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Synthesis and characterization of $\text{CuFeO}_{2+\delta}$ delafossite powders

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Abstract

Effects of oxygen off-stoichiometry have been investigated on $\text{CuFeO}_{2+\delta}$ delafossite-type powders prepared by solid state reaction. Materials annealed at different temperatures under air atmosphere were compared. Thermogravimetric analysis coupled with X-ray structural analysis showed that a powdered CuFeO_2 can be oxidized up to $\text{CuFeO}_{2+\delta}$ with $\delta=0.18$. Electrical measurements confirm the existence of oxidized $\text{CuFeO}_{2+\delta}$ phases. Particular attention is paid to the correlation between oxidation process and phase stabilities in the CuFeO_2 and copper spinel phase system.

Keywords: Delafossite; Copper iron oxide; Non-stoichiometry; Spinel; Ferrite

1. Introduction

Off-stoichiometry in metal oxides has been of great interest because it significantly affects the chemical and physical properties of solid state materials [1]. This way, ABO_2 delafossite compounds are quite interesting materials because of their capabilities to be stabilized with a large number of A and B cations and within a wide range of off-stoichiometry values. Delafossite structure can accommodate trivalent cations B^{3+} with ionic radii varying from 0.535 Å (octahedral Al^{3+} ion) up to 1.032 Å (octahedral La^{3+} ion) [2,3], according to Shannon's table of effective ionic radii [4]. They can be perfectly stoichiometric with the ABO_2 formula as well as highly oxidized with the $ABO_{2+\delta}$ formula whereas δ can reach 0.50 [5–7].

In delafossite structure, BO_6 octahedra are edge-connected leading to BO_2 layers, which are stacked along the c axis of the hexagonal structure (Fig. 1). The BO_2 layers can be stacked in different ways along the c direction, so that delafossites crystallize in the hexagonal 2H (space group: $P6_3/mmc$) or rhombohedral 3R (space group: $R\bar{3}m$) structures. These BO_2 layers are connected together with triangular metallic planes of monovalent element A whereas $A = \{\text{Cu}, \text{Pt}, \text{Pd}, \text{Ag}\}$. This A^+

cation is linearly twofold-coordinated with oxygen of upper and lower BO_6 layers.

Delafossite compounds have attracted much attention due to their unusual magnetic and conducting properties for more than 30 years [8–10]. More recently, the first report of p-type conductivity in transparent CuAlO_2 thin films [11] has attracted much attention and several similar thin films that share its delafossite structure have been reported with various interesting conductivities and transparencies [12–16]. Therefore, delafossite compounds ABO_2 are interesting oxides for fundamental researches on non-stoichiometry and mixed valencies as well as interesting compounds for modern technology applications.

The copper mixed valencies $\text{Cu}^I/\text{Cu}^{II}$ govern transport properties in delafossite compounds [17,18]. In $\text{CuBO}_{2+\delta}$, $\text{Cu}^I/\text{Cu}^{II}$ ratio is directly controlled by the δ off-stoichiometry value. The copper delafossite compounds CuBO_2 have been shown to accommodate oxygen species into the crystal lattice. A large amount of interstitial extra oxygen can be inserted into triangular Cu planes for CuMO_2 with large M^{3+} cations. Moreover, structural studies show that ordered delafossite-type superoxides can be obtained with $\delta \approx 0.33$ or $\delta \geq 0.50$ [5–7,19–21] with $M = \{\text{Y}$ or lanthanides $\}$. Contrary thereto, CuMO_2 with small M^{3+} cations cannot accommodate a large amount of extra oxygen. Zhao et al. [22,23] have only obtained pure single crystal phase of $\text{CuFeO}_{2+\delta}$ up to $\delta=0.08$. No other studies reported off-stoichiometric values for CuFeO_2 .

