Thermochimica Acta, 93 (1985) 481-484
Elsevier Science Publishers B.V., Amsterdam

STRUCTURAL, TRANSPORT AND THERMOANALYTICAL STUDIES OF SOME COPRECIPITATED SPINELS

P.M. Khopkar, J.A.Kulkarni and V.S.Darshane*
The Institute of Science,Bombay 400 032,INDIA

ABSTRACT

The work deals with several substituted copper, nickel and zinc manganite spinels synthesised by a new coprecipitation technique using H_2O_2. X-ray diffraction, electrical resistivity, thermoelectric power and thermoanalytical studies have been carried out. Compositional dependence of reaction temperature has been discussed with reference to site preference energy of individual cations.

INTRODUCTION

Spinels are the compounds represented by general formula AB_2O_4, where A and B are tetrahedral and octahedral summetric oxygen sites in which divalent and trivalent cations are accomodated. These compounds have a lot of commercial importance due to their interesting structural, electrical and magnetic properties. Desired applicability in these compounds can easily be achieved by substituting various cations partially or fully in tetrahedral or octahedral sites.

Conventionally ceramic method is used for the preparation of spinels. In this method compounds are needed to be heated at elevated temperatures (1000 - 1200°C) for a long time (50 - 100 hrs). This is certainly expensive and time consuming process. Hence many investigations have been carried out to reduce the cost and time of manufacturing of these materials.[1-4] The coprecipitation is one of the widely used methods.

In the present investigation several spinels have been prepared by coprecipitation method from the soluble salts. Various substituted manganites of copper, nickel and zinc have been synthesised by this technique. Novelty of our preparation technique lies in the use of hydrogen peroxide as an oxidizing agent.

MATERIALS AND METHODS

The compositions of compounds listed in Table were prepared by proportionately dissolving the salts in distilled water, followed by a precipitation using sodium hydroxide (pH - 9 to 9.5). Digested precipitate was oxidized with 30% H_2O_2 solution till the precipitate changed its color to black or

---

Proceedings of ICTA 85, Bratislava

dark brown. The precipitate was thoroughly washed and dried under vacuum.

X-ray powder diffraction analysis was carried out using Ni filtered CuK$_\alpha$ radiation. DTA and TG analysis was carried out on MOM Derivatograph. DC resistivity and thermoelectric power measurements were carried out on the samples in a hard circular pellet form. Details of setup and measurements are given elsewhere[5].

RESULTS AND DISCUSSION

X-ray analysis of the samples showed very small amount of spinel formation ($<$ 10%) in the above synthesis. DTA & TGA showed the extent of formation of constituent oxides in various compounds at room temperature to be 72 - 96% - Table. Individual oxide reflections in X-ray analysis could be characterized separately from the spinel reflections. The reaction temperatures for the compounds were determined from the DTA curves and are listed in Table. The samples were then transferred to furnace and heated at the reaction temperatures for 2 hrs.X-ray analysis thereafter showed spinel as the major phase with small peaks of unreacted oxides. The single phase spinels could only be obtained after 4 hrs. of heating. Thus eventhough the reaction temperature could not be brought down, the time for spinel formation was successfully cut down by 1/15 times or more. The formation of spinels was also confirmed by chemical analysis, which showed an excellent agreement between observed and calculated values. IR spectra showed charecteristic spinel absorbtions near 600 cm^{-1} and 400 cm.$^{-1}$

The spinel formation in the above process takes place by solid state reaction in which cations diffuse through the lattice during heating. Diffusivity and the reaction temperature entirely depend on the particle size of reactants. In our case as the compounds can form in just 4 hrs. the fast diffusivity can be attributed to the mixing of component cations on a atomic scale during oxidation with H_2O_2. The results of Yamamoto et. al.[6] are interesting in this context. They have shown that in the case of $CoMn_2O_4$ the spinel formation takes place at room temperature when air is used as an oxidizing agent for 40 hrs. Each particle of the precipitate was found to be a single cubic spinel crystal with an average diameter 5000A.

