JOURNAL OF
Materials
CHEMISTRY

Formation of the $Bi_2Sr_2CaCu_2O_{8+\delta}$ superconductor with $Mg_{1-x}Cu_xO$ inclusions: the phases compatibility and the effect of the preparation route on the material microstructure and properties†

Pavel E. Kazin,[*a] **Yuri D. Tretyakov,**[a] **Vasili V. Lennikov**[a] **and Martin Jansen**[b]

[a] *Chemistry Department, Moscow State University, 119899 Moscow, Russia*
[b] *Max-Plank-Institut für Festkörperforschung, D-70569 Stuttgart, Germany*

Received 7th April 2000, Accepted 2nd June 2000
First published as an Advance Article on the web 6th October 2000

A compatibility between $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) and MgO was investigated, and the Bi-2212–$Mg_{1-x}Cu_xO$ composite materials were obtained and characterised. It was established that Bi-2212 interacts with the MgO powder at 850 °C producing $(Sr,Ca)_{4-y}Bi_2O_z$ and the $Mg_{1-x}Cu_xO$ solid solution, while single crystal MgO is stable against Bi-2212 solid and melt up to 1100 °C. The Bi-2212 phase is found to coexist with $Mg_{1-x}Cu_xO$, where $x \geqslant 0.08$, at 850 °C in air. Magnesium oxide content is estimated to be under 1 mol% in the solid Bi-2212 phase, as well as in the phases formed *via* the Bi-2212 peritectic decomposition, and in the Bi–Sr–Ca–Cu–O melt. The Bi-2212–$Mg_{1-x}Cu_xO$ superconducting composites were prepared by melt-processing using different precursors. The effect of the precursor on the material microstructure and superconducting properties was investigated. The $Mg_{1-x}Cu_xO$ submicron particles were found to be rather uniformly distributed in the Bi-2212 matrix, their size depending on the preparation conditions. Application of the nanosize MgO powder as a precursor indicated substantial coarsening of the magnesium oxide particles during the composite processing, the average particle size exceeding 0.2 μm. The composites exhibited higher critical current density as well as better field stability at enhanced temperatures in comparison with the Bi-2212 samples.

1. Introduction

An opportunity for the improvement of high-T_c superconductor parameters such as critical current density (J_c) and mechanical strength is connected with the formation of composite materials consisting of a superconductor matrix and homogeneously distributed inclusions of non-superconducting phases.[1–4] The second phase inclusions can act as effective pinning centres for magnetic flux providing an increase in the critical current and its stability in the magnetic field. The problem of low pinning energy especially concerns the $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) superconductor which in other ways is very suitable for the production of long items such as wires, tapes and rods.[5–7]

Magnesium oxide is often used as an additive to Bi-2212 owing to its stability and ability to retain the materials superconductivity.[8–16] Introduction of micrometer size whiskers of MgO provided a better texture and mechanical strength for the Bi-2212 melt-processed material, and thus a several fold increase in J_c.[8–10] 10 vol.% of the MgO powder was added to keep the sample form and prevent second phase separation during the peritectic melting in a magnetic field.[11] It led to bulk textured samples with J_c as high as 1650 MA m^{-2} at a temperature of 4 K.[12] Addition of nanosize MgO powder was found to increase the material magnetization hysteresis width at low temperatures.[13] A similar increase in the magnetization was observed below 20 K in the Bi-2212 single crystal with imbedded MgO particles which was attributed to a high density of dislocations within the sample.[14] Interesting results were obtained by Yang and Lieber,[15] a film of Bi-2212 was deposited on the MgO substrate covered by a "forest" of MgO whiskers with a diameter of 20–30 nm. Such a microstructure is very effective for pinning the flux lines, and the J_c increased by an order of magnitude at 77 K reaching 100 MA m^{-2} in a field of 0.1 T.

At the same time, both the MgO chemical compatibility with Bi-2212 and its behaviour in the material processing have not been closely investigated. Doping of Bi-2212 with MgO was briefly discussed in our previous works.[3,16] In the present paper we report a study on the compatibility between Bi-2212 and MgO and on the formation of the superconductor composites starting from different precursors.