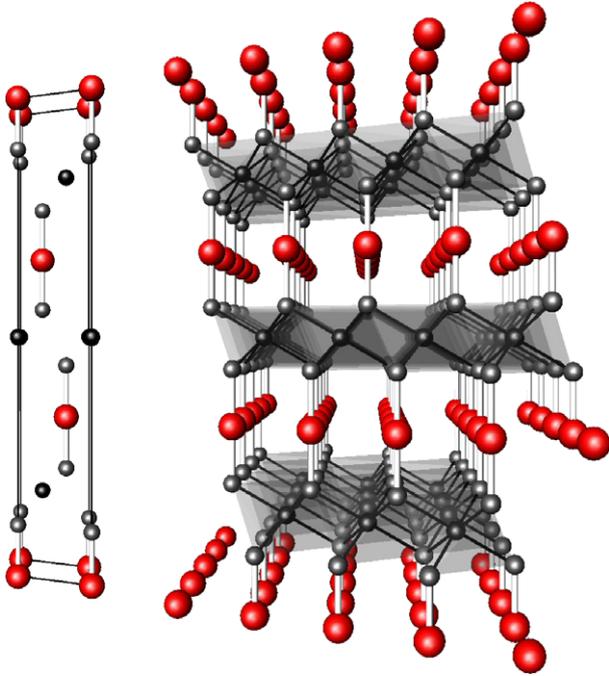


Fig. 1. 3R-CuFeO₂ delafossite structure with the hexagonal *c* axis vertical.

The great interest of delafossite compounds is without any doubt connected to the TCO applications, which involve delafossite with small *B* cations for p-type conductivity and optical transparency. As a result, oxidizing CuBO₂ compounds with small *B* cations without changing the crystal symmetry is an important challenge.

The purpose of this present work was to demonstrate the possibility to prepare CuFeO_{2+δ} with high δ ($\delta > 0.1$) on the basis of simple thermogravimetric and structural analyses.

2. Experimental

Polycrystalline CuFeO₂ was synthesized by solid state reaction from stoichiometric mixtures of Cu₂O and Fe₂O₃ commercial powders. The starting mixture has been heated in an argon flow at 900 °C for 24 h (150 °C/h heating rate) with intermediate regrinding and leads to the so-called as-synthesized CuFeO₂ compound. This as-synthesized CuFeO₂ was then annealed in air in the 0 < *T* < 800 °C temperature range (150 °C/h heating rate) and immediately cooled down to room temperature. The samples are annotated in the following by the letter A for annealed and the corresponding temperature leading to, for example, A-400 for the 400 °C air annealed sample.

Powder X-ray diffraction (PXRD) patterns for phase analysis and Rietveld refinements are obtained at room temperature using a Seifert XRD 3003 TT diffractometer employing copper radiations as the X-ray source. Fluorescence is avoided by using a graphite secondary monochromator. The Rietveld method implemented in the FullProf program [24] was used for crystal structure refinements and pattern matching analysis. Specific quantitative phase analysis by PXRD was performed on multiphase compositions

according to the equation $c_k = \frac{s_k(ZMV)_k}{\sum s_i(ZMV)_i}$ [25] where c_k (or wt.%) is the mass concentration of phase *k*, s_k is the phase depending refundable Rietveld scale factor and ZMV are the number, mass and volume of the formula unit in each phase, respectively.

The thermal analysis of the as-synthesized and annealed samples was carried out in a TG-DTA 92 SETARAM. The samples were first treated at 150 °C for 2 h in air to eliminate adsorbed water, and then heated at 5 °C/min up to 900 °C under the same atmosphere.

DC electrical properties were qualitatively estimated with a specific apparatus: 0.3 g of powder was filled into an insulating cylindrical matrix in between two metallic copper probes of 1 cm in diameter. External pressure was then applied on probes with an Eurolabo 25011 uniaxial press. Pressure was slowly increased up to 30 bars with constant steps in time. The measurements were carried out using a Keithley 175 A autoranging multimeter. As the pressure increases resistance quickly decreases because of a closer contact of the grains. At high pressure, resistance values tend to stabilize at an intrinsic value that is reproducible: it is then possible to compare homogeneous series of compounds. The value shown was measured once the resistance had become unaffected by the increase in pressure.

3. Results and discussion

The X-ray pattern of the as-synthesized sample shows that it is delafossite single phase (Fig. 2). The CuFeO₂ phase remains PXRD pure until *T*=480 °C. At 480 °C, a very small peak which corresponds to the *111* Bragg peak of tenorite (CuO), appears at $2\theta \approx 38.8^\circ$. For temperature *T* ≥ 500 °C, a third phase identified as copper spinel ferrite also appears (see inset Fig. 2). As temperature increases up to 900 °C, tenorite and copper ferrite rates increase within a proportional decrease of delafossite phase. The weight, and then the molar, percentage of each phase can be determined by PXRD quantitative phase analysis. The results are summarized in Table 1 within *T* ≤ 550 °C temperature

