JOURNAL OF SOLID STATE CHEMISTRY 88, 476–484 (1990)

# Low Temperature Syntheses of $NbFeO_4$ and $TaFeO_4$: Influence of Recrystallization on the Magnetic Properties

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Received May 18, 1990

Hydroxides of iron and niobium, or iron and tantalum, precipitate by adding $NH_4OH$ to the metal oxalate solutions and give $NbFeO_4$ and $TaFeO_4$ by decomposition. Owing to the thermal treatment, different samples are obtained. $NbFeO_4$ of $\alpha$-$PbO_2$-type structure crystallizes at 700°C with large diffraction lines while a very well-crystallized disordered phase is obtained by heating the precipitate at 1100°C for half an hour and quenching it down to room temperature. The wolframite ordered form is obtained at 1000°C. A pure rutile $TaFeO_4$ is obtained at 1100°C by avoiding annealings between 700 and 900°C. The low temperature phase of $\alpha$-$PbO_2$ structure crystallizes in very small quantities at 1000°C. The ordered $NbFeO_4$ wolframite sample is antiferromagnetic below 50 K unlike the complete disordered ones. Intermediate behaviors are observed owing to the thermal treatment, particularly a ferromagnetism within iron clusters. The Curie constants extracted from the Curie–Weiss behavior are very below the theoretical Curie constants for disordered samples and for $TaFeO_4$ indicating strong interactions between irons.

## Introduction

The compounds $NbFeO_4$ and $TaFeO_4$ are known for several decades. $NbFeO_4$ is reported to have three types of structure, rutile (quadratic; space group $P4_2/mnm$) above 1380°C, $\alpha$-$PbO_2$ type (orthorhombic; space group *Pbcn*) between 1085 and 1380°C, and wolframite (monoclinic; space group $P2/c$) below 1085°C (*1*). $TaFeO_4$ generally crystallizes in the rutile structure under normal conditions of pressure (*2*), while the wolframite form has been pointed out under pressure (*3*). The three structures are characterized by strings of octahedra sharing an edge, straight in the *c* axis in the rutile, staggered along the *c* axis in the two other arrangements (Fig. 1). The wolframite form is an ordered and slightly distorted variant of the $\alpha$-$PbO_2$ structure in which every zigzag chain contains either Fe or Nb atoms (Fig. 2).

Until now, $NbFeO_4$ and $TaFeO_4$ have been synthesized using a solid state reaction between $Nb_2O_5$ or $Ta_2O_5$ and $\alpha$-$Fe_2O_3$, most of the time under air and at temperatures higher than 1100°C. However, this route presents a major drawback, the reduction of $\alpha$-$Fe_2O_3$ into $Fe_3O_4$, leading to an incomplete reaction between the starting oxides. Koenitzer *et al.* (*5*) have detected small amounts of $\alpha$-$Fe_2O_3$ after a sintering of Nb $FeO_4$ at 1330°C for 24 hr, consistent with the formation of $FeNb_2O_6$ in solution with $NbFeO_4$. Roth and Waring (*1*) pointed out an increase of unit cell dimensions of Nb $FeO_4$ when the temperature from which the samples have been quenched (1085°C <

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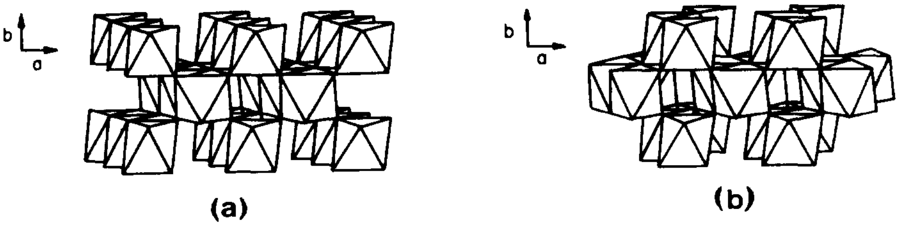

FIG. 1. Schematic representation of rutile (a) and $\alpha$-$PbO_2$-type (b) structures.

