**In situ** high-energy synchrotron x-ray diffraction investigation of phase formation and sintering in MgB$_2$ tapes

M Vignolo$^1$, G Romano$^1$, E Bellingeri$^1$, A Martinelli$^1$, D Nardelli$^2$, A Bitchkov$^3$, C Bernini$^1$, A Malagoli$^1$, V Braccini$^1$ and C Ferdeghini$^1$

$^1$ CNR-SPIN Genova, Corso Perrone 24, 16152 Genova, Italy
$^2$ Former CNR-SPIN, now ASG Superconductors S.p.A., C.so Perrone 73r, 16152 Genoa, Italy
$^3$ ESRF-6, rue Jules Horowitz, 38000 Grenoble, France

E-mail: maurizio.vignolo@spin.cnr.it

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Abstract

In the present paper we report an **in situ** high-energy x-ray diffraction analysis of MgB$_2$ tapes during the preparation process. The experiment was performed in a specifically designed furnace working in a reducing atmosphere, compatible with the Laue diffraction condition. The MgB$_2$ synthesis was realized starting from MgH$_2$ and amorphous B in powder form as precursors, varying reaction temperature and testing different cooling processes. We analysed both the MgB$_2$ synthesis and the sintering process of tapes prepared with these powders. Phase evolution, micro- and crystallographic structure were monitored during the different thermal treatments. Among the main results we observed the formation of MgB$_2$ at an extraordinary low temperature (300$^\circ$C), probably as a result of a solid-state reaction between MgH$_2$ and B. Furthermore, we studied the dependence of the microstructure upon the thermal treatment and its effect on the critical current performance of the superconducting tapes.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

MgB$_2$ conductors are now fabricated in long lengths and commercialized for some particular applications such as low field MRI systems: if on one side the technological advancement has been significant, still a strong research effort is required. In fact, in order to be able to widen the application range of MgB$_2$ conductors, a significant enhancement of $J_c$ is needed, which came to a standstill and does not look like a trivial task at the moment [1]. If it has been shown that $H_{c2}$ can be as high as 60 T [2] in thin films, although numerous attempts have been made it remains below 35 T in polycrystals [3] while at the same time $J_c$ looks limited. The research should be focused then on understanding how it is possible to efficiently add different pinning centres and/or new pinning mechanisms.

So far, the most successful results in terms of $J_c$ reached in polycrystals have been obtained via doping with carbon under different forms [4], or combining carbon doping and mechanical alloying [5]. Concerning the preparation of **ex situ** powder-in-tube (PIT) MgB$_2$ conductors for applications, we obtained good $J_c$ values by applying high-energy ball milling [6] and adding carbon [7] or by lowering the synthesis temperature [8]. Given that the main pinning mechanism in MgB$_2$ is due to grain boundaries [9], the reduced grain size obtained through these two ways helped significantly in improving the critical current in-field behaviour.

In a previous work, the influence of the synthesis temperature ($T_S$) and processing atmosphere during the cooling process on the MgB$_2$ grain size were investigated and correlated to **ex situ** PIT tape performances [10]. In this work we will closely examine these topics, with particular focus on the formation of the phase. In order to clarify all the aspects related to the thermal treatments in the tape realization we performed high-energy x-ray diffraction (HEXRD) during both the synthesis of MgB$_2$ and the tape sintering process of an **ex situ** MgB$_2$ tape. To reduce the probability of uncontrolled
oxidation during the synthesis we used, as suggested in the literature [11–13], MgH₂ instead of metallic Mg as a precursor.

The use of an in situ analysis like neutron or HEXRD is a powerful tool [14–17] for studying the synthesis and the sintering processes involved during the preparation of MgB₂ tapes. These techniques have been already applied to investigate the stress induced during the deformation process and the subsequent re-crystallization as a function of the sintering temperature [14]; as a result the optimal sintering temperature was identified to be 920°C because, at higher temperatures, Ni reacts with magnesium diboride forming a layer of Ni₂.5MgB₂. MgB₂ formation was previously studied by HEXRD. In particular, it was observed that the reaction time is decreased from 100 up to 2 min if the temperature is increased from 670 up to 900°C [15]. The formation of MgO and MgB₂ was observed at 450°C and 575°C, respectively, investigating the synthesis of MgB₂ applying the in situ PIT method [16]. Finally the MgB₂ formation in the Mg–B–N system at high pressure (5.5 GPa) and temperature (1900 K) was studied, revealing that the MgB₂ formation starts with a solid-state reaction [17].

