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# Quasi-reversible transformations and thermal stability of $\text{BiPbSr}_{2-x}\text{Ca}_x\text{FeO}_{6+z}$ with $x=0$ and 1

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## Abstract

A Mössbauer spectroscopy study of the products of the quasi-reversible reaction Fe-2201 phases  $\rightleftharpoons$  Fe-2212 phases was performed. Differences in the values of the hyperfine field at 4.2 K and drastic changes of the Néel temperatures offered evidence for deviations in the Bi:Pb:Sr:Fe ratios of the Fe-2212 phases obtained during 30 h annealing at 700 °C from the as-prepared  $\text{Bi}_2\text{PbSr}_2\text{Fe}_2\text{O}_{9+z}$  and  $\text{Bi}_2\text{PbSrCaFe}_2\text{O}_{9+z}$  compounds. Only slight differences in Néel temperature and hyperfine field parameters were found by comparing the as-prepared  $\text{BiPbSr}_2\text{FeO}_{6+z}$  and  $\text{BiPbSrCaFeO}_{6+z}$  with the Fe-2201 products obtained after a subsequent annealing for 24 h at 850 °C. In all Fe-2201 compounds, besides the majority of Fe present in the form of  $\text{Fe}^{3+}$  with a hyperfine field of 50–51 T at 4.2 K, about 11–12% of Fe nuclei exhibited a hyperfine field of 19–20 T, which could be attributed to the valency state  $\text{Fe}^{4+}$ . From the analysis of the values of the quadrupole splitting at 4.2 K and above the Néel temperature a spin arrangement parallel to the *c*-axis for the Fe-2201 phases but in the basis plane for the Fe-2212 ones could be inferred.

**Keywords:** Quasi-reversible transformations; Thermal stability; Mössbauer spectroscopy

## 1. Introduction

In the last few years new complex iron oxides of type  $((\text{Bi,Pb})\text{O})_2\text{Sr}_2\text{Bi}_{n-1}\text{Fe}_n\text{O}_{3n+1+z}$  ( $n=1, 2, 3, 4$ ) have been synthesized and studied [1–8]. Structurally these compounds are similar in many aspects to the high- $T_C$  superconductor series  $((\text{Bi,Pb})\text{O})_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+z}$ . The main difference is that in the Fe series the oxygen is in excess, the iron ions being always octahedrally surrounded by oxygen. Recently, the substitution of calcium for strontium, leading to the compositional series  $((\text{Bi,Pb})\text{O})_2\text{Sr}_{2-x}\text{Ca}_x\text{Bi}_{n-1}\text{Fe}_n\text{O}_{3n+1+z}$  ( $n=1, 2, 3, 4$ ), has also been reported [9].

During the study of these new compounds evidence was found for a quasi-reversible temperature-dependent reaction in oxygen atmosphere by which the members of the series with  $n=1$ , here denoted as Fe-2201, give rise to one with  $n=2$  (denoted as Fe-2212 in the following), which at higher temperatures transforms again to a Fe-2201 phase [9]. The conclusions of the

authors were mainly based on room-temperature X-ray study of the products of the reactions occurring at several temperatures with different durations.

In our study we undertook another approach based on the high Fe content of these compounds. It is indeed possible to use  $^{57}\text{Fe}$  Mössbauer spectroscopy in order to perform a quite reliable phase analysis of Fe-containing systems, especially when the studied compounds order magnetically below a critical temperature. And in the case when Mössbauer spectroscopy measurements are technically feasible in the temperature range of the investigated reactions even a direct in situ study of the chemical processes and of the products of reaction becomes possible. Here we report on the quasi-reversible transformation of both series' members with  $x=0$  and  $x=1$ , and in a second part [10] we discuss the influence of temperature and duration on the reversible transformation.

## 2. Experimental

For our study we prepared four samples as follows: (1) sample A with the nominal composition  $\text{BiPbSr}_2\text{Fe}_{6+z}$ ;

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(2) sample B with the nominal composition  $\text{BiPb-SrCaFeO}_{6+z}$ ;

(3) sample C with the nominal composition  $\text{Bi}_2\text{Pb-Sr}_2\text{Fe}_2\text{O}_{9+z}$ ;

(4) sample D with the nominal composition  $\text{Bi}_2\text{Pb-SrCaFe}_2\text{O}_{9+z}$ .

The details of the preparation procedures were the same as the ones described in [1] and [2].

