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Low-temperature synthesis of $CuFeO_2$ (delafossite) at 70 °C: A new process solely by precipitation and ageing

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ABSTRACT

This study presents a new low temperature synthesis method to obtain pure delafossite ($Cu^{1+}Fe^{3+}O_2$) at a temperature of 70 °C within 24 h. For the first time delafossite is synthesized solely by precipitation and subsequent ageing process and without usage of any additives controlling the oxidation state of copper. The synthesized material, called LT-delafossite, consists of pure $Cu^{1+}Fe^{3+}O_2$ exclusive of any side products. Rietveld analysis confirms the presence of both 3R (space group (SG): ***R***-3m) and 2H (SG: **P6$_3$**/mmc) polytypes in LT-delafossite. Electron microscopy images show nanometer-sized hexagonal plates with a diameter <500 nm and a thickness of <30 nm. Measurements of the magnetic susceptibility from 2 K to 350 K in zero-field show one peak ~18.5 K, which is attributed to an AFM phase transition. Zero-field-cooled magnetization data between -14 T and $+14$ T at 2 K revealed an s-shape form around the origin having no remanent magnetization.

1. Introduction

Delafossite ($Cu^{1+}Fe^{3+}O_2$) is a stable compound in the Cu–Fe–O system with nonmagnetic monovalent metal cations and magnetic trivalent cations [1]. Its structure is constructed with alternating layers of slightly distorted edge-shared $Fe^{3+}O_6$ octahedra and 2-dimensional (2D) close-packed Cu^{1+} (Fig. 1). Both Fe^{3+} and Cu^{1+} layers are connected with linear O–Cu^{1+}–O bonds perpendicular to their 2D sheets. Each O^{2-} is bonded to one Cu^{1+} and three Fe^{3+}. According to the stacking sequences of those Fe^{3+} and Cu^{1+} layers delafossite crystallizes in two polytypes: the rhombohedral phase 3R-delafossite (SG # 166: ***R***-3 m) and the hexagonal phase 2H-delafossite (SG # 194: **P6$_3$**/mmc). $CuFeO_2$ also exists in a third phase ($Cu^{2+}Fe^{2+}O_2$) containing Cu^{2+} and Fe^{2+} crystallizing in ***R***-3m.

Delafossite-type oxides (ABO_2) have received much attention due to the flexible chemistry, variability of size and valence charge at sites of A and B cations, enabling diverse technical applications, e.g. as a catalyst, in p-type conduction oxides, as a cathode in Li-ion batteries [1–3], or as luminescent materials [4,5]. Furthermore, delafossite has special magnetic [6], photo- and electrochemical [7] and antiviral [8] properties. A strong anisotropy of those structural and physical properties makes this family of materials highly interesting. Therefore various methods for the synthesis of the delafossite-type materials have been developed.

High-temperature (>500 °C) syntheses of delafossite-type compounds have been preferred to prevent side products. Syntheses have been reported via solid state reactions at 1100–1200 °C [2,6,9], sol–gel methods with high temperature after treatment at 900 °C [10] and hydrothermal syntheses at 500–700 °C and 3000 atm [11]. Recently two hydrothermal methods were presented to prepare pure $CuFeO_2$ (3R-delafossite) powders (1) in autoclaves at a temperature of 180 °C in the presence of propionaldehyde as reducing agent [8] or (2) at a temperature of 280 °C with an ageing time of 96 h [12]. Using hydrothermal synthesis at >200 °C 2H-delafossite was formed, together with Cu_2O, as a byproduct during syntheses of iron–copper–arsenates [13].

In this study we present a new low-energy and short-time consuming synthesis method to gain high crystalline $Cu^{1+}Fe^{3+}O_2$ (we call LT-delafossite) at 70 °C without applying any additional

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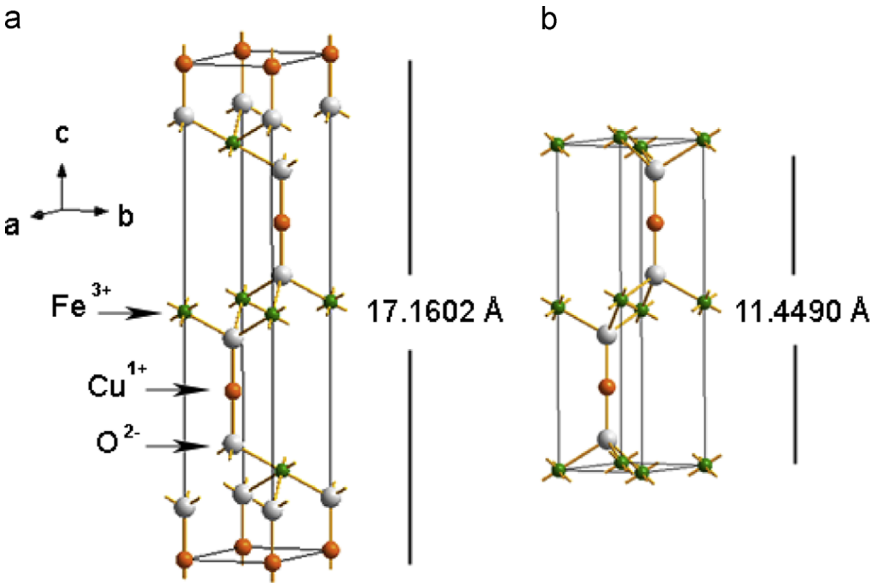

Fig. 1. Two polytypes of delafossite $Cu^{1+}Fe^{3+}O_2$; (a) 3R-polytype in ***R***-3m; (b) 2H-polytype in $\mathbf{P6_3/mmc}$.

reducing agent. This new, effective synthesis route of $Cu^{1+}Fe^{3+}O_2$ as well as characterization are described herein.