2. Experimental

The precursor powders with cation stoichiometry corresponding to $Bi_{2.1}Sr_2CaCu_2O_{8+\delta}$ and $Bi_{2.1}Sr_2CaCu_2O_{8+\delta}+0.8MgO$ were prepared using nitrate and sol–gel methods.

In the former method a nitrate solution of all metal cations was evaporated and decomposed at 200–400 °C. The residue was annealed at 800 °C for 6 h, reground and annealed at 850 °C for 6 h (precursor 1).

In the sol–gel method 1 g of precursor 1 was added to 6 ml of a solution containing 3 g of citric acid on heating with subsequent dropwise addition of a solution of 25% NH_3 to obtain a clear solution. The solution was gently evaporated, the homogeneous solid was decomposed at 250–600 °C and annealed at 800 °C for 24 h.

The glassified samples were prepared by melting precursor 1 at 1100 °C for 15 min and quenching it between copper plates.

The Bi-2212 ceramics were prepared using precursor 1 which was pelletised and annealed at 860 °C for 24 h.

The nanocrystalline MgO powders were obtained: (i) by thermal decomposition of $Mg(OH)_2$ at 340 °C for 6 h; (ii) by thermal decomposition of MgC_2O_4 at 550 °C for 12 h.

The Bi-2212–$Mg_{1-x}Cu_xO$ composites with nominal composition Bi-2212+0.8MgO were prepared *via* melt processing using the following precursors: the glassified material (sample

---

†Basis of a presentation given at Materials Discussion No. 3, 26–29 September, 2000, University of Cambridge, UK.

DOI: 10.1039/b002795m

A), the oxide products obtained by the sol–gel method (sample B), the oxide products obtained by the nitrate method (sample C), the mixture of commercial Bi-2212 (Hoechst) and nanosize MgO prepared from MgC_2O_4 (sample D) or $Mg(OH)_2$ (sample E). The pellets produced from the precursors ground in an agate mortar were heated in air on a MgO single crystal substrate for several hours up to 890–910 °C, and kept at this temperature for 1 h (optionally heated to 920–950 °C and kept at this temperature for 0.2 h with fast cooling to 880–890 °C at 300 °C h^{-1}) and slowly solidified by cooling to 850 °C at 1 °C h^{-1}. The maximum heating temperature was varied to optimise the superconductor T_c and J_c values. For comparison, the Bi-2212 materials without the MgO additive were prepared under the same conditions utilising the procedures used for samples A–D.

For the phase compatibility study, two kinds of experiments were carried out. In the first one, the fine commercial MgO powder (99%) was annealed at 1400 °C for 1 h to achieve 0.5–1 micron size MgO grains. Then it was mixed with Bi-2212 to obtain the Bi-2212 + 10MgO composition, pressed into pellets and annealed at 850 °C for 24 h. In the second experiment, the small pieces of Bi-2212 ceramic were placed on the MgO single crystals with *ca.* 1 mm thickness. The separate specimens were annealed in air at either: 850 °C for 120 h, 900 °C for 24 h, 1000 °C for 1 h or 1100 °C for 1 h, and quenched in liquid nitrogen. The polished cross-sections of the specimens were examined by scanning electron microscopy.

Powder X-ray diffraction was performed on a DRON-3M diffractometer with CuK_α radiation.

Microstructure and chemical composition of the phases were studied using scanning electron microscopes (a Philips ESEM and a Zeiss DSM device) equipped with options for energy dispersive X-ray analysis (EDX). The samples were cut and polished prior to the investigation.

AC magnetic susceptibility was measured on a specially designed susceptometer[17] in the temperature range of 15–100 K in AC fields of 0.1 and 10 mT and a frequency of 27 Hz. Magnetisation was measured on a Quantum Design MPMS device at temperatures of 5, 30 and 60 K in fields up to 5 T. For the magnetic measurements, the samples were cut to get rectangular bars of *ca.* 1 mm thickness, which were placed along the field.

3. Results and discussion

3.1. Compatibility between Bi-2212 and MgO

In our earlier work, we mentioned that in the melt-processed Bi-2212 with inclusions of MgO, the latter, keeping its crystal structure, incorporates some Cu-cations.[16] That must change the cation ratio in the Bi–Sr–Ca–Cu–O part of the system, and the secondary phases may appear. At the same time there is evidence that even for a large MgO content the composites exhibit very good superconducting properties.[10,12] These facts initiated us firstly to clear up the aspects of the compatibility between Bi-2212 and MgO.