For the preparation of the enriched samples a corresponding quantity of a  $^{57}\text{Fe}$  solution in  $\text{HNO}_3$  was used and evaporated to dryness in the presence of the additional starting materials. The samples were characterized with a Philips XRD powder diffractometer (Cu  $K\alpha$  radiation) in the as-prepared state. In addition, selected samples were X-ray checked after performing subsequent thermal treatments and recording the Mössbauer spectra.

In order to study the predicted transitions two procedures were used:

(1) The samples A and B were heated in air at 700 °C, 740 °C and 850 °C for different durations and then quenched. The Mössbauer spectra were recorded at 4.2 K and room temperature (RT) using a standard set-up. In some cases temperature-dependent measurements over larger intervals were also performed.

(2) In situ Mössbauer measurements were performed at different temperatures in the 20–900 °C range. Because of the relatively long measurement time (>20 h), necessary in order to give good statistics at temperatures higher than RT, the recorded spectrum at a given temperature offers a cumulative picture of the changes occurring during the whole recording time. The result of this study will be presented in a further paper [10].

The Mössbauer parameters were obtained by computer analysis using a least-squares method. For each subspectrum the Lorentzian lines were constrained to have equal widths and the opposite peaks were restricted to have the same intensity.

### 3. Results and discussion

The Mössbauer spectra of samples A, B, C and D, taken at 4.2 K, are shown in Fig. 1(a). They are similar to the ones reported earlier by Sinnemann et al. [11,12] and could be fitted in a similar way. In the case of sample A, as already mentioned by Sinnemann et al. in [11], the relatively large values of the line widths allowed in principle a fit with two sextets and closely lying values of the hyperfine field (HF), the quadrupole splitting (QS) and the isomer shift (IS). The better resolution of the spectrum shown in Fig. 1 allowed us to try a fit to two subspectra, and because of the extra intensity evident between about  $-3 \text{ mm s}^{-1}$  and  $+4 \text{ mm s}^{-1}$ , to build in even a third sextet with a low HF

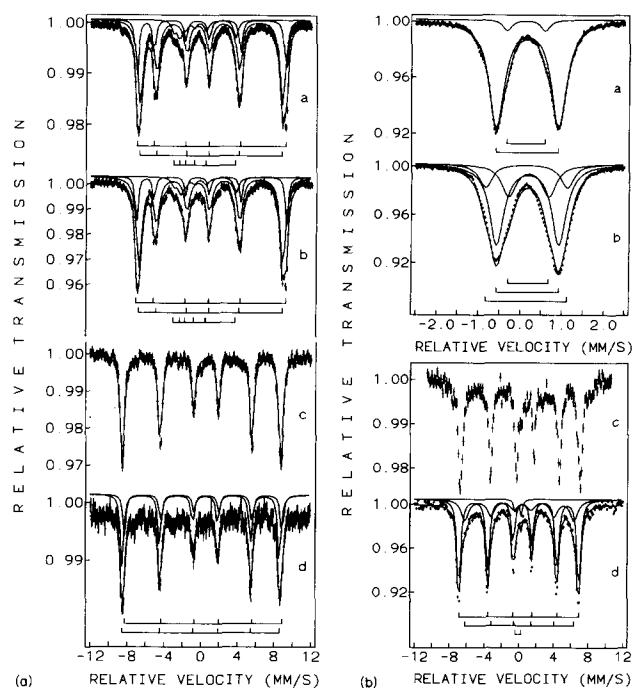


Fig. 1. (a) The 4.2 K Mössbauer spectra of samples A, B, C and D. (b) The RT Mössbauer spectra of samples A, B, C and D (in the sequence a, b, c and d).

value. A similar fit to three sextets was used for sample B, and the Mössbauer parameters of these fits are given in Table 1.

Whereas the Mössbauer spectra of samples A and B recorded at room temperature were paramagnetic doublets, the one of sample C was still magnetically split (Fig. 1(b)), with a hyperfine value of 42.8 T. These findings are in excellent agreement with the values of the Néel temperatures of 212 K and 512 K for  $\text{Bi-PbSr}_2\text{FeO}_{6+z}$  and  $\text{Bi}_{2.5}\text{Pb}_{0.5}\text{Sr}_2\text{Fe}_2\text{O}_{9+z}$  respectively [11,12].

The 4.2 K Mössbauer spectra of samples C and D shown in Fig. 1(a) are very similar. Nevertheless, in the latter case the fit with two sextets with very close values of the hyperfine field and quadrupole splittings was a better option for the description of the experimental data.

