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Experimental Study of the Bi_2O_3-Fe_2O_3 Pseudo-Binary System

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As part of a general contribution to the study of accelerator driven system (ADS) nuclear reactor feasibility, a study of the five-component system Bi-Fe-Hg-O-Pb was undertaken. New results about the quasi-binary Bi_2O_3-Fe_2O_3 are presented in this paper. The phase diagram was reinvestigated by differential scanning calorimetry, x-ray diffraction, and electron probe microanalysis. A new compound was discovered and characterized: $Bi_{25}FeO_{40}$. Its crystallographic structure was refined. Invariant and transition temperatures are given, as well as phase compositions.

1. Introduction

Among the nuclear reactors for power generation of the future, accelerator driven systems (ADS) will use a proton accelerator, on the one hand, and a liquid metal target, on the other hand, to yield neutrons that will sustain the fission reaction in a subcritical core. The liquid will be the eutectic alloy Pb + 55.2 wt.% Bi. It will be both the fast neutron source (spallation reactions with the incident energetic protons) and a heat carrier [2000Kne].

To predict the long-term behavior of the structural material (T 91 steel, 9 Cr, 1 Mo), containing the liquid bath, thermodynamic knowledge of the five-component system Bi-Fe-Hg-O-Pb is needed:

- In the liquid proton target, spallation reactions may yield impurities [2002Vil] and especially non negligible quantities of mercury.
- On the surface of T 91 samples subjected to long term corrosion tests in conditions reproducing those of the reactor [2001Bar, 2001Faz, 2002Maî1], products like Fe_3O_4, $Fe_{(1-x)}Cr_xFe_2O_4$, $Bi_{25}FeO_{40}$, and PbO have been found.

The subsystem Pb-Bi-Hg has already been studied in the laboratory [2002Mai2], and a new compound with a stoichiometry around $Bi_7Hg_4Pb_9$ has been found. Its stability range is below 37 °C. A strong diminution of the liquidus temperatures is induced by small additions of mercury (<1 wt.%).

To continue the description of the ternary subsystems of Bi-Fe-Hg-O-Pb, we have undertaken the study of Bi-Fe-O. Very few papers dealing with this system are found in the literature. At first, the isopleth Bi_2O_3-Fe_2O_3, which includes several corrosion products of the T91 was characterized. Koizumi et al. [1964Koi] and Speranskaya et al. [1965Spe] have published two contradictory versions (Fig. 1a and 1b); the main points being the intermediate compound near Bi_2O_3, the invariants, and the allotropic transformation in $BiFeO_3$. In more recent works concerning Bi_2O_3-Fe_2O_3, physico-chemical characteristics have been determined without questioning the phase equilibria [1989Dim, 1989Tan, 2000Luo, 2000Pas].

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2. Experimental

The raw materials used were supplied by Riedel-de-Haën (St. Louis, MO) (Fe_2O_3, 99.99 wt.%) and Alfa (Ward Hill, MA), (Bi_2O_3, 99.99 wt.%). Their main characteristics are given in Table 1. Scanning electron microscopy (SEM) was used to determine the morphology of the powders (Fig. 2a and 2b).

Mixtures of oxides were prepared under air by weighing and mixing the components in an agate mortar before introducing them into platinum crucibles, which were then sealed by arc welding to limit weight losses, i.e., composition changes during heat treatments.

The first treatment of heating at 1 °C min^{-1} up to 1000 °C, several hours at that temperature, and then cooling at 1 °C min^{-1} ensured the reaction between the components. Then differential scanning calorimetry (DSC) from room temperature to 1000 °C with a calorimeter designed and built in the laboratory [1986Gac] gave the temperatures of transformation and the relative quantities of products in the samples. The temperature cycles were composed of heating and cooling at a rate of 2 °C min^{-1} with an annealing of 15 min at the top temperature (Fig. 3a). After DSC experiments, the products were subjected to x-ray diffraction (Philips X'pert Pro, Eindhoven, The Netherlands, λ = 0.154056 nm), SEM (Hitachi S-2500, Tokyo, Japan), and electron probe microanalysis (EPMA; CAMECA SX100, Courbevoie, France). For EPMA, the instrument operating conditions were 10 kV accelerating voltage and 10 mA probe current, and the size of the excited zone was about 1 μm^3. Accumulation times on standards and samples were determined to achieve good accuracy for the element content analyses. In addition, EPMA on samples heat-treated

Table 1 Main Characteristics of the Oxides

Oxide (manufacturer)	Purity, wt.%	Specific Mass, gcm^3	Specific Area BET, m^2 g^{-1} min	Size (from Manufacturer, μm)	Size from BET, μm (a)
Bi_2O_3 (Riedel-de-Haën)	99.99	8.90	4.7	1-5	0.14
Fe_2O_3 (Alfa)	99.99	5.25	3.0	1-5	0.38

(a) The mean diameter of the grains is deduced from $d_m = 6 \times \rho/S_{BET}$ with S_{BET} the specific area determined by the BET method.