3.1.1. Interaction of Bi-2212 with MgO in the mixture at 850 °C. Annealing the pellet of Bi-2212 + 10MgO caused a partial decomposition of the Bi-2212 phase. In an XRD pattern a few new peaks appeared (Fig. 1). They correspond to the monoclinic phase $(Sr,Ca)_4Bi_2O_7$[18] which was also considered as having somewhat different stoichiometry $Sr_{11-x}Ca_{5+x}Bi_9O_z$.[19,20] The EDX analysis suggests its approximate composition to be $(Sr,Ca)_{4-y}Bi_2O_z$ with $y \approx 0.4$ that is close to the one reported in the latter work. The major part of the magnesium oxide resides in submicron particle agglomerations from a few to a hundred microns in size. The analysis of different regions in the agglomerations revealed that they contain 0–1 at.% of Bi, Sr, Ca and about 8 at.% of Cu in reference to Mg. The Cu content did not appreciably depend on the size of the agglomerate or on the distance from the interface between the agglomerate and the Bi–Sr–Ca–Cu–O matrix. That confirms that the reaction between MgO and Bi-2212 is virtually complete. The observed compound $Mg_{1-x}Cu_xO$ ($x = 0.08$) retains the MgO crystal structure. Its composition belongs to a solid solution range of CuO in MgO, which was reported to extend at 850 °C to $x = 0.2$, according to Assal *et al.*,[21] or to $x \approx 0.12$, according to Paranthaman *et al.*[22] In the Bi-2212 and $(Sr,Ca)_{4-y}Bi_2O_z$ phases the magnesium oxide content was under the EDX sensitivity level of about 1 mol%.

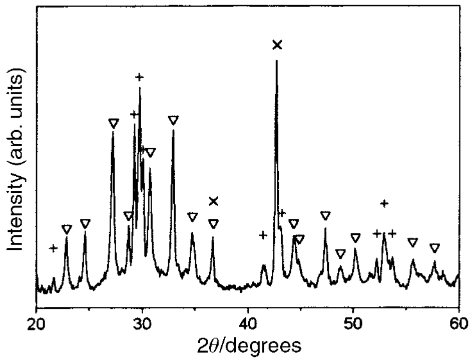

Fig. 1 X-Ray diffraction pattern of the Bi-2212 + 10MgO sample after the annealing: Bi-2212 (triangles), $(Sr,Ca)_{4-y}Bi_2O_z$ (plus symbols), $Mg_{1-x}Cu_xO$ (crosses).

From the cation ratio consideration one can expect formation of additional phases, but that was not observed. This can be explained by taking into consideration the existence of a solid solution range for $Bi_{2+y}Sr_2CaCu_2O_z$ with $0 < y < 0.3$.[23] The initial sample had a bulk composition close to $Bi_2Sr_2CaCu_2O_{8+x}$. After the annealing, the Bi content was slightly increased, *i.e.* Bi-2212 was able to accept the Bi surplus that appeared as a result of the formation of the Sr,Ca-rich bismuthate. The change in the phase composition during the reaction is shown in Fig. 2. With decreasing Cu content, the configuration point A moves to the two-phase region: Bi-2212 solid solution–$(Sr,Ca)_{4-y}Bi_2O_z$ (point B). At lower Cu contents, one can expect a transition to the three-phase region including the $Bi_2(Sr,Ca)_2CuO_z$ (Bi-2201) phase and possibly to a four-phase region.

3.1.2. Interaction of the Bi-2212 melt with a single crystal of MgO. After 120 h annealing at 850 °C there was no noticeable change at the interface between the Bi-2212 ceramics and the MgO single crystal. For the samples annealed at and above 900 °C, the Bi–Sr–Ca–Cu–O part represented a drop of melt wetting the MgO substrate. At 900 °C, the quenched melt