As expected from the chemical and structural data, as mentioned earlier [11,12], iron in the studied compounds is predominantly trivalent, according to the values of HF (49–53 T) and IS ( $0.3\text{--}0.4 \text{ mm s}^{-1}$ ). The contribution of about 11% of Fe with a low hyperfine value found in samples A and B can be interpreted in terms of overoxidation and evidence for  $\text{Fe}^{4+}$  [13]. The absence of this contribution in the paramagnetic spectrum taken at RT (Fig. 1(b)), which could be fitted to two doublets with large quadrupole splittings (sample A), can be due to the difficulty of separating it inside the doublet with rather large intensity and line width, or to the fast electron hopping between ions with variable valence, which are accommodated in our structure. A

Table 1  
Mössbauer parameters of initial samples

Sample	Temperature	Subspectrum	Relative intensity (%)	Line width (mm s <sup>-1</sup> )	Isomer shift (mm s <sup>-1</sup> )	Quadrupole splitting (mm s <sup>-1</sup> )	Hyperfine field (T)
A	4.2 K	1	25	0.42	0.32	1.53	50.5
		2	64	0.72	0.32	1.44	48.2
		3	11	0.56	-0.28	1.92	18.9
	RT	1	95	0.45	0.17	1.57	-
2		5	0.25	0.14	0.91	-	
B	4.2 K	1	19	0.36	0.31	1.55	50.8
		2	70	0.74	0.33	1.41	48.7
		3	11	0.63	-0.27	1.99	18.9
	RT	1	16	0.38	0.14	1.95	-
		2	60	0.42	0.17	1.49	-
		3	24	0.42	0.19	0.96	-
C	4.2 K	1	100	0.51	0.35	-0.57	53.7
	RT	1	100	0.55	0.23	-0.54	42.8
D	4.2 K	1	65.5	0.40	0.27	-0.23	53.3
		2	34.5	0.38	0.47	-0.17	53.4
	RT	1	66.5	0.49	0.23	-0.20	42.9
		2	30.5	1.03	0.25	-0.18	39.0
		3	3	0.32	-0.05	0.66	-

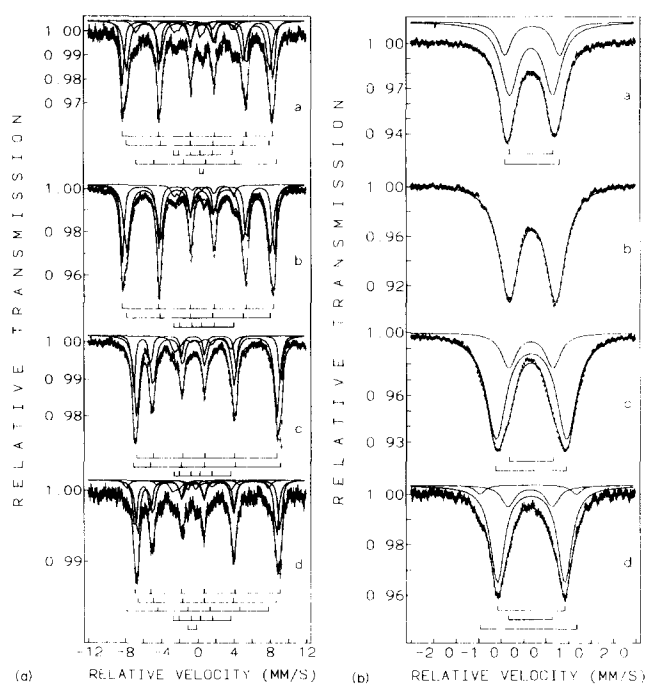


Fig. 2. (a) The 4.2 K Mössbauer spectra of samples treated at 700 °C for 30 h and later at 850 °C for 24 h: A<sub>2</sub>, B<sub>3</sub>, A<sub>4</sub>, B<sub>8</sub>. (b) The RT spectra for samples A<sub>2</sub>, B<sub>3</sub>, A<sub>4</sub> and B<sub>8</sub> (in the sequence a, b, c and d).

more detailed analysis of the Fe<sup>4+</sup> contribution will be presented in a forthcoming paper [10].

A scrutiny of the Mössbauer parameters of samples A and B determined at 4.2 K and given in Table 1 shows that besides the values of the hyperfine fields,

which are slightly larger for sample B, one can consider the shapes of the spectra with an unusually large value of the quadrupole splitting as a good fingerprint for the compounds with only one Fe atom per unit formula (Fe-2201).

