Low temperature structural studies of zinc substituted copper ferrite using synchrotron X-ray powder diffraction

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Abstract. Two samples of the spinel ferrite system $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ with $x = 0.0$ and $x = 0.1$ were synthesised by a combustion method. The effect of zinc ion substitution for copper on low temperature structural properties of CuFe_2O_4 ferrite is reported. Synchrotron X-ray measurements have been performed in the temperature range 300K – 15K. It was found that for $\text{Cu}_{0.9}\text{Zn}_{0.1}\text{Fe}_2\text{O}_4$, the sample begins to transform from cubic to tetragonal at about 250K, with the coexistence of both phases down to 15K. No phase transition was observed in the CuFe_2O_4 spinel below room temperature.

Introduction

Spinel ferrites, which have vast application from microwave to radio frequencies is of great importance from both fundamental and applied research points of view [1-5]. The spinel structure is based on a cubic close-packed array of oxide ions (32e), with $\frac{1}{2}$ of the octahedral sites (16d) and $\frac{1}{4}$ of tetrahedral sites (8a) occupied by cations. The general chemical formula is AB_2O_4 , and there are two ideal structures with different cation ordering schemes: $(\text{A})_{8a}[\text{B}_2]_{16d}\text{O}_4$ (*normal spinel*) and $(\text{B})_{8a}[\text{AB}]_{16d}\text{O}_4$ (*inverse spinel*). Copper ferrite crystallizes in a tetragonal (T) or cubic (C) symmetry depending on the cation distribution among interstitial sites of spinel structure. The T-phase is an inverse spinel, with the cation distribution that can be presented by the formula: $(\text{Fe})[\text{CuFe}]\text{O}_4$. The Cu^{2+} ions occur copper only octahedral B-sites and this causes the tetragonal distortion due to the cooperative Jahn-Teller effect [6-7]. The Jahn-Teller distortion in copper ferrite has established that the critical number of octahedral site Cu^{2+} ions per formula unit for a cooperative distortion to tetragonal symmetry at room temperature is 0.8 [7]. One way to reduce the Jahn-Teller effect, could be the addition of other 3d-cations to the tetragonal CuFe_2O_4 lattice [3,7]. Since the zinc ion has a stronger tetrahedral site preference than Fe^{3+} in the normal spinel $\text{Zn}[\text{Fe}_2]\text{O}_4$, we may assume it also does so in Zn^{2+} doped copper ferrite. In this work, the structural change with decreasing temperature below ambient condition polycrystalline $\text{Cu}_{0.9}\text{Zn}_{0.1}\text{Fe}_2\text{O}_4$ compound has been compared with that of undoped copper ferrite.

Experimental details

Powder samples having nominal composition CuFe_2O_4 and $\text{Cu}_{0.9}\text{Zn}_{0.1}\text{Fe}_2\text{O}_4$ were prepared by a combustion method using citrate-nitrate precursors. The stoichiometric quantities of starting materials, viz., $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{C}_6\text{H}_8\text{O}_7 \cdot 6\text{H}_2\text{O}$ (Merck), were dissolved in distilled water. The mixed citrate-nitrate solution was heated at 120°C with continuous stirring. After evaporation of excess of water a highly viscous gel was obtained. Ultimately, the particles were sintered at different temperatures (300 , 600 , 900°C) for five hours and slow cooled down to room temperature. The investigations on the temperature phase transition, using high-resolution powder diffractometer, equipped with He-cryostat and Image Plate OBI detector were carried out at the Desy/HASYLAB at the B2 beam-line [8-9]. The wavelength applied during measurements, determined by calibration using NIST silicon standard, was $0.49342(1)\text{\AA}$. The polycrystalline samples placed in glass capillaries of diameter 0.3 mm were cooled within a temperature range from 300 K to 15 K . Refinement of the diffraction data, collected as a function 2-theta were performed using the FullProf [10] and UnitCell [11-12] programs. The program WinPLOTR-2006 (version 0.5 – April 2009) was used for the powder diffraction graphic representation [13].

Results and discussion

Figure 1 displays the RT XRD patterns of the as-prepared samples CuFe_2O_4 , (A) and $\text{Cu}_{0.9}\text{Zn}_{0.1}\text{Fe}_2\text{O}_4$, (B). The results of indexing XRD patterns has shown that the nominal composition structures with different concentrations are single phase with no additional lines corresponding to any other phase. Tetragonal structure is obtained only for copper ferrite and all of the peaks are indexed with space group $I4_1amd$ in the standard data (JCPDS no. 34-0425). In our communication we use the face-centred ($F4_1ddm$) unit cell, with the eight CuFe_2O_4 content, as in the spinel ($Fd3m$) unit cell, allows us to demonstrate the degree of tetragonal distortion of the crystal lattice.

Figure 1. X-ray powder diffraction patterns for A: CuFe_2O_4 (indexing for the tetragonal $F4_1ddm$ space group) and B: $\text{Cu}_{0.9}\text{Zn}_{0.1}\text{Fe}_2\text{O}_4$ (indexing for the cubic $Fd3m$ space group) at room temperature.