$T < 1380°C$) increases. They assigned this phenomenon to either a change in the Fe/Nb ratio of the phase with temperature or to a reduction of $Fe^{3+}$ to $Fe^{2+}$. This reduction can be avoided by annealing the powders in a pure oxygen atmosphere (*6*) or by decreasing the reaction temperature. This latter is easily obtained when the starting oxide powders are very fine: $\alpha$-$Fe_2O_3$ resulting from the decomposition of iron(II) oxalate in air at 750°C and $Ta_2O_5$ or $Nb_2O_5$ from $Ta(OH)_5$ or $Nb(OH)_5$ dried in air at 700°C (*7*). The solid state reaction occurs at 1000°C and $\alpha$-$Fe_2O_3$ is invisible in X-ray diffraction patterns. Nevertheless, the lack of its diffraction lines is not the proof of its nonexistence since the reduction begins at about 880°C (*8*).

To avoid completely this reaction, low-temperature syntheses must be used. Two of them have been already reported. Impregnation of FeOOH by adsorbed niobium (or tantalum) and exchange reaction between $K_3NbO_4$ and $Fe(NO_3)_3$ give $NbFeO_4$ under 1000°C and at about 600°C, respectively (*9, 10*). But some $\alpha$-$Fe_2O_3$ is present with the first method and substitutions for $K^+$ are difficult to avoid in the second one. We present here a third low-temperature method, the coprecipitation of metal hydroxides. The influence of recrystallization on the magnetic properties is then reported.

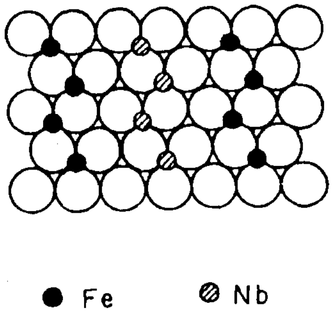

FIG. 2. Order between niobium and iron atoms in the wolframite structure (after Leiva *et al.* (*4*)).

## Experimental

Niobium or tantalum chloride is dissolved in alcohol. By adding $NH_4OH$, the hydroxides $Ta(OH)_5$ or $Nb(OH)_5$ precipitate. Those precipitates are filtered, carefully washed with water, and thrown immediately into a solution of oxalic acid (10 wt%). This solution is then stirred until all is dissolved. The amount of niobium or tantalum hydroxides and the volume of acid solution are calculated in order to obtain a metal concentration of about 2 wt%. After calculating the accurate quantity of metal in the solution, an appropriate amount of ferrous oxalate $Fe(COO)_2$ is added. The iron is oxidized with $H_2O_2$. Then, the mixture, iron and niobium (or tantalum) oxalate, is slowly poured (drop by drop) into a great quantity of $NH_4OH$ heated at about 60°C, giving a claret precipitate of mixed hydroxide $FeNb(OH)_8$ or $FeTa(OH)_8$. After filtration, the hydroxides are dried first up to 120°C for 4 hr, then up to 700°C in silica crucibles. At this temperature, the precipitates are no more

TABLE I

Thermal Treatments Performed on the $NbFeO_4$ Precipitate Dried at 700°C and Their Structures and Magnetic Properties

| Sample | Annealings | | Quenching | Structure | Maximum of $XT$ | Curie–Weiss law | |
|---|---|---|---|---|---|---|---|
| | Temperature | Time | | | | $C$ | $\Theta$ |
| a | 700°C | 3 hr | No | $\alpha$-$PbO_2$ type | 130 K | | |
| b | 800°C | 3 days | No | $\alpha$-$PbO_2$ type | | | |
| c | 1100°C | $\frac{1}{2}$ hr | Yes | $\alpha$-$PbO_2$ type | 104 K | | |
| d | 1200°C (100°C/hr) | | No | | | | |
| | 1200°C (100°C/hr) | | Yes | | | 3.61 | 68 K |
| e | 1000°C | 16 hr | No | Wolframite | | 4.27 | 92 K |

amorphous. Then the samples, put into platinum crucibles, are submitted to different thermal treatments (Tables I and II). The cristallographic structures are determined on powders by means of X-ray diffraction using a Kristalloflex Siemens diffractometer and cobalt radiation. Parameters are calculated using $Al_2O_3$ as internal standard. Thermal gravimetric analyses are performed in platinum crucibles under air using a Setaram 92 apparatus. The loss or gain of weight are calculated after removing the signal of the empty crucible. Magnetic measurements are performed with a pendulum-type magnetometer designed in our laboratory in the temperature range 4.2–300 K and magnetization measurements using a Foner. $^{57}Fe$ Mössbauer spectra have been recorded at room temperature using conventional mechanical drives synchronized with a multichannel analyzer operating in multiscaling mode.

