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Yttrium iron garnet and Y, Fe binary oxides synthesized by microwave monomode energy transfer

J. Ostoréro[a,*], M. Gasgnier[b], A. Petit[b]

[a] Laboratoire de Chimie Métallurgique et Spectroscopie des Terres Rares, CNRS, UPR 209, 1 Place A. Briand, 92195 Meudon Cedex, France

[b] Laboratoire des Réactions Sélectives Sur Supports, URA 478, ICMO, Bat. 410, Université Paris-Sud, 91405 Orsay Cedex, France

Abstract

Polycrystalline yttrium iron garnet (YIG) has been synthesized from Y_2O_3/Fe_3O_4 mixtures at a low temperature (below 900 K) in a few minutes by using microwave monomode at ambient atmosphere. Yttrium orthoferrite $YFeO_3$ and surprisingly YFe_2O_4 have also been synthesized. Under conventional solid state reactions all these Y, Fe binary oxides are synthesized at a much higher temperature and under low partial oxygen pressure in the case of YFe_2O_4. We discuss briefly this apparent discrepancy. The MW method was equally extended to the synthesis of a scandium-doped YIG compound. This demonstrates the interest of this method for the syntheses of inorganic compounds. © 1997 Elsevier Science S.A.

Keywords: Microwave; Synthesis; Yttrium iron garnet; YFe_2O_4

1. Introduction

Yttrium iron garnet ($Y_3Fe_5O_{12}$ or YIG) and derived compounds constitute a very important class of materials due to their magnetic and magneto-optic properties [1] leading to numerous applications in telecommunications and data storage. Numerous works have been devoted to the synthesis of this compound either as polycrystalline or single crystals, in bulk as well as thin films. Polycrystalline synthesis of bulk material is performed using classical solid state reaction methods between Y_2O_3 and α-Fe_2O_3 at high temperature ($T \sim 1500$ K) with lengthy sintering time (several hours) and grinding steps. We present here a new method to synthesize polycrystalline Y-Fe-O binary compounds, taking place at much lower temperature and with reaction time of the order of a few minutes. This method is based on the microwave (MW) monomode energy transfer which has been used for several years to study the oxidation-reduction reactions of various oxides, and also the formation of binary oxides [2-4]. Under these conditions, Fe_3O_4 is known to react violently to form α-Fe_2O_3. The aim of our experiments was thus to synthesize YIG by submitting several mixtures of Y_2O_3 and Fe_3O_4 to the MW energy. We obtained nearly pure YIG and, depending on the experimental conditions, yttrium orthoferrite $YFeO_3$ and surprisingly YFe_2O_4 were also synthesized. To our knowledge, it is the first time that YFe_2O_4 has been observed during YIG synthesis at ambient atmosphere because this oxide is generally difficult to prepare under low oxygen partial pressure [5,6]. It is also to be noted that all three binary oxides are synthesized at high temperature ($T \sim 1500$ K) according to classical thermodynamic conditions, which is at least 700 K higher than temperatures recorded during our MW experiments. We will briefly discuss this apparent discrepancy.

2. Experimental

The MW apparatus (Prolabo Cy, Maxidigest 350) is equipped with a magnetron with the following charac-

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[*] Corresponding author.

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teristics: $f = 2.45$ GHz ($\lambda = 12.2$ cm) and $P = 300$ W. The electromagnetic beam is propagated along a wave-guide in which a standing wave system is established. This allows the energy to be focused within a small volume of powder, closely around the central axis of a Pyrex glass (or a quartz) test tube localized in front of the wave-guide (Fig. 1). Sample temperature is measured by means of an IR pyrometer located in front of a mirror positioned beneath the test tube containing the powder. Temperature recordings are carried out by means of a computer. The pyrometer was calibrated as reported elsewhere [2] and the temperatures indicated in the text are the corrected ones. It is to be noted that the MW power is automatically cut off when the recorded temperature is higher than 823 K.

