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THERMAL EFFECTS ON CATION DISTRIBUTION OF $CuCr_2O_4$

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Thermal studies on $CuCr_2O_4$ spinel indicated the phase present above 870 K to be cubic $CuCr_2O_4$. However, when the substance was quenched from 1023 K, 1173 K, 1273 K and 1473 K, only the tetragonal phase of $CuCr_2O_4$ was obtained. This is because the first-order, diffusionless, tetragonal to cubic phase transition at 865 K occurs reversibly at a very fast rate. The c/a ratio for $CuCr_2O_4$ present in the various quenched samples did not change when the quenching temperature was raised. A strong preference of the Cr^{3+} ion for the B site prevents it from interchanging sites with Cu^{2+} ions, thus keeping the lattice parameters c and a unchanged.

Copper(II) chromite ($CuCr_2O_4$) and copper(II) ferrite ($CuFe_2O_4$) are tetragonally distorted spinels with $c/a < 1$ and $c/a > 1$, and the transition to the cubic form occurs at 873 K and 633 K, respectively [1–4]. The distortion in these spinels is due to the Cu^{2+} Jahn–Teller ion [5, 6]. Cr^{3+} and Cu^{2+} both have a strong preference for octahedral coordination, but the former has a comparatively higher octahedral site preference energy [7] and so $Cu[Cr_2]O_4$ is a normal spinel, whereas $Fe[CuFe]O_4$ is almost an inverse spinel. However, the degree of inversion of $CuFe_2O_4$ changes at higher temperatures, due to a change in the cation distribution, as indicated by the c/a values of $CuFe_2O_4$ quenched from various temperatures, and cubic $CuFe_2O_4$ can be obtained by quenching from above 1033 K [4]. Such changes in cation distribution at higher temperatures may also be expected in $CuCr_2O_4$ and the present work is an attempt to study the thermal effect on the cation distribution of $CuCr_2O_4$, and the preparation of quenched cubic $CuCr_2O_4$.

Experimental

$CuCr_2O_4$, referred to as sample (1) in the text, was prepared from reagent grade copper(II) carbonate and chromium(III) oxide. The reactants were mixed thoroughly and fired in the form of pellets at 973 K for 12 h. The product was subsequently cooled to room temperature at a rate of 4°/min.

Samples Q_1,Q_2, Q_3 and Q_4: These were prepared by heating portions of sample (1) at 1023 K, 1173 K, 1273 K and 1423 K, respectively, for 1 h and then quenching to room temperature. Quenching was done by plunging the samples from the furnace into ice-cold water. The entire process took 10 to 15 sec. This procedure has been successfully adopted by us to obtain cubic $CuFe_2O_4$ and cubic Fe_2MoO_4 [8]. Sample Q_5 was prepared from cupric carbonate and chromic oxide. The reactants were mixed thoroughly and fired at 1273 K for 2 hrs, and the product was subsequently quenched to room temperature.

Room temperature X-ray diffraction patterns of sample (1), Q_1, Q_2, Q_3, Q_4 and Q_5 were taken with a Dron-I X-ray diffractometer, using CuK_α ($\lambda = 1.542$ Å) radiation and a nickel filter. A Philips X-ray diffractometer with an MRC model X-86-N3 high-temperature attachment described elsewhere [9] was used for X-ray diffractogram of sample (1) at 927 K*. Lattice parameters c and a were evaluated using Hull's charts for tetragonal structures. The error in c/a values thus obtained is within ±0.5%. DTA plots of sample (1) were obtained with a VEB Laborelectronic DTA apparatus between 298 K and 1273 K at a rate of 5°/min.

Results and discussion

Sample (1) is single phase tetragonal $CuCr_2O_4$, as shown by the room temperature X-ray pattern. The X-ray pattern at 927 K is that of cubic $CuCr_2O_4$. DTA plots of this sample indicated the tetragonal to cubic phase transition to occur between 858 and 868 K. Room temperature X-ray patterns of Q_2, Q_3, Q_4 and Q_5 showed the presence of Cr_2O_3 and $Cu_2Cr_2O_4$ in addition to the spinel phase.