The spectra of samples C and D were magnetically split at both 4.2 K and RT (Table 1). From the paramagnetic region one obtains different values for the quadrupole splittings (QS) of the compositions Fe-2201 and Fe-2212. The former one reached at RT an average value of 1.50 mm s<sup>-1</sup>, whereas the values obtained above  $T_N$  for samples C [14,15] and D [15] were in the range 0.98–1.06 mm s<sup>-1</sup>.

It is worth mentioning the close values of the Néel temperatures for two members of each pair of compounds with either 2Sr or 1Sr and 1Ca ( $x=0$  and  $x=1$  but with different numbers of Fe–O layers). For the Fe-2201 pair A and B we have  $T_N$  values of 212 K [11] and 238 K [15]. For the Fe-2212 pair we find 512 K [12] for  $x=0$  and an extrapolated but similar value for  $x=1$  obtained from the temperature dependence of the hyperfine field in the range 4.2–300 K.

A comparison of the quadrupole splittings found at 4.2 K and room temperature in the case of the Fe-2201 phases A and B (Table 1) allowed us to find the probable direction of the Fe spins below the magnetic ordering temperature  $T_N$ . As already argued previously [11] from simple geometrical considerations one can assume that the tensor of the electrical field gradient at the Fe sites of the Fe-2201 phases has an uniaxial symmetry with the  $V_{zz}$  component along the  $c$ -axis. In

such a case the quadrupole splitting in the magnetically ordered state is given by

$$(QS)_{\text{mag}} = \frac{1}{4} eQ V_{zz} (3 \cos^2 \phi - 1) \quad (1)$$

where  $Q$  is the nuclear  $^{57}\text{Fe}$  quadrupole moment;  $V_{zz}$  is the  $z$ -component of the electrical field gradient (EFG); and  $\phi$  is the angle made by the Fe spins with the direction of  $V_{zz}$ , i.e. in our case the  $c$ -axis.

Above  $T_N$  the quadrupole splitting in the paramagnetic state is given by

$$(QS)_{\text{para}} = \frac{1}{2} eQ V_{zz} \quad (2)$$

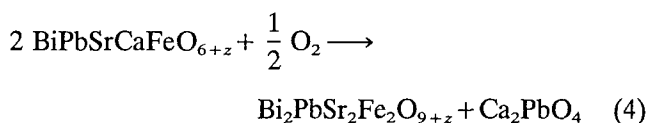
In the case when the Fe spins order in such a way that they orient themselves parallel to the direction of  $V_{zz}$

$$(QS)_{\text{mag}} = \frac{1}{2} eQ |V_{zz}| \quad (3)$$

That is, the modulus of the quadrupole splitting does not change when the spin system undergoes the antiferromagnetic transition. And in fact a 'glance' at Table 1 shows that for samples A and B the values of QS are about the same in both the antiferromagnetic and paramagnetic regimes. At this point it is worth mentioning that the orientation of the spins parallel to the  $c$ -axis of the Fe-2201 phases occurs only at low temperatures. As shown in [11], strong evidence for a Morin-like spin reorientation was found for  $\text{BiPbSr}_2\text{FeO}_{6+z}$  and later on for  $\text{BiPbSrCaFeO}_{6+z}$ , an aspect which will be treated in more detail in a forthcoming paper [10].

No direct conclusions about the spin direction in the Fe-2212 phases C and D could be drawn from the 4.2 K and RT quadrupole splitting data because of the magnetic ordering lying above RT for both samples C and D. The negative QS values given in Table 1 mean that either the spin direction is this time perpendicular to the  $c$ -axis, or the  $V_{zz}$  component of the EFG is negative. But in the already mentioned previous study of a Fe-2212 compound with a parent composition  $\text{Bi}_{2.5}\text{Pb}_{0.5}\text{Sr}_2\text{Fe}_2\text{O}_{9+z}$  having  $T_N = 512$  K [12], values of  $(QS)_{\text{mag}} = -0.42$  mm s $^{-1}$  and  $(QS)_{\text{para}} = 0.99$  mm s $^{-1}$  were found. The former is quite close to  $QS = -0.46$  mm s $^{-1}$  found at 4.2 K for sample D, for instance, and therefore offers a strong argument in favour of an orientation of the spins perpendicular to the  $c$ -axis at temperatures below  $T_N$  in the Fe-2212 phases C and D. As will be seen further, the occurrence of Fe-2212 phases with  $T_N$  below RT and the values of QS in the magnetic ordered state similar to the ones of the samples C and D offer complementary support for the proposed spin arrangement in Fe-2212 compounds.

