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INVESTIGATION OF MAGNETIC, ELECTRIC AND OPTICAL PROPERTIES OF LEAD COBALT PHOSPHATE - $PbCo_2(PO_4)_2$

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This paper presents data on synthesis and investigation of physical properties of a not previously investigated substance - $PbCo_2(PO_4)_2$. The investigation is performed on a polycrystalline material. The unit cell parameters are determined by means of the x - ray diffraction analysis. The optical reflection spectrum is plotted and the observed peaks are identified. Dependence of magnetic susceptibility, dielectric permittivity and electric resistance on temperature is investigated.

INTRODUCTION

This paper comprises first results obtained in the investigation of $PbCo_2(PO_4)_2$ and at the same time is a continuation of the previously started investigations of the phosphates of transition metals /1/.

SYNTHESIS AND CRYSTALLIZATION

$PbCo_2(PO_4)_2$ is synthetized by mixing the following substances: $PbCO_3$, $CoCl_2 \cdot 6H_2O$ and $NH_4H_2PO_4$ and their heating till the melting point. In the melt undergoing intensive mixing, a chemical reaction followed by a release of gaseous products occurs. The melting point of the substance obtained is 810^oC.

By means of the Bridgman - Stockbargers method and the change of experimental conditions we have tried to obtain larger monocrystals. The substance shows extremely anisotropic characteristics - during its solidification from the melt a sample of layered structure is formed what makes it difficult to obtain larger monocrystal samples.

Due to the mentioned difficulties in the obtainment of monocrystals the investigations presented in this paper are performed on the polycrystalline samples.

CRYSTAL STRUCTURE

The information on the crystal structure has been obtained by means of the x - ray diffraction analysis. Diffraction pattern of the powdered sample is acquired by use of G.M. - diffractometer and CuK_{α}-radiation.

Investigation of the diffraction pattern shows the possibility for indexing of lines if the substance is taken to have the monoclinic unit cell with the following parameters:

$$a = 10{,}50\ \text{Å},\quad b = 4{,}77\ \text{Å},\quad c = 6{,}60\ \text{Å},\quad \beta = 91^{\circ}.$$

A reliability factor (R - factor) /2/ can be used as a criterion of accuracy of the values of parameters. The calculations show that the agreement between the experimental and calculated values of intrplanar spacings (for 21 line) can be represented as R = 0,01.

Comparison of the values obtained for parameters and diffraction pattern with the x - ray diffraction data for the phosphates investigated show that the substance under investigation can be compared to $MnFe_2(PO_4)_2$- Sarkopside mineral belonging to a group of Graftonite minerals /3/. The Sarkopside Crystals have C_{2h}^5 - $P2_{1/}$ symmetry while the crystal structure of this substance is similar to that of Olivine /3/. A fact that there is a structural analogy of other phosphates with that of particular silicate /3,4/ supports this assertion.

OPTICAL SPECTRUM AND CRYSTAL FIELD

The optical reflection spectrophotometry method is applied in further investigation of $PbCo_2(PO_4)_2$. Investigation of the spectrum is done in the optical range of 350 to 1000 nm with respect to $BaSO_4$ used as etalon (Fig.1). For the sake of comparison the spectrum of $CoSO_4 \cdot 7H_2O$, the substance that contains $Co(OH_2)_6^{2+}$ - ions /5/ is plotted also. Comparison of these two spectra shows that they are very similar, as could have been expected, since according to the postulate on the crystal structure, Co^{2+} ions in $PbCo_2(PO_4)_2$ should be in the octahedral coordination of CoO_6. At the same time it is evident that phosphate spectrum is substantially shifted toward lower energies with respect to the sulphate spectrum what correspnds to the weaker crystal field. This effect can be explained as weakening og Co-O bond going from phosphates to sulphates.

The interpretation of the spectra obtained is not simple as is shown by the analysis of literature considering this problem /6,7/. The graph Tanabe - Sugano for $3d^7$ ion /6/ is used for the interpre-

tation of this spectra. A good agreement with our spectrum is found although the applicability of this graph is a bit doubtfull /8/.