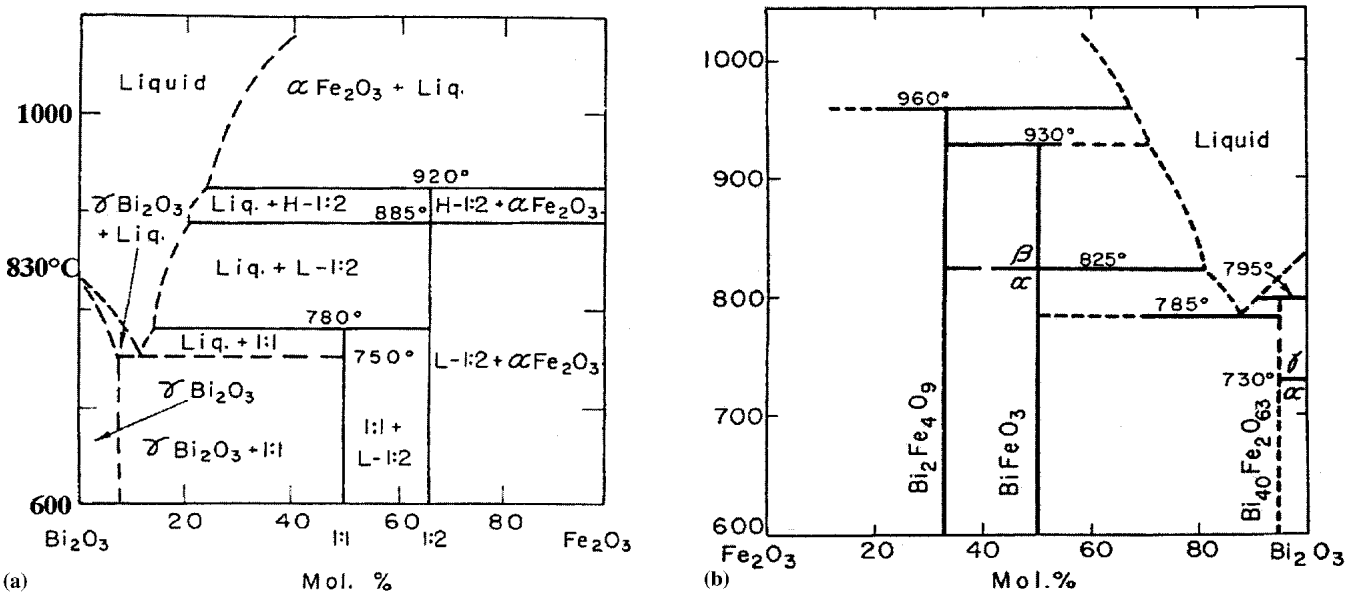

Fig. 1 Bi_2O_3-Fe_2O_3 phase diagrams as proposed by **(a)** [1964Koi] and **(b)** [1965Spe]