Fe_3O_4 (Johnson Matthey 99.99%) and Y_2O_3 (Johnson Matthey 99.99%) powders were employed as starting materials. Four different compositions of Y_2O_3/Fe_3O_4 powders mixtures were studied with a metallic ratio $r = Y/Fe = 3/[5(1+x)]$ in the vicinity of 0.6 corresponding to stoichiometric YIG: x = 0, 5, 10 and 20% ($0.6 \geq r \geq 0.5$).

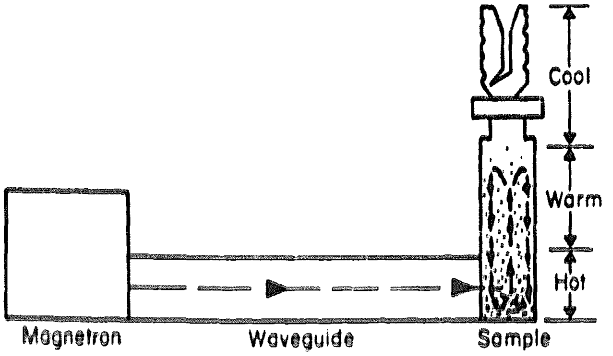

Fig. 1. Schematic drawing of a wave-guide design for focused MW digestion.

Desired ratios Y_2O_3/Fe_3O_4 powders (3–5 g in our case) were thoroughly mixed, then poured into the test-tube and finally exposed to the MW beam at ambient atmosphere. During the experiment, the test tube is rotated at ~30 rev./min in order to obtain a good homogeneity of the MW energy absorption in the material. In some experiments, a small amount of carbon was added to enhance the reaction [3]. In order to reduce the number of experimental parameters, the MW power was fixed to 300 W and exposure time to 150 s.

3. Results and discussion

3.1. MW synthesis

The measured temperature vs. time curves for the reacting mixture are plotted in Fig. 2. As shown in Fig. 2a and b (x = 0 and 10%, respectively), the temperature increases in an exponential manner [7]. When $T \sim 543$ K, strong burstings are heard and simultaneously white, red and purple flashes are clearly observed. Finally, the mixture becomes incandescent white near 900 K in less than 3 min. It is to be noted that when small amounts of carbon graphite addition

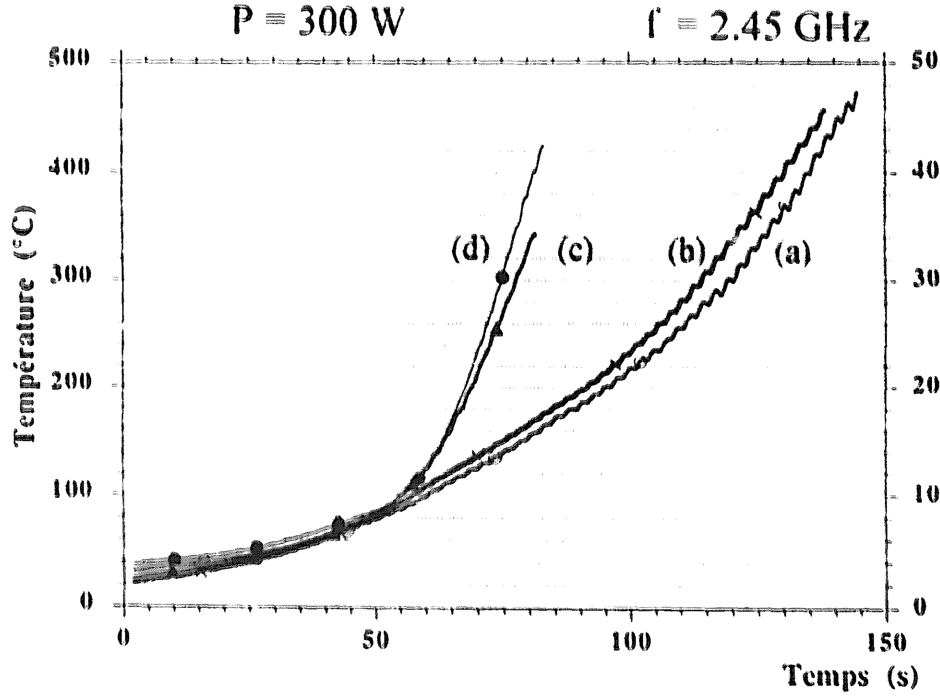

Fig. 2. Temperature vs. time curves during MW heating of Y_2O_3-Fe_3O_4 mixtures for different ratios: (a) x = 0%; (b) 10%; (c) 0% + C; (d) 10% + C. C indicates that a small amount of C graphite was added to the mixture prior to MW exposure.