These results clearly indicate that the phase transition occurs below 870 K, and cubic $CuCr_2O_4$ may be obtained by quenching $CuCr_2O_4$ from temperatures above 870 K) However, the X-ray diffraction pattern of sample Q_1 (quenched from 1023 K) is that of tetragonal $CuCr_2O_4$. Thus, in spite of the formation of cubic $CuCr_2O_4$ above 870 K, it is not possible to obtain it at room temperature by quenching. This may occur if the time required to cool the sample even by quenching is not short enough to prevent the cubic form from transforming back into the tetragonal form. From this, one can conclude that the tetragonal to cubic phase transformation in $CuCr_2O_4$ at 870 K, which is reported to be first order, diffusionless and reversible [4, 10], occurs at a fast rate. A similar behaviour has also been observed in $CuFe_2O_4$, which undergoes a diffusionless, tetragonal to cubic, first order phase transition at about 633 K. At higher temperatures, however, transition occurs by diffusion of Cu^{2+} ions from octahedral (B) sites to tetrahedral (A) sites, as shown by the change in the c/a ratio for high temperature quenched samples. This diffusion is considerable at 1033 K, and the c/a value of $CuFe_2O_4$ quenched from this temperature becomes equal to one. Hence, cubic $CuFe_2O_4$ was obtained by quenching from temperatures only above 1033 K and so cubic $CuCr_2O_4$ may probably be obtained by raising the quenching temperature. However, at temperatures above 1173 K $CuCr_2O_4$ decomposes into $Cu_2Cr_2O_4$ and Cr_2O_3

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[11]. Moreover, the *c*/*a* values of the $CuCr_2O_4$ phase in Q_2 and Q_3 indicate that the degree of tetragonality of $CuCr_2O_4$ remains unaltered with increasing quenching temperature. Thus, it appears that no appreciable interchange among A and B sites by Cu^{2+} and Cr^{3+} ions occurs in this spinel even at a temperature of 1273 K. The plausible reasons for this may be (i) strong affinity of Cr^{3+} ion for B site or (ii) a larger lattice energy of normal $CuCr_2O_4$ than that of inverse $CuCr_2O_4$ at all temperatures. Since the energy difference between normal and inverse spinels is quite small [12], (ii) may not be the deciding factor here and it is the strong affinity of Cr^{3+} ions for B sites, even at temperatures above 1200 K, which prevents the *c*/*a* ratio from changing in quenched $CuCr_2O_4$. Thus, it may be concluded that the tetragonal to cubic transition in $CuCr_2O_4$ is a first order, diffusionless, reversible and very fast transition, not only at 860 K but also at higher temperatures.

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Résumé — L'étude des propriétés terhmiques du spinelle $CuCr_2O_4$ indique que la phase présente au-dessus de 870 K consiste en $CuCr_2O_4$ cubique. Cependant, en refroidissant très rapidement à partir de 1023, 1173, 1273 et 1473 K on n'a obtenu que la phase tétragonale de $CuCr_2O_4$. Ce résultat est dû au fait que la transition sans diffusion du premier ordre de la phase tétragonale en la phase cubique s'effectue réversiblement, à une vitesse très élevée, à 865 K. Le rapport *c*/*a* de $CuCr_2O_4$ présent dans les divers prélèvements refroidis rapidement, n'a pas été modifié en augmentant la température de départ du refroidissement rapide. Une forte préférence de l'ion Cr^{3+} pour les sites B empêche celui-ci d'échanger ses sites avec les ions Cu^{2+}, maintenant ainsi les paramètres du réseau "*c*" et "*a*" inchangés.

Zusammenfassung — Thermische Untersuchungen am $CuCr_2O_4$ Spinell zeigten, daß die Phase oberhalb von 870 K aus kubischem $CuCr_2O_4$ besteht. Wenn jedoch von 1023 K, 1173 K, 1273 K und 1473 K schnell abgekühlt wurde, entsteht nur die tetragonale Phase von $CuCr_2O_4$. Der Grund hierfür ist, daß der diffusionsfreie Übergang erster Ordnung von der tetragonalen zur kubischen Phase bei 865 K reversibel mit sehr großer Geschwindigkeit vor sich geht. Das Verhältnis *c*/*a* von $CuCr_2O_4$ in den verschiedenen schnell abgekühlten Phasen verändert sich durch das Erhöhen der Ausgangstemperatur der Abkühlung nicht. Ein starker Vorrang des Cr^{3+}-Ions für die B Plätze verhindert den Austausch von Plätzen mit Cu^{2+}-Ionen, wodurch die Gitterparameter "*c*" und "*a*" unverändert bleiben.

Резюме — Термическое исследование шпинели $CuCr_2O_4$ показало, что выше 870 К для нее характерна кубическая структура. Однако, при охлаждении от температур 1023 К, 1173 К, 1273 К и 1473 К получается только тетрагональная фаза этой шпинели. Это является следствием того, что происходящий при 865 К бездиффузионный переход первого порядка тетрагональной фазы до кубической обратии с очень большой скоростью. Отношение параметров решетки c/a в различных охлажденных образцах шпинели не изменяется при повышении термпературы охлаждения. Значительное предпочтение иона Cr^{3+} к стороне Б подрешетки, предохраняет их от взаимного обмена с ионами Cu^{2+}, сохраняя талим образом неизменными параметры решетки «*c*» и «*a*».