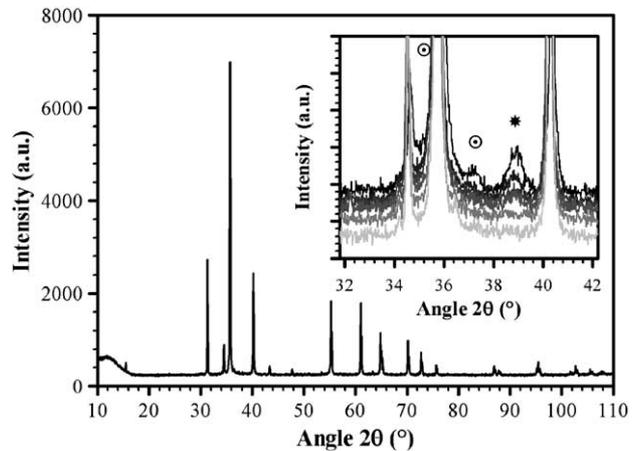


Fig. 2. PXRD pattern of as-synthesized sample with pure CuFeO₂ phase. Inset, zoom of the annealed samples at *T*=400 (light grey), 450, 480, 500, 520 and 550 °C (black) with appearance of tenorite (*) and spinel (○) extra phases.

Table 1
Thermogravimetric and PXRD data for $\text{CuFeO}_{2+\delta}$ over-stoichiometry calculations

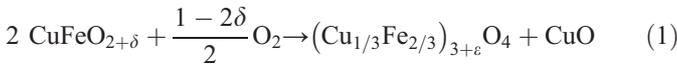
Sample	$\Delta m^{\text{th}} - \Delta m^{\text{exp}}$ (%)	Phases	δ^{tot}	CuFeO_2 (% ^{mol})	$\text{CuFeO}_{2+\delta}$
As-syn.	0.084	Delafossite	0.008	100	$\text{CuFeO}_{2.008}$
A-400	0.084	Delafossite	0.008	100	$\text{CuFeO}_{2.008}$
A-450	0.114	Delafossite	0.011	100	$\text{CuFeO}_{2.011}$
A-480	0.494	Delafossite + ϵ CuO	0.047	≈ 100	$\text{CuFeO}_{2.047}$
A-500	0.654	Delafossite + CuO + CuFe_2O_4	0.062	99	$\text{CuFeO}_{2.061}$
A-520	1.295	Delafossite + CuO + CuFe_2O_4	0.122	93	$\text{CuFeO}_{2.114}$
A-550	1.874	Delafossite + CuO + CuFe_2O_4	0.177	85	$\text{CuFeO}_{2.150}$

range. At 900 °C, only CuFe_2O_4 and CuO phases are observed. One can note that for the A-480 and the A-500 samples, tenorite and spinel phases are present (see inset Fig. 2) but not really quantifiable by PXRD quantitative analysis due to the weakness of the diffraction peaks. In Table 1, these oxidized phases are fixed at 1% that is the accuracy of the technique.

The 3R-delafossite phase is refined in the rhombohedral $R\bar{3}m$ (N°166) space group using the hexagonal axes. It leads to unit cell parameters a and c summarized in Table 2. The oxygen atoms are located in a $6c$ crystallographic site with the θ , θ , z coordinates. The oxygen z value is the only refinable parameter for atomic positions in CuFeO_2 and then directly governs the interatomic distances: $d(\text{Fe}-\text{O})$ and $d(\text{Cu}-\text{O})$. These distances are in accordance with those calculated with the Shannon ionic radii [4] whereas $d(\text{Fe}-\text{O})=2.04$ Å and $d(\text{Cu}-\text{O})=1.86$ Å.

As temperature increases, the unit cell parameters are quite constant until $T=400$ °C. For higher temperature, the a parameter is quite constant and the c parameter slightly increases leading to a global increase of the c/a ratio (Fig. 3).