(0.3 g) are added to the oxide mixtures (Figs. 2c and d), they become red hot at very low temperature ($T \sim 493$ K) after 1 min which is roughly half the time needed by the mixtures without C to reach the same temperature. The same light emission and acoustic phenomena previously observed for the mixtures without C occur but at temperatures lower by 100–150 K. In all cases, the exposure to the MW beam is then stopped at a temperature close to 900 K. It is to be noted that this addition of C has no significant influence on the resulting reaction products. Nevertheless, the results discussed below concern only the oxide mixtures without C addition.

In all the experiments, the final product, obtained after cooling down to 300 K, shows the coexistence of a dark red powder (~ 30% weight) and hard melted blocks (~ 70%). They exhibit a metallic reflexion and appear as melted aggregates. After a coarse crunching, these aggregates are reduced into grains of various sizes (up to a few mm) which can be magnetically separated at room temperature fairly easily. The melted part thus corresponds to a mixture of polycrystalline 'magnetic' and 'non-magnetic' grains. X-ray diffraction experiments were performed on the powders and also on mm-size individual grains of the magnetically separated melted aggregates. These grains are very hard to crunch into powder for the diffraction experiments.

3.2. X-ray diffraction analyses

The X-ray diffraction results concerning the MW synthesis products obtained from the four compositions x = 0, 5, 10, and 20% (without carbon addition) are presented in Table 1. The diffraction patterns confirm a good crystallinity of the different phases.

The red-brown powder part is always constituted of a mixture of α-Fe_2O_3, Y_2O_3 and traces of $YFeO_3$ and YIG. This confirms that Fe_3O_4 is unstable under MW exposure and transforms mainly into α-Fe_2O_3,

Table 1
Approximate compositions of the different binary Y, Fe oxides synthesized after MW exposure

x (%) Y/Fe = 3/[5(1 + x)]	Magnetic	Non-magnetic part part	Powder
0	$Y_3Fe_5O_{12}$ (50) $YFeO_3$ (50)	$YFeO_3$ (90) Y_2O_3 (10)	α-Fe_2O_3 Y_2O_3
5	$Y_3Fe_5O_{12}$ (40) $YFeO_3$ (60)	YFe_2O_4 (60) $YFeO_3$ (40)	α-Fe_2O_3 Y_2O_3
10	$Y_3Fe_5O_{12}$ (90) $YFeO_3$ (10)	YFe_2O_4 (85) Y_2O_3 (15)	α-Fe_2O_3 Y_2O_3
20	$Y_3Fe_5O_{12}$ (70) $YFeO_3$ (30)	YFe_2O_4 (50) $YFeO_3$ (50)	α-Fe_2O_3 Y_2O_3

