

STUDY OF MAGNETIC BEHAVIOUR AND CONDUCTION MECHANISM OF CuNiTiO_4

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ABSTRACT

A compound CuNiTiO_4 is prepared by solid diffusion method in the laboratory using standard chemical crystallographic of CuNiTiO_4 . The magnetic susceptibility of compound is measured by Gauy's method. The molar susceptibility is obtained with curie molar constant with respect to temperature. The Magnetic properties are studied under which the variation of Magnetic susceptibility with respect to temperature. The compound is found to be paramagnetic at room temperature. The paramagnetic behaviour is studied by plotting $1/\chi_m$, vs temperature.

Key words:- Magnetic susceptibility, CuNiTiO_4 ,

INTRODUCTION

On the basis of structure, solids can be classified into two main categories or ions are stacked in a regular manner. By choosing a single point within the crystal, all the identical points in a environment can be found out. A group of oxides with chemical formula XY_2O_4 that has crystal structure of magnesium aluminate (MgAl_2O_4) or mineral hausmannite (Mn_3O_4) is known as 'spinel'. The crystal structure of MgAl_2O_4 has been determined completely by Bragg and Nishikowa independently in the year 1915, which was found to be cubic crystal. It is interesting to note that all the compounds with chemical formula X_2O_4 do not necessarily have the spinel structure. The essential condition for the formation of oxidic spinels is that the cationic radii should be between 0.45 Å to 0.95 Å.

In spinel structure it is seen that there are two types of interstices, available, one formed by four anions of the vertices of tetrahedron and other by six anions of the

vertices of an octahedron. These interstices are called the tetrahedral (A) site and octahedral (B) site respectively. The positions of the anions are variable and are specified by the symmetry of the structure.

Site distribution of cations in the spinels plays an important role in the understanding of electrical and magnetic properties. Much theoretical as well as experimental work has been done for finding out the distribution. It was first believed in an oxidic spinels the metal ions would tend to occupy the same sites as in the oxides. Thus the metal oxides having zinc blend and rock salt structure would tend to occupy Tetrahedral and a Octahedral sites respectively. However belief was found to have limited applicability.

Several workers have classified the cations according to their distribution in the spinels. Verway and Heilmann have classified the cations assuming a purely ionic model. According to them the presence of the ions for A and B sites is as follows

- a) Zn^{+2} , Cd^{+2} , Ga^{+3} , In^{+3} , Ge^{+4} prefer A sites
 b) Ni^{+2} , Cr^{+3} , Ti^{+4} , Sn^{+4} , prefer B sites
 c) Mg^{+2} , Fe^{+2} , Co^{+3} , Mn^{+2} , Fe^{+3} are indifferent ions.

In the present work we have prepared spinel containing copper, zinc and titanium. It is found that Ni^{+2} has large A site preference energy while Ti^{+4} have B site preference energy and Cu^{+2} distribution also have A site. Therefore the study of site distribution is highly interesting. Here the electrical conductivity of the spinel is studied.

Cationic radii of the elements used in the present works

Element	Ionic radii
Cu^{+2}	0.72 Å
Ni^{+2}	0.74 Å
Ti^{+4}	0.68 Å

EXPERIMENTAL

2.1 Preparation of Pellets :

For making pellets for electric conductivity measurement, the sample was finally powdered in an agate mortar, and then mixed with 5% polyvinyl acetate solution in A.R. grade, which serves as binder. It was found that about 2 cc of the binder per gram of the sample was required to give well modulated pellets suitable size for studying it. The plastic mass was obtained by mixing sample with binder was pressed in hydrauline press of 0.9 cm diameter die under the pressure of 5 - 8 tones per square meter.

The pellets thus prepared was placed in ceramic boat and slowly heated in air upto 400°C when the binder either evaporated or burn off. The pellet was maintained at this temperature for one one and half hour then temperature of furnace was rised 800°C to 900°C. The pellet was maintained at sintering temperature for 3 - 4½ hours and finally

quenched at room temperature in air, which form the suitable pellets for study of electrical conductivity.

2.2 Magnetic Behaviour And Measurmets :

When substance is placed in magnetic field H, a inagnetic moment M per unit volume results. M is called the magnetization. Susceptibility χ , defined by $\chi = M/H$, is then a scalar quantity. In anisotropy substance χ is a tensor. in this case M refer to gram molecule, one may introduce molar susceptibility χ_m .

Spinel type compound containg ions belongining to the first transition series have recently becomes important. Magnetically they exhibit a wide variety of a phenomenon because of several possibility of a site and charge distribution of cation in such compounds. In case of spinel containing magnetic ion, the magnetic interaction which depend on the type of ion, their distance, location and temperature of investigation decide the nature of their magnetic properties.

The diamagnetic substance posses no net permanent magnetic moments and they exhibit negative susceptibility.

In paramagnetic substance, quantum mechanical interactions among them are absent. Strong magnetism exhibited by compound having localized momens interaction through what is known as Heisenberg xchange. Positive exchange integrals favours parallel alignments of magnetic moments giving rise to ferromagnetism.

Antiferromagnetism is common in and e of transition elements In many such instance eg Mno the origin of interaction between the moments of cations is described by the "super exchange". As consequence of super exchange interaction, the moments of transition metal ion are lined at antiparrallel resulting in a cancellation of their magnetic moments. This interaction is the strongest in the cations are diamagnetically located with respect to interveming anions Mn-O-Mn. In $\text{CdFe}_2\text{CaO}_4$, spinel the B-B interaction result in antiferromagnetism.