The δ off-stoichiometry value for as-synthesized and annealed samples was checked by TGA in oxidizing atmosphere (air) up to $T=900$ °C. At the end of the TG analysis, all the products are identified by PXRD as a mixture of iron copper spinel (CuFe_2O_4) and tenorite (CuO) phases. The oxidation reaction of CuFeO_2 in these conditions can be globally expressed with reaction (1):



Even if spinels, such as $\text{Fe}_{3-\epsilon}\text{O}_4$, are known to exhibit cation vacancies, copper ferrite is generally stoichiometric when slowly cooled from high temperatures, or displays a slight excess of cations when quenched from temperatures higher than about 700 °C [26]. For instance, powders quenched from 710 °C in air,

Table 2
Crystallographic data for as-synthesized and annealed $\text{CuFeO}_{2+\delta}$ samples

Sample	a (Å)	c (Å)	c/a	$d(\text{Fe}-\text{O})$ (Å)	$d(\text{Cu}-\text{O})$ (Å)
As-syn.	3.0351(1)	17.1691(3)	5.6569(2)	2.02	1.86
A-400	3.0352(1)	17.1702(2)	5.6571(2)	1.99	1.92
A-450	3.0354(1)	17.1728(2)	5.6575(2)	2.00	1.90
A-480	3.0359(1)	17.1785(3)	5.6585(2)	1.99	1.92
A-500	3.0352(1)	17.1781(3)	5.6596(2)	1.98	1.94
A-520	3.0345(1)	17.1778(4)	5.6607(3)	1.98	1.94
A-550	3.0339(1)	17.1783(7)	5.6622(5)	2.00	1.94

have an excess of oxygen close to 0.007 due to the formation of about 0.02 Cu^+ cations [26]. The chemical formula of the copper ferrite is then $(\text{Cu}_{1/3}\text{Fe}_{2/3})_{3+0.007}\text{O}_4$. Because of the quite low cooling rate (5 °C/min) during thermal analyses, the spinel phase formed according to reaction (1) was assumed to be very close to the stoichiometry ($\epsilon \rightarrow 0$). From this assumption, the theoretical weight gain due to reaction (1) is estimated by $\Delta m^{\text{th}}=(5.28-10.56\delta)\%$. Many reproducible experiments on various as-synthesized CuFeO_2 compounds have given experimental weight gain of $\Delta m^{\text{exp}}=5.20\%$ leading to a nominal off-stoichiometry value $\delta=0.008$ for $\text{CuFeO}_{2+\delta}$. After air annealing, all the samples were analyzed in the same experimental conditions and exhibit smaller Δm^{exp} . The difference between Δm^{exp} and Δm^{th} is then representative of the oxidation value due to the air annealing treatment. Data are shown in Fig. 4 for all the samples between A-400 and A-550.

Just as compounds were pure delafossite phases, the off-stoichiometry value is due to an oxidation of copper species inside the delafossite phase according to reaction (2):



For temperatures higher than 480 °C, the oxidation process related to reaction (2) is coupled with a phase transition due to reaction (1).

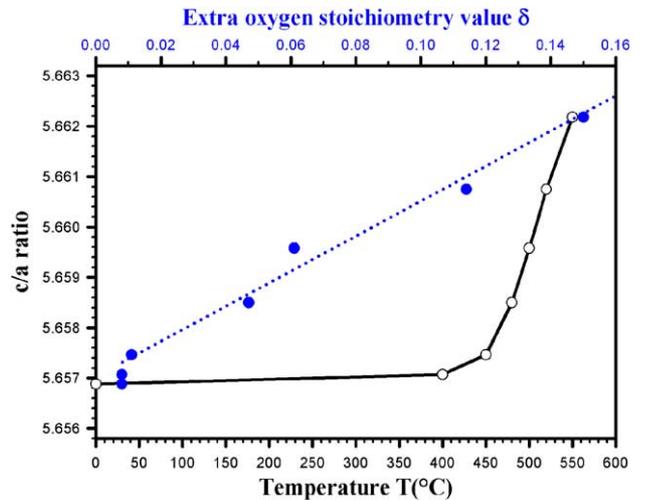


Fig. 3. Temperature dependence (lower scale) and extra oxygen stoichiometry value δ dependence (upper scale) of the ratio c/a between lattice parameters a and c of the $\text{CuFeO}_{2+\delta}$ as-synthesized and annealed samples. The lines are only a guideline for the eyes.

