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Structural & Electrical Study of $CuCrTiO_4$

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ABSTRACT: *The Spinel $CuCrTiO_4$ is prepared with reactants Cu_2O, Cr_2O_3 and TiO_2 mixed in proper molar ratio . Compound identification is confirmed by X-ray diffraction pattern which points towards single phase spinel structure with cubic unit cell. The site distribution of cations in spinels plays an important role in understanding of electrical and magnetic properties. The observed electrical conductivity is explained on the basis of Verway model of hopping of charge carriers between the nearest cations . The electrical measurements between 350 °K to 775°K indicates the semiconducting behavior of the sample.*

I. INTRODUCTION

A group of oxides with chemical formula XY_2O_4 which has crystal structure of magnesium aluminate ($MgAl_2O_4$) is known as spinel. The essential condition for the formation of oxide spinel is that the cationic radii should lie between 0.45A° to 0.95A°. Spinels are in general divided into three groups as normal, inverse and random.

The spinels have attracted the attention of technologists due to their remarkable electrical and magnetic properties. The spinels have numerous applications in industries and in the various branches of physics. These properties are best understood with the help of site and charge distribution of cations. The site distribution of cations depends upon relative site preference energies of all the cations in the lattice . It is found to be in good agreement with the observed results.

The Spinels have widely varying electrical properties . The mechanism of electrical conductivity in pure and mixed 3d transition metal oxides have attracted much attention and has been subject of investigation by many workers . A recent review of the electrical conduction mechanism of various ferrite spinels and other transitions metal oxides is given by kumashiro. Verway , was the first to propose a hopping mechanism to explain the electronic conduction in a magnetic and other ferrites. According to him the ferrites are semiconductors and their d.c. resistivity decreases with increasing temperature as per the relation

$$\rho=\rho_\alpha \exp(\Delta E/KT)$$

Where ΔE is the activation energy to release an electron from the ion for a jump to the neighboring ion, giving rise to electrical conductivity.

An examination of spinel structure reveals that the normal distance between the tetrahedral –octahedral or tetrahedral- tetrahedral cations is so large that the overlapping between the electronic wave functions on such adjacent pair is negligible and the probability of electronic exchange between the cations on these sites is small. The electrical conduction can takes place by electron exchange (or hopping) amongst the octahedral ions , the distance between octahedral –octahedral ions being relatively small. Thus the electrical behavior of the spinel is mostly governed by the octahedral ions.

Experimental Details -

In the present work the oxide spinels were prepare by ceramic method .The reacting oxides were mixed in their molar percentage and were grounded for 4 to 5 hours. These crushed powders were heated for 100 to 110 hours at 900°C continuously. And then the temperature of furnace was reduced at the rate of 100°C per hour. Then the mixtures were taken out of furnace & grounded for about 1 hour. After grinding the samples were tested for confirmation of formation using X-ray diffraction . From the X-ray diffraction the compounds were found to be single phase with spinel structure.

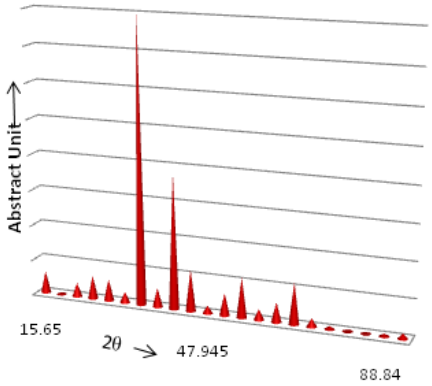
For Electrical conductivity measurements the pallets of the samples were prepared and then coated with silver to have good contacts during measurements .The pallet was inserted in the two electrodes of the sample holder which is connected to LCR meter bridge . The measurement of temperature was facilitated by use of cromel / Alumel thermo couple which was connected to sample holder . Thus the resistance was measured from 300° K to 773° K

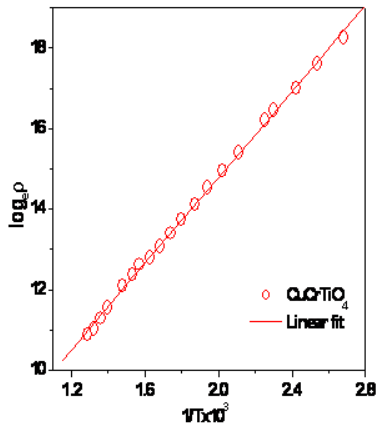
II. RESULT & DISCUSSION

The X-ray pattern of the compound indicates formation of single phase spinel with cubic structure. The cubic structure of compounds were confirmed from the planes calculated in table (1). Lattice parameter for the compound is found to be 9.82A° which is slightly higher than the reported value of various other ferrites which is about 8.4A° .This may be due to the larger ionic radii of the cations forming these compounds. The calculated d-values and observed d – values are found to be nearly same and matches with that of spinel structure. The X-ray density of sample is found to be 3.1898gm/cm^3.

Table (1) XRD Calculations for Lattice Parameter

d-value observe d(A^0)	d-value Calculate d (A^0)	Intensity Observed	Bragg's Angle $2\theta^0$	(h k l)
5.6577	5.6695	8.4	15.650	(1 1 1)
3.2373	3.2733	9	27.530	(3 0 0)
3.1537	3.1053	8.4	28.275	(1 0 3)
2.8395	2.8347	100	31.480	(2 2 2)
2.4535	2.4550	48.5	36.595	(4 0 0)
2.1980	2.1958	15.4	41.030	(4 2 0)
1.6846	1.6841	8.6	54.420	(5 3 0)
1.6385	1.6366	14.8	56.085	(6 0 0)
1.4233	1.4173	15.4	65.530	(4 4 4)





Variation of resistivity with temperature Graph (2)

The conductivity of spinel is usually measured on polycrystalline specimen, it depends to some extent on physical nature of the sample , such as porosity, and the surface grain boundary in homogeneities. Thus the conductivity of spinel is found to vary from sample to sample. The activation energy values are however fairly reproducible and can give information on conductivity mechanism. It is found for intrinsic semiconductors the influence of the temperature on the concentration of the conduction carriers is relatively small. This means that the temperature influence on the conductivity is a result of change of mobility of electrons or holes with temperature. In most cases a straight line relationship is found between $\log_e\rho$ vs.1/T. The slope of the line corresponding to the activation energy ΔE which lies between 0.1 ev to 0.7 ev . In few cases a change in slope is found in the curves which points out to two parallel conductivity mechanism with differing activation energies. As general rule high activation energy is associated with high resistivity at room temperature.

The electrical measurements are carried out & found to obey Wilson's law indicating the semiconducting nature of compound under investigation. The plot of $\log_e\rho$ versus 1/T° K $X10^{-3}$ indicates that the logarithm of resistivity increases linearly with 1/T° K. The value of activation energy obtained from slope is found to be 0.4782 eV which means it the energy required to make electrons free to take part in electrical conductivity and this conductivity is mainly due to copper ions.

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