TABLE II

Thermal Treatments Performed on the $TaFeO_4$ Precipitate Dried at 700°C and Phases Observed

| Sample | Annealings | | Quenching | Phases |
|---|---|---|---|---|
| | Temperature | Time | | |
| a | 700°C | 3 hr | No | Undetermined |
| b | 700°C | 170 hr | No | $\alpha$-$Fe_2O_3$ |
| c | 700°C | 170 hr | No | $\alpha$-$Fe_2O_3$, $Ta_2O_5$, $Fe_3O_4$ |
| | 1000°C | 15 hr | No | Rutile $TaFeO_4$ |
| d | 1000°C | 75 hr | No | Rutile $TaFeO_4$<br>Orthorhombic $TaFeO_4$ |
| e | 1100°C | 1 hr | Yes | Rutile $TaFeO_4$ |

## Results

*Crystallization of $NbFeO_4$.* X-ray diffraction patterns recorded after every thermal treatment are given in Fig. 3. Niobium iron hydroxide changes into $NbFeO_4$ at 700°C with the orthorhombic structure of $\alpha$-$PbO_2$ type (space group *Pbcn*). No $Nb_2O_5$ or $\alpha$-$Fe_2O_3$ is detected by X-ray diffraction measurements (Fig. 3a). A better crystallized sample of the same structure is obtained after heating at 800°C for 3 days (Fig. 3b). The most narrow diffraction lines are observed after annealing at 1100°C for half an hour or increasing the temperature of 100°C per hour up to 1200°C, both followed by a rapid quenching down to room temperature (Figs. 3c and 3d). The diffraction lines 001 and 110, characteristic of the wolframite structure, are hardly detectable. The most ordered sample is obtained after an annealing of 16 hr at 1000°C (Fig. 3e). A further heating at 900°C for 3 days does not improve

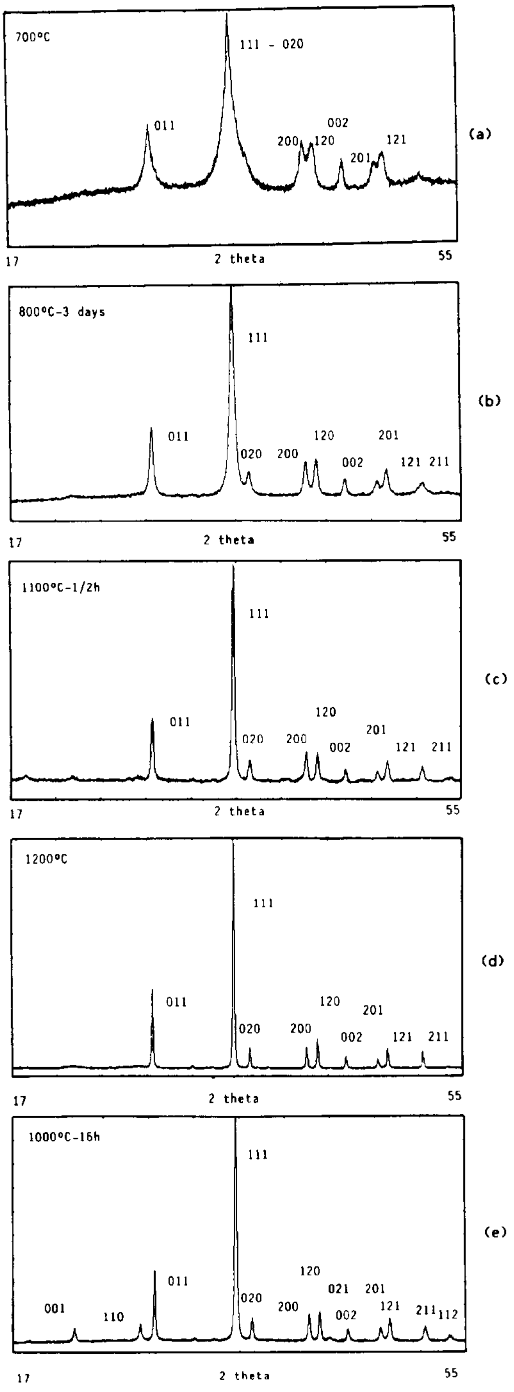

FIG. 3. X-ray diffraction patterns of samples of Nb $FeO_4$ submitted to the thermal treatments described in Table I.