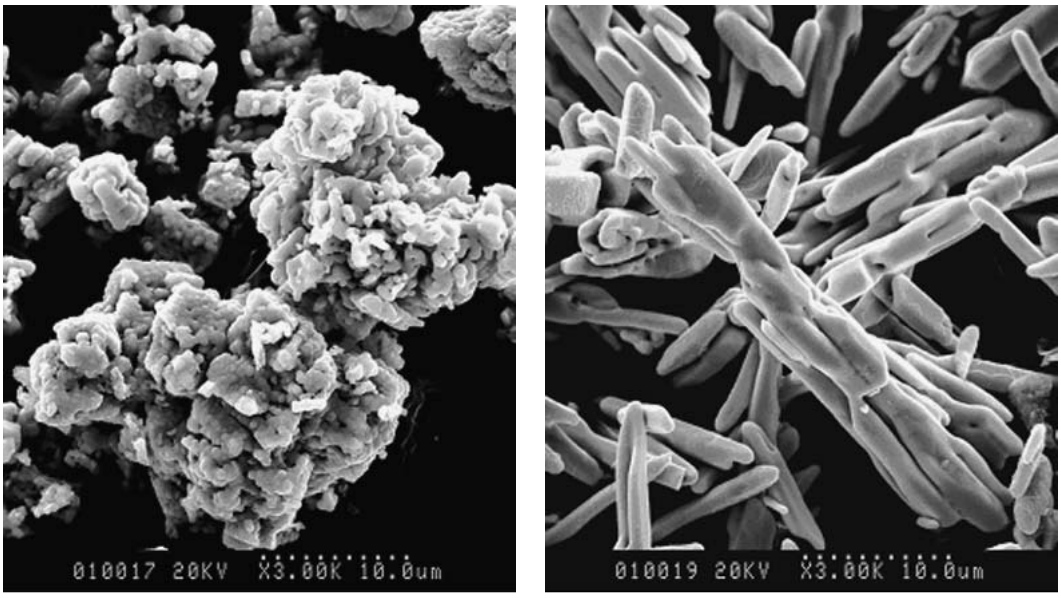

Fig. 2 SEM photomicrographs of **(a)** Fe_2O_3 and **(b)** Bi_2O_3 powders

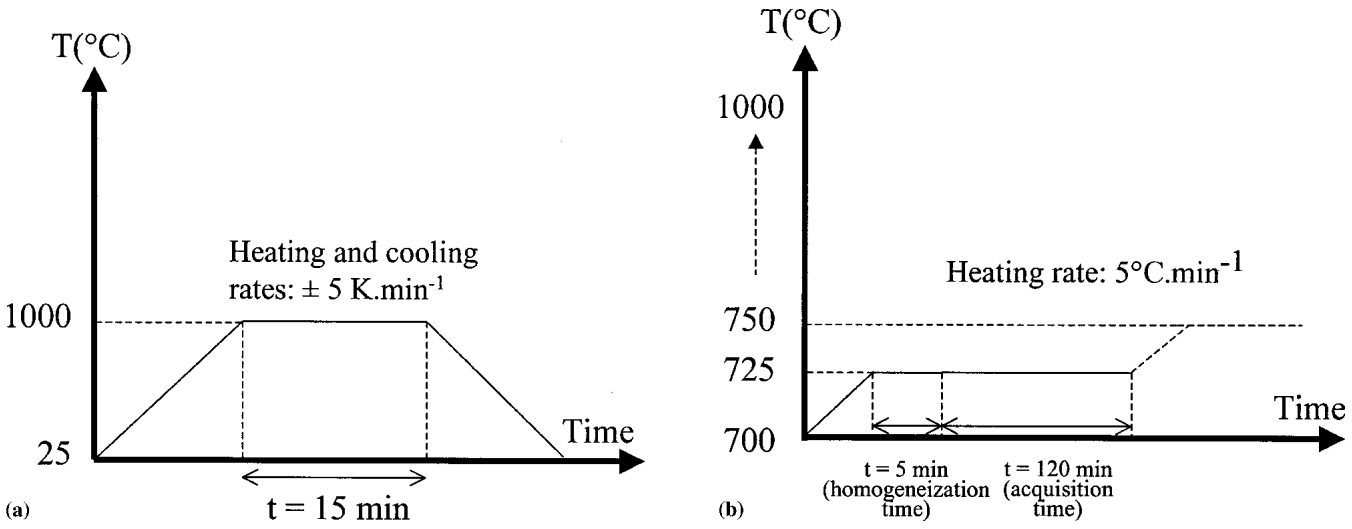

Fig. 3 Temperature programs used during **(a)** DSC and **(b)** HTXRD experiments.

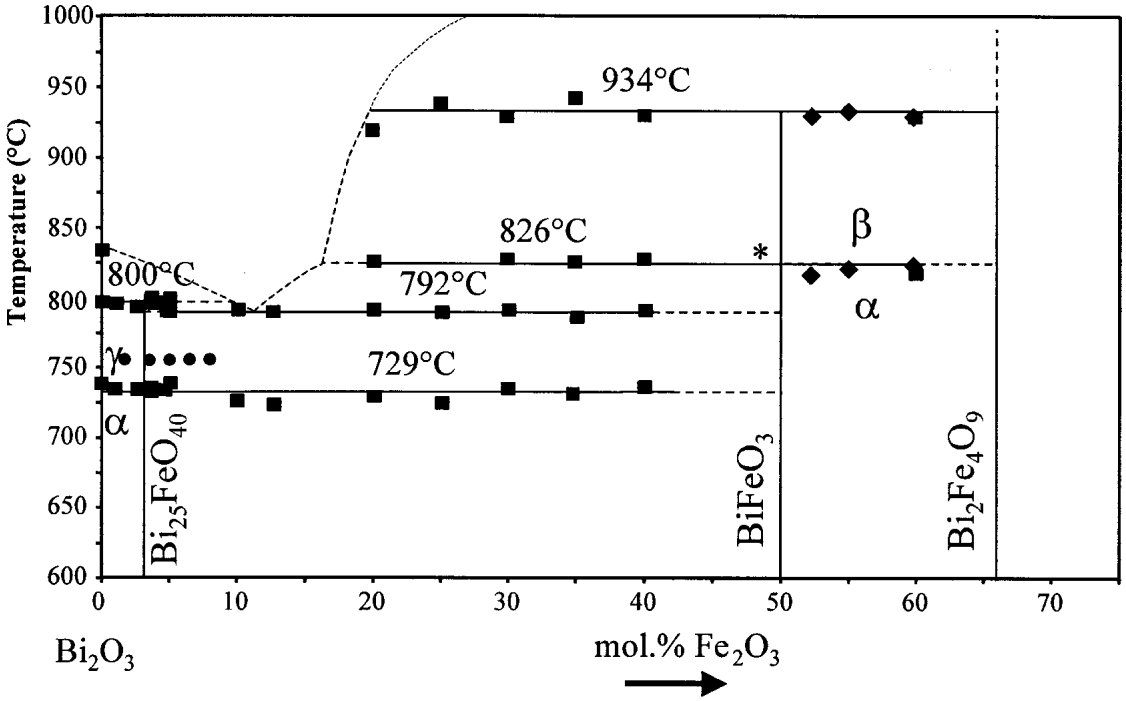

Fig. 4 Phase diagram Bi_2O_3-Fe_2O_3 in the temperature range 600-1000 °C. Equilibria (●) were characterized after long annealings. Invariant temperatures (■) were determined by DSC runs. Allotropic transitions (♦) were studied by HTXRD and DSC. The DSC arrests near 729 °C on either side of $Bi_{25}FeO_{40}$ possibly represent an allotropic transition in that phase though x-ray patterns (see Fig. 9) at T > 729 °C and T < 729 °C imply that the structural change is not major. Alternatively, these arrests may mean that the DSC samples in the composition range between $Bi_{25}FeO_{40}$ and $BiFeO_3$ retained some unreacted Bi_2O_3. This hypothesis seems also to be ruled out by our EPMA studies. Detection thresholds were such that the results did not give theoretically any possibility of mistaking one phase for another. It is necessary to perform new experiments to decide definitively on this point. (*): It is impossible, given the uncertainty of the temperature measurements, to characterize any temperature difference between the two invariants on the left and the right of $BiFeO_3$.

for several days at temperatures between 800 and 900 °C and quenched in ice gave the equilibrium concentrations. Furthermore, the morphology of the samples was also examined by optical microscopy (Olympus VANOX AHMT, Hamburg, Germany).