2. Experimental

For the synthesis, 9.8218 g $CuSO_4 \cdot 5\ H_2O$ (VWR, analytical grade) were dissolved in 250 ml water with high purity (5 μS/cm). Then the solution was heated up to a reaction temperature of 70 °C. While continuously stirring, $FeSO_4 \cdot 7\ H_2O$ (VWR, analytical grade) was added to the starting solution to reach a mole ratio Cu^{2+}:Fe^{2+} = 1:1. As a next step a pH value of 11 was adjusted using Na(OH) (VWR, analytical grade). The solution was continuously stirred and kept at 70 °C for this step. Afterwards the solution containing the precipitates was filled in a conventional laboratory bottle. Then the bottle was sealed and stored at 70 °C for 24 h or 7 days.

The synthesized fine particles were filtered, washed 3 times with water (5 μS/cm), and dried at room temperature (RT) for 24 h. For pH measurements and adjustments a Titrator TL 7000 (SI Analytics) was used. Within one synthesis > 5 g delafossite were produced.

Scanning electron microscopy (SEM) and energy dispersive analysis (EDS) was performed at the Department of Experimental Physics, University of Augsburg on a type GEMINI 982 manufactured by LEO (now Zeiss). For SEM the sample was pre-treated with isopropanol in an ultrasonic bath for 4 min. The solution was deposited at a Si single crystal waver and coated with 10 nm Au to ensure good electron conduction. SEM images were taken at an acceleration voltage of 20 kV in the working distance of 8–9 mm. Energy dispersive spectra (EDS) were analyzed with the software package Inca.

X-ray powder diffraction (XRD) data were collected in Debye–Scherrer geometry using Mo$K_{\alpha 1}$ radiation on a GE diffractometer, XRD 3003 TT. The diffractometer is located at the Department of Earth and Environmental Sciences, Ludwig-Maximilians-University Munich. Using a position-sensitive, semiconductor-based 1D-detector (Meteor) all XRD data sets of LT-delafossite samples were collected three times in a 2θ range of 12–34° in every 0.013° (2θ) steps for an exposure time of 100 s/count and summed to increase the signal/noise ratio. The glass capillary sample holder (⌀ 0.5 mm) was rotated during the data collection for better counting statistics. Qualitative phase identification was conducted by comparison of XRD data with the data bank Inorganic Crystal Structure Database on its user interface program, FindIt [14]. Quantitative phase analysis was succeeded by Rietveld refinements with XRD data using the program package FullProf Suite [15].

Fourier transform infrared spectroscopy (FTIR) was applied to identify low crystalline phases. For FTIR analysis 1 mg sample was pressed in KBr pellets. All FTIR spectra were acquired on a spectrometer, EQUINOX55 (Bruker) located at the Department of Earth and Environmental Sciences, Ludwig-Maximilians-Universität München. Raw spectra were corrected for atmospheric influences and baseline corrected before fitting absorption bands using the software Peakfit. The peak assignment was done based on the RRUFF database. Additionally, a reference spectrum was attained with a naturally occurring delafossite sample originating from Bisbee, Arizona for qualitative assignment of FTIR bands observed in synthesized LT-delafossite samples.

Transmission electron microscopy (TEM) and energy dispersive analyses (EDS) were carried out using a JEOL JEM-2100F transmission electron microscope (located at the Department of Experimental Physics, University of Augsburg) equipped both with a Gatan imaging filter for energy filtered microscopy and an EDAX EDS detector for recording EDS spectra. Samples were prepared on Au-grids to avoid Cu-signals from the grid in EDS measurements. Particle size and shape investigations were carried out in the imaging mode, supplemented by electron diffraction for structural analysis. Electron diffraction patterns were recorded using the image plate scanner system DITABIS.

Magnetic responses at RT to the applied magnetic field between −900 mT and +900 mT were characterized on a variable field translation balance (VFTB) located on the Department of Earth and Environmental Sciences, Ludwig-Maximilians-Universität München.

Physical properties measurement system of Quantum Design (PPMS) was used to record zero-field-cooled (ZFC) AC susceptibility at 1 KHz with 1 mT amplitude from 350 K down to 2 K, as well as ZFC magnetization between −14 T and +14 T at 2 K. The PPMS is located at the Physics Department, Technical University Munich.

Mößbauer spectra were recorded at the Department of Materials Research & Physics, University of Salzburg using a