In order to reproduce the chemical reaction  $\text{Fe-2201} \rightarrow \text{Fe-2212}$  studied in [9] at 700 °C for 15 h, we performed several treatments at the same temperature or at 740 °C. The parameters of the Mössbauer spectra obtained with samples A and B, treated for 30 h at 700 °C and denoted as samples  $A_2$  and  $B_3$  in Table 2, are presented in Table 3. The opposite reaction  $\text{Fe-2212} \rightarrow \text{Fe-2201}$  was studied as a result of the subsequent treatment of the samples  $A_2$  and  $B_3$  for 24 h at 850 °C (samples  $A_4$  and  $B_8$  in Table 2). According to the idealized mechanism of reaction proposed in [9] one has



That is, the sample B has to transform completely in the sample C plus calcium plumbate.

The 4.2 K and RT Mössbauer spectra of sample  $B_3$  are shown in Figs. 2(a) and 2(b). Even a superficial inspection of the spectrum taken at 4.2 K shows that it is very similar to the one for sample C (Fig. 1(a)), i.e. of the initial compound  $\text{Bi}_2\text{PbSr}_2\text{Fe}_2\text{O}_{9+z}$ . But at variance with the latter, about 5% of the Fe, with a hyperfine field of 19.7 T, is in the  $\text{Fe}^{4+}$  state.

Despite the strong similarity of the 4.2 K Mössbauer spectra of the Fe-containing product of reaction with the ones of sample C ( $\text{Bi}_2\text{PbSr}_2\text{Fe}_2\text{O}_{9+z}$ ), slight but relevant differences especially in the HF and QS values are obvious. And a more striking new aspect is that, as mentioned above, for sample C the RT Mössbauer spectrum is still magnetically split (i.e. magnetic order present at RT), whereas the Mössbauer spectrum of sample  $B_3$  at RT is purely paramagnetic (Fig. 2(b)). Under these circumstances, the suspicion arises that the Fe-containing phase that appears at 700 °C after a longer treatment and, as sample C, contains two Fe atoms per unit formula, is not identical with the latter (C) one. In fact we found that the Néel temperature of the Fe-2212 phase ( $B_3$ ) obtained after 30 h treatment at 700 °C of the initially prepared Fe-2201 sample (B) reached only 290 K, therefore lying sensibly lower than

Table 2  
Starting compositions of the samples treated for 30 h at 700 °C and subsequently for 24 h at 850 °C

No.	S	SC <sup>a</sup>	TT <sup>b</sup>
5	$A_2$	A	30 h/700 °C
6	$A_4$	A	30 h/700 °C + 24 h/850 °C
7	$B_3$	B	30 h/700 °C
8	$B_8$	B	24 h/850 °C 30 h/700 °C

<sup>a</sup>Starting composition of the treated sample.

<sup>b</sup>Thermal treatment.

the critical temperature of 512 K of the freshly prepared Fe-2212 compound containing only Sr (sample C).

This circumstance allows us, as in the case of the Fe-2201 phases, to compare the QS in both antiferromagnetic and paramagnetic regions for an Fe-2212 phase, this time the B<sub>3</sub> sample A. A glance at Table 3 shows that in a good approximation the average QS at 4.2 K is negative and close to half the RT quadrupole splitting (paramagnetic) value. According to Eqs. (1) and (2) the Fe spins at 4.2 K have to lie perpendicular to the *c*-axis, i.e. in the basal plane. This finding corroborates the already-mentioned earlier results on Bi<sub>2.5</sub>Pb<sub>0.5</sub>Sr<sub>2</sub>Fe<sub>2</sub>O<sub>9+z</sub> [12], making it plausible to conclude that this type of spin arrangement, opposite to the one arising in the Fe-2201 phases, occurs in a large variety of Fe-2212 phases with Néel temperatures in the interval 200–520 K.

At this point one has to mention that by increasing the temperature from about 200 K the paramagnetic component in the Mössbauer spectrum of sample B<sub>3</sub> steadily increases in intensity, reaching for instance 60% at about 260 K. It seems that the treatments leading to this sample give rise to a distribution of iron environments and therefore to a rather broadened magnetic phase transition.