The polymorphic transformations in $BiFeO_3$ and $Bi_2Fe_4O_9$ were checked by x-ray diffraction at high temperatures. The scans were carried out with a Philips X'Pert Pro diffractometer (Eindhoven, The Netherlands) in the Bragg Brentano θ-2θ geometry. A high-temperature cell

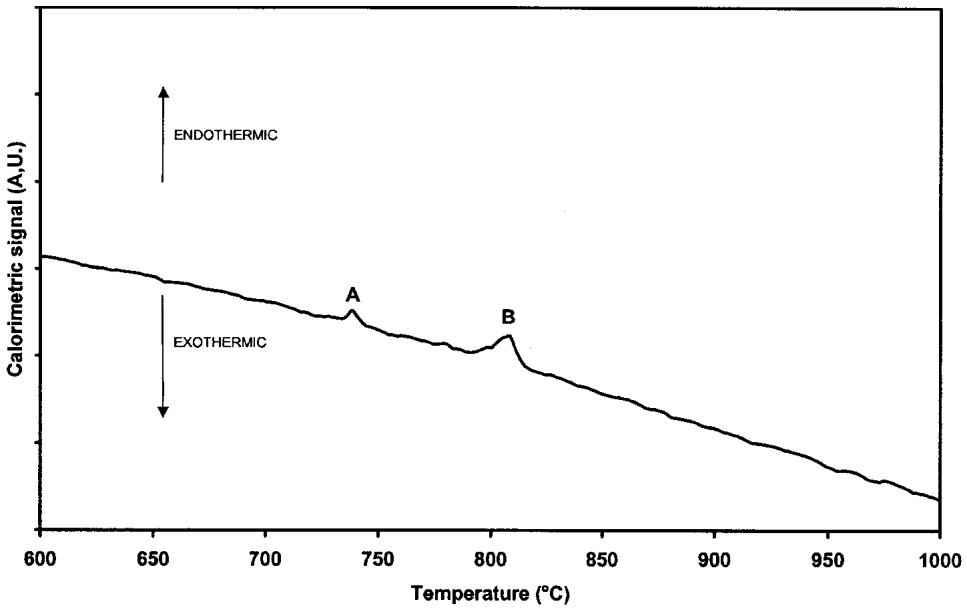

Fig. 5 DSC recording of the heating at 2 K min^{-1} of a sample with 1.3 mol.% Fe_2O_3

HTK 1200 from Anton Parr (Graz, Austria) was used and was equipped with a Kanthal APM furnace (Sandriken, Sweden), copper radiation ($\lambda_{K\alpha(Cu)} = 0.14056$ nm), kapton windows, and a rotating sample holder (30 rpm). This device is capable of working under vacuum or imposed atmosphere up to 1200 °C. For $BiFeO_3$, each pattern was recorded between 20 and 70° (2θ) with steps of 0.02° and 1.5 s counting time. Figure 3(b) gives schematically one step of the temperature program. To identify the phases, the search routine of the Diffract-AT software (Socabim, Paris, France) [1994Nus] was used. Moreover, the phases such as α-$BiFeO_3$, β-$BiFeO_3$, and $Bi_{25}FeO_{40}$ were indexed from the JCPDS files 71-2494 [1971Mor], 72-2112 [1960Zas], and 46-0416 [1990Rad], respectively. To study the allotropic transformation in $BiFeO_3$, the patterns recorded at 800 and 825 °C are analyzed by the Rietveld method with use of the program FULLPROF (Laboratoire Leon Brillouin, Saclay, France) [2000Rod]. The starting parameters were taken from [1969Mor] for the refinement of the low-temperature crystallographic structure (800 °C) and from [1969Tut] for the high-temperature structure (825 °C). Interatomic distances were calculated by using the IVTON software (Bioson Research Institute, Groningen, The Netherlands) [1988Vic].

3. Results and Discussion

The Bi_2O_3-Fe_2O_3 phase diagram was determined with the results from around twenty-five samples whose compositions were chosen between 0 and 75 mol.% Fe_2O_3. Figure 4 presents the interpretation of all the experimental results.

3.1 Phase Limits and Invariants

On the Bi_2O_3 side of the system, no traces of iron in the phase Bi_2O_3 were detected, which means that the solubility of Fe_2O_3 is probably lower than the detection threshold of the EPMA. As a consequence, the shape and size of the α + γ domain was out of reach. DSC experiments did not give any clear indications of either liquidus shape or composition. Reaction between the liquid products and the platinum crucible is a probable cause of this fact.

