INVESTIGATION OF PHYSICAL PROPERTIES OF LEAD COBALT PHOSPHATE - $Pb_2Co(PO_4)_2$

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This paper presents the results of investigations of polycrystalline samples of the compound $Pb_2Co(PO_4)_2$. The temperature dependence of magnetic susceptibility, dielectric permitivitty and electric resistance were determined. The optical reflection spectrum of this sompound was also registred and the observed peaks are identified. The data obtained are compared with those for the previously investigated compound $PbCo_2(PO_4)_2$.

INTRODUCTION

The investigation of $Pb_2Co(PO_4)_2$. whose properties are described in this paper, is a part of a study of mixed phosphates of divalent metals, started in our laboratory several years ago (e.g.[1,2]).

SYNTHESIS AND CRYSTALLIZATION

The synthesis of $Pb_2Co(PO_4)_2$ is similar to that of $PbCo_2(PO_4)_2$ [2]. The problems encountred in the crystallization of the mixed phosphates are reported elsewhere[2,3]. Due to difficulties in obtaining monocrystals, in the present paper only the results for polycrystalline samples are presented.

CRYSTAL STRUCTURE

Using the x-ray diffraction method powder sample of $Pb_2Co(PO_4)_2$ was examined. Diffraction pattern of the powdered sample is aquired by use of G.M. - diffractometer and CuK_α - radiation. The diffraction pattern obtained differs from those corresponding to the mixed phosphates with known structure[3,4].This difraction pattern resembles the pattern of $Sr_2Co(PO_4)_2$, whose structure is not determined [5] . For the time being it is not possible to draw reliable conclusions on the symmetry and crystal structure of $Pb_2Co(PO_4)_2$.

OPTICAL SPECTRUM AND CRYSTAL FIELD

The diffuse reflection spectrophotometry method was used for recording the optical spectrum of $Pb_2Co(PO_4)_2$ in the range from 350 to 1000 nm. The spectrum obtained (fig. 1) has the distinctive features for the Co^{2+}-ion in the octahedral crystal field. This fact and the position of the spectrum on the wavelength scale suggest that the Co^{2+}-ion in $Pb_2Co(PO_4)_2$ is surrounded by octahedron formed by the oxygen atoms from the Po_4^{3-}-ions.

The Tanabe-Sugano method [6] for the interpretation of the spectrum was used. The best values obtained for the energies of the electronic transition from the ground state $^4T_{1g}$ (^4F) are

$^4T_{1g} \rightarrow$ $^4A_{2g}$ ...... E = 13500 cm^{-1}
$^2T_{2g}$ ...... 16800 cm^{-1}
$^2T_{1g}$ ...... 17500 cm^{-1}
$^4T_{1g}(^4P)$ .. 18650 cm^{-1}
$^2A_{1g}$ ...... 22500 cm^{-1}.

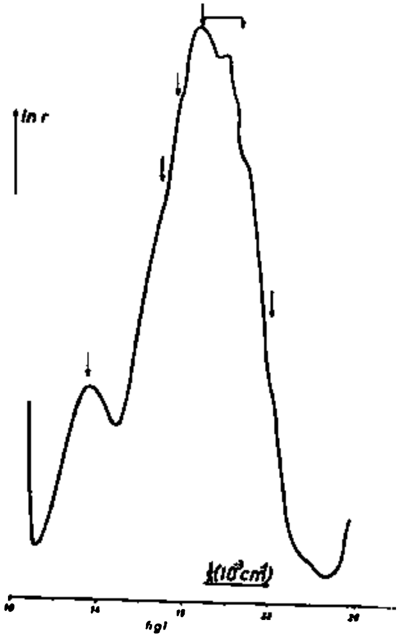

fig1

The positions of these calculated transitions in the spectrum (fig. 1) are indicated by arrows. From these calculations one obtains for the coefficient β [7] the value β = 0,91, which corresponds to the appreciably ionic character of the Co-O bond as is the case with the $PbCo_2(PO_4)$ compound [2]. Finally, from the analysis of the spectrum the value for the parameter 10 Dq [7] is derived. The calculation gives 10 Dq = 6940 cm^{-1}. This value is larger than that for $PbCo_2(PO_4)_2$. This fact is not unexpected. In $Pb_2Co(PO_4)_2$ the greater content of Pb^{2+}-ions with bigger ionic radius causing the PO_4^{3-}-ions to have the role of bidentate or tridentate ligands for the Co^{2+}-ions, and for this reason the crystal field is stronger [7].