It can be seen from Table that the reaction temperature for copper spinels is lowest whereas that for Zn spinels is highest. It can be said that the cations capable of stabilizing in more than one oxidation states can react easily than that of cations with stable oxidation states. Strong preference for a particular site by the cations shows a certain influence on the reactivity. According to the Miller's values of site preference energies Zn is most stable ion in the tetrahedral whereas, Ni and Cr are most stable in an octahedral coordination[7] Other ions however, can change their sites depending on relative energies. Here a definite relation is observed between reaction temperature and site preference energies.

Transport properties showed all the compounds to be semiconductors. Electrical resistivity measurements showed straight line plots of log (ρ/T) vs 10^3/T upto 650°C without any break or inflexion. A temperature independent thermoelectric power is observed for all the compounds upto 400°C. This behaviour has been attributed to the polaron hopping conductivity in these compounds. The values of activation energy (Q) for conduction and thermoelectric coefficient (α) are reported in Table. The values of activation energy are found slightly lower than those for the compounds prepared by ceramic method owing to smaller particle size and thereby reducing the effects of porosity and grain boundaries in polycrystalline samples. The values should however be the same in the case of single crystals. The activation energies are low for the compounds possessing cation pairs such as Cu - Mn, Mn - Co or Mn - Mn, which are capable of showing mixed valencies. Whereas, other cations with the stable valencies such as Zn,Ni,Cr, Cd and Al showed high values.

The compounds in which electrons are the charge carriers have shown n-type semiconductivity (-ve α) and the others where electron holes are charge carriers showed p - type semiconductivity (+ve α). The low values of α in the case of $ZnMnCoO_4$ (-20µV/°C) and $CuMnFeO_4$ (+30µV/°C) signify presence of both the types of charge carriers in the compounds in which majority of charge carriers determine the sign of α.[8]

TABLE

Compound	Lattice constant (Å)		% Oxide formed at room temp.	Reaction temperature (°C)	Activation energy (ev)	Thermoelectric coefficient (μV/°C)
	a	c			Q	α
$CuMn_2O_4$	8.33	8.33	95	790	0.16	+80
$CuMnCrO_4$	8.32	8.32	90	810	0.16	+70
$CuMnFeO_4$	8.41	8.41	96	760	0.20	+30
$CuMnCoO_4$	8.33	8.63	90	740	0.23	-51
$NiMn_2O_4$	8.40	8.40	90	780	0.18	-80
$NiMnCrO_4$	8.35	8.35	82	800	0.36	-80
$NiMnCoO_4$	8.35	8.35	88	820	0.22	-70
$NiMnCuO_4$	8.32	8.32	88	760	0.18	+47
$NiMnZnO_4$	8.25	8.25	80	810	0.52	-115
$NiMnCdO_4$	8.60	8.60	85	800	0.48	-100
$NiMnAlO_4$	8.28	8.28	72	820	0.58	-120
$ZnMnCrO_4$	8.30	8.73	85	980	0.40	+180
$ZnMnFeO_4$	8.29	8.71	82	910	0.47	+130
$ZnMnCoO_4$	8.37	8.37	89	940	0.34	-20

REFERENCES

1 Inorganic Synthesis, 9 (Ed.-S.young Tyree, McCrow Hill, 1967) 152.
2 D. Gajapathy and K.C. Patil, Mat. Chem. and Phys. 9 (1983) 423.
3 B.A. Mulla and V.S. Darshane, Indian J. Chem. 22A (1983)143.
4 B.A. Mulla, P.S. Jain, K.A. Deshpande and V.S. Darshane, Indian J.Chem., 23A (1984) 339.
5 J.A. Kulkarni, Ph.D. Thesis, Univ. of Bombay (1985).
6 N. Yamamoto, S. Kawano, N. Achiwa, M. Kiyama and T. Takada, Jap J.Appl. Phys. 12 (1973) 1030.
7 A.Miller, J. Appl. Phys.30 (1959) 245
8 J.A Kulkarni, K Muraleedharan, J.K. Srivastava, V.R. Marathe V.S Darshane, C.R.K. Murty and R. Vijayaraghavan J.Phys. C Solid State Phys. (IN PRESS).