Figure 5 shows the DSC record obtained by heating sample with a 1.3 mol.% Fe_2O_3. Two endothermic peaks (A and B) exist at 739 and 798 °C, respectively. Above the temperature T_B, crossing the liquidus does not give any appreciable signal. It must be noted that

- The peak A corresponds to the polymorphic trasnformation in Bi_2O_3: $\alpha \leftrightarrow \gamma$
- The peak B can be attributed to the peritectic: Bi_2O_3 + liq. $\leftrightarrow$ $Bi_{25}FeO_{40}$

$Bi_{25}FeO_{40}$ is a stoichiometric phase that was detected during the course of this work. Speranskaya et al. [1965Spe] had already suspected a compound close to Bi_2O_3, but they failed to accurately determine its chemical composition. A microprobe observation of a sample with 12.5 mol.% (Fig. 6a), after slow cooling (−2 K min^{-1}), shows the presence of two phases: $Bi_{25}FeO_{40}$ and $BiFeO_3$. XRD on the same sample (Fig. 6b) confirmed the two compounds, with the majority being $Bi_{25}FeO_{40}$, which is cubic [1990Rad]. The stochiometric designation as $Bi_{25}FeO_{40}$ is based on the analysis of the gray phase in Table 2.

Using all the experimental results, the invariant equilibria have been determined and compared with what was available in literature (Table 3). Obviously, the earlier results of Speranskaya et al. [1965Spe] are close to ours, the transformation temperatures found by these authors differ by less than 10 °C from those determined in this work.

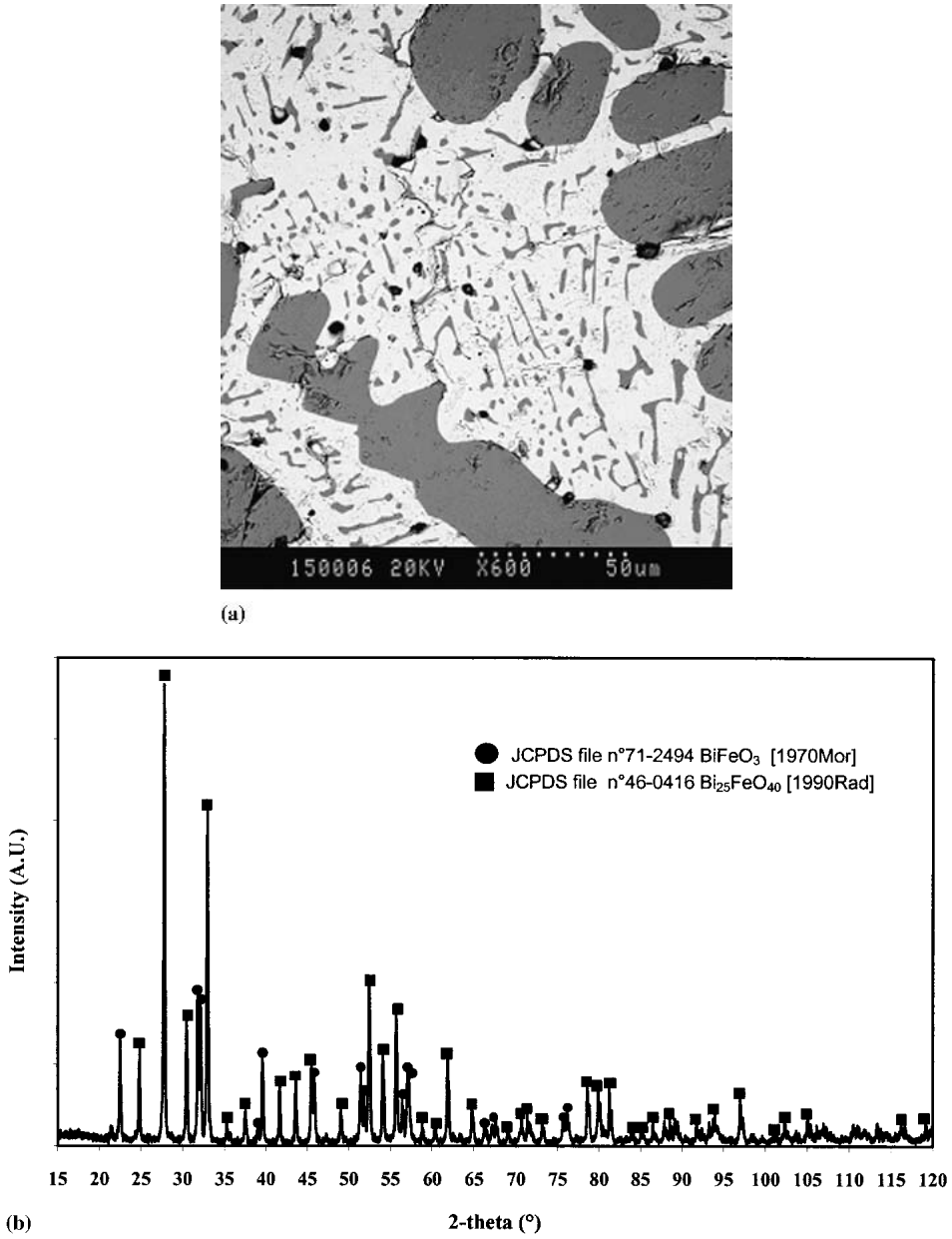

Fig. 6 **(a)** SEM micrograph of the sample 0.125 mol·(Bi_2O_3)-0.875 mol·(Fe_2O_3), heat-treated in the calorimeter up to 1000 °C, then slowly cooled, and **(b)** XRD pattern at room temperature of the same product. The two phases are distinguished: $BiFeO_3$ gray and $Bi_{25}FeO_{40}$ light gray. Chemical analyses are given in Table 2.

3.2 Allotropic Transformations

Allotropic transformations were studied by high-temperature x-ray diffraction (HTXRD) for both $Bi_{25}FeO_{40}$ and $BiFeO_3$. These experiments allowed us to check the temperatures already determined by DSC runs, but the values given by HTXRD are considered as only indicative due to the difficulty to ascertain the surface temperature of the sample.