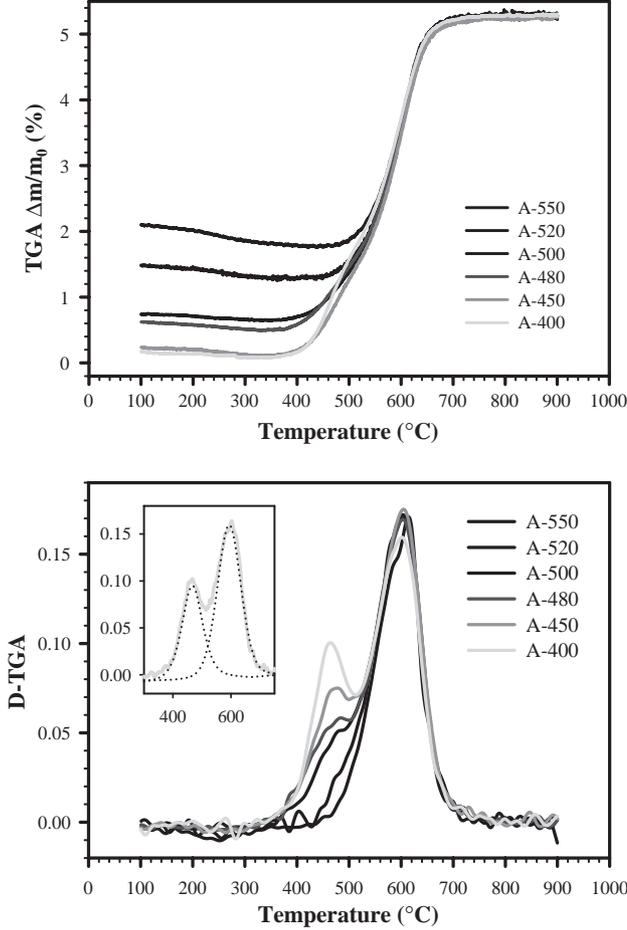


Fig. 4. TGA and DTGA curves of as-synthesized and annealed $\text{CuFeO}_{2+\delta}$ samples. Inset, Gaussian fit of the A-400 sample DTGA curve with 2 separate peaks.

The off-stoichiometry value δ for $\text{CuFeO}_{2+\delta}$ phases is easily calculable and accurate for $T < 480$ °C according to reaction (2). For $T > 480$ °C, Δm^{exp} is the result of both reactions (1) and (2) and δ can be calculated only with X-ray quantitative phase analysis. The results are summarized in Table 1.

The electrical properties were also estimated. Fig. 5 reports the resistance values of all the annealed samples divided by that of the as-synthesized sample. Resistance decreases as temperature increases for more than 1 order of magnitude from A-400 to A-550 °C.

Intercalation of oxygen into delafossite structure always takes place in Cu atomic planes [21]. The crystallographic site for intercalated oxygen is at the center of a triangle of Cu atoms (inset Fig. 6). Then, the effective size of intercalated oxygen site D_{Ox} can be calculated. Assuming that Cu atoms are monovalent and twofold-coordinated in the CuFeO_2 pristine phase, $r(\text{Cu}_{\text{II}}^+) = 0.46$ Å and D_{Ox} can be expressed as follow:

$$D_{\text{Ox}} = a \frac{\sqrt{3}}{3} - r(\text{Cu}_{\text{II}}^+) = a \frac{\sqrt{3}}{3} - 0.46 \quad (3)$$

Moreover, in the delafossite structure, the unit cell parameter a is directly correlated to the B cation size because

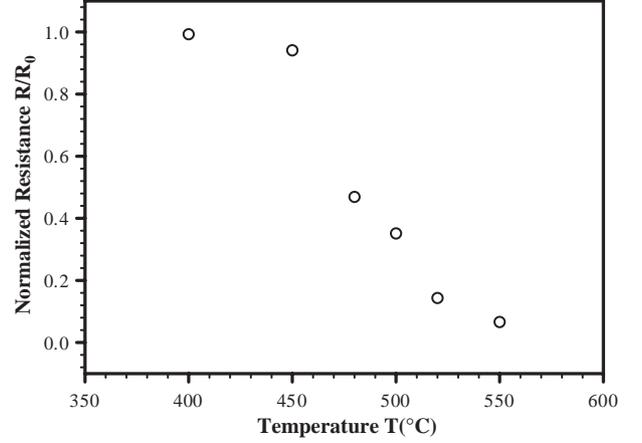


Fig. 5. Temperature dependence of the normalized resistance R/R_0 whereas R_0 is the resistance measured for the as-synthesized sample.