In the present work, the given compound CaNiTiO_4 is paramagnetic at room temperature so paramagnetic susceptibility has been determined by Gouy's Method. The graph of $1/\chi_m$ Vs $T^\circ\text{K}$ has been plotted from the slope of the graph, the Curie molar constant has been calculated from the measurements.

Langevin in 1905, the expression, gives the paramagnetic susceptibility

$$\begin{aligned}\chi_m &= N\mu^2/3KT \\ \chi_m &= C_m/T\end{aligned}\quad (1)$$

N is the total no. of atoms or ions, μ is the magnetic moment of an atom, T is temperature in $^\circ\text{K}$. C_m is Curie molar constant.

$$\chi_m = Ng^2 J(J+1) \mu^2 B / 3KT \quad (2)$$

Equation (2) gives quantum theory of paramagnetism, leads to paramagnetic susceptibility. This equation can be written as

$$\chi_m = Np_{\text{eff}}^2 \mu^2 B / 3KT = C_m / T \quad (3)$$

$$p_{\text{eff}} = g \sqrt{J(J+1)} \quad (4)$$

Equation (4) is valid for rare earth elements but not iron group elements.

Since for iron ions the crystal field exerts a greater influence on the direction of the orbital momentum L than does the spin coupling between L and S .

Thus for iron group $L=0$ and hence $J=3$ and $g=2$
Giving

$$p_{\text{eff}}^2 = 4S(S+1)$$

Leading to

$$C_m = P_{\text{eff}}^2 / 8 = S(S+1) / 2 \quad (5)$$

For n ions per molecule

$$C_m = \sum C_j$$

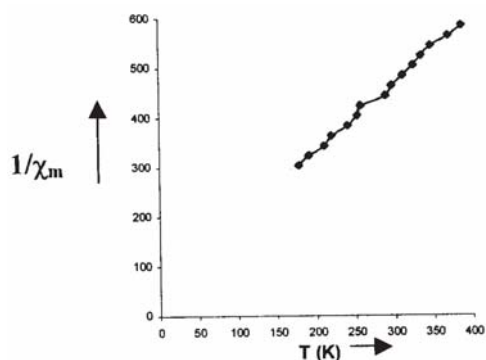
Where C_j is the Curie molar constant for the i^{th} ion. The experimentally observed value of

C_m agrees with theoretically calculated spin only value and provides information about valence state of cations. However variation of C_m value from theoretically calculated values is observed which is attributed to contribution per ion or by exchange information between the ions.

2.4 Experimental Procedure:

The empty Gouy's tube is suspended from the monopan balance in such a way that it is totally free inside the furnace and its lower end coincides with the center of the pole pieces. The mass of thoroughly clean and dried empty tube is recorded on the monopan balance and pulls on it due to magnetic fields are recorded to ensure the existence of magnetic correlation, if any.

When the same tube is filled with the calibrant $\text{HgCo}(\text{CNS})_4$ up to specific mark. The pulls on the calibrant due to magnetic fields are recorded at different temperatures and the data is used in calculating tube constant β for the tube. The calibrant is then removed. And tube is cleaned with HCL and then with distilled water and is dried properly using acetone. The finely powdered sample is filled up to mark by gently tapping on wooden tube. The tube is hanged to the pan of the balance with the hanger and the mass of sample is recorded at room temperature without magnetic field and then by applying magnetic field at room temperature. To study the paramagnetic behaviour, the temperature of the tube was allowed to rise from room temperature onwards by providing gradually higher current to the furnace. The mass of the tube with the sample is measured for different currents. The same procedure is repeated for different temperatures. The table of mass sample and change in mass for zero field and field of current 1A, 2A and 3A is constructed and susceptibility (χ) is calculated for that temperature. The graph of $1/\chi_{\text{molar}}$ Vs temperature is plotted and from the slope the Curie molar constant is calculated.



RESULT AND DISCUSSION

There are several methods to be used for the interpretation of the conduction mechanism. These include hot probe method, Hall effect and thermoelectric power method. But the simplest one is hot probe method. We use this method to determine the type charge carriers and p-type charge carriers find to compound under study.

Magnetic susceptibility measurement is carried out from 304 °K to 554 °K using

balance. The compound is found to be paramagnetic at room temperature. The paramagnetic behaviour of sample is studied by plotting $1/\chi_m$ vs temperature. From the slope of the graph curie molar constant (C_m) is calculated and is found to be 0.360. Theoretical value of C_m for the sample is also calculated by considering spin only and is found to be 0.375. By indexing the diffractogram, the compound CuNiTiO_4 is found to be $a = 8.67 \text{ \AA}$ and $c = 8.59 \text{ \AA}$. From XRD pattern it is observed the compound is single phase. The diffractogram does not contain peak for the reacting oxides, checked from the standard data sheet. (Hand Walt 1936).

By observing the values of $h k l$ it is clear that the Bravias lattice is primitive since all $h k l$ are mixed. Thought the ionic radii of Ni^{2+} , Cu^{2+} , Ti^{4+} lie in the range 0.45 - 0.96 Å. Which is essential condition for the formation of oxidic spinels is satisfied, the formation of spinel structure is not favored. This may probably be attributed to the difference in the electro negativities of the ions concerned.

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