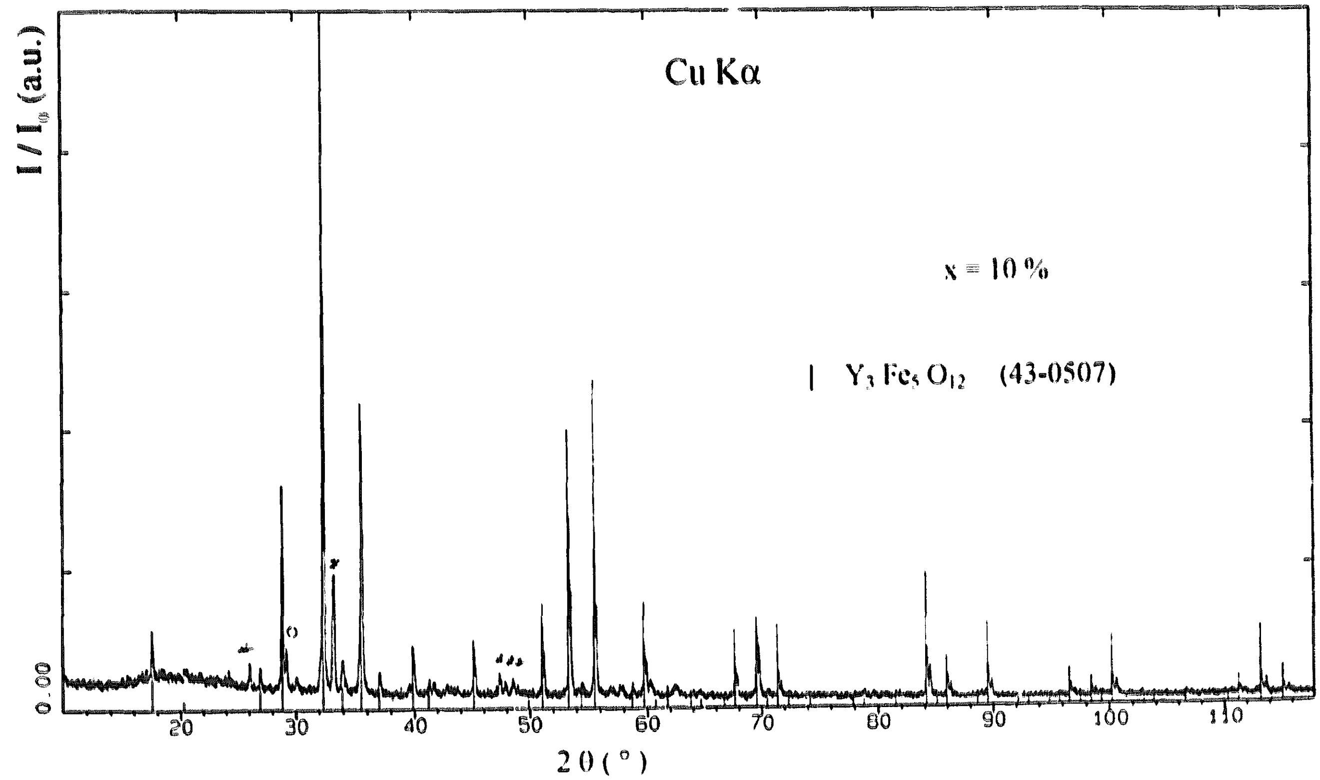

Fig. 3. X-ray diffraction pattern of the 'magnetic' part of the melted aggregate after MW exposure corresponding to the mixture Y_2O_3-Fe_3O_4 with x = 10%. The reference spectrum corresponds to $Y_3Fe_5O_{12}$ (vertical bars ICDD-JCPDS card 43-0507). Small amounts of $YFeO_3$ (stars) and traces of Y_2O_3 (O) are also observed.

and Y_2O_3, as mostly white powders, has not reacted, in agreement with previous results [2–4].

The main constituents of the melted aggregates were found to be binary oxides of Y and Fe whose relative ratios vary according to the composition of the initial charge (Table 1). The products and the crystal data are as follows: $Y_3Fe_5O_{12}$ (cubic *Ia3d* $a_0 = 1.2378$ nm), yttrium orthoferrite $YFeO_3$ (orthorhombic *Pnma* $a = 0.5595$ nm, $b = 0.7605$ nm and $c = 0.5282$ nm), and YFe_2O_4 (trigonal $R\bar{3}m$ with $a = 0.6090$ nm and $c = 2.4788$ nm in a hexagonal crystallographic system).

YIG is always found in the magnetic grains of the melted aggregates and is absent in the non-magnetic ones, which allows an easy means of separation. It coexists with the yttrium orthoferrite. When $x = 10\%$, nearly pure YIG is obtained (Fig. 3). To our knowledge, it is the first time that polycrystalline YIG powder has been synthesized by this method. The quasi omnipresence of $YFeO_3$ both in magnetic and non-magnetic parts confirms that this compound plays a central role in the synthesis of YIG. It is well known that YIG melts incongruently in air at 1823 K into $YFeO_3$ and α-Fe_2O_3, and orthoferrite is a frequent impurity phase found in ferrimagnetic garnets [8,9].