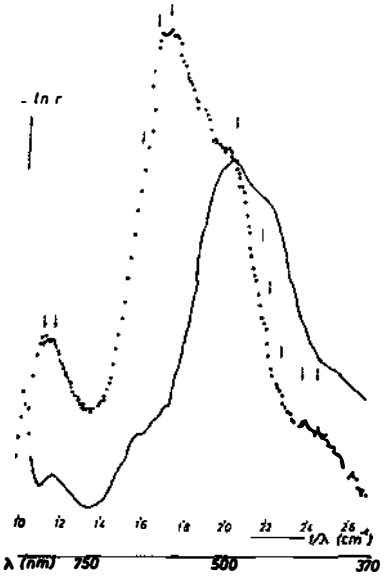

Fig. 1.

The calculation done on the basis of this graph yields values for the energies of electronic transitions from the ground state $^4T_{1g}$:

$^4T_{1g}$ $^2E_{1g}$ ..... 11300 cm^{-1}
$^4A_{2g}$ ..... 11800cm^{-1}
$^4T_{1g}$ ..... 17200cm^{-1}
$^4A_{1g}$ ..... 20200cm^{-1}

The values of these energies are presented in Fig. 2. The energy of 6030cm^{-1} is calculated for the first transition, $^4T_{1g}$- $^4T_{2g}$, that lie in the infrared region. The weakly pronounced peaks in the region (14-16) 10^3cm^{-1} correspond to the forbidden transitions $^2T_{2g}$(15700 s^{-1}) and T_{18} (16.600 s^{-1}). The weakly pronounced peaks above 21000 s^{-1} also correspond to the forbidden transitions. From such a distribution of electronic transitions it follows that Racah parameter B /6/ for Co^{2+} ion in the crystal field has a value of B = 833 cm^{-1}, while for the free Co^{2+}- ion B_o= 971 cm^{-1}.

Therefore $\beta = B/B_o = 0,86$

what corresponds to the ionic character of the bond of Co^{2+} ion /9/.

Finally, for the parameter of level separation Δ /6/ the calculations yield

$$\Delta = 6100\ cm^{-1}.$$

MAGNETIC PROPERTIES

The dependence of the magnetic susceptibility on temperature is determined by means of the Gouy method. (Fig. 2.). The dependence can be represented by the Curie - Weiss law

$$X = \frac{C}{T - \Theta}$$

The calculation yields Θ = -50,3K. For the oxides, fluorides, sulphides and sulphates of 3d - metals $T_n = \frac{1}{2}$ /Θ/ /10/; if this relation is applied to the substance investigated it follows that in the region

of low temperatures it is an antiferomagnet with the Neel temperature of T_N = 25K.

Furthermore, the calculation yields C = 5,64 CGS units. If this value is used for the calculation of the effective magnetic moment of Co^{2+} ion, we obtain (in Bohr magnetons μ_B)

$$M = 4{,}75\ \mu_B.$$

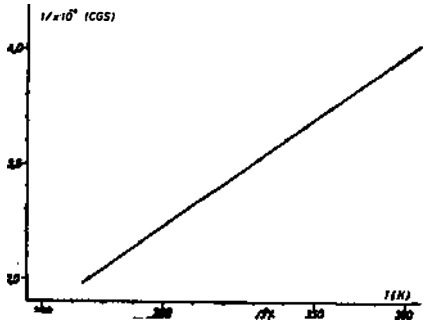

Fig. 2.

This value lies between the pure spin magnetic moment (3,87) and the total magnetic moment (5,20) /11/ what is often obtained in experiments /12/ and corresponds to the partial "quenching" of the orbital moment /11/.

MEASUREMENT OF DIELECTRIC PERMITTIVITY

Dependence of the dielectric permittivity ε_r on temperature is measured (Fig. 3) from the ambient temperature by means of a resonant bridge (at 800Hz). On the room temperature (T = 300K) ε_r = 29. With the increase of temperature ε_r at first increases slowly and then quickly so that at 930K it is 19 times greater. This type of ε_r(T) dependence is also found for phosphates of a different type of structure /1/. A discontinuity in the ε_r(T) dependence at 850K can probably be related to a particular structural phase transition. The appropriate investigations are yet to be done.