Summarizing, in this paper we studied the MgB₂ synthesis at various temperatures by in situ HEXRD, using MgH₂ and amorphous B as precursors and analysed the effect of different atmospheres during the cooling process. Moreover, the sintering process of tapes prepared with these powders was also examined relating micro-and crystallographic structure with the critical current performance of superconducting tapes.

2. Experimental details

HEXRD analysis was carried out at the ID11 beamline of the European synchrotron radiation facility (ESRF) in Grenoble. The set-up of the experiment, similar to that reported in [18, 19], is sketched in figure 1. A tubular furnace has been placed in the high energy x-ray beam path (88 K eV, λ = 0.137 Å) for transmission measurements. The quartz tube, with a inner diameter of 60 mm, was sealed with Kapton windows on appropriate PVC caps at both ends. The caps were equipped with a gas inlet or outlet, respectively, to maintain a controlled Ar-5% H₂ atmosphere during each heat treatment. Two perforated discs of refractory material were mounted in order to limit irradiation and maintain higher homogeneity in the central zone of the furnace, where the sample is placed. The samples were aligned throughout an optical system.

Laue diffraction patterns were acquired by a CCD camera (10 patterns min⁻¹) and were integrated to obtain the diffracted intensity as a function of the diffracting angle (I–2θ diffraction patterns). Rietveld refinement [20] was carried out using FULLPROF software [21]. By means of an LaB₆ polycrystalline standard an instrumental resolution file was obtained and applied during refinements. In this way the variation of the cell parameters as a function of the reaction time/temperature was investigated as well as the phase evolution.

The apparatus described above and the HEXRD measurement technique were used to study the various steps of the process preparation of an ex situ MgB₂ tape [22].

The ex situ PIT process is a very flexible method to tailor the properties of superconducting powder and can be divided into the following steps:

(i) MgB₂ synthesis from precursors,
(ii) possible powder treatments (mechanical, thermal, oxidation),
(iii) filling of the tube with powders followed by tube sealing,
(iv) mechanical deformation to obtain tapes, wires or cables,
(v) final sintering process.

In this experiment we studied the thermal treatments performed during the ex situ PIT process, i.e. steps (i), (ii) and (v). We analysed this last step both for the powders prepared in an inert atmosphere and for the powders exposed to oxygen in step (ii). In fact, it is during these heat treatments that it is possible to tune the MgB₂ properties from the chemical point of view.

Regarding the MgB₂ synthesis (i), HEXRD data were acquired during two reactions at 760°C (LT) and 910°C (HT), respectively. We then studied the oxidation process during cooling (ii). The deformation process applied was the `standard` one [22] optimized for maximizing the critical current for our powders. Summarizing, three kinds of tapes were analysed, as shown in table 1.

In the following we will refer to the different typologies with the sample names from table 1.
earlier, in this experiment we tested two different MgH2 sources by opening the upper part of the split furnace. As mentioned earlier, many Fe peaks lie on the same angular positions of crucial MgB2 and MgO peaks. Then we also analysed some pellets of pressed precursor powders without any sheath material. The pellets, with 1 cm diameter and height, were prepared mixing the precursors and pressing them with a 2 ton force. Both syntheses were carried out under an inert atmosphere (IA) at two different synthesis temperatures: 760 °C (low temperature inert atmosphere or LTIA sample) and 910 °C (high temperature inert atmosphere or HTIA sample).

Great care was employed in order to reproduce the standard preparation conditions applied at the SPIN laboratories; however, we underline how during the experiment at ESRF it was necessary to carry out parts of the process in air and not in an inert atmosphere glove box: in some respects this could make a difference. Moreover, it should be noted that the actual temperature of the pellet can be significantly different from that of the furnace. In figure 2(a) we show the furnace thermal profile compared with the pellet temperature measured by a thermocouple in direct contact with the powders in a similar system to figure 1. Here, the heating rate was 10 °C min⁻¹, up to the reaction temperature, the same conditions we used for the experiment. At low temperatures (time) the two temperatures significantly differ; the difference between the furnace and pellet temperature tends to decrease at higher temperatures (time) but still remains appreciable. This is the reason why in the following figures we prefer to put on the x axis the time and not directly the temperature. The estimated temperature is reported, for clarity, on the upper x axis only as a reference. Looking in detail at figure 2 an endothermic peak is observed in the temperature range between 450 and 550 °C in both curves, due to the MgH2 decomposition (figure 2(b)), as described later. A small exothermic peak is present around 700 °C (figure 2(c)) in both thermal profiles (up to 760 °C and up to 910 °C): this peak results from the superposition of an endothermic peak, originated by Mg melting, and a stronger exothermic peak, resulting from the reaction between Mg and B. This thermal effect is indicative of the fact that, as soon as Mg melts, it spreads throughout the B powders and reacts with them, forming MgB2.