MAGNETIC SUSCEPTIBILITY

The dependence of the magnetic susceptibility (χ) on temperature was determined by the Gouy method. The measurements were performed in the region from 120 to 670 K. The dependence can be represented by the Curie-Weiss law $\chi = C(T-\theta)^{-1}$ with θ = 26 K. From this value of θ it follows that ferromagnetic ordering may be expected at low temperatures. The magnetic moment of Co^{2+}-ion (in Bohr magnetons μ_B) determined from the value of C is M = 4,65 μ_B. This value corresponds to the partial quenching of the orbital moment [8]. It is smaller than the value of M(Co^{2+}) obtained for $PbCo_2(PO_4)_2$ [2]; the difference is probably caused by the difference in the crystal field strength [8].

ELECTRIC CONDUCTIVITY

The measurement of the electric resistance (R) was performed using a digital electrometer circuit (with two leads). The sample used for this measurement was a plate cut from a greater polycrystalline piece of examined substance. At room temperature the resistivity of $Pb_2Co(PO_4)_2$ is $\rho = 7{,}8\cdot 10^{8}$ ohm m. The measurement of the resistance in the temperature range from 300 to 900 K and the plot lnR from 1/T (where lnR = $\log_e R$) shows that in this range there are three regions with different activation energy (fig. 2.) Boundary temperatures for these three regions are 419 K($1/T = 2{,}18\cdot 10^{-3}K^{-1}$) and 769 K($1/T = 1{,}3\cdot 10^{-3}K^{-1}$). The activation energies for these three regions, beginning with low temperatures, are $E_1 = -{,}44$ eV, $E_2 = 0{,}21$ eV and $E_3 = 0{,}72$ eV, respectively.

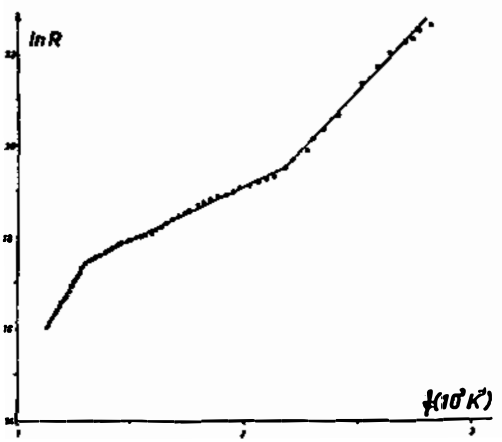

fig.2.

DIELECTRIC PERMITTIVITY

The dielectric permittivity (ε_r) in the temperature interval from 300 to 670 K was measured by means of a resonant bridge (at 800 Hz). At room temperature $\varepsilon_r = 27$. The permittivity increases with temperature (fig. 3) and at T = 670 K it reaches the value $\varepsilon_r = 320$. The measurements at higher temperatures were not possible because of very large dielectric losses. This kind of dependence $\varepsilon_r(T)$ is probably caused by a structural phase transition. The existence of such transformations are characteristic for several phosphates [9]. The other mixed phosphates examined in our former experiments show similar behaviour [1]. The change of the shape of dependence lnR = f(1/T) at 769 K corresponds probably to the same transition.

The break of the dependence lnR = f(1/T) at 419 K corresponds to the weakly pronounced change of the shape od function $\varepsilon_r(T)$. Finally, the deviation of the curve $\varepsilon_r(T)$ from the hyperbolic shape in

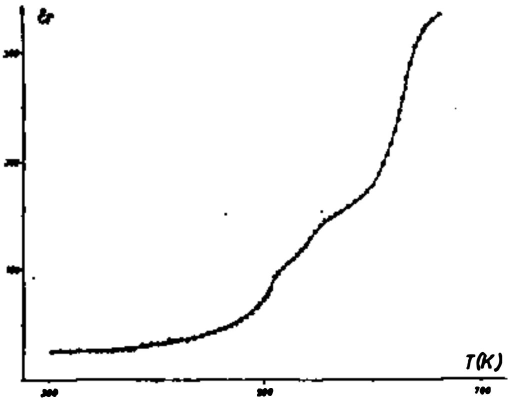

fig.2

the region between 500 and 600 K corresponds to the deviation of the dependence lnR = f(1/T) from the straight line in the region 1/T = (1,6 - 2) $10^{-3}K^{-1}$ (fig. 2).

It should be underlined that the values of $1/\chi$, obtained on the basis of the measurement in the same temperature interval, can be presented by a straight line which corresponds to the Curie-Weiss law. In the examined temperature region does the breaks do not exists which may correspond to any change in the examined substance. This can be explained by the fact that the dominant contribution to the magnetic susceptibility comes from the Co^{2+}-ion in the octahedral surroudning, which changes very little in this temperature region.

FINAL REMARKS

In this paper the first results of investigation of $Pb_2Co(PO_4)_2$ are reported. The investigations will be continued and the intended measurements on monocrystalline samples will be performed.

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