a is equal to the edge of the $[\text{BO}_6]$ octahedra. This correlation between a and $r(B_{\text{VI}}^{3+})$ is evidenced in Fig. 6 and can be expressed by following first order equation fit:

$$a = 1.77 + 1.96 r(B_{\text{VI}}^{3+}) \quad (4)$$

From Eqs. (3) and (4), $r(B_{\text{VI}}^{3+})$ can be expressed versus D_{Ox} . If we assume that $D_{\text{Ox}} = r(\text{O}_{\text{III}}^{2-}) = 1.36$ Å, one can calculate the critical radius $r_c(B_{\text{VI}}^{3+})$ of B cation below which it is not possible to intercalate oxygen anion, without any lattice distortion. In this case, $r_c(B_{\text{VI}}^{3+})$ is close to 0.70 Å. As a result, when B is taken among trivalent cations such as Fe^{3+} , Cr^{3+} , Al^{3+} , Ga^{3+} , etc. . . , which display a ionic radius lower than $r_c(B_{\text{VI}}^{3+})$, the crystallographic site for intercalated oxygen is too small. By contrast, when B^{3+} is Sc^{3+} , Y^{3+} or La^{3+} , the corresponding CuBO_2 phase can easily accept oxygen intercalation.

Fig. 7, which is plotted from bibliographical data [2,3,27], shows that no $\text{Cu}^{\text{II}}\text{B}_2^{\text{III}}\text{O}_4$ spinel is encountered, when B^{3+} cation radii are larger than 0.665 Å. These spinel phases are however stable for lower B^{3+} radii. In other words, oxidation of cuprous ions in delafossite leads to non-stoichiometric $\text{CuBO}_{2+\delta}$ phases for big B^{3+} cations, and to spinel and CuO

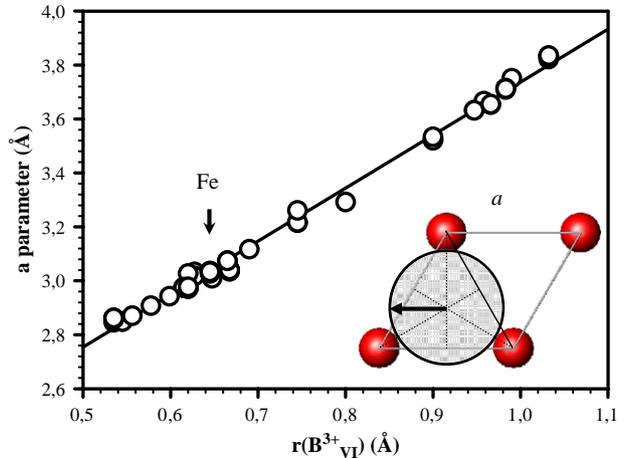


Fig. 6. a parameter of the 3R- CuBO_2 delafossite compounds versus B_{VI}^{3+} cationic size. Inset, schematic draw of available space for intercalated oxygen in the Cu plane of CuBO_2 delafossite.

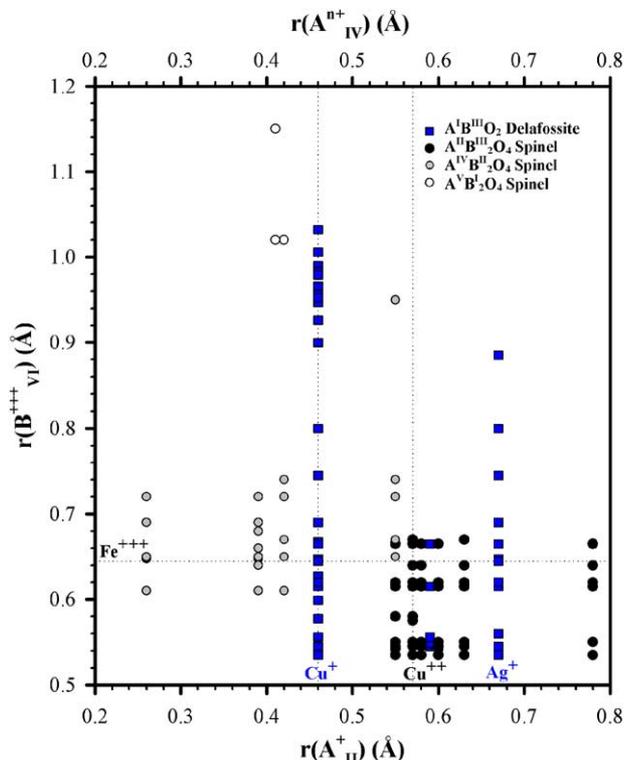


Fig. 7. Plot of r_B versus r_A for various ABO_2 Delafossite and AB_2O_4 spinel phases.

phases for small B^{3+} cations. It can then be deduced that non-stoichiometric $CuBO_{2+\delta}$ phases are always transformed into $Cu^{II}B_2^{III}O_4$ spinel and CuO each time the spinel phase is stable. By this approach, the critical $r_c(B_{VI}^{3+})$ radius is 0.665 Å, very close to previous value determined by a geometric method.