### Table 1. List of samples analysed through HEXRD.

| Sample name | Powder reaction temperature (T_r) (°C) | Power oxidized during cooling process |
|-------------|---------------------------------------|--------------------------------------|
| LTIA        | 760                                   | No                                   |
| LTOA        | 760                                   | Yes                                  |
| HTIA        | 910                                   | No                                   |

### 3. Results and discussion

#### 3.1. Powder synthesis and phase evolution

As suggested in the literature [11–13] and with the aim to reduce the possible uncontrolled oxidation, we used MgH2 instead of metallic Mg as a precursor for synthesizing MgB2 involved in the ex situ process. In this way a possible oxygen source is eliminated since it is well known that metallic Mg is easily oxidized by atmospheric O2, both during storage and manipulation. Furthermore, the formation of H2 by MgH2 reduction produces a reducing atmosphere which hinders oxygen contamination.

The reactions involved in the MgB2 synthesis can be summarized by the following main reactions (1)–(3):

\[
\text{MgH}_2(s) = \text{Mg}(s) + \text{H}_2(g) \quad \text{at } T = 450 \, ^\circ\text{C} \\
\text{Mg}(s) = \text{Mg}^0(l) \quad \text{at } T = 650 \, ^\circ\text{C} \\
\text{Mg}^0(l) + 2\text{B}(s) = \text{MgB}_2(s)
\]

In our experiment, the heating rate for the synthesis reaction was 10 °C min⁻¹ and samples were kept for 1 h at the regime temperature (T_r); then they were cooled at 10 °C min⁻¹ down to 500 °C and then freely down to room temperature by opening the upper part of the split furnace. As mentioned earlier, in this experiment we tested two different T_r: 760 and 910 °C.

In order to investigate the synthesis reaction with the same experimental set-up used at SPIN laboratories we tried to study the MgB2 powder synthesis into very thin walls, i.e. 100 μm Fe crucibles. Unfortunately, many Fe peaks lie on the same temperature. The estimated temperature is reported, for clarity, on the upper x axis only as a reference. Looking in detail at figure 2 an endothermic peak is observed in the temperature range between 450 and 550 °C in both curves, due to the MgH2 decomposition (figure 2(b)), as described later. A small exothermic peak is present around 700 °C (figure 2(c)) in both thermal profiles (up to 760 °C and up to 910 °C): this peak results from the superposition of an endothermic peak, originated by Mg melting, and a stronger exothermic peak, resulting from the reaction between Mg and B. This thermal effect is indicative of the fact that, as soon as Mg melts, it spreads throughout the B powders and reacts with them, forming MgB2.

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**Figure 2.** Thermal profile of the MgB2 synthesis reaction: (a) temperature profile of the thermal treatments for the low and high synthesis temperature. (b) Details of MgH2 decomposition and of MgB2 formation (c).
Figure 3. Phase volume fraction evolution as a function of the time during the synthesis of MgB$_2$ at low temperature (760 °C).

Figure 3 shows the phase evolution as volume percentage versus time for MgB$_2$ synthesis at 760 °C as obtained from Rietveld refinement of HEXRD data. Metallic Mg (full triangle) is already present (7%) at the beginning of the reaction. This is probably due to an incomplete hydrogenation reaction or a decomposition reaction of MgH$_2$ during its storage. The formation of MgB$_2$ (full square) takes place at very low temperature (less than 300 °C), around 30 min after the beginning of the thermal treatment. This exceptionally low temperature formation is probably due to a solid–solid reaction between MgH$_2$ and B: indeed, the MgH$_2$ amount slightly decreases after 30 min (full circle), whereas the metallic Mg remains constant. Unfortunately, being that boron is too light an element to be detected with the HEXRD technique, it was not possible to monitor the phase evolution of elemental B.