3.2.1 $BiFeO_3$ phase. Figure 7 shows the results of HTXRD tests between 725 and 1000 °C for a sample with 60 mol·% Fe_2O_3. Between 800 and 825 °C, a split of some lines of $BiFeO_3$ denotes a crystallographic transition. The temperature detected by DSC (824 °C) is in accordance with the HTXRD measurements. Figure 8 shows the Rietveld analyses at 800 and 825 °C and the corresponding structural

Table 2 Electron Probe Microanalysis Results of the Mixture 0.125 mol.(Bi_2O_3)-0.875 mol.(Fe_2O_3) Shown in Fig. 6

Element	Bi	Fe	O
Detection threshold, at.%	0.14	0.21	0.25
Gray phase, at.%	19.87	19.81	60.32
Light gray phase, at.%	37.16	1.51	61.33

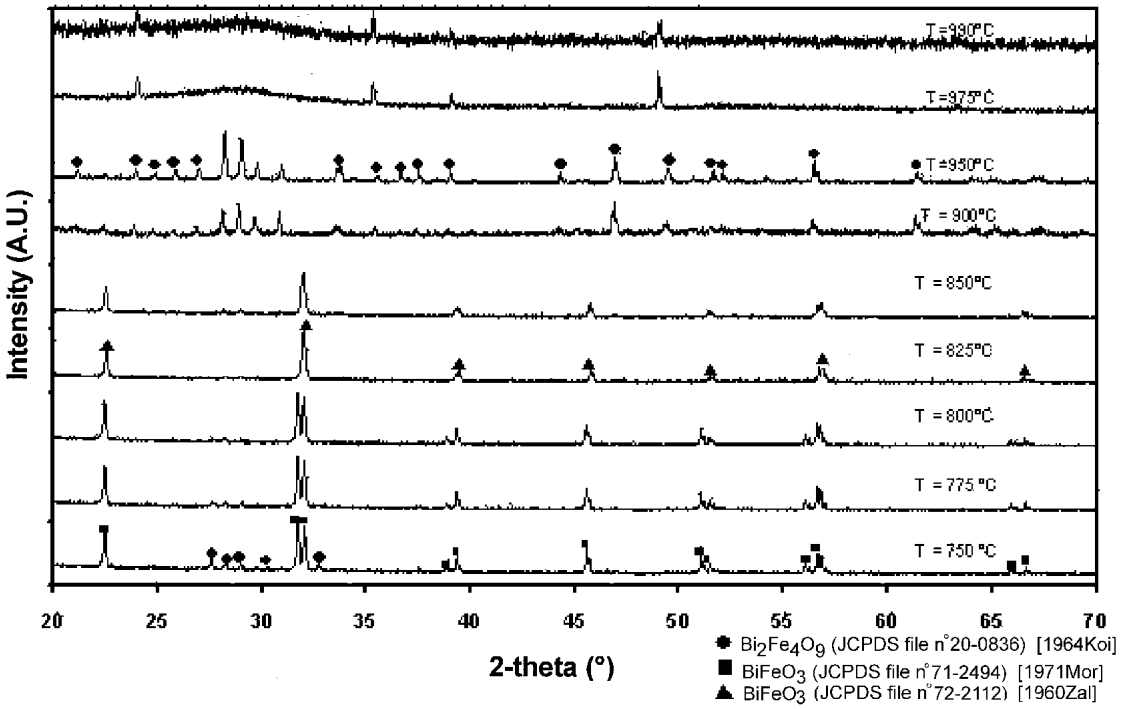

Fig. 7 High-temperature XRD patterns of a sample with 0.6 mol. Fe_2O_3. The temperature program, which has been followed, is schematically illustrated in Fig. 3(b). It has not been noted that temperatures given are only indicative and less accurate than those given by DSC.

Table 3 Characteristics of the Main Invariant in the System Bi_2O_3–Fe_2O_3, This Work and Literature Data

	Temperatures, °C, Observed by DSC, Heating Rate, 2 K min^{-1}											
	$Bi_{25}FeO_{40}$ + $BiFeO_3$ ↔ Liq			$Bi_{25}FeO_{40}$ ↔ Liq + Bi_2O_3			$BiFeO_3(\alpha)$ ↔ $BiFeO_3(\beta)$			$BiFeO_3(\beta)$ ↔ Liq + $Bi_2Fe_4O_9$		
Composition, Molar% Fe_2O_3	This Work	[1964 Koi]	[1965 Spe]	This Work	[1964 Koi]	[1965 Spe]	This Work	[1964 Koi]	[1965 Spe]	This Work	[1964 Koi]	[1965 Spe]
0.000	…	…	…	800	…	795	…	…		…	…	…
0.050	791	…	…	798	…	795	…	…		…	…	…
0.100	792	750	785	…	…	…	…	…		…	…	…
0.125	792	750	785	…	…	…	…	…		…	…	…
0.200	792	750	785	…	…	…	826	885	825	919	920	930
0.250	790	750	785	…	…	…	826	885	825	939	920	930
0.300	792	750	785	…	…	…	828	885	825	928	920	930
0.350	787	750	…	…	…	…	826	885	825	942	920	930
0.400	792	750	…	…	…	…	828	885	825	930	920	930
0.600	…	…	…	…	…	…	…	885	825	928	920	930

model with the FeO_6 octahedra representation. Below 824 °C, α-$BiFeO_3$ may be described as rhombohedral (*R*3*c*) with cell parameters, which were refined:

At 800 °C, $a = b = 0.5694(2)$ nm, and $c = 0.6885(2)$ nm.

