

Thermal instability of the tetragonally distorted structure of copper-iron materials

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Abstract. Polycrystalline CuFe₂O₄ samples have been successfully prepared using a simple combustion method starting from citrate-nitrate precursors. All the ferrite samples studied were prepared at the same temperatures (300, 600, 900°C), but one series was slowly cooled from 900°C to room temperature, and another was quenched in solid CO₂. The nature of the structural transition in inverse spinels has been investigated by the synchrotron XRD technique. Slowly cooled samples are subjected to a diffusionless order-disorder transformation, due to the modified of the orientation of the Jahn-Teller distortions, and to the migration of Cu²⁺ ions from octahedral to tetrahedral sites. This phenomenon transforms the tetragonally distorted spinel structure (*F4₁/ddm*) into a cubic lattice (*Fd $\bar{3}$ m*). It occurs at temperatures from ~ 360°C to ~ 420°C.

Introduction

Copper ferrite is known to exist in tetragonal and cubic structure. Since Cu²⁺ is a Jahn-Teller ion (JT), it gives the anomalous favorable properties and also exhibits phase transition from tetragonal to cubic, depending on the temperature. The JT transition is argued to be order-disorder in character, but its exact nature is still not fully understood [1-4]. CuFe₂O₄ can be described as a cubic close-packed arrangement of oxygen ions, with Cu²⁺ and Fe³⁺ ions at two different crystallographic sites. From a structural standpoint, the formula unit of stoichiometric ferrite can be written as: (Cu_x²⁺Fe_{1-x}³⁺)_A[Cu_{1-x}²⁺Fe_{1+x}³⁺]_BO₄, where (A) denotes tetrahedral sites, [B] represents octahedral sites [2-3]. The parameter of inversion, x, is equal to 0 for inversion spinels, and to 1, when the spinel is normal. The temperature of the order-disorder transformation depend on the content of octahedral cupric ions and on the non-stoichiometry [5]. When the spinel is synthesized using classical ceramic technologies (sufficiently high temperature treatment of the initial oxides of the metal cations) with strict stoichiometry, it has a tetragonal structure of hausmannite type with crystal cell parameters *a* = 8.20Å and *c* = 8.60Å; *c/a* ~ 1.05. The *c/a* ratio can be changed via decreasing the copper concentration, or alternatively by heat treatment temperature and cooling rate [2]. Part of the

Cu^{2+} ions can be frozen in tetrahedral sites when the ferrites are quenched in air from above 400°C. The resulting ferrites show a smaller tetragonal distortion since a great proportion of the cupric ions are located on tetrahedral sites. Moreover, quenching treatments in air from temperature higher than 750°C lead to the formation of oxygen-deficient spinel ferrites, the nonstoichiometry arising from the reduction of some Cu^{2+} ions to Cu^+ ions [2, 6-7]. Some authors [2-3] consider that the Cu^+ ions are located in the interstitial sites (i.e., sites normally not occupied in the spinel structure). Recently, it has been found, that Cu-ferrite films can be stabilized in either tetragonal or cubic phase even at room temperature depending on deposition conditions and post-deposition heat treatment; the samples annealed in air at high temperatures (>800°C) and slowly cooled to room temperature were tetragonal, while those rapidly quenched in liquid nitrogen were cubic [8-9].

In this work, bulk copper ferrites samples were prepared by a simple combustion method using citrate-nitrate precursors. A citrate process as an alternative synthesis route has been successfully employed to synthesize such materials with improved properties for specific applications, such as magnetic powder for massive storage devices [10].