Referring to Table 1, it is to be noted that YFe_2O_4 is obtained only when $x > 0$. The synthesis of YFe_2O_4 (Fig. 4) is surprising. This compound, which shows a composition zone from $YFe_2O_{3.9}$ to YFe_2O_4 (at present the exact composition of the MW synthesized compound is not known) was studied by different authors [5,10–14]. Indeed it is synthesized at high temperature under very low partial oxygen pressure. Therefore, our experimental conditions: ambient atmosphere and low temperature cannot be compared to the references mentioned above.

We will now briefly discuss the apparent discrepancy between the temperatures needed to synthesize the Y, Fe binary oxides by solid state reaction and the MW recorded ones. During MW exposure the evaluation of the sample temperature is a very difficult problem. Compared to classical thermodynamics the temperature gradient is reversed: the heart of the material is heated at once. So each grain is annealed from the centre up to the surface [7] and the part of the powder absorbing the MW energy becomes red-hot in a very short time (~ 1 min) [15]. The true response of the IR-pyrometer is hidden first by the powder around the central heated zone, and second by the tube wall which plays a shielding role. In order to have a good evaluation of this temperature, an optical pyrometer located in front of the upper part of the test-tube shows no deviation during our experiments indicating that the temperature of the samples

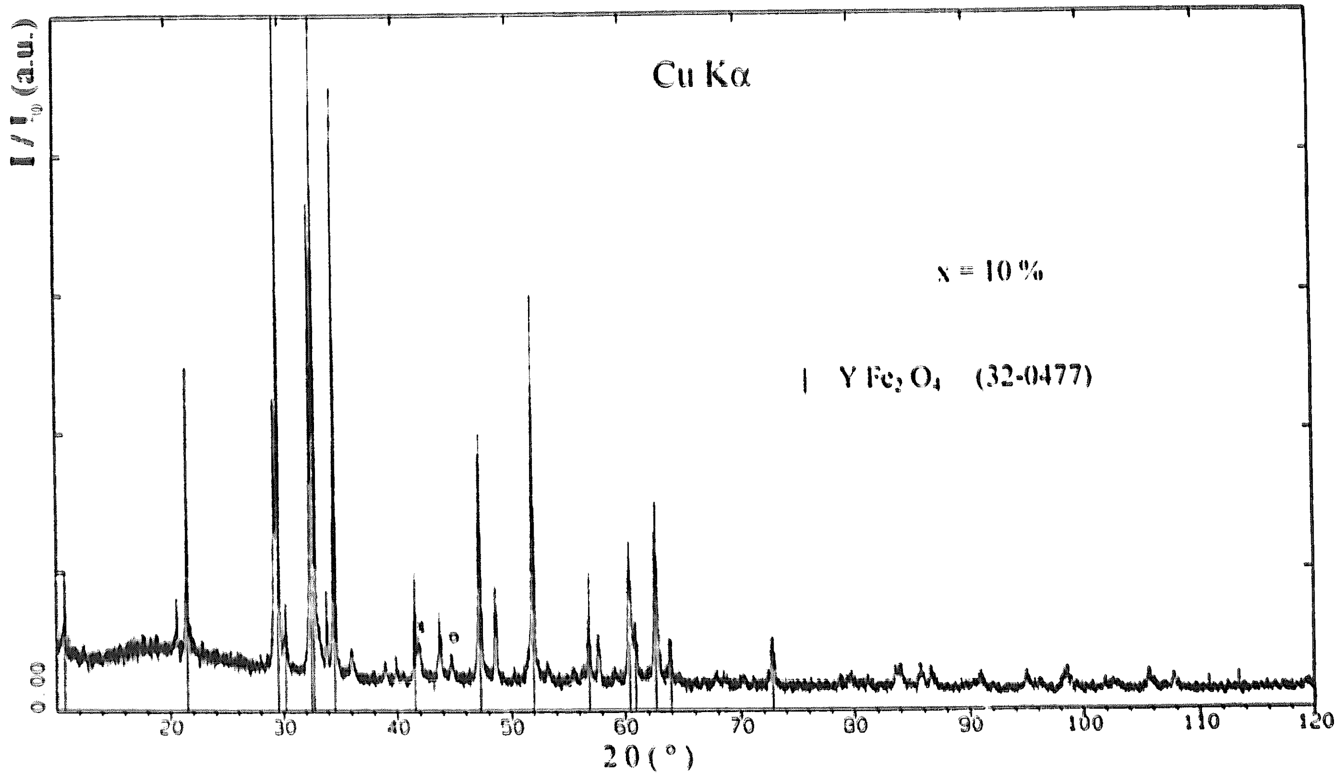

Fig. 4. X-ray diffraction pattern of the 'non-magnetic' part of the melted aggregate after MW exposure corresponding to the mixture Y_2O_3-Fe_3O_4 with $x = 10\%$. The reference spectrum corresponds to YFe_2O_4 (vertical bars ICDD-JCPDS card 32-0477 ($2\theta < 74°$). Traces of impurity phases FeO (*) and Fe (○) are also possible. Other peaks: Y_2O_3 and/or YFe_2O_4 ($2\theta > 74°$).

is less than 1020 K (low temperature limit of the pyrometer). It is therefore possible that the reactions taking place under focused MW energy depend greatly on the very local conditions of temperature and oxygen pressure. These local parameters may thus be strongly different from the macroscopic measured ones.

