Journal of Thermal Analysis, Vol. 35 (1989) 1079–1082

THERMAL STUDIES ON ALUMINIUM SUBSTITUTED $CuCr_2O_4$

N. Padmanaban, B. N. Avasthi and **J. Ghose*

DEPARTMENT OF CHEMISTRY, INDIAN INSTITUTE OF TECHNOLOGY
KHARAGPUR, 721 302, INDIA

Thermal studies on aluminium substituted copper chromite spinel oxide, $CuCr_{2-x}Al_xO_4$ ($x = 0.2$ to $x = 0.8$) by DSC show that with 20% replacement of Cr by Al, the phase transition temperature of the spinel is lowered but on further increasing the percentage of Al the phase transition temperature becomes higher than that of $CuCr_2O_4$. The enthalpy change for phase transition however decreases gradually with increasing x.

Copper chromite is a tetragonally distorted normal spinel with $C/a < 1$ [1]— Extensive studies have been done on the crystallographic phase transition of $CuCr_2O_4$ [2–5] and it has been established that the tetragonal →cubic transition occurs around 823 K. Electrical resistivity measurements [6] have shown that there is a thermal hysteresis near the transition temperature indicating a diffusionless, reversible and first order phase transition.

The present work is a thermal study of aluminium substituted tetragonal $CuCr_2O_4$ using differential scanning calorimetry.

Experimental

The solid solution samples $CuCr_{2-x}Al_xO_4$ ($x = 0$, 0.2, 0.4, 0.6 and 0.8) were prepared by decomposing the metal nitrate solutions following the procedure reported in a previous paper [7].

X-ray diffraction analyses of all the samples were carried out using a Philips X-ray diffraction unit model PW 1012/00. A Cr-target was used with a vanadium filter for Cr-rich compounds and Cu-target with Ni-filter for Cu rich samples.

DSC studies were carried out with about 5 mg of the samples using a DuPont 9000 Differential Scanning Calorimeter between 305 K to 823 K at a heating rate of 10 deg/min in a flowing N_2 atmosphere.

* To whom correspondence may be addressed.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Results and discussion

X-ray diffraction studies show that all the samples are single phase tetragonal spinels. The lattice parameters and cation distribution [7] are shown in Table 1. The results of the DSC measurements are given in Figs 1, 2 and 3.

For NA2 ($x = 0.2$) Fig. 1 shows that the curve gradually falls as the temperature is increased and at about 673 K a small endothermic peak appears. On further heating, a second endothermic change appears between 727 K and 790 K with the peak at 759 K. The resistivity *vs.* temperature plots of this compound have shown a break in the linearity of the curve at about 750 K due to phase transition and so the second endothermic peak could be attributed to tetragonal to cubic phase transition in $CuCr_{1.8}Al_{0.2}O_4$. As expected, this temperature is lower than the phase

Table 1 Ratio of lattice parameter, cation distribution and phase transition temperatures of $CuCr_{2-x}Al_xO_4$

Sample	Code	C/a	Fraction of metal ions on B sites			T_t
			Cu	Al	Cr	
$CuCr_2O_4$	NA0	0.912	0	0	2.0	823 K
$CuCr_{1.8}Al_{0.2}O_4$	NA2	0.918	0.06	0.14	1.8	759 K
$CuCr_{1.6}Al_{0.4}O_4$	NA4	0.924	0.09	0.31	1.6	804 K
$CuCr_{1.4}Al_{0.6}O_4$	NA6	0.932	0.13	0.47	1.4	873 K
$CuCr_{1.2}Al_{0.8}O_4$	NA8	0.943	0.18	0.62	1.2	873 K

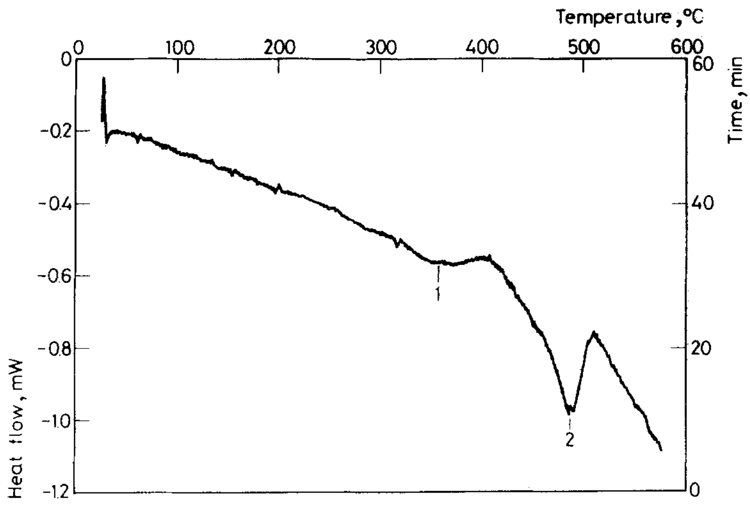

Fig. 1 DSC curve for $CuCr_{1.8}Al_{0.2}O_4$ (NA2)