the ordering much more, i.e., the intensities of the diffraction lines 100 and 011 do not appreciably increase. Cell parameters are in agreement with those given by Roth and Waring (*1*). The parameters of our orthorhombic samples are in agreement with those they have found for samples heated up to 1100°C: $a = 5.004 \pm 0.005$ Å, $b = 5.613 \pm 0.005$ Å, and $c = 4.651 \pm 0.005$ Å (*1*).

*Crystallization of* $TaFeO_4$. X-ray diffraction patterns recorded after every thermal treatment are given in Fig. 4. At first sight, the precipitate of iron and tantalum behaves completely differently. The phase which crystallizes at 700°C does not look like a rutile or an orthorhombic phase. Moreover, no $Fe_2O_3$ and $Ta_2O_5$ are detected (Fig. 4a). A further annealing at 700°C, for 7 days, allows the crystallization of $\alpha$-$Fe_2O_3$. Two other phases similar to a rutile phase and an orthorhombic phase isomorphous of Nb $FeO_4$ seem to crystallize (Fig. 4b). Nevertheless, it can be noted that the intensities of the rutile phase are not preserved compared to those usually observed for $TaFeO_4$. Indeed, the diffraction lines corresponding to $d = 3.31$ Å (110) is weaker than that corresponding to $d = 2.51$ Å (011) and $d = 1.73$ Å (121). A further heating at 1000°C for one night shows that a segregation between tantalum and iron occurs at 700°C. Indeed, $\alpha$-$Fe_2O_3$, $Fe_3O_4$, $Ta_2O_5$, and rutile $TaFeO_4$ are present (Fig. 4c). Annealings of precipitate at 800 and 900°C for 15 hr are not more successful: the rutile phase $TaFeO_4$ crystallizes, but $Ta_2O_5$ appears, although the step at 700°C has been avoided. The easiest way to obtain pure rutile $TaFeO_4$ is to introduce the precipitate into a furnace heated at 1100°C, for 1 hr (Fig. 4d). At 1000°C, a small quantity of orthorhombic phase of $\alpha$-$PbO_2$ type crystallizes with the rutile phase (Fig. 4e). These reflections do not increase when heating between 900 and 1000°C for 15 days.