The phase equilibria in the Fe-Fe_2O_3-Y_2O_3 system at 1473 K have already been established [5]. Depending on the partial oxygen pressure, complex chemical equilibria exist among these three binary oxides and Y_2O_3, α-Fe_2O_3, Fe_3O_4, FeO and Fe. As stated in [9], generally in a ternary system such as the Y-Fe-O system, where the bulk composition of a condensed phase assemblage varies with the oxygen partial pressure in the atmosphere, it is often observed that two solid phases, or even three, coexist in equilibrium with a liquid phase at the solidus temperature. This leads us to tentatively ascribe a few intense unassigned peaks of the diffraction patterns to the reflections of these latter compounds. For instance, FeO and Fe might be impurity phases as a few intense unassigned peaks (star and circle in Fig. 4) correspond to the principal peaks of these compounds. This is also in agreement with the fact that FeO [9] and metallic Fe [11] were found as impurity phases in YFe_2O_4 single crystals.

3.3. Application to the synthesis of YIG:Sc compounds

In order to extend the method to practical applications, we tried to synthesize a ternary YIG compound such as the Y-Sc-Fe garnet. Sc is known to enter the garnet lattice by substitution in the Fe^{3+} octahedral sublattice leading to interesting magneto-optical applications [1]. In this experiment, a mixture of Sc_2O_3, Y_2O_3 and Fe_3O_4 corresponding to the atomic ratios $Y/Sc = 2/1$ and $(Y+Sc)/Fe = 3/5$ was exposed to the MW beam in the same experimental conditions as described in the preceding sections. The X-ray diffraction pattern of a magnetic mm-size polycrystal of the melted part is shown in Fig. 5. The lattice parameter $a_0 = 1.2463$ nm is deduced from the garnet phase lines. Assuming that Sc ions substitute only to Fe ions [16], this indicates that the formula of the garnet can be written $Y_3Fe_{5-t}Sc_tO_{12}$ with $t = 1$. It is known that the t-value cannot exceed 1.5. The ratio of orthoferrite and other impurity phases is very low (Fig. 5).

4. Conclusion

From our experiments, we can conclude that it is possible to synthesize nearly pure YIG and substituted YIG compounds at less than 900 K in a few