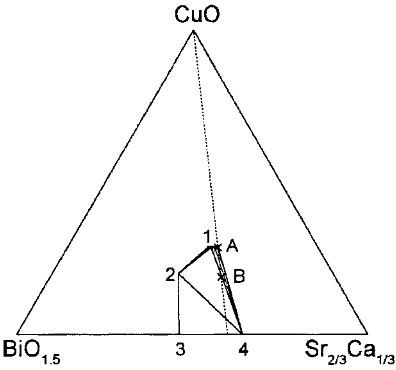

Fig. 2 Part of the $BiO_{1.5}$–CuO–$Sr_{2/3}Ca_{1/3}O$ phase diagram. (1) $Bi_{2+y}Sr_2CaCu_2O_{8+\delta}$ solid solution, (2) $Bi_2(Sr,Ca)_2CuO_6$, (3) $(Sr,Ca)_6Bi_7O_{16.5}$, (4) $(Sr,Ca)_{3.6}Bi_2O_z$. Point A (cross) — initial composition of the Bi–Sr–Ca–Cu–O part of the Bi-2212 + 10MgO sample, point B — the composition after the sample annealing.

contained $(Sr,Ca)CuO_2$, $(Sr,Ca)_{4-y}Bi_2O_z$ and Bi-2201 crystals distributed in the glassy matrix; at 1000 °C, only grains of CaO were found in the matrix; and at 1100 °C, the Bi–Sr–Ca–Cu–O part represented homogeneous glass. In all the cases no additional cations were found in the MgO part starting from 2 µm from the interface with Bi-2212. That limits the possible contents of Bi, Sr,Ca and Cu oxides in MgO to *ca.* 0.5 mol%. At smaller distances from the interface the cations are detected due to X-ray emission from the adjacent Bi–Sr–Ca–Cu–O part. In the Bi–Sr–Ca–Cu–O parts magnesium oxide was not observed above 1 mol%.

Therefore, the experiments described above allow us to conclude that magnesium oxide in the form of micrometer powder extracts CuO from Bi-2212, thus causing its decomposition toward strontium–calcium bismuthate. In the equilibrium between Bi-2212 and $Mg_{1-x}Cu_xO$ the copper content x in the latter phase cannot be less than 0.08. However, cation diffusion from Bi–Sr–Ca–Cu–O into the MgO single crystal is not observed. Hence, the composition of magnesium oxide based inclusions in the superconductor may depend on the route of the MgO introduction.

3.2. The Bi-2212–$Mg_{1-x}Cu_xO$ composites

3.2.1. Microstructure and phase composition. The typical SEM micrographs of the Bi-2212–$Mg_{1-x}Cu_xO$ composites are shown in Fig. 3, the XRD pattern in Fig. 4. All the composites contain two main phases: Bi-2212 and magnesium oxide. The Bi-2212 phase forms large plate-like grains, several hundred microns in size. Small quantities of secondary phases $(Sr,Ca)CuO_2$, $(Sr,Ca)_2CuO_3$, $(Sr,Ca)_{4-y}Bi_2O_z$, and Bi-2201 are observed, which are usually present in the melt-processed Bi-2212.

The magnesium cations are not detected in the Bi-2212 phase as well as in the secondary phases. The magnesium oxide submicron particles are found to be rather uniformly distributed inside the Bi-2212 matrix without any agglomeration on the Bi-2212 grain boundaries. Such a behaviour of MgO differs from that of the particles of many other stable phases such as $SrZrO_3$, $(Sr,Ca)SnO_3$, $(Sr,Ca)In_2O_4$ and $BiSr_{1.5}Ca_{0.5}Al_2O_z$ which have been found to agglomerate partially between Bi-2212 lamella.[3,24–27]

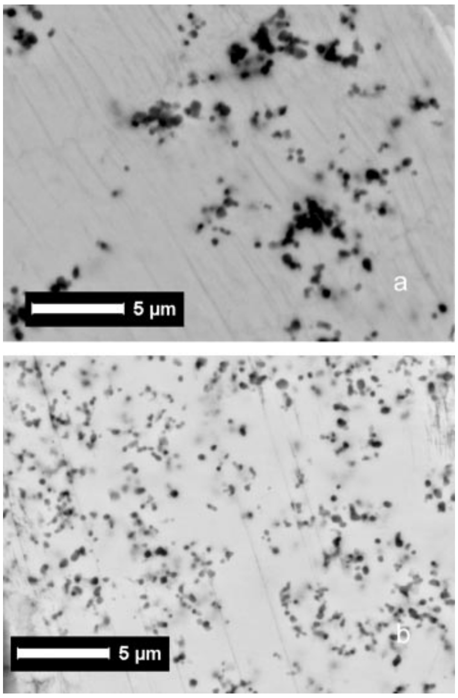

Fig. 3 SEM (BSE) micrographs of the Bi-2212–$Mg_{1-x}Cu_xO$ composites: a) sample D, b) sample E. Light-grey area — Bi-2212, black submicron particles — $Mg_{1-x}Cu_xO$.