*Mössbauer study of* $TaFeO_4$. The Mössbauer spectra of samples a, d, and e are

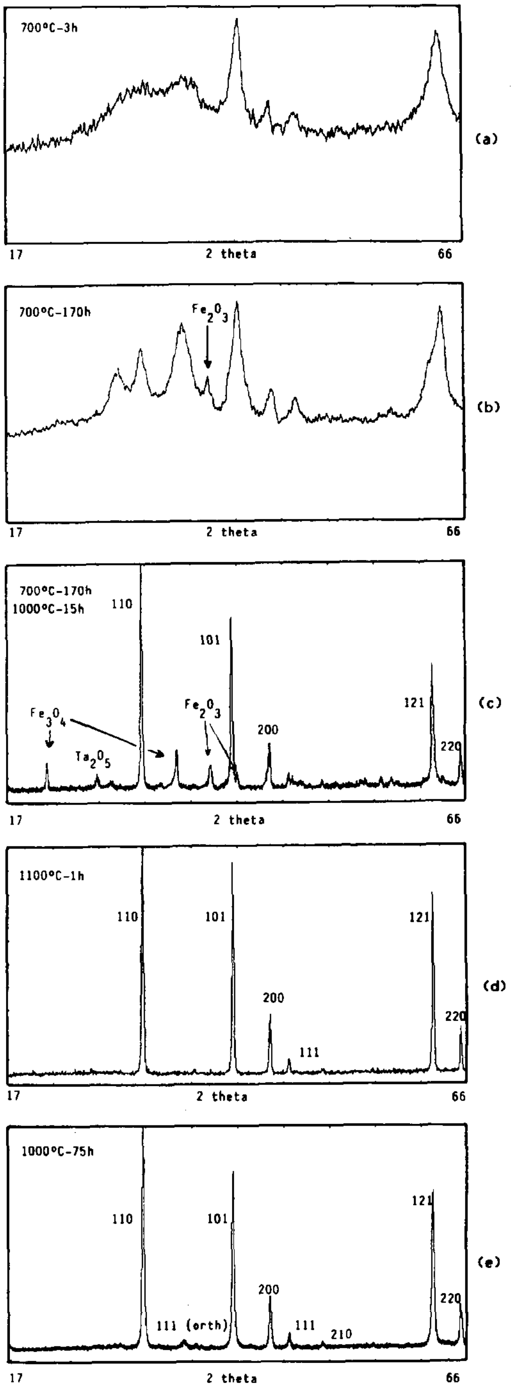

FIG. 4. X-ray diffraction patterns of samples of Ta $FeO_4$ submitted to the thermal treatments described in Table II.

TABLE III

MÖSSBAUER PARAMETERS OF THE $Fe^{3+}$ IONS IN $TaFeO_4$ SAMPLES

| | $Fe^{3+}$ in a paramagnetic site | | | $Fe^{3+}$ in a magnetic site | | |
|---|---|---|---|---|---|---|
| Sample: | a | d | e | a | d | e |
| $\delta_{IS}$ | 0.41 | 0.41 | 0.41 | 0.33 | 0.28 | — |
| $\Delta$ EQ | 0.62 | 0.52 | 0.52 | — | — | — |
| $H_{hf}$ | — | — | — | 511 | 527 | — |
| $W$ | 0.48 | 0.39 | 0.36 | 0.6 | 0.3 | — |
| % | 84 | 92 | 100 | 16 | 8 | 0 |

*Note.* $\delta_{IS}$, isomer shift; $\Delta$ EQ, quadrupole splitting; $H_{hf}$, hyperfine field; $W$, linewidth.

characterized by one broadened quadrupole doublet indicating the presence of $Fe^{3+}$ ions in a paramagnetic site. The isomer shifts and quadrupole splittings characterizing $Fe^{3+}$ ions are given in Table III. A signal arising from $Fe^{3+}$ in a magnetic site appears in the samples a and d and is assigned to $\alpha$-$Fe_2O_3$. The concentration of $Fe^{3+}$ in this magnetic site is estimated to be 16% in sample a and 8% in sample d. However, it becomes zero in sample e.

*Thermogravimetric study.* After the first crystallization, a small loss of weight is observed by thermogravimetric analysis performed under air: about 0.2 wt% for the niobium powder and about 0.3 wt% for the tantalum powder above 790°C. The following thermal treatment 20°C → 1200°C → 20°C → 1200°C with an increment of 100°C per hour shows that no increase or decrease of weight is noticeable during the cooling and the second heating. The final $TaFeO_4$ and $NbFeO_4$ present the rutile structure and the orthorhombic structure of $\alpha$-$PbO_2$ type respectively because of the final quenching.

*Magnetic behavior of $NbFeO_4$ samples.* All the $NbFeO_4$ samples do not exhibit the same magnetic behavior. For the samples a, b, and c, the susceptibility always increases when the temperature decreases up to 4.2 K. The sample d, for which the diffraction lines 001 and 110 are almost invisible, pres-

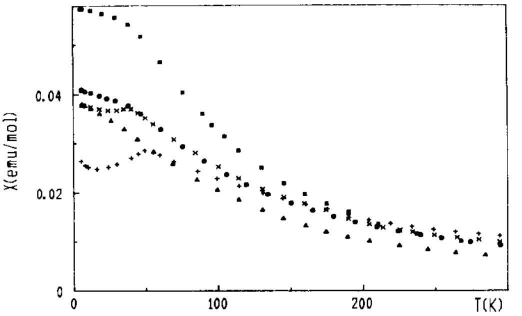

FIG. 5. Susceptibility variations versus temperature for NbFeO$_4$ samples heated at 700°C (▲), 800°C (●), 1100°C for half an hour (■), 1200°C (×), and 1000°C for 15 hr (+).

