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Relations between the synthesis conditions, composition, microstructure and superconducting properties of Bi-2212 based composites

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The variation of synthetic conditions, the composition of a Bi-2212 matrix, and the nature of dispersed phases was found to impact on the distribution of non-superconducting inclusions and the flux pinning in the superconducting composites.

The formation of non-superconducting defects in the Bi–Sr–Ca–Cu–O superconductors is a perspective way for increasing flux pinning and, therefore, critical current density.[1,2] The inclusions of fine non-superconducting phases can work as high-energy pinning centres at temperatures approaching the critical transition temperature.[3–10] The chemical compatibility of embedded non-superconducting phases with a superconducting matrix is of primary importance to obtain stable materials with advanced properties.[10] Among others, the $SrAO_3$ (A = Ti, Zr or Hf) phases are found to be compatible with $Bi_2Sr_2CaCu_2O_{8+x}$ (Bi-2212),[5,6,10] while no systematic study on the introduction of Mo- or W-containing non-superconducting phases as pinning centres into Bi–Sr–Ca–Cu–O superconductors was reported. Here we consider Ti-, Zr-, Hf-, Mo- and W-containing oxides as pinning additives to Bi-2212 and report on the preparation conditions and superconducting properties of the corresponding composites.

To estimate the compositions of M-containing phases (M = Mo or W) compatible with Bi-2212, the interaction of Bi-2212 with 5 mol% MO_3 was investigated. The pellets of the powder mixture were partially molten in air and slowly crystallised in air at cooling rates of 2 and 5 K h^{-1}.

Precursors with the nominal compositions $\{Bi_{2.1}Sr_{1.9}CaCu_2O_{8+x} + 0.5SrAO_3\}$ (A = Zr, Hf) and $\{Bi_{2.1}Sr_{1.9}CaCu_2O_{8+x} + 0.25Sr_2CaMO_6\}$ were prepared *via* a sol–gel technique. The $Bi_{2.1-x}Pb_xSr_{1.9}Ca_{1-y}Y_yCu_2O_{8+x}$ (x = 0–0.4; y = 0–0.2) phases (BSCCO) and the $\{Bi_{2.1}Sr_{1.9}CaCu_2O_{8+x} + 0.5SrTiO_3\}$ precursor were prepared by the thermal treatment of nitrates mixture. Fine powders of $SrAO_3$ were obtained by oxalate decomposition at 800–1000 °C and then mixed with BSCCO. Afterwards, all the samples were pressed into pellets, heated above the melting temperature and crystallised as described above.

The amount of a dispersed phase trapped within the superconducting grains in respect to the full amount of the phase (trapping ratio) was calculated using the ratio of the corresponding areas in the SEM images. To quantify pinning, the mean effective activation energy <*E*> was estimated from the time dependence of magnetisation at 4.2 K and 1 T.[11,12] To characterise pinning at temperatures close to T_c the τ parameter was calculated as T_{max}/T_c, where T_{max} was the temperature of the maximum at the imaginary part of magnetic susceptibility *vs.* temperature at H_{AC} = 100 Oe.

Table 1 Magnetic properties of the $Bi_{2.1}Sr_{1.9}CaCu_2O_{8+x}$–$SrAO_3$/$Sr_2CaMO_6$ composites.

A/M	Trapping ratio	T_c/K	τ (%)	<*E*> (4.2 K, 1 T)/meV
—	—	92	70	17.4
Zr	43	92	76	18.7
Hf	22	92	75	17.8
Mo	100	96	71	17.9
W	18	94	80	19.5
Ti	42	68	< 25	—

In the thermally treated mixtures of Bi-2212 with MO_3, along with the main Bi-2212 phase, phases close to Sr_2CaMO_6 in composition were found. These phases were assumed as chemically compatible with Bi-2212 and for the preparation of the composites the corresponding surpluses of oxides were used. Therefore, five composites with the nominal compositions $\{$Bi-2212 + $0.5SrAO_3\}$ and $\{$Bi-2212 + $0.25Sr_2CaMO_6\}$ were obtained.