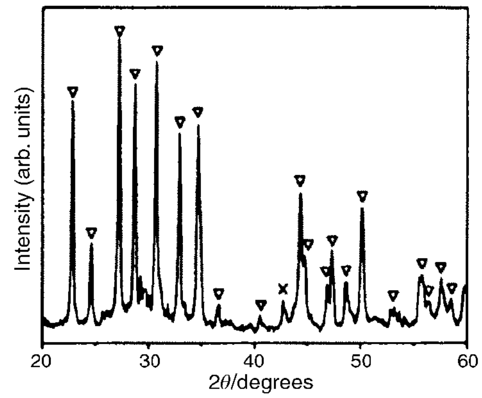

Fig. 4 X-Ray diffraction pattern of the Bi-2212–$Mg_{1-x}Cu_xO$ composite (sample E): Bi-2212 (triangles), $Mg_{1-x}Cu_xO$ (crosses).

Sometimes magnesium oxide particles of the same size are observed in the grains of the secondary phases. These phases were formed on the Bi-2212 peritectic melting and partly remained in the sample after the solidification process. It appears that the magnesium oxide particles had existed in the melt and were captured by formed grains of the secondary phases and afterwards by the growing Bi-2212 crystallites.

The composition of the inclusions in all the cases except sample A corresponds to $Mg_{1-x}Cu_xO$ with $x = 0.08$–0.1, *i.e.* the magnesium oxide has acquired a composition close to an equilibrium one with Bi-2212, rather than staying inert. That implies a 4% deficiency of Cu-ions in the Bi–Sr–Ca–Cu–O part, but it seems to be rather small to affect the sample phase composition and properties, since after the peritectic formation of Bi-2212 some amount of unreacted phases resides both in the undoped Bi-2212 material and in the composite.

In the sample A the x-value is increased to 0.12. Most probably, MgO has acquired additional CuO during the precursor melting at 1100 °C. The solubility of CuO in MgO increases with temperature up to 1050 °C,[22] and one should expect an increase in the cation diffusivity at higher temperature. All this promotes the CuO transfer from the Bi–Sr–Ca–Cu–O melt into the MgO particles.

The size of the included $Mg_{1-x}Cu_xO$ lies within a rather narrow range of 0.1–2 µm and varies with the composite preparation method (Table 1). The biggest particles of 1 µm in size were formed from the glassified precursor (method A). Melt-processing of the "single source" precursors (methods B and C) led to somewhat smaller particles. The application of a mixture of Bi-2212 and the nanosize MgO powders provided the smallest grain size of 0.2–0.4 µm.

The size of the initial MgO nanoparticles was of the order of 10 nm, according to transmission electron microscopy. Ana-

Table 1 Superconducting parameters of the melt processed materials and the included $Mg_{1-x}Cu_xO$ particle size in the Bi-2212–$Mg_{1-x}Cu_xO$ composites

Material	$Mg_{1-x}Cu_xO$ size/µm	T_c/K	J_c at 60 K/MA m^{-2}
Bi-2212–$Mg_{1-x}Cu_xO$:			
Sample A	1.06	89	13
Sample B	0.80	93	17
Sample C	0.58	91	34
Sample D	0.43	92	46
Sample E	0.26	89	48
Bi-2212:			
Method A		93	10
Method B		94	3
Method C		91	26
Method D		90	20

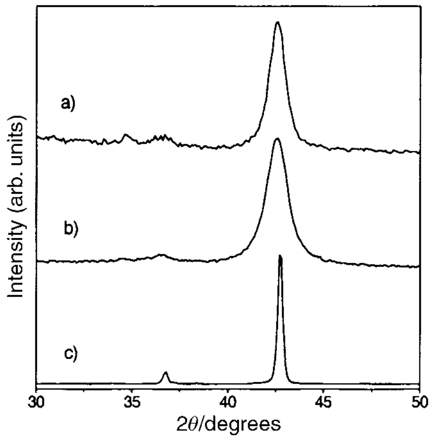

Fig. 5 X-Ray diffraction patterns of the MgO nanopowders: a) prepared from MgC_2O_4, b) prepared from $Mg(OH)_2$, and c) the reference MgO powder with 0.5–1 μm grain size.