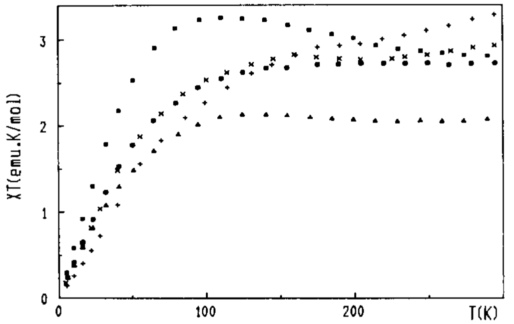

FIG. 7. Variation of the magnetic moment versus temperature for NbFeO$_4$ samples heated at 700°C (▲), 800°C (●), 1100°C for half an hour (■), 1200°C (×), and 1000°C for 15 hr (+).

ents a maximum at 40 K in the susceptibility curve. The most ordered, of wolframite structure (e), is also antiferromagnetic; its susceptibility curve presents a sharp maximum at $T = 50$ K, much more pronounced than for sample d (Fig. 5). The variations of the inverse of the susceptibility are presented for all the samples in Fig. 6. The antiferromagnetic samples d and e follow a Curie–Weiss law above 200 K: $X = 3.61/(T + 68)$ and $X = 4.27/(T + 92)$, respectively. One can note for the disordered samples that the Curie constants are lower than the theoretical value ($C_{\text{exp}}$ between 2.74 and 2.02; $C_{\text{th}} = 4.375$). The samples a and b are distinguished from the others, since the variations of magnetic moments are characterized by a maximum at 130 and 104 K, respectively (Fig. 7). However, magnetization measurements performed at 4.2 K do not point out a field-dependent susceptibility up to a field value of 2 $T$.

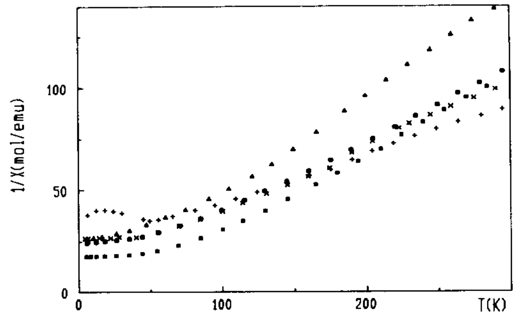

FIG. 6. Variation of the inverse susceptibility versus temperature for NbFeO$_4$ samples heated at 700°C (▲), 800°C (●), 1100°C for half an hour (■), 1200°C (×), and 1000°C for 15 hr (+).

*Magnetic behavior of TaFeO$_4$ samples.* Susceptibility measurements of pure rutile TaFeO$_4$ are similar to the previous published results (*7*). It is characterized by a maximum at about 10 K. Let us note the shoulder between 100 and 150 K, already observed in previous measurements performed on a sample prepared using the ceramic process (Fig. 8). Above 200 K, the inverse susceptibility versus temperature is expressed by $X = 3.1/(T + 354)$ (Fig. 9). As for the dried precipitate, its susceptibility follows the law $X = 1.98/(T + 90)$ in all the temperature range.

## Discussion

Our results confirm that niobium and tantalum do not have the same behavior, although they belong to the same column in the Mendeleev table. The hydroxide of iron and niobium crystallizes into an $\alpha$-PbO$_2$

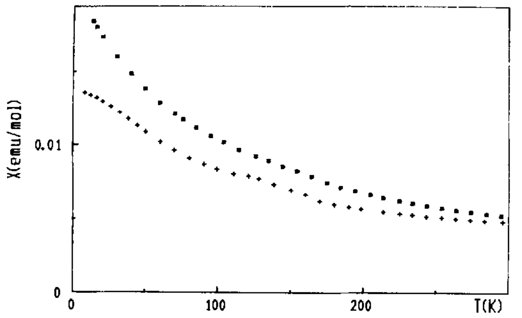

FIG. 8. Susceptibility variations versus temperature for $TaFeO_4$ samples heated at 700°C (■) and 1100°C for 1 hr (+).

structure at 700°C. The intensities of the diffraction lines are in agreement with those of $NbFeO_4$, but their shapes indicate that the crystallization is bad. A very well-crystallized disordered compound of $\alpha$-$PbO_2$ structure is obtained at 1100°C after a short heating of half an hour followed by a quenching. In agreement with the previous structural studies, the wolframite form is obtained at 1000°C (*1*). Using this coprecipitation method, $NbFeO_4$ crystallizes first in a disordered arrangement of $\alpha$-$PbO_2$ type (Fig. 3a) and not in the most stable structure which is the wolframite one (Fig. 3e). This is due both to the disordered distribution of iron and niobium in the precipitate and to the thermal energy which is not great enough at 700°C to allow rapid jumps of atoms from one site to another.