In order to study the transition back in the single Fe–O layer phase (Fe-2201) found at 850 °C in [9], we tried to reach the complete transformation and to check the whole reversibility by increasing the duration of the treatment at 850 °C up to 24 h following the first one at 700 °C. In fact, as one can see in Fig. 2(a), the 4.2 K Mössbauer spectra of samples A<sub>4</sub> and B<sub>8</sub> are practically identical with those of samples A and B (Fig. 1). However, it is worth mentioning that, for instance, the Fe-2201 phase thus formed (sample B<sub>8</sub>) had a Néel temperature of about 204 K, i.e. lower than the 238 K of the originally prepared single-phase Fe-2201 sample (B), whereas the Fe-2212 (B<sub>3</sub>) phase was paramagnetic at RT, in strong discrepancy with the initially double Fe–O layer compound (sample C) with a magnetic critical temperature of 512 K.

As already mentioned in [9], the quasi-reversible reaction Fe-2201 → Fe-2212 → Fe-2201 also occurs when starting with BiPbSr<sub>2</sub>FeO<sub>6+z</sub> (sample A), i.e. no presence of Ca is needed for it. And in fact we found both steps of the reaction. From the Mössbauer parameters presented in Table 3 one can see that the Fe-2212 phase (*x*=0) built during the reaction at 700 °C (A<sub>2</sub>) has values of HF and QS which again are only slightly different from the ones characterizing sample C. And as in the case of the Ca-containing sample (B) after

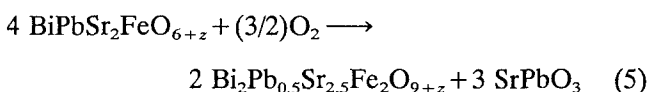
Table 3  
Mössbauer parameters of the products resulting from the thermal treatment of sample A (BiPbSr<sub>2</sub>FeO<sub>6+z</sub>) and sample B (BiPbSrCaFeO<sub>6+z</sub>)

Sample	Temperature	Subspectrum	Relative intensity (%)	Line width (mm s <sup>-1</sup> )	Isomer shift (mm s <sup>-1</sup> )	Quadrupole splitting (mm s <sup>-1</sup> )	Hyperfine field (T)
A <sub>2</sub>	4.2 K	1	37	0.45	0.33	-0.52	51.6
		2	44	0.70	0.30	-0.42	49.0
		3	10	0.73	0.32	1.36	48.2
		4	7	0.43	-0.094	1.75	20.0
		5	2	0.30	0.41	0.36	-
A <sub>2</sub>	RT	1	26	0.34	0.20	1.22	-
		2	74	0.46	0.17	0.96	-
B <sub>3</sub>	4.2 K	1	39	0.46	0.34	-0.48	52.0
		2	56	0.78	0.33	-0.37	49.2
		3	5	0.36	-0.13	1.88	19.7
B <sub>3</sub>	RT	1	100	0.53	0.20	1.04	-
A <sub>4</sub>	4.2 K	1	39	0.46	0.33	1.56	49.2
		2	35	0.42	0.31	1.48	49.0
		3	10	0.51	-0.24	1.78	18.7
		4	16	0.94	0.38	0.20	49.5
A <sub>4</sub>	RT	1	80	0.53	0.18	1.57	-
		2	20	0.39	0.17	0.99	-
B <sub>8</sub>	4.2 K	1	32	0.44	0.30	1.64	49.8
		2	43	0.54	0.30	1.53	47.7
		3	7	0.62	0.10	-0.12	48.6
		4	7	0.53	-0.23	1.69	19.0
		5	11	1.04	-0.53	1.76	-
B <sub>8</sub>	RT	1	5	0.25	0.11	2.14	-
		2	78	0.35	0.17	1.50	-
		3	17	0.38	0.15	0.98	-

30 h treatment at 700 °C the synthesized Fe-2212 phase (sample A<sub>2</sub>) no longer has a magnetically split Mössbauer spectrum at RT, but a simple paramagnetic one (Fig. 2(b)), the Néel temperature being 240 K.

The treatment at 850 °C again led to a Fe-2201 phase (sample A<sub>4</sub>), this time with a Néel temperature of 250 K, higher than the 212 K of the initially synthesized sample A, but with a spectrum (Fig. 2(a)) having the same shape as the one of sample A, with similar values of the hyperfine interaction parameters HF and QS.