Bi-2212 and the corresponding dispersed phases were found to be the main constituents of the composites. According to EDX, Zr, Hf, Mo and W were not observed in the Bi-2212 matrix within the measuring accuracy (better than 1 at% of cations). 2 at% Ti was observed in the matrix, which resulted in decreased T_c = 68 K. In the Hf- and Zr-containing composites, the superconducting transition temperature remained the same as that in pure Bi-2212, while it increased in the Mo- and W-containing samples (Figure 1), reaching 97 K for Bi-2212-Sr_2CaMoO_6. This may suggest that a small amount (less than 1 at%) of Mo and, probably, W enters the Bi-2212 matrix.

The composites consist of Bi-2212 plate-like crystallites with smaller grains of secondary phases distributed inside and between the crystallites. In case of separate precursors, some initial aggregates of $SrHfO_3$ do not decompose during melt processing, while the $SrZrO_3$ aggregates decompose completely. The majority of the secondary phases found are the added ones.

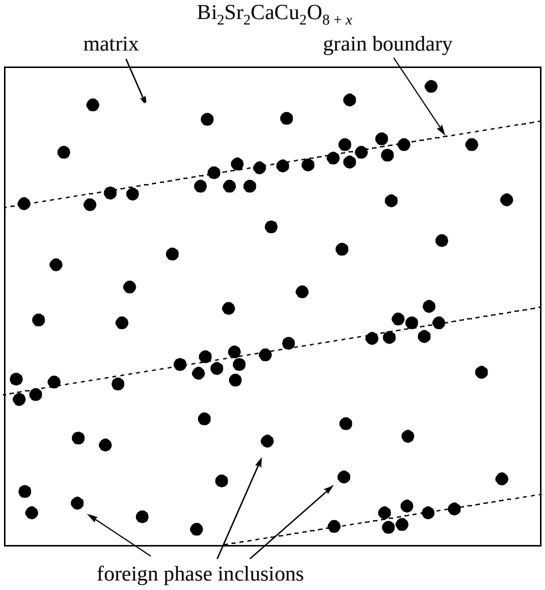

Figure 1 Segregation of the fine admixture particles at the grain boundaries.

The Bi-2212 crystallites are disordered and have a wide size distribution. The largest average grain size is found for undoped Bi-2212. This may be connected with the fact that the foreign phases supply new nuclei for Bi-2212 crystallisation, as well as hinder the liquid flow to the growing superconducting crystals in both cases resulting in a reduced Bi-2212 grain size.

Sr_2CaMoO_6 forms particles of a few micrometres in size. The other foreign phases form submicron particles with the size dependent on the synthesis route. A large size of the molybdate phase particles may indicate some solubility of Mo in the BSCCO melt, which results in particle coarsening during the melt processing.

The foreign phases tend to segregate mainly at the Bi-2212 grain boundaries. The segregation can be described by the Uhlmann–Chalmers–Jackson (UCJ) theory, stating that small admixture particles tend to be pushed out from a crystal, which grows with a rate of v below the critical value v_{cr}.[13] For $v > v_{cr}$, the particles are effectively trapped by the growing crystal. The critical rate v_{cr} depends on the admixture particle size r as follows: $v_{cr} \propto \Delta\sigma/(\eta r)$, where η is the viscosity of the liquid, $\Delta\sigma = \sigma_{crystal/particle} - \sigma_{liquid/particle} - \sigma_{crystal/liquid}$ is the difference between the corresponding surface energies.[14] To trap finer admixture particles, higher crystallisation rates are required.

According to our observations, the particles of 1–5 μm in size (Sr_2CaMoO_6 and coarse $SrZrO_3$) did not segregate at all, which may be connected with the sufficient particle size for the crystallisation rate determined by particular processing conditions. Other foreign phases are partially segregated.

The trapping ratio T_c the parameter τ, and the effective activation energy $<E>$ (4.2 K) for the test samples are given in Table 1. The Zr-, Hf- and W-containing composites differ markedly from the reference Bi-2212 sample by increased τ, while $<E>$ increased only slightly. The Mo-containing composite has pinning parameters close to those of the reference sample. The Ti doping strongly decreases τ.

Table 2 Trapping ratio and pinning parameter τ for the $Bi_{2.1-x}