The second compound ($\text{Cu}_{0.9}\text{Zn}_{0.1}\text{Fe}_2\text{O}_4$), crystallizes in the cubic space group $Fd\bar{3}m$. The structure refinement by the Rietveld method was carried out to determine the cation distribution over tetrahedral and octahedral spinel sites at the room temperature (figure 2). The distribution of cations in $\text{Cu}_{0.9}\text{Zn}_{0.1}\text{Fe}_2\text{O}_4$ can be expressed as $(\text{Cu}_{0.071}\text{Zn}_{0.125}\text{Fe}_{0.804})_{\text{Tet}}[\text{Cu}_{0.804}\text{Fe}_{1.196}]_{\text{Oct}}\text{O}_4$ and shows a critical number of copper ions in the octahedral spinel sublattice for the tetragonal symmetry in copper ferros spinel. Substitution with zinc ions clearly restrains Jahn-Teller effect, owing to the reduction of $\text{Cu}^{2+}/\text{Fe}^{3+}$ ratio in octahedral sites in CuFe_2O_4 . The unit cell volume is found to increase with addition of zinc in copper ferrite (table 1). This is due to the fact that the ionic radius of Zn^{2+} (0.83 Å) is greater than that of Cu^{2+} (0.70 Å)[14].

Figure 2. Observed, calculated and difference profiles from the Rietveld analysis of X-ray powder diffraction data of the sample $\text{Cu}_{0.9}\text{Zn}_{0.1}\text{Fe}_2\text{O}_4$, at the room temperature.

Table 1. Lattice parameters and volume for samples with tetragonal and cubic unit cell at the room temperature. a^* and V^* - value converted to $F4_1ddm$ space group.

Sample	c (Å)	a (Å)	c/a	V (Å ³)
CuFe_2O_4	8.7047(8)	8.2307(3)*	1.057	589.69 (0.11)*
$\text{Cu}_{0.9}\text{Zn}_{0.1}\text{Fe}_2\text{O}_4$	-	8.3943(1)	1.000	591.498 (0.012)

The structure of the copper ferrite can be changed via decreasing the copper concentration, or alternatively, by temperature treatments. Annealing can modify the cationic distribution in spinel lattice – Cu^{2+} ions from octahedral sites migrate to the tetragonal positions. This phenomenon transforms the tetragonally distorted CuFe_2O_4 structure into a cubic lattice in the temperature range from $\sim 360^\circ\text{C}$ to $\sim 420^\circ\text{C}$ [15]. In a previous work, we have studied the structure properties of small quantities zinc ions substituted CuFe_2O_4 , which revealed that the

structural transformation for $\text{Cu}_{0.95}\text{Zn}_{0.05}\text{Fe}_2\text{O}_4$ from tetragonal to cubic space group occurs in the temperature range from $\sim 50^\circ\text{C}$ to $\sim 200^\circ\text{C}$ [16].

Research in the framework of Hasylab (Desy, Hamburg) project made possible the investigations on the low temperature phase transition for both samples using the high-resolution X-ray diffractometer. Figure 3 shows the (113), (311) and (222) reflections for CuFe_2O_4 , from the synchrotron X-ray powder diffraction data, recorded in the temperature range from 300K to 15K. There is no phase transition effect with decreasing temperature, and the sample remains tetragonal in the whole temperature range. The volume parameter, V , of the tetragonal phase ($F4_1ddm$) decreases with temperature from $589.69(0.11) \text{ \AA}^3$ to $588.04(0.11) \text{ \AA}^3$.

Figure 3. Low temperature evolution of the X-ray powder diffraction patterns for CuFe_2O_4 .

Low temperature X-ray diffraction patterns for the $\text{Cu}_{0.9}\text{Zn}_{0.1}\text{Fe}_2\text{O}_4$ oxide are shown in figure 4. With decreasing temperature the formation of the tetragonal polymorph was indicated at about 255K. The splitting of the lines and their intensity reveal clearly the tetragonal structure (space group $F4_1ddm$). The coexistence of two phases in a whole measurements range of temperature may be observed.

Figure 4. Low temperature evolution of the X-ray powder diffraction patterns for $\text{Cu}_{0.9}\text{Zn}_{0.1}\text{Fe}_2\text{O}_4$.

Concluding remarks

The CuFe_2O_4 and $\text{Cu}_{0.9}\text{Zn}_{0.1}\text{Fe}_2\text{O}_4$ were synthesized by a combustion method using citrate-nitrate precursors. The formation of the tetragonal CuFe_2O_4 , and the cubic $\text{Cu}_{0.9}\text{Zn}_{0.1}\text{Fe}_2\text{O}_4$ phases were confirmed by X-ray diffraction studies. Substitution with Zn^{2+} ions reduces the total concentration of Cu^{2+} , suppressing the Jahn-Teller effect, and stabilizes the cubic structure. The substitution of divalent zinc ions in $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ spinel oxides increases the lat-

tice parameters of the system. No phase transition has been observed in the CuFe_2O_4 spinel below room temperature. The sample remains tetragonal when cooled in the range 300K – 15K. On the other hand the compound with small quantities of Zn^{2+} ions undergoes at 250K temperature region a structural transformation from cubic ($Fd3m$) to tetragonal ($F4_1ddm$) lattice, with the coexistence of both phases down to 15K. Further investigation on the structure properties of the $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ system are indispensable.

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