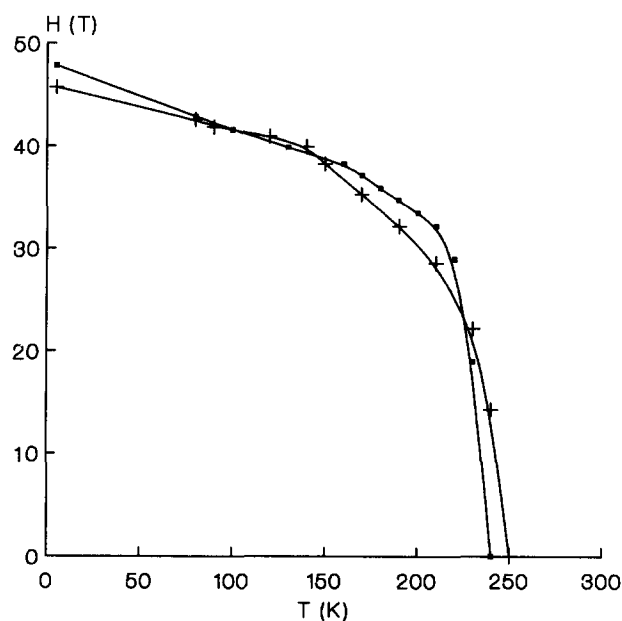
As mentioned in [9], when starting from BiPbSr<sub>2</sub>FeO<sub>6+z</sub> the reaction of the formation of the Fe-2212 phase takes place according to another mechanism than the one described by Eq. (1) for BiPbSrCaFeO<sub>6+z</sub>. This time evidence for a perovskite phase of SrPbO<sub>3</sub> type was found. Such a reaction can be tentatively described by the idealized equation



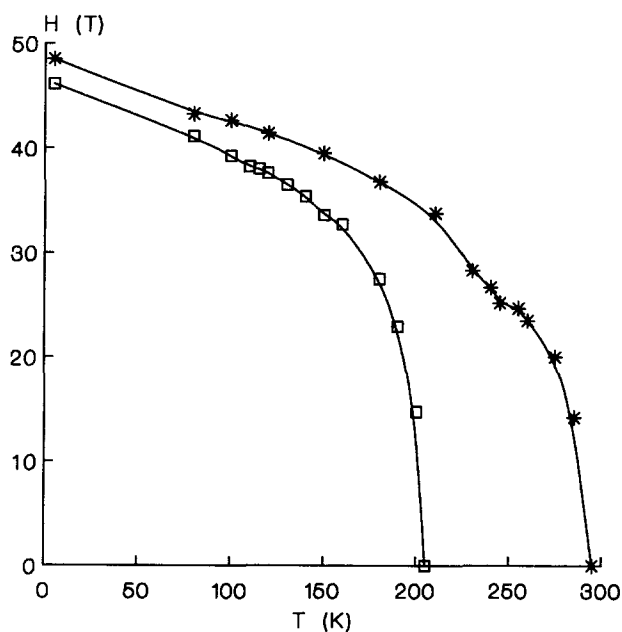
It is obvious that the resulting Fe-2212 phase has a different Pb and Sr content than sample C, i.e. the Fe-2212 phase formed according to Eq. (4). This time the Fe-2212 phase would contain 0.5 Pb and 2.5 Sr atoms per formula unit, instead of 1 Pb and 2 Sr as in the case of sample C. The paramagnetic pattern of the RT Mössbauer spectrum of the Fe-2212 phase, sample A<sub>2</sub> (Fig. 2(b)), obtained after the heat treatment at 700 °C of the Fe-2201 phase A ( $x=0$ ), shows that the Néel temperature of that phase lies below RT. Therefore, as was the case when starting from BiPbSrCaFeO<sub>6+z</sub> (sample B), this Fe-2212 phase is not identical with the directly synthesized compounds Bi<sub>2</sub>PbSr<sub>2</sub>Fe<sub>2</sub>O<sub>9+z</sub> (C) or Bi<sub>2</sub>PbSrCaFe<sub>2</sub>O<sub>9+z</sub> (D) with Néel temperature of 512 K. Differences between the lattice parameters of an  $x=0$  sample with Fe–O double layer and the C sample were clearly mentioned in [8], therefore pointing most probably to changes in the Bi:Pb:Sr:Fe ratio, in the direction assumed tentatively by reaction (5). And in fact, as has been shown in [16], changes in the ratio Bi:Pb:Sr can drastically alter the value of  $T_N$ , which for compositions such as PbSr<sub>4</sub>Fe<sub>2</sub>O<sub>9.03</sub>, Bi<sub>2.25</sub>Sr<sub>2.75</sub>Fe<sub>2</sub>O<sub>9.32</sub> and Bi<sub>2.75</sub>Sr<sub>2.25</sub>Fe<sub>2</sub>O<sub>9.48</sub>, lies in the range 30–50 K.