Nevertheless, previous experimental TGA and PXRD results show that oxidation of cuprous cations can be achieved according to reaction (2) inside the delafossite, even if Fe^{3+} cation radius (0.645 Å) is slightly lower than the above determined $r_c(B_{VI}^{3+})$ values from geometric calculations or from bibliographical data analysis.

At 450 °C, the delafossite phase is PXRD pure and off-stoichiometry parameter δ ($\delta=0.011$) is higher than that of A-400 sample ($\delta=0.008$). For higher temperatures, phase transition occurs according to reaction (1) and a competition takes place between (1) and (2) oxidation reactions. By plotting the DTG curves, all the samples annealed at $T < 500$ °C exhibit a two-step oxidation process. For the experimental conditions carried out, the first process is always centered at $T=480$ °C and the second one at $T=600$ °C. By convolution according to a Gaussian fit, we can define the start and the end of each peak when $I/I_{max} > 5\%$ (inset Fig. 4b). The first one starts at $T=380$ °C and ends at 550 °C. The second one starts at 500 °C and ends at 700 °C. This is in accordance with the PXRD phase analysis, showing oxidation (2) starts at about 400 °C and ends at 550 °C. The beginning of oxidation (1), which leads to spinel ferrite and copper monoxide precipitation, was found at about 480 °C from XRD measurements for the experimental conditions of oxidation carried out.

The c/a ratio also indicates that an oxidation occurs inside the delafossite. The a parameter is quite constant because a is controlled by the Fe^{3+} cation which is unaffected by the oxidation process. The $d(Fe-O)$ distance is quite stable at 2.02 Å for all the samples (Table 2). On the other hand, $d(Cu-O)$ significantly increases from 1.86 Å for A-400 to about 1.94 Å for A-500-520-550 (Table 2). This is in good agreement with the increases of average oxidation states (from Cu^I to Cu^{II}) and cation coordinations (from 2-fold to 3-fold or 4-fold) which tend to increase the average copper ionic radius: $r(Cu^{II})=0.46$ Å and $r(Cu^{IV})=0.57$ Å [4]. By plotting now the c/a ratio versus δ instead of T , one observes a quite linear dependence of the increase in c/a ratio versus δ (Upper scale in Fig. 3). For $T > 550$ °C, oxidation according to reaction (2) does not occur any more and delafossite phase vanishes. The c/a ratio does not evolve for $T > 550$ °C as well as it is possible to measure it.

Electrical resistance values present a significant decrease as annealing temperature increases (Fig. 5). This is in accordance with the increase of Cu^{II} species on Cu^I planes which favors hopping mechanism [17,18]. The resistance does not