Experimental details

Powder samples with nominal composition CuFe_2O_4 were prepared by the combustion method. The stoichiometric quantities of starting materials, viz., $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, (Merck) and $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, were dissolved in distilled water. The mixed citrate-nitrate solution was heated at 120°C, with continuous stirring. After the evaporation of excess of water, a highly viscous gel was obtained. Ultimately, the powder was sintered in air at different temperatures (300, 600, 900°C) for 5h. After heating, the preparations were either cooled slowly (SC) to room temperature or rapidly quenched (QC) in solid CO_2 . The compounds formation and crystallinity of the materials were identified by XRD patterns, which were recorded on a Bruker D8 Advance diffractometer, with $\text{CuK}\alpha$ radiation. Finally, investigations on the temperature phase transition for product formed as a result of slow cooling of CuFe_2O_4 sample were carried out at the synchrotron beamline B2 at HASYLAB (DESY, Hamburg). The diffractometer was equipped with capillary furnace (STOE) and the on-site readable image-plate detector OBI. The polycrystalline samples placed in quartz capillaries of diameter 0.3 mm were heated and cooled at the temperature range from RT to 500°C. The wavelength, determined by calibration using a NIST silicon standard, was 0.493421 Å. Analysis of the XRD data was undertaken with a full-pattern fitting procedure based on the Rietveld method. Structure refinement was performed using *FullProf* program [11].

Results and discussion

The XRD studies show that the slow cooled and quenched in solid CO_2 samples displayed different thermal behavior (figure 1). In spite of the fact that a quench cooling process usually leads to the cubic structure of CuFe_2O_4 [2-3, 12], from structural analysis results based on the powder diffraction data we confirmed that the rapidly quenched sample showed a dominant cubic phase (76.4%) with a minor tetragonal component (23.6%). The slowly cooled sample crystallizes in the tetragonal system and at room temperature it could be indexed as a single-phase tetragonal spinel with space group $I4_1/amd$. The unit cell with lattice constants

$a = 5.8111(5)\text{\AA}$ and $c = 8.6888(9)\text{\AA}$ consists of four CuFe_2O_4 units. It is, however, much more informative to consider the crystal lattice as a tetragonally distorted spinel structure with the non-standard face-centred space group $F4_1/d\bar{d}m$. In that case the unit cell is doubled, with $a_s = 8.2387(5)\text{\AA}$ and $c/a_s = 1.055$, containing eight CuFe_2O_4 , and the copper ions occupy the octahedral sites of the spinel lattice, leading to a structural formula close to $(\text{Fe}^{3+})_A[\text{Cu}^{2+}\text{Fe}^{3+}]_B\text{O}_4$, corresponding to the equilibrium distortion at room temperature.

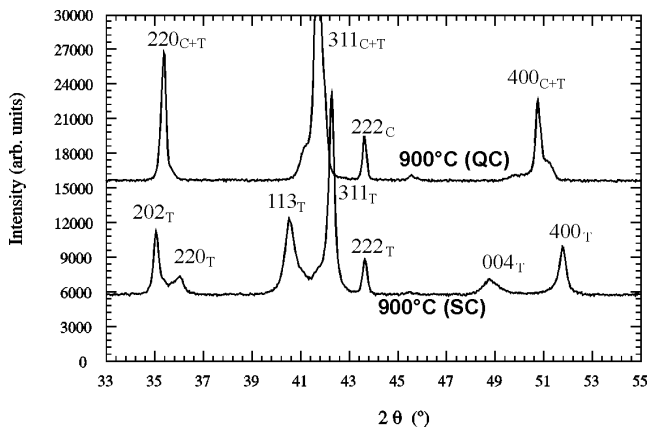


Figure 1. X-ray diffraction patterns of samples CuFe_2O_4 obtained by slow cooling (SC) or by rapid quenching in CO_2 (QC), measured at room temperature.

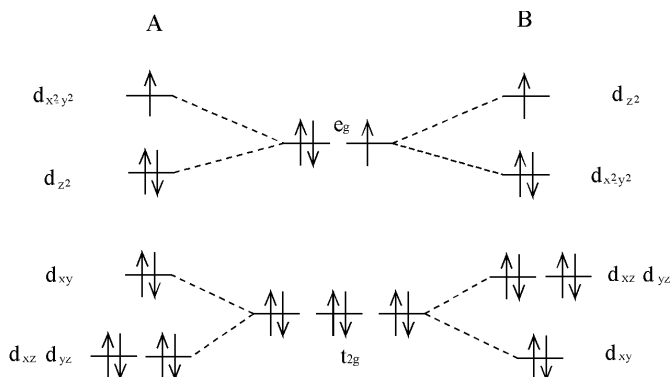


Figure 2. Orbital splitting of the d -energy levels within the copper ion (d^9) diagram showing the two possible Jahn-Teller distortion in an octahedral complex.