lysis of the widening of the XRD lines (Fig. 5) gave a particle size of ≈7 nm for the sample prepared from hydroxide, and ≈14 nm for the sample prepared from oxalate. Hence, considerable coarsening of the MgO particles took place during the material processing. This is probably connected with their recrystallisation in the melt. Thus, the highest temperature applied in method A (1100 °C) caused an almost two-fold increase in the particle size in comparison with method C in which the same precursor was used, but without high-temperature melting. Apparently MgO is soluble in the Bi–Sr–Ca–Cu–O melt to some extent, although its solubility appears to be low even at 1100 °C.

3.2.2. Superconducting properties. In Fig. 6 the AC susceptibility curves are shown for two of the samples. They are typical for all the samples prepared. The composites exhibit $T_c = 89$–93 K, which is virtually the same as for the undoped Bi-2212 materials (Table 1). At the same time the composites show the sharper transition on the $\chi'(T)$ curves, and the $\chi''(T)$ peak at a higher temperature. Only one $\chi''(T)$ peak and nearly full screening at low temperature allows us to suggest that the supercurrent flows around the whole sample.

The critical current density was estimated using the imaginary part of the AC susceptibility at the field of 10 mT and applying Bean's model for the flux penetration in the superconductor using expressions described in ref. 28. The composites normally show higher critical current density than the corresponding Bi-2212 samples (Table 1). In Fig. 7 the J_c values are plotted *vs.* the average $Mg_{1-x}Cu_xO$ particle size in the composites. The critical current density increases with decreasing particle size. This is quite expected, because at a constant inclusion phase content the number of the inclusions and correspondingly of the flux pinning sites increases, and J_c will be proportional to $1/a$, where a is the inclusion size.[2] A certain scatter of the J_c data can be connected with other factors, such as defect structure and T_c.

J_c at different magnetic fields was estimated from magnetisation data using the expression $J_c = 2\Delta M/d$ (corresponding to the Bean's model for a slab geometry[29]) in SI units, where ΔM is the hysteresis magnetisation width at a certain field, and d is the sample thickness. The field dependence of J_c is presented in Fig. 8 for sample D and the Bi-2212 sample (prepared *via* method C), showed the best characteristics. At $T = 5$ K, the J_c values are slightly higher for the Bi-2212–$Mg_{1-x}Cu_xO$ sample. At $T = 60$ K the composite reveals a J_c value twice as high at 10 mT and an order of magnitude higher at 80 mT in

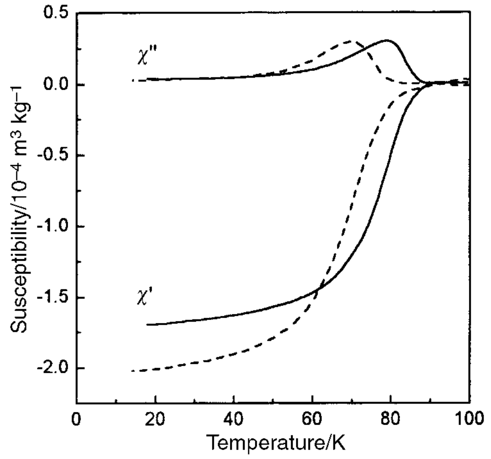

Fig. 6 Temperature dependence of AC susceptibility at an AC field of 10 mT: broken line — the Bi-2212 sample prepared by method C, solid line — the Bi-2212–$Mg_{1-x}Cu_xO$ composite (sample D).