In the light of these results we must consider another reaction involved in the MgB$_2$ synthesis, when MgH$_2$ is employed, which must be temporally placed before step (i) and can be represented by the following equation:

$$\text{MgH}_2(s) + 2\text{B}(s) = \text{MgB}_2(s) + \text{H}_2(g)$$

The solid-state reaction between Mg and B was already reported in previous papers [23–26] but located at about 500 °C. Furthermore, in those cases, metallic Mg was used instead of MgH$_2$. This lower reaction temperature may be due to a catalytic effect of H$_2$, even if this evidence has not been verified yet. The MgB$_2$ content exhibits a slight increase as the decomposition of MgH$_2$ takes place, in the temperature range 400–500 °C, confirming what was reported in [27]. At higher temperatures (times) only metallic Mg is present. The MgB$_2$ amount undergoes a dramatic increase when the temperature reaches the melting point of Mg (650 °C) and for a further 10 min. When the oven temperature reaches 760 °C (after 76 min), the formation of MgB$_2$ is complete (97% volume). The remaining 3% is represented by MgO, whose formation starts at the Mg melting point. A small amount of oxygen is always present, probably due to the refractory material used as a shield in thermal insulation or physically absorbed during the making of the pellet.

The phase evolution analysis is in qualitative agreement with thermal analysis obtained during the low and high synthesis temperatures in a similar furnace at the SPIN laboratory (figure 2). The synthesis reaction of MgB$_2$ described by equation (3) is complete in the temperature range 700–780 °C. We did not record any significant difference in the phase evolution when the process has been carried out up to 910 °C for the HTIA sample except for a slightly reduced MgB$_2$ formation time due to the higher temperature. Differences, however, are present in the microstructure: in figure 4 we show the granulometry distribution for the two MgB$_2$ powders fitted with a Lorentzian function. Such a distribution was obtained from statistics on about 700 particles taken from several points of the two samples with a scanning electron microscope in order to estimate the average diameter of the powders. As is clearly shown, the granulometry distribution is more homogeneous and has a lower maximum (0.3 μm versus 1.4 μm) for the powders synthesized at low temperature, as a natural consequence of the different grain growth at different temperatures. Other microstructural differences are also shown during the subsequent sintering process of the tape as described in the next paragraph.

3.2. Tape sintering

The importance of the final sintering heating treatment is based on the necessity of recovering the lattice strain induced by the prolonged cold working procedure applied in the PIT process and improving the grain connectivity and the $T_c$ as well (the cold deformation working alone can lower $T_c$ down to 32 K [22]). We therefore investigated the sintering process in an inert atmosphere by in situ HEXRD analysis to see its influence on the structural features. Figure 5 shows the $a$ and $c$ cell parameter evolution during the sintering process, obtained by refinement of the HEXRD data. The upper panels refer to the tapes realized with LT powders and lower panels to the ones realized with HT powders. The $a$ and $c$ parameters for...
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Figure 5. MgB$_2$ lattice parameter evolution during the sintering process for LTIA (upper panel) and HTIA (lower panel) samples.

Figure 6. Broadening of the 100 peak of MgB$_2$ as a function of sintering time for different synthesis temperature and atmosphere. The continuous lines represent the exponential fit of each dataset.

Figure 7. $J_c$ measurements for the wires of [6] (synthesis temperature for LTIA = 745 °C).

HT samples closely follow the temperature profile, different from what is observed for LT where a strong rearrangement of the cell edges is observed in the temperature region 750–900 °C. This effect is due to a greater stress recovery in the sample synthesized at low temperatures whereas the HT sample has a more relaxed structural parameter already after synthesis. In figure 6 we show the broadening of the 100 peak during the sintering for the LTIA and HTIA samples. In both cases a structural relaxation trend is evident which ends with a higher value for the LTIA sample. This means a lower stress recovery and/or a reduced crystallite size for the LTIA sample. This trend is in good agreement with the data previously published in [14], where it was established that the cold working brings on a progressive peak broadening, indicating the loss of crystallinity, followed by a recovery of crystallinity during the final heat treatment when the peaks became narrower again. It is interesting to note how the LTIA sample, at the end of the process, shows a more stressed structure and/or smaller grains than HTIA. Figure 7 shows $J_c$ (from [6]) for two wires synthesized at low and high temperature in an inert atmosphere. To correlate these data with those obtained from the HEXRD study we can speculate that the increased $J_c$ corresponding to the LTIA sample is due to a reduced granulometry which leads to an enhanced connectivity at all fields; furthermore, a higher contribute at high magnetic fields can be given by a bigger stress content.