The crystallization of $TaFeO_4$ is less simple at 700°C. The phases which appear first do not look like a rutile or an $\alpha$-$PbO_2$-type phase (Fig. 4a). $\alpha$-$Fe_2O_3$ or $Ta_2O_5$ are invisible in the X-ray diffraction pattern. However, Mössbauer studies of sample a point out that some $Fe^{3+}$ is in a magnetic site, similar to that encountered in $\alpha$-$Fe_2O_3$. As $\alpha$-$Fe_2O_3$ does not appear in the X-ray diffraction pattern, it can be concluded that this phase has just begun to crystallize in sample a, and that the grains are small. Nevertheless, the major part of iron has an octahedral environment similar to that encountered in the rutile structure as the Mössbauer studies show (*11*). A further annealing of the powder at 700°C allows $\alpha$-$Fe_2O_3$ to crystallize showing that a segregation occurs (Fig. 4b). This phase segregation is pointed out definitely by a heating up to 1000°C, since $Ta_2O_5$, $\alpha$-$Fe_2O_3$, and $Fe_3O_4$ are detected at this temperature (Fig. 4c). Let us note on the X-ray diffraction pattern that the quantity of $Ta_2O_5$ is very low compared to those of iron oxides, since the former diffracts much more than the latter. This allows us to conclude that the iron is thrown out at 700°C in greater quantities than tantalum, so that the stoichiometry of this rutile phase is not one tantalum for one iron. This step must be avoided by a rapid heating up to 1100°C for 1 hr in order to synthesize pure rutile $TaFeO_4$ (sample e). Mössbauer studies confirm the great purity of our sample e, since $\alpha$-$Fe_2O_3$ detected in sample a has disappeared. The rutile structure is not the low temperature form, since the thermal treatment performed at 1000°C points out that the $\alpha$-$PbO_2$ arrangement already encountered under pressure (*3*) appears in very small quantities. Unfortunately, the orthorhombic structure is not more developed after a long heating of 15 days between 900 and 1000°C.

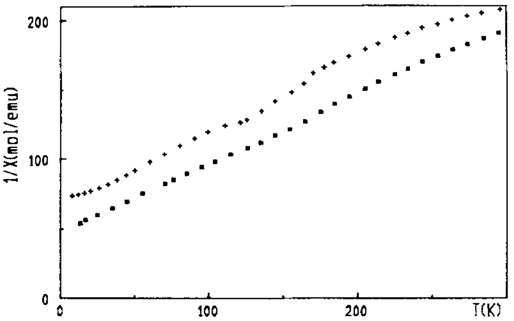

FIG. 9. Variation of the inverse susceptibility versus temperature for $TaFeO_4$ samples heated at 700°C (■) and 1100°C for 1 hr (+).

The loss of weight detected by the thermogravimetric analysis at 700°C is assigned to residual water. As the $NbFeO_4$ and $TaFeO_4$ powders do not gain or lose any weight during the first cooling and the second heating up to 1200°C, an annealing at 1100°C during 1 hr is not destructive toward the compounds. The reduction of iron is avoided, so that the cristallographic parameters found for the orthorhombic samples are in agreement with the smallest values given by Roth and Waring (*1*). That is why the method is a real improvement in the synthesis of pure $TaFeO_4$ and pure $NbFeO_4$. No oxygen atmosphere is required and the thermal treatment is much more shorter than by solid state reactions. Furthermore, the grains are smaller, making the powder more reactive for use as starting compounds.

