co(II) and Ni(II) compounds, literature known (for example /3,4/), it can be concluded that the spectra do not correspond to the most frequent coordination surroundings of Co(II) and Ni(II) - ions in the different structures. The forme of the spectra recorded might mean that M(II)-ions are in coordination surroundings of a very low symmetry /3,4/ or that M(II)-ions in the investigated crystals could be found simultaneously in two different surroundings, which was established for certain phosphates (for example /5/). Spectroscopy does not render a reliable answer to these questions /3/.

MAGNETIC, DIELECTRIC AND ELECTRIC MEASUREMENTS

Temperature dependence is studied within the wide temperature interval of:

- a. Magnetic (mass) susceptibility (χ_m) by Gouy method; measuring results are given in Fig.2.
- b. Dielectric (relative) permittivity (ϵ_r) with high-frequency measuring bridge (at 1 MHz); measuring results are given in Fig.3.
- c. Specific electric resistivity (ρ) by electrometric method; measuring results are given in Fig.4.

Measurements under b. and c. are made on pellets of powder pressed under 5 MPa pressure. General form of obtained dependences $1/\chi_m$, ϵ_r and

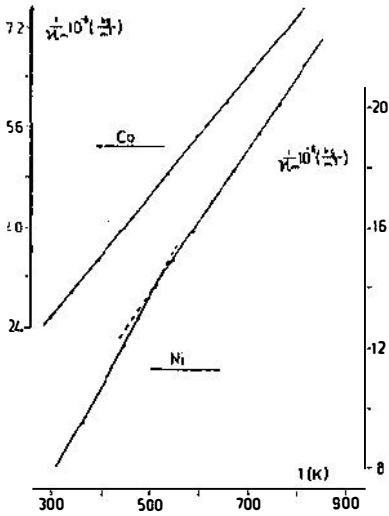


Fig. 2.

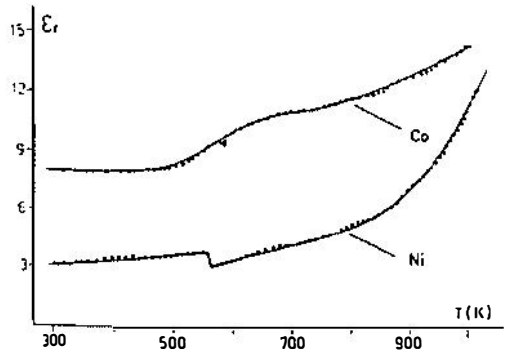


Fig. 3.

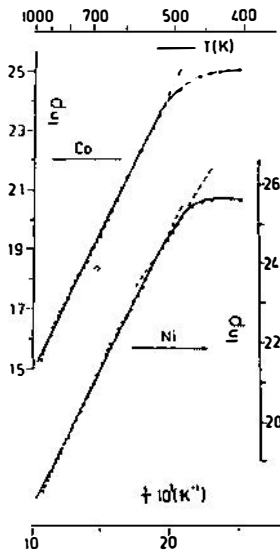


Fig. 4.

$\ln \rho$ on temperature (T), presented by the curves in Figs. 2 + 4, is typical for paramagnets, linear dielectrics and weak electronic conductivity systems. However, a small discontinuity can be noticed on the curves corresponding to Ni-compound. This discontinuity corresponds to the structural phase transition which temperature (mean value of 3 measurements) is $T=532K$. Let us say that one phase transition at $T=580K$ could be attributed, with less reliability, to Co-compound; however, additional investigations are needed for this.

CONCLUSION

The compounds not described so far are synthesized and a series of investigations is performed. Crystal symmetry is established and unit cell parameters are determined; crystal field spectra are recorded on the basis

of which the complexity of the problem related to the symmetry of the coordination polyhedrons is defined. Temperature dependence of some physical properties is studied and the existence of one structural phase transition for Ni-compound is established, while the case of Co-compound requires additional investigation. Those structural transitions are characteristic for numerous simple and mixed phosphates /6/.

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