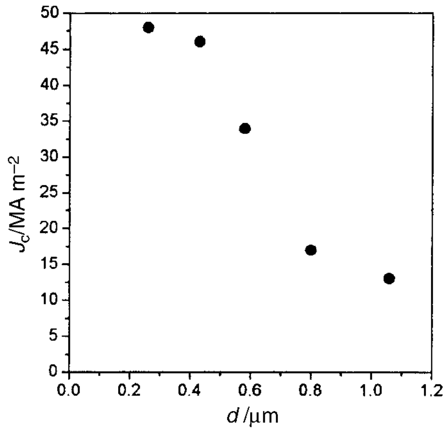

Fig. 7 Critical current density J_c at $T = 60$ K *vs.* average $Mg_{1-x}Cu_xO$ particle size d in the Bi-2212–$Mg_{1-x}Cu_xO$ composites.

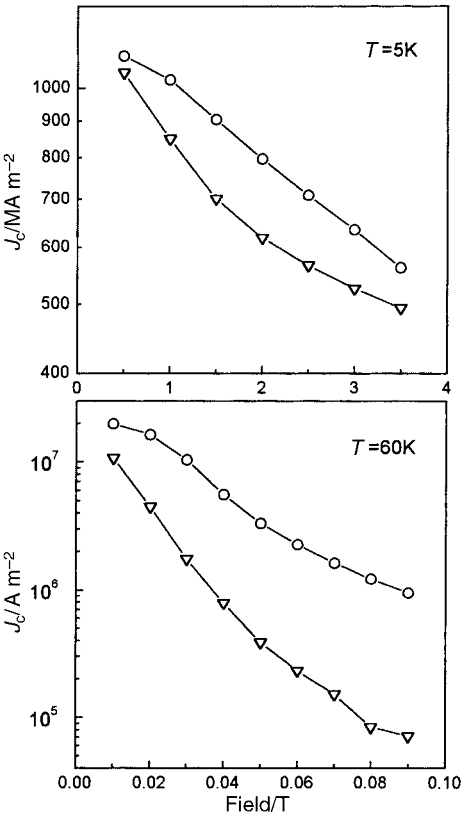

Fig. 8 Field dependence of the critical current density: the Bi-2212 sample prepared by method C (triangles), the Bi-2212–$Mg_{1-x}Cu_xO$ composite (sample D, circles).

comparison with the Bi-2212 sample. Relative enhancement in J_c and its field stability at increased temperatures is commonly attributed to the increase in the number of pinning centres with high energy, which remain active at high temperature.[4,24] Such pinning centres are quite easy to identify with the $Mg_{1-x}Cu_xO$ submicron inclusions.

4. Conclusions

The Bi-2212 phase interacts with the MgO powder yielding $Mg_{1-x}Cu_xO$ and $(Sr,Ca)_{4-y}Bi_2O_z$. The Bi-2212 phase coexists with $Mg_{1-x}Cu_xO$ at $x \geqslant 0.08$. In contrast to that, single crystal MgO is chemically stable against the Bi-2212 solid and melt up to 1100 °C. The solubility of magnesium oxide in solid Bi-2212, $(Sr,Ca)CuO_2$, $(Sr,Ca)_2CuO_3$, $(Sr,Ca)_{4-y}Bi_2O_z$, Bi-2201, as well as in the Bi–Sr–Ca–Cu–O melt up to 1100 °C is limited to low values, under 1 mol%. The composites Bi-2212–$Mg_{1-x}Cu_xO$ obtained using different precursor preparation methods consist mainly of the Bi-2212 matrix with uniformly distributed submicron inclusions of $Mg_{1-x}Cu_xO$, their size depending on the precursors used. When applying even nanocrystalline MgO, the $Mg_{1-x}Cu_xO$ grains in the composites attain sizes above 0.2 μm due to recrystallisation in the Bi–Sr–Ca–Cu–O melt. The Bi-2212–$Mg_{1-x}Cu_xO$ composites exhibit both higher critical current density and better field stability of J_c at enhanced temperatures in comparison with Bi-2212, that discriminates the $Mg_{1-x}Cu_xO$ inclusions as effective pinning centres.

Acknowledgements

The work is supported by Russian Fund for Basic Research (projects 97-03-33249a, 00-03-32597a) and Russian Ministry of Science (project "Composite").