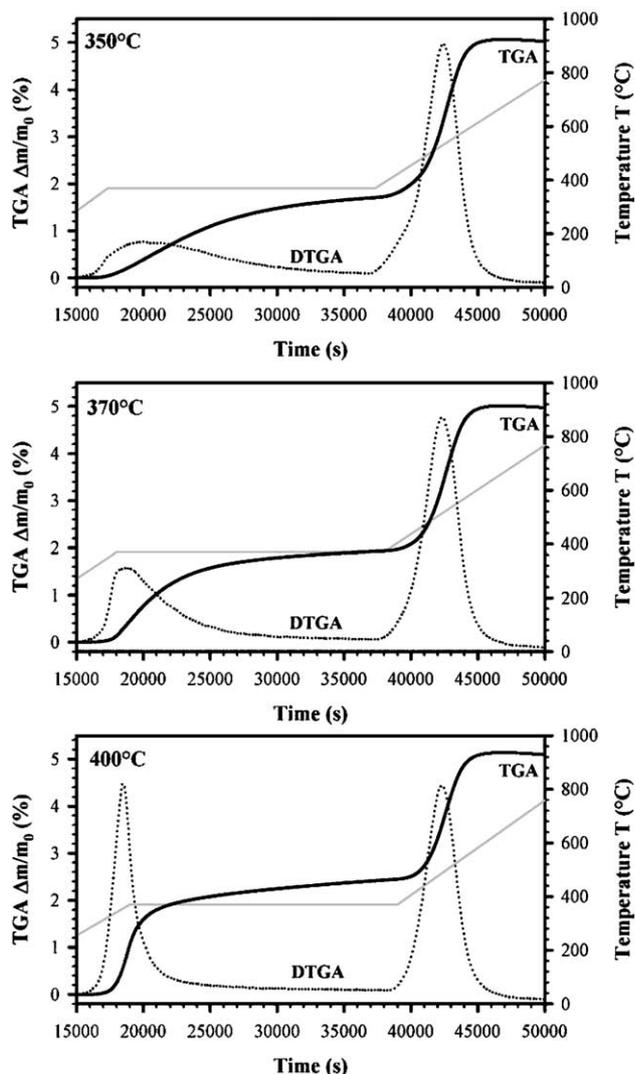


Fig. 8. TGA and DTGA curves of 900 °C air-annealed $CuFeO_{2+\delta}$ samples with intermediate 5 h 30 steps at $T=350, 370$ and 400 °C.

evolve significantly between A-520 and A-550 in agreement with the almost total disappearance of oxidation according to reaction (2).

Finally, two-step air annealings were performed in order to separate reactions (2) and (1) and to determine experimental conditions to get pure and highly oxidized delafossite phase. As-synthesized samples were heated up to 350, 370 or 400 °C and kept for 400 min at these temperatures to try to reach the maximal oxidation state for delafossite, without any spinel ferrite and copper monoxide precipitation (reaction (2)) (Fig. 8). After this dwell, the samples were heated at 5 °C/min up to 900 °C to entirely oxidize cuprous ions as in previous thermogravimetric analyses, i.e., to get spinel and copper monoxide phases only.

The 400 min dwell at 350 °C is insufficient to reach the maximal state of non-stoichiometry as demonstrated by the positive slope of TGA curve (DTGA>0) at dwell end. On the other hand, spinel phase and CuO precipitation (reaction (1)) occurs during annealing at 400 °C. A single and highly non-stoichiometric delafossite is however obtained after 400 min dwell at 370 °C as revealed by X-ray diffraction patterns. The reactions (2) and (1) can be well discriminated in this case (Fig. 8). Δm^{exp} at the end of this dwell step is equal to 1.96% leading to the formation of $\text{CuFeO}_{2.18}$ off-stoichiometric delafossite. This non-stoichiometric phase displays quite broad X-ray diffraction peaks suggesting a bad crystallization state due to many stacking faults induced by oxygen anions intercalation in the delafossite structure. That makes the crystalline organization not much stable. It is the reason why it seems difficult to reach higher off-stoichiometry for the powders studied, without any secondary phases precipitation. To our knowledge $\text{CuFeO}_{2.18}$ is the copper–iron delafossite phase with the highest off-stoichiometry degree obtained up to now.

4. Summary

Pure CuFeO_2 delafossite powders have been prepared by solid state reaction at 900 °C in inert atmosphere. The study of their reactivity towards oxygen has revealed that these powders can be oxidized. By heating in air at 5 °C/min, oxidation of cuprous ions leads to oxygen intercalation from 400 to about 500 °C. Off-stoichiometric $\text{CuFeO}_{2+\delta}$ delafossite phases are then formed. Above 500 °C, oxidation leads also to spinel ferrite and CuO precipitation.

From geometrical considerations and bibliographical data analysis, it could be deduced that oxygen intercalation in CuFeO_2 is impossible. This study however demonstrated that oxygen can be significantly intercalated, making possible the formation of $\text{CuFeO}_{2+\delta}$ delafossite phases, with δ varying from 0 to 0.18. This partial oxidation of cuprous ions inside the delafossite lattice seems to be permitted because the ionic radius of Fe^{3+} cations is just slightly smaller than the critical radius below which it is not possible to intercalate oxygen.

Added oxygen anions tend, however, to distort the lattice along the *c* axis.

Comparative electrical measurements show that cuprous cations oxidation leads to a decrease in resistivity, in agreement with the formation of $\text{Cu}^+/\text{Cu}^{2+}$ pairs, which favors electronic hopping in the copper planes. It will be however necessary, in future studies, to go deeper in this matter by further techniques, for instance powder-solution-composite technique coupled with impedance spectroscopy [28].

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