In agreement with the different X-ray diffraction patterns, the $NbFeO_4$ samples do not present the same magnetic behavior. No magnetic order occurs in the susceptibility curves of samples a, b, and c, while the samples d and e are antiferromagnetically ordered. The magnetic behaviors of samples a, b, and c are in agreement with previous magnetic measurements performed on orthorhombic $NbFeO_4$ samples quenched from temperatures between 1085 and 1350°C (*12*). The slopes of straight lines drawn above 200 K in the curves $1/X = f(T)$ are further below the theoretical Curie constants, indicating that the paramagnetic domain is still not reached at 300 K. Thus, iron atoms are probably aggregate, these aggregates proceeding from the coprecipitation, since this method leads to an homogeneous mixture of small grains of iron hydroxide and niobium hydroxide. When looking at the variations of magnetic moments (Fig. 7), it can be noted that the samples a and b do not behave as the sample c, since a maximum of XT is observed for the former. As magnetization measurements performed at 4.2 K show that no tridimensional ferromagnetic order exists in these compounds, these maxima can be assigned to ferromagnetic interactions within small iron clusters. These clusters are probably the intermediate form between the disorder and the ordered wolframite form. Indeed, at 700 and 800°C, the wolframite structure is thermodynamically favored. As ferromagnetic interactions within metal planes (100) have been pointed out in wolframite structures, particularly in $FeWO_4$, it can be imagined that this ferromagnetism proceeds from parts of iron planes isolated among niobium atoms (*13*).

The tridimensional antiferromagnetic coupling is the leading effect for the magnetic behavior of $NbFeO_4$ samples d and e. Their susceptibilities are characterized by a maximum at 40 and 50 K, respectively. The susceptibilities increase again below 16 and 40 K, respectively, revealing a weak disorder with some isolated $Fe^{3+}$ in the niobium chains. This phenomenon has already been encountered for the disordered $WV_2O_6$ (*14*, *15*) and $WVO_4$ (*16*). The total order would be probably reached with longer annealings at 1000°C and a slow cooling down. The susceptibility measurements of samples d and e are in agreement with the cristallographic studies. The most ordered sample, the wolframite sample e, presents a better antiferromagnetic order, with a more pronounced maximum and a less important increase of susceptibility at very low temperatures. The experimental Curie constant of sample d less ordered than sample e, $C_{\text{exp}} = 3.27$, is low but close to those of disordered samples a, b, and c. The experimental Curie constant $C_{\text{exp}} = 4.27$ of sample e is close to the theoretical one $C_{\text{th}} = 4.375$, showing that the paramagnetic domain is hardly reached at 200 K.

The magnetic properties of $TaFeO_4$ samples do not present the evolution previously observed, since no structural transition occurs. All our attempts in obtaining the $\alpha$-$PbO_2$ structure failed. So, measurements of magnetic susceptibility of samples a and d were only of interest. No magnetic order is observed for the precipitate, while the rutile phase is antiferromagnetic. The difference between the experimental and theoretical Curie constants are larger for the iron tantalum oxide than in the niobium case. The experimental Curie constants $C_{\text{exp}} = 1.98$ for sample a and $C_{\text{exp}} = 3.08$ for sample d very below the theoretical one even for the very well-crystallized rutile sample indicate that stronger interactions between $Fe^{3+}$ ions occur in the tantalum compound than in the niobium one. This difference can be explained by a greater covalency of tantalum allowing an easier exchange between iron ions.

## Conclusions

The low temperature syntheses of $NbFeO_4$ and $TaFeO_4$ described in this paper have the great advantages to give pure compounds by avoiding the reduction of iron, although the thermal heating are performed under air. Moreover, the short annealing at 1100°C preserves the fine granulometry of the powders.

From the cristallographic and magnetic studies of $NbFeO_4$, it can be concluded that the state of order or disorder within a structure has a stronger effect on the magnetic properties than on the X-ray diffraction pattern. While the susceptibility curves of samples b and d are completely different, their X-ray diffraction patterns both correspond to the $\alpha$-$PbO_2$ structure. Only the diffraction lines are a little larger for sample b than that for sample d. The wolframite surstructure diffraction lines are absent in Fig. 3d and the susceptibility presents a maximum as if the compound is ordered. So, this study points out that the magnetic behavior is very sensitive to the order, more than X-ray diffraction measurements.

## Acknowledgment

We thank J. P. Kappler, I.P.C.M.S. Groupe des Matériaux Métalliques, 3 rue de l'Université, 67084 Strasbourg Cedex, France, for recording magnetization measurements.

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