Above 824 °C, β-$BiFeO_3$ is rhombohedral (*R*3*m*), and its cell parameters are

At 825 °C, $a = b = 0.56314(2)$ nm, and
$c = 1.39850(7)$ nm.

This variety may also be described as a nearly ideal perovskite structure (cell angles $\alpha = \beta = \gamma \approx 90°$). In addition, atoms positions are specified: Bi and Fe are on 1*a* positions while O is on 3*b*. Atomic positions and distances are given in Table 4 and 5.

From a crystallographic point of view, the α ↔ β allotropic transition corresponds to:

- A lifting of degenerescency for the Fe-O distances. In the β high temperature form, Fe octahedral surrounding is defined by 6 equivalent Fe-O distances of 0.1992(1)

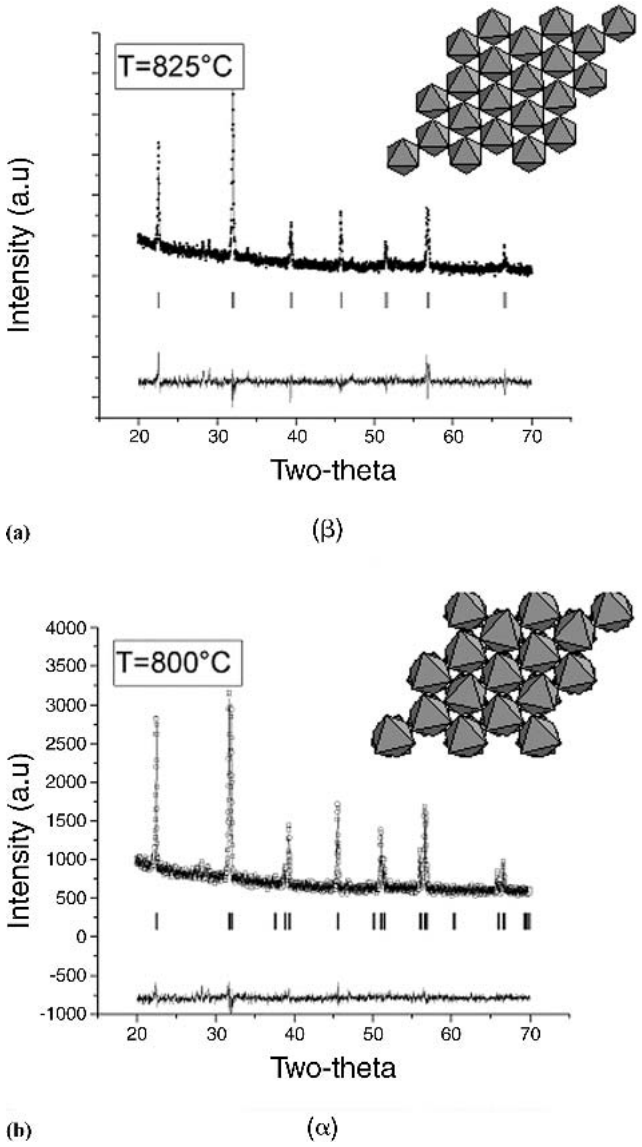

Fig. 8 Experimental (points) and computed (line) x-ray diffraction patterns for high (β) and low (α) temperature forms of $BiFeO_3$

nm. On the contrary, the α low temperature form is characterized by two different Fe-O distances of 0.197(5) and 0.218(5) nm, respectively.

- Rotations of the FeO_6 octahedra around the ternary axis (00*z*) leading to a superstructure of order two along this axis (Fig. 8a and 8b).

Above 900 °C, β-$BiFeO_3$ disappears to give $Bi_2Fe_4O_9$ and an amorphous (liquid) phase. Then, $Bi_2Fe_4O_9$ disappears above 975 °C.

3.2.2 $Bi_{25}FeO_{40}$ phase. A similar procedure was followed for several mixtures with different compositions in the two phase field $Bi_{25}FeO_{40}$-$BiFeO_3$. Results are presented for a 30 mol.% Fe_2O_3 mixture (Fig. 9), which gave the more clear patterns. $BiFeO_3$ lines are still of relative low intensities but at the same time give reference points.

Table 4 Interatomic Distances, nm, in $BiFeO_3$ for the Low Temperature (α, 800 °C) and the High-Temperature (β, 825 °C) Structures

Atom–Atom	*d*, nm, at 800 °C	*d*, nm, at 825 °C
Fe-O	6 × 0.1992 (1)	3 × 0.197 (5)
		3 × 0.218 (5)
Bi-O	6 × 0.2814 (1)	3 × 0.225 (6)
	6 × 0.2820 (1)	3 × 0.250 (5)
		3 × 0.332 (6)
		3 × 0.353 (6)
Bi-Fe	2 × 0.3443 (1)	1 × 0.313 (2)
	6 × 0.3452 (1)	3 × 0.3348 (5)
		3 × 0.3594 (9)
		1 × 0.386 (2)

Table 5 Structural Parameters of $BiFeO_3$ for the Low-Temperature (α, 800 °C) and the High-Temperature (β, 825 °C) Structures