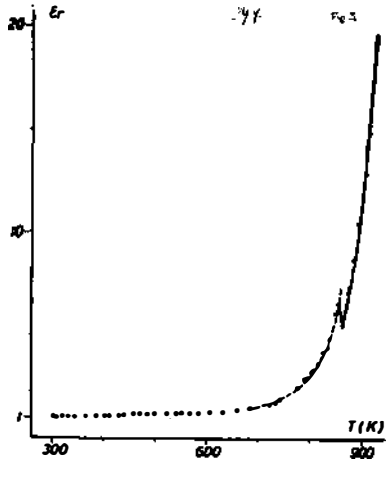

Fig. 3.

ELECTRIC CONDUCTIVITY

Measurements of the electric resistance in DC - regime have shown that this substance has a specific resistance

$$\rho = 4{,}7 \cdot 10^{18}\ \text{ohmcm}$$

at the ambient temperature.

Dependence of the electric resistance on temperature is shown in Fig. 4. It can be noticed that at $T^{-1} = 1{,}17 \cdot 10^{-3} K^{-1}$ there is a weakly pronounced break on the curve. This break corresponds to the descontinuity shown in Fig. 3. The activation energy changes from 1,16 eV to 1,54 eV while passing this temperature. Finally, a very pronounced break appears at $1{,}02 \cdot 10^{-3} K^{-1}$ (i.e. at 980K) which correspnds to a great change in the mechanism of conductance. For the regions above this temperature the activation energy is 8,1 eV.

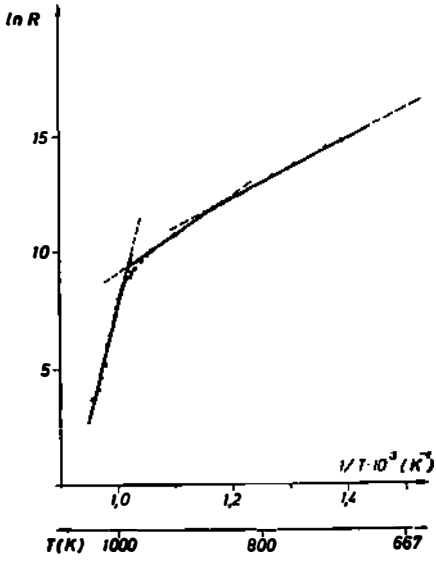

Fig. 4.

FINAL REMARKS

The investigations performed show that the substance under investigation has very interesting properties. Explanation of some of these properties (Fig.3) requests a more detailed information on the crystal structure and interatomic distances which will soon be obtained.

REFERENCES

1. Napijalo M.Lj., Dojčilović J., Žižić B., Rodić M. and Žikić A., Fizika, 8 Supplement, 1976, Procedings of the V Yugoslav Symposium of the Physics of Condensed Matter, Sarajevo, October 1976., p. 274.
2. Hejker, D.M. and Zevin L.S., Rentgenovskaya diffraktometriya, FIZMATGIZ, Moskva, 1963.
3. Povarennykh, A.S., Kristallokhimicheskaya klassifikaciya mineral'nykh vidov, "Naukovaya dumka", Kiev, 1966.
4. Wyckoff, R.W.G., Crystal Structures, 3, Interscience Publ., New York, 1960.
5. Holmes, O. and McClure, D.S., J. Chem. Phys., 26, 1686 (1957).
6. Sviridov D.T., Sviridova R.K. and Smirnov, Y.F.,

Opticheskie spektry ionov perekhodnykh metallov v kristallakh, "Nauka", Moskva, 1976.
7. Hush, N.S. and Hobbs, R.J.M., Progr. Inorg. Chem., ed F.A.Cotton, vol 10., pp. 259 - 486, 1969.
8. Ballhausen, C.J., Introduction to Ligond Field Theory, McGraw-Hill, New York, 1962.
9. Lever, A.B.P., Inorganic Electronic Spectroscopy, Elsevier, Amserdam, 1968.
10. Vonsovskii, S.V., Magnetizm, "Nauka", 1971.
11. Mabbs, F.E. and Machin D.J., Magnetism and Transition Metal Complexes, Chapman and Hall, London, 1973.
12. Weiss A. and Witte H., Magnetochemie, Verlag Chemie, Weinheim, 1973.