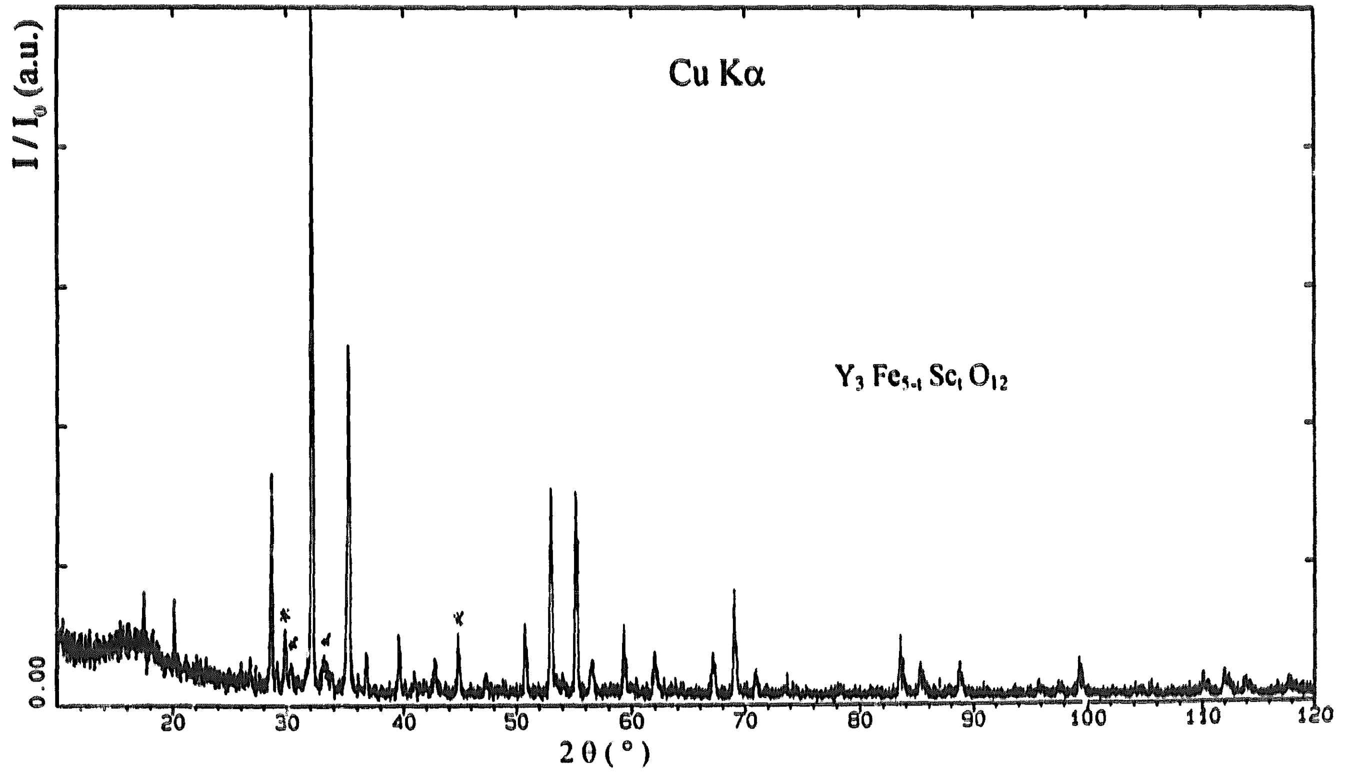

Fig. 5. X-ray diffraction pattern of the 'magnetic' part of the melted aggregate after MW exposure corresponding to the mixture Y_2O_3-Sc_2O_3-Fe_3O_4. The spectrum corresponds mainly to the garnet $Y_3Fe_{5-t}Sc_tO_{12}$ with $a_0 = 1.2463$ nm indicating that $t = 1$. A few intense lines marked with (*) correspond to non-garnet impurity phases.

minutes by means of monomode MW treatment in air. The second very important result proceeds from the formation of the YFe_2O_4 compound which is obtained under low partial oxygen pressure ($\sim 10^{-10}$ atm) at 1473 K under classical thermodynamic conditions [5]. As observed by Worner [17], 'the MW energy apparently stimulates endothermic reactions just as it hastens exothermic reactions; and chemical reactions (such as smelting) seem to take place at significantly lower temperature than when conventional means of heating are involved'. Finally, in MW ovens, the MW energy is absorbed instantaneously, and internal and volumetric heating occur. Sutton [7] has claimed that: 'the heat is generated internally within the material instead of originating from external heating sources'.

We observe in the case of an intermediary oxide such as Pr_6O_{11} that both the oxidation reaction (PrO_2) and the reduction reaction (Pr_2O_3, Pr_7O_{12}) occur at the same time under MW exposure [3]. This is to be compared to the chemical reactions observed in this work for Fe_3O_4.

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