Parameter	At 800 °C, *R3c*	At 825 °C, *R3m*
a_h, nm	0.56314 (2)	0.5639 (1)
c_h, nm	1.3985 (1)	0.6886 (2)
a_r, nm		0.3984 (1)
α_r, °		90.11 (5)
Iron	In site (6a)	In site (3b)
z, Fe	0.224 (2)	0
Oxygen	In site (18b)	In site (9e)
x (O)	0.44 (1)	0.5
y (O)	0.023 (8)	0
z (O)	0.949 (4)	0
Bismuth	In site (6a) fixed at $z = 0$	In site (3a)

HTXRD patterns in the range 620-760 °C do not show any noticeable crystallographic modification, specially for $Bi_{25}FeO_{40}$ (Fig. 9). The face-centered-cubic (fcc) cell parameter of $Bi_{25}FeO_{40}$ changes from 1.0294(2) nm at 620 °C to 1.0318(3) nm at 760 °C, which is only due to thermal expansion. Consequently, from these results, it is not possible to confirm a crystallographic transition already suspected by DSC for $Bi_{25}FeO_{40}$. If a lattice parameter distortion occurs due to lowering of the symmetry, it might be of very small amplitude. In this case, the XRD pattern with the high resolution given by synchrotron radiation is necessary for determining the structural changes.

4. Conclusion and Future Work

The overall shape of the phase diagram deduced from this work is close to the one already proposed by Speranskaya et al. [1965Spe], but some points that were uncertain are now firmly established:

- The presence and chemical composition of $Bi_{25}FeO_{40}$ in the quasi binary system Bi_2O_3-Fe_2O_3 were deter-

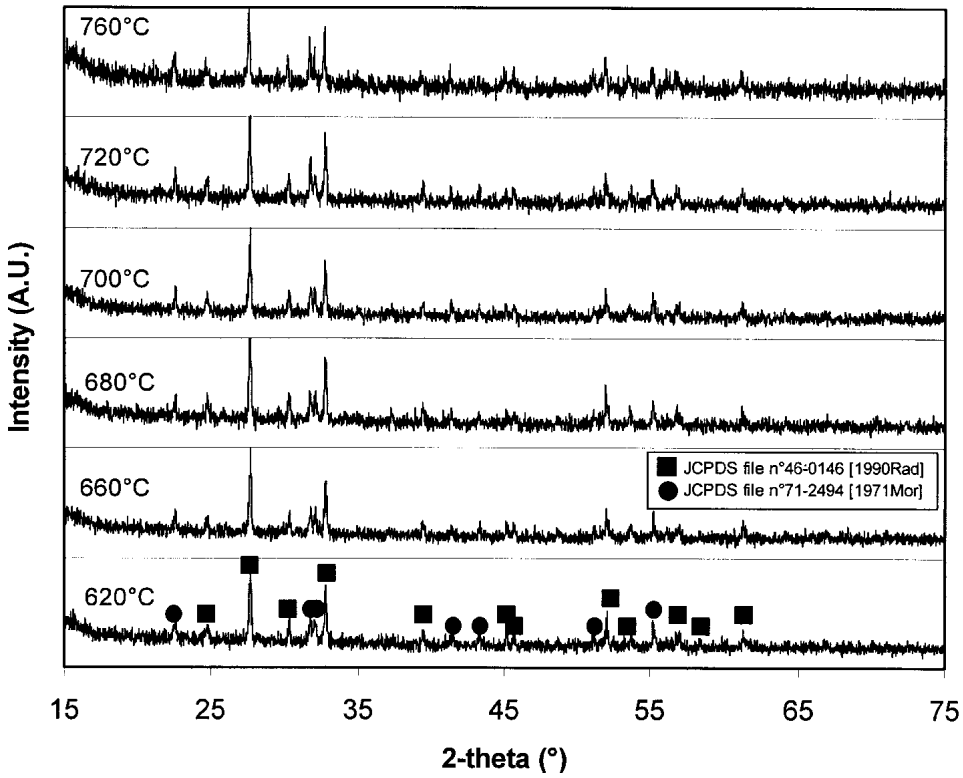

Fig. 9 XRD patterns between 620 and 760 °C for the composition like 0.3 mol.% Fe_2O_3 [with (■) for $Bi_{25}FeO_{40}$ and (●) for $BiFeO_3$]

mined by HTXRD and EPMA, which contradicts [1964Koi] and corrects [1965Spe].

- Eutectic and peritectic invariant temperatures were defined more accurately than before. The differences found between this work and those of [1964Koi] and [1965Spe] may be due to product purity and the sensitivity of the calorimeter which was used, not a differential thermal analysis device but a truly quantitative calorimeter [1986Gac].
- $BiFeO_3$ $\alpha \leftrightarrow \beta$ allotropic transition was established and structurally characterized.
- $Bi_{25}FeO_{40}$ was isolated.

There are still some points that need clarification:

- The liquidus shape is still unknown. The DSC experiments did not give indications about it, and its worth mentioning that the higher the temperature, the higher the uncertainty. The products, when above 1000 °C for a long time, attack the platinum crucible, and experiments become meaningless just before they destroy the calorimeter. A CALPHAD optimization may help on this point.
- An allotropic transition in $Bi_{25}FeO_{40}$ may exist.
- Oxygen pressure effects on the system have not yet been investigated.

Acknowledgments

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