3.3. Oxidation effects

Finally, we studied the effect of an oxidizing atmosphere during the cool down of the powders during step (ii) of the
Figure 8. Enlarged view of the HEXRD patterns of samples synthesized under different atmospheres (IA and OA) both at low temperature (LT). The patterns have been acquired during the sintering process of the respective tapes; here only the last pattern for each is reported.

Figure 9. Magnetic $J_c$ of the sample synthesized at low temperature in different atmosphere, [10].

process. For this purpose we investigated using HEXRD tapes synthesized at low temperature in inert (IA) and oxidizing (OA) atmospheres during the cooling process (i.e. for $T < 400^\circ$C).

In [8] we reported that MgO is present as a thin layer covering the MgB$_2$ grains: this layer hinders the grain growth during the sintering process. The same MgO layer (with a thickness comparable to the MgB$_2$ coherence length) can act as pinning centres enhancing the in-field $J_c$ performance of the tape.

To confirm the grain growth inhibition among IA and OA samples we have estimated the lattice rearrangement during the sintering process through the broadening of the full width at half-maximum (FWHM) of the 100 peak because it is more sensitive to the sintering process from a structural arrangement point of view. The evolution with time of the FWHM of the 100 peak for the LTOA sample is reported in the same figure.

From the plot a higher peak broadening for the LTOA sample is clearly visible after sintering with respect to LTIA, whereas both the LT samples show the same recrystallization trend during the whole process.

Figure 8 shows the comparison of the HEXRD patterns around the angular position of the 110 reflection of the MgB$_2$ phase of LTOA and LTIA samples after the sintering process. It is clearly visible that the MgO amount is higher in the OA sample. This is consistent with the different critical current behaviour shown in figure 9, where we report the data of [10] for two samples realized as LTOA and LTIA.

We note how the best $J_c$ shown at low field is measured in the sample with the smallest MgO content (LTIA) and the best $J_c$ behaviour in high fields belong to the LTOA sample, which shows the highest MgO content and the more stressed structure. In reference [10] we showed how the grain boundary pinning is the main pinning mechanism in these powders, namely when the oxygen introduction inhibits the grain growth. This is in agreement with the data of figure 6 where the peak broadening clearly increases after sintering for the oxidized sample. In addition the LTIA and LTOA samples presented the same critical temperature and the same critical field but considerable differences in the average grain size after sintering being nearly double in the case of LTIA [10]. The MgO at the grain boundaries decreases the connectivity (as results from the Rowell analysis of $\Delta \rho$ [28]), being 14% for LTIA and only 4% for LTOA. We conclude that $T_c$ and $H_{c2}$, which are related to the crystallite properties, are not affected by oxidation. On the other hand, the critical current at high fields seems to be favoured by an increasing of grain boundary pinning force, being improved by the presence of MgO at the grain surface despite the decreasing of connectivity. We speculate that the presence of an MgO layer of 4–5 nm [8], just of the scale of the coherence length, can favour this effect.

4. Conclusions

We carried out a detailed study realized by HEXRD on the phase formation and sintering in MgB$_2$ ex situ PIT tapes. The analysis was performed during the MgB$_2$ synthesis realized starting from MgH$_2$ and amorphous B in powder form as precursors: we focused on the effects of the reaction temperature, the oxidation process and sintering process of the tapes on the phase composition and the microstructure and tried to correlate these properties with the critical current in-field in the final tapes. We have found that a solid-state reaction between the precursors occurs at quite low temperature, below 300$^\circ$C, leading to the formation of MgB$_2$, while the synthesis is complete in the temperature range 700–780$^\circ$C. We investigated the sintering process of the tapes in an inert atmosphere and found that the cell parameters $a$ and $c$ for the sample synthesized at HT closely follow the temperature profile, while the sample synthesized at LT undergoes a strong rearrangement of the cell edges in the temperature range 750–900$^\circ$C due to a greater stress recovery. We also estimated the lattice rearrangement during the sintering process through the broadening of the FWHM of the 100 peak, which resulted in broadening for the sample cooled in an oxidizing atmosphere below 400$^\circ$C. From the comparison of the HEXRD patterns of samples synthesized under different atmospheres (IA and OA) we saw that the OA sample has higher MgO content, being
consistent with showing better $J_c$ behaviour at higher magnetic fields.