The tetragonal distortion in the CuFe_2O_4 compounds is attributed to the cooperative distortion that is driven by the octahedrally coordinated Cu^{2+} ($3d^9$) [2, 6, 13]. The electron configura-

ration of Cu^{2+} located at octahedral sites is $(t_{2g}^6)e_g^3$. While six electrons with antiparallely aligned spins occupy the triplet, three electrons on the orbital e_g can be distributed in two ways (double degeneracy) see figure 2. The first alternative (figure 2B) leads to an axially flattened octahedron ($c/a < 1$); the second one (figure 2A) causes elongating of the octahedron ($c/a > 1$) e.g., CuFe_2O_4 .

Investigations of the thermal phase transition of the product formed as a result of slow cooling of copper ferrite sample were carried out at the synchrotron beamline B2 at HASYLAB (DESY, Hamburg).

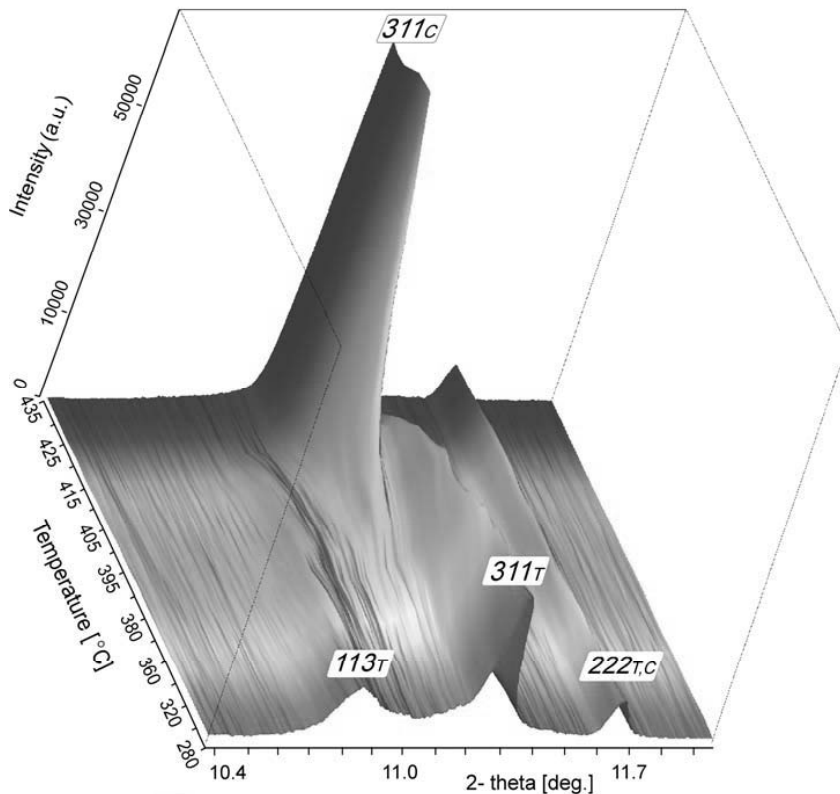


Figure 3. Temperature evolution of the X-ray diffraction patterns for CuFe_2O_4 (SC). Data were measured at beamline B2, Synchrotron DESY HASYLAB, Hamburg. The shift of reflections 113_T , 311_T at the tetragonal \rightarrow cubic phase transition can clearly be observed. For the graphic representation the program EVA (DIFFRAC plus BASIC Evaluation Package, Bruker AXS) was used.

The synchrotron powder diffraction scans (figure 3) reveal that the structural phase transition at approximately $\sim 340^\circ\text{C}$ to $\sim 420^\circ\text{C}$ is manifested by the shift and disappearance of the reflections 113_T , 311_T (tetragonally distorted spinel, $F4_1/ddm$) and appearance of a new re-

flection 311_C (cubic spinel, $Fd\bar{3}m$) in the investigated temperature range. Evidence is given that above 420°C the JT-distortion disappears in the structure.