In order to better characterize the Fe-2212 compounds A<sub>2</sub> and B<sub>3</sub> magnetically, and to determine the Néel temperature  $T_N$ , we performed a temperature-dependent Mössbauer study. The change of the average HF with temperature for the Fe-2212 samples A<sub>2</sub> and B<sub>3</sub> is shown in Fig. 3(a). One can see that the Néel temperature reached only 240 K and 295 K respectively, i.e. far below the 512 K found for the Fe-2212 samples C and D.

At this point one can also mention the differences found in the values of the hyperfine fields at 4.2 K.



(a)



(b)

Fig. 3. (a) Hyperfine field vs.  $T$  for samples A<sub>2</sub> and A<sub>4</sub>. (b) Hyperfine field vs.  $T$  for samples B<sub>3</sub> and B<sub>8</sub>.

Whereas for Bi<sub>2</sub>PbSr<sub>2</sub>Fe<sub>2</sub>O<sub>9+z</sub> the HF was as high as 53.7 T, the average values of HF reached only 50.9 and 52.0 T for samples A<sub>2</sub> and B<sub>3</sub> respectively.

As one can see from Fig. 3 and Table 3, the phases (samples A<sub>4</sub> and B<sub>8</sub>) obtained by the 24 h treatment at 850 °C restore the one Fe–O layer structure but obviously with small changes in the composition. The Néel temperatures of 250 K for sample A<sub>4</sub> and 205 K

for sample B<sub>8</sub> differ only slightly from the ones of the as-prepared Fe-2201 compositions A and B with critical temperatures of 212 and 238 K respectively. The value of HF at 4.2 K lying around 50 T is practically the same for all the Fe-2201 compounds A, B, A<sub>4</sub> and B<sub>8</sub>. And even the 5–11% iron in the Fe<sup>4+</sup> state with HF = 20 T in the as-prepared samples A and B is also present in the A<sub>4</sub> and B<sub>8</sub> samples representing the end products of the quasi-reversible reaction Fe-2201 → Fe-2212 → Fe-2201.

#### 4. Conclusions

A Mössbauer spectroscopy study of the previously found quasi-reversible transformation of Fe-2201 phases into Fe-2212 ones with increasing temperature in the interval 700–850 °C [1] allowed us to perform a more detailed analysis of the compounds arising during the different steps of these processes.

Comparison of the Mössbauer energetical parameters hyperfine field HF, quadrupole splitting QS and isomer shift IS, and of the Néel temperatures of the as-prepared BiPbSr<sub>2</sub>FeO<sub>6+z</sub> (A), BiPbSrCaFeO<sub>6+z</sub> (B), Bi<sub>2</sub>PbSr<sub>2</sub>Fe<sub>2</sub>O<sub>9+z</sub> (C) and Bi<sub>2</sub>PbSrCaFe<sub>2</sub>O<sub>9+z</sub> (D), with the product of the first transformation of the Fe-2201 compounds A and B confirmed the formation of Fe-2212 phases, but with compositions which are probably slightly different from those of the as-prepared samples C and D. The new Fe-2212 compounds A<sub>2</sub> and B<sub>3</sub> exhibit lower values of HF at 4.2 K than the as prepared Fe-2212 samples C and D, and Néel temperatures of 420 and 205 K, far below the 512 K of the as-prepared samples.

These findings point to changes in the Bi:Pb:Sr ratios in a direction assumed tentatively by the reaction described in Eq. (5).

The products of the second step of the quasi-reversible transformation give rise to Fe-2201 phases (A<sub>4</sub> and B<sub>8</sub>) with values of the hyperfine parameters quite close to those of the as-prepared compositions A and B. Even the amount of Fe<sup>4+</sup> found in samples A and B is again present in the samples A<sub>4</sub> and B<sub>8</sub>.

From analysis of the QS values at 4.2 K and above T<sub>N</sub> one can see that at low temperatures the Fe spins

are oriented along the *c*-axis in the Fe-2201 phases, whereas they lie in the basal plane of the Fe-2212 phases.

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