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References

[1] Iwasa Y, Larbalestier D C, Okada M, Penco R, Sumption M D and Xi X X 2005 IEEE Trans. Appl. Supercond. 16 1457
[2] Braccini V et al 2005 Phys. Rev. B 71 012504
[3] Malagoli A, Braccini V, Tropeano M, Vignolo M, Bernini C, Fanciulli C, Romano G, Putti M, Ferdeghini C, Mossang E, Polianskii A and Larbalestier D C 2008 J. Appl. Phys. 104 103908
[4] Shcherbakova O V, Pan A V, Dou S X, Nigam R and Wexler D 2010 J. Appl. Phys. 107 09E147 and references therein
[5] Herrmann M, Haessler W, Rodig C, Gruner W, Holzapfel B and Schultz L 2007 Appl. Phys. Lett. 91 082507
[6] Romano G, Vignolo M, Braccini V, Malagoli A, Bernini C, Tropeano M, Fanciulli C, Putti M and Ferdeghini C 2009 IEEE Trans. Appl. Supercond. 19 2706
[7] Braccini V, Malagoli A, Tumino A, Vignolo M, Bernini C, Fanciulli C, Romano G, Tropeano M, Siri A S and Grasso G 2007 IEEE Trans. Appl. Supercond. 17 2766
[8] Vignolo M, Romano G, Malagoli A, Braccini V, Bernini C, Tropeano M, Martinelli A, Cubeda V, Tumino A, Putti M, Ferdeghini C and Siri A S 2008 IEEE Trans. Appl. Supercond. 18 1175
[9] Kitaguchi H, Matsumoto A, Kumakura H, Doi T, Yamamoto H, Saitoh K, Sossiati H and Hata S 2005 Appl. Phys. Lett. 85 2842
[10] Vignolo M, Romano G, Malagoli A, Braccini V, Tropeano M, Bellingeri E, Fanciulli C, Bernini C, Honkimaki V, Putti M and Ferdeghini C 2009 IEEE Trans. Appl. Supercond. 19 32718
[11] Nakane T, Kitaguchi H, Fugjii H and Kumakura H 2006 Physica C 445–448 764
[12] Nakane T, Fugjii H, Matsumoto A, Kitaguchi H and Kumakura H 2005 Physica C 426–431 1238
[13] Jiang C H, Hatakeyama H and Kumakura H 2005 Supercond. Sci. Technol. 18 L17–22
[14] Bellingeri E, Malagoli A, Modica M, Braccini V, Siri A S and Grasso G 2003 Supercond. Sci. Technol. 16 276
[15] De Fouw J D, Quintana J P and Dunand D 2006 Acta Mater. 56 1680
[16] Grivel J C, Pinholt R, Andersen N H, Kováč P, Husék I and Homeyer J 2006 Supercond. Sci. Technol. 19 96
[17] Baranov A N, Solozhenko V L, Lathe C, Turkevich V Z and Park Y W 2003 Supercond. Sci. Technol. 16 1147
[18] Giannini E et al 2000 Int. J. Mod. Phys. B 14 2688
[19] Flukiger R et al 1999 IEEE Trans. Appl. Supercond. 9 2430
[20] Young R A 1993 The Rietveld method (Oxford: Oxford University Press)
[21] Rodriguez-Carvajal J 2001 Program FULLPROF Laboratoire Léon Brillouin Saclay, France
[22] Grasso G, Malagoli A, Ferdeghini C, Roncallo S, Braccini V, Siri A S and Cimberle M R 2001 Appl. Phys. Lett. 79 230
[23] Ma Z, Liu Y C and Huo J 2009 Supercond. Sci. Technol. 22 12500
[24] Ning B Q, Jiang H and Yan Z S 2009 J. Mater. Sci. 44 666
[25] Yan S C, Yan G, Liu C F, Lu Y F and Zhou L 2007 J. Alloys Compounds 437 298
[26] Liu Y C, Shi Q Z, Zhao Q and Ma Z Q J 2007 Mater. Sci. 43 855
[27] Ershova O G, Dobrovolsky V D, Solomin Y M and Khyzhun O Y 2009 Carbon Nanomaterials in Clean Energy System Chemistry and Material Science (Berlin: Springer) pp 473–83
[28] Rowell J M 2003 Supercond. Sci. Technol. 16 R17