References

1 L. D. Cooley and L. R. Motowidlo, *Supercond. Sci. Technol.*, 1999, **12**, R135.
2 M. Murakami, *Prog. Mater. Sci.*, 1994, **38**, 311.
3 P. E. Kazin, V. V. Poltavets, V. V. Lennikov, R. A. Shuba, E. A. Eremina, Yu.D. Tretyakov, M. Jansen, B. Freitag, G. F. la Fuente and A. Larrea, *Formation of stable phase inclusions in Bi-2212 and Bi(Pb)-2223 materials*, in *High-Temperature Superconductors and Novel Inorganic Materials*, eds. G. Van Tendeloo, E. V. Antipov and S. N. Putilin, Kluwer Academic Publishers, Dordrecht, 1999, p. 69.
4 P. Majewski, *Appl. Supercond.*, 1995, **3**, 289.
5 E. E. Hellstrom, *JOM*, 1992, 48.
6 H. Miao, H. Kitaguchi, H. Kumakura, K. Togano, T. Hasegawa and T. Koizumi, *Physica C*, 1998, **303**, 81.
7 J. C. Diez, L. A. Angurel, H. Miao, J. M. Fernandez and G. F. de la Fuente, *Supercond. Sci. Technol.*, 1998, **11**, 101.
8 B. Soylu, N. Adamopoulos, W. G. Clegg, D. M. Glowacka and J. E. Evetts, *IEEE Trans. Appl. Supercond.*, 1993, **3**, 1133.
9 D. R. Watson, M. Chen and J. E. Evetts, *Supercond. Sci. Technol.*, 1995, **8**, 311.
10 N. Adamopoulos, B. Soylu, Y. Yan and J. E. Evetts, *Physica C*, 1995, **242**, 68.
11 S. Pavard, C. Villard, D. Bourgault and R. Tournier, *Supercond. Sci. Technol.*, 1998, **11**, 1359.
12 S. Pavard, D. Bourgault, C. Villard and R. Tournier, *Physica C*, 1999, **316**, 198.
13 W. Wei, J. Schwartz, K. C. Goretta, U. Balachandran and A. Bhargava, *Physica C*, 1998, **298**, 279.
14 B. Zhao, W. H. Song, X. C. Wu, W. D. Huang, M. H. Pu, J. J. Du, Y. P. Sun and H. C. Ku, *Supercond. Sci. Technol.*, 2000, **13**, 165.
15 P. Yang and C. M. Lieber, *Science*, 1996, **273**, 1836.
16 V. V. Lennikov, P. E. Kazin, V. I. Putlayev, Yu. D. Tretyakov and M. Jansen, *Zh. Neorg. Khim. (Russ.)*, 1996, **41**, 911.
17 P. E. Kazin, T. E. Os'kina and Yu.D. Tretyakov, *Appl. Supercond.*, 1993, **1**, 1007.
18 C. J. Rawn, R. S. Roth, B. P. Burton and M. D. Hill, *J. Am. Ceram. Soc.*, 1994, **77**, 2173.
19 B. Hong, J. Hahn and T. O. Mason, *J. Am. Ceram. Soc.*, 1990, **73**, 1965.
20 R. Müller, M. Cantony and L. J. Gauckler, *Physica C*, 1995, **243**, 103.
21 J. Assal, B. Hallstedt and L. J. Gauckler, *Z. Metallkd.*, 1996, **87**, 568.
22 M. Paranthaman, K. A. David and T. B. Lindemer, *Mater. Res. Bull.*, 1997, **32**, 165.
23 P. Majewski, *Adv. Mater.*, 1994, **6**, 460.
24 P. E. Kazin, M. Jansen, A. Larrea, G. F. de la Fuente and Yu. D. Tretyakov, *Physica C*, 1995, **253**, 391.
25 P. E. Kazin, R. A. Shuba, Yu.D. Tretyakov, A. V. Knotko, M. Jansen and B. Freitag, *Supercond. Sci. Technol.*, 2000, **13**, 134.
26 P. E. Kazin, V. V. Poltavets, M. S. Kuznetsov, D. D. Zaytsev, Yu.D. Tretyakov, M. Jansen and M. Schreyer, *Supercond. Sci. Technol.*, 1998, **11**, 880.
27 P. E. Kazin, V. V. Poltavets, Yu.D. Tretyakov, M. Jansen, B. Freitag and W. Mader, *Physica C*, 1997, **280**, 253.
28 F. Gömöry, *Supercond. Sci. Technol.*, 1997, **10**, 523.
29 C. P. Bean, *Rev. Mod. Phys.*, 1964, **36**, 31.