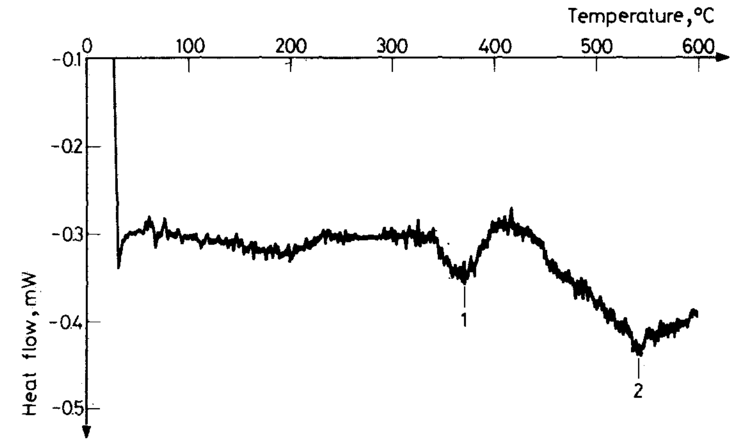

Fig. 2 DSC curve for $CuCr_{1.6}Al_{0.4}O_4$ (NA4)

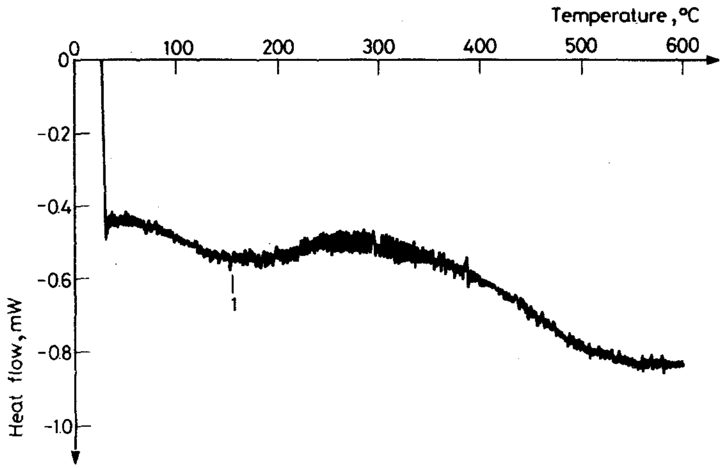

Fig. 3 DSC curve for $CuCr_{1.2}Al_{0.8}O_4$ (NA8)

transition temperature reported for $CuCr_2O_4$ (823 K): with the introduction of Al^{3+}, the Cu^{2+} ions distribute between the tetrahedral and octahedral sites (Table 1) and hence the number of copper ions on the tetrahedral sites is reduced, which is likely to weaken the co-operative J–T effect thereby reducing the tetragonal to cubic phase transition temperature. However, on further increasing the Al^{3+} content in NA4 (x = 0.4; Fig. 2) the first endothermic peak shifts to 641 K while the second endothermic peak which indicates the phase transition appears at 804 K. The phase transition temperature of samples with higher aluminium content, that is, for NA6 (x=0.6) and NA8 (x=0.8; Fig. 3) were probably above 873 K and could not ne recorded as the DSC studies could not be carried out above this temperature. The endothermic peak preceding the phase transition was, however, recorded for all the samples. The curves show that there is a shift to lower temperatures with increasing aluminium content. These endothermic peaks were not due to any chemical change as the X-ray patterns of the heat treated samples indicated them to be similar to the original ones. If it is due to a structural change, then it seems to be a reversible one, which has no effect on the electrical resistivity. Thermogravimetric analysis did not show any weight change in the studied temperature range either. Further investigations are being carried out using high temperature X-ray and DTA technique to determine the origin of this endothermic change preceding the phase transition.

From these results it may be concluded that like $CuCr_2O_4$, the aluminium substituted tetragonal spinels also undergo reversible thermal changes.

* * *

The authors thank Mrs P. P. De of Rubber Technology Centre, Indian Institute of Technology, Kharagpur for her help with the DSC studies.

Reference

1 E. Prince, Acta Crystallogr., 10 (1957) 554.
2 G. G. Robbrecht and C. M. Iserentant, Bull. SBP, 4(5) (1955) 347.
3 H. Ohmishi and T. Teranishi, J. Phys. Soc. Japan, 16 (1961) 35.
4 S. Miyahara, J. Phys. Soc. Japan, 17 Suppl. B (1962) 181.
5 P. J. Woztowicz, Phys. Review, 116 (1959) 32.
6 K. S. De, J. Ghose and K. S. R. C. Murthy, J. Solid State Chem., 43 (1982) 261.
7 K. S. De, J. Ghose and K. S. R. C. Murthy, J. Solid State Chem., 47 (1983) 264.

Zusammenfassung — Mittels DSC wurde ein aluminium-substituiertes Kupferchromitspinelloxid, $CuCr_{2-x}Al_xO_4$ mit x = 0,2–0,8 thermisch untersucht. Wird 20% des Cr durch Al ersetzt, sinkt die Phasenübergangstemperatur ab, bei weiterem Anwachsen des Aluminiumgehaltes steigt sie jedoch über die von $CuCr_2O_4$ hinaus an. Die Enthalpieänderung des Phasenüberganges steigt mit anwachsendem x allmählich an.

Резюме — Проведенное методом ДСК термическое исследование алюминий замещенной хромитмедной шпинели $CuCr_{2-x}Al_xO_4$ (x = 0,2–0,8) показало, что при 20% замещении хрома на алюминий, температура фазового перехода шпинели понижается, но при дальнейшем увеличении процентного содержания алюминия, температура фазового перехода становится более высокой, чем для $CuCr_2O_4$. Однако, изменение энтальпии фазового перехода постоянно уменьшается с увеличением x.