Annealing treatment can modify the cationic distribution in the spinel lattice. Structural analysis results indicated that above 350°C copper ions partially occupy the tetrahedral sites and the structural ($F4_1/ddm$) \rightarrow ($Fd\bar{3}m$) phase transition appears. On heating the sample, the copper ions migrate to tetrahedral sites (figure 4A) and the structural formula of the ferrite changes to $(\text{Cu}_x^{2+}\text{Fe}_{1-x}^{3+})_A[\text{Cu}_{1-x}^{2+}\text{Fe}_{1+x}^{3+}]_B\text{O}_4$. The resulting decrease in Cu^{2+} ions in the octahedral sites gives rise to a less distorted crystalline structure. The redistribution Cu^{2+} ions in the spinel lattice is revealed by the variation of the tetragonal distortion (c/a of the unit cell). For the slow cooled sample, the c/a ratio of the tetragonal spinel phase is reported in figure 4A as a function of temperature. In this case, the c/a ratio diminishes as the temperature increases up to 415°C . In particular, Cu^{2+} intersite cationic migration is also correlated with the decrease in the c/a ratio. More precisely, the migration of Cu^{2+} ions from octahedral to tetrahedral sites is responsible for this decrease. It has been shown that placed in the octahedral sites Cu^{2+} ions migrate to the tetrahedral sites. Such migration occurs above 350°C (figure 4B).

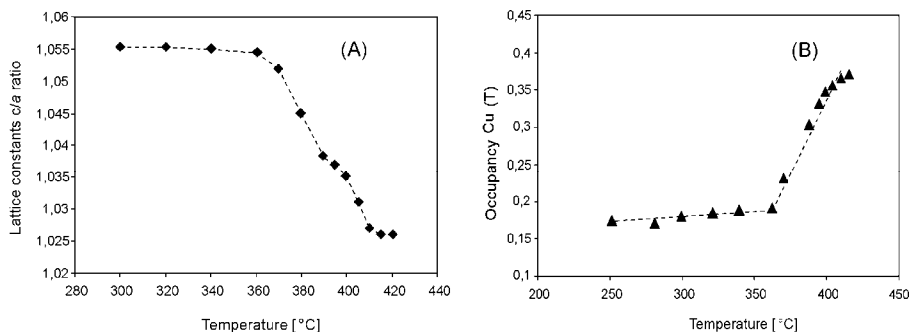


Figure 4. Evolution of the c/a ratio for the tetragonally distorted spinel phase CuFe_2O_4 (SC) as a function of temperature (A), and the occupancy of Cu^{2+} at the spinel tetrahedral sites (B). Dashed lines are guides for the eyes.

Concluding remarks

Polycrystalline CuFe_2O_4 samples have been successfully prepared by a simple combustion method using citrate-nitrate precursors. All the ferrite samples studied were prepared at the same temperatures, but one series was slowly cooled from 900°C to room temperature, and another was quenched from 900°C . The most striking effect observed in this experiment was the dependence of the reaction products on the preparation conditions. The SC and QC sample displayed different thermal behavior. The nature of the structural transition in inverse spinels has been investigated using the synchrotron XRD technique. Slow cooled samples are subjected to order-disorder transformation, due to the migration Cu^{2+} from octahedral to tetrahedral sites. This phenomenon transforms the tetragonally distorted spinel structure

($F4_1/ddm$) into a cubic lattice ($Fd\bar{3}m$). The tetragonal→cubic phase transition occurs in the temperature range from $\sim 360^\circ\text{C}$ to $\sim 420^\circ\text{C}$. The resulting cubic lattice cannot be stabilized at room temperature by quenching. Annealing can modify the cationic distribution in spinel lattice - it has been shown that placed in the octahedral sites Cu ions migrate to the tetrahedral positions. The resulting decrease in copper ions in the octahedral sublattice gives rise to a less distorted crystalline structure, and above 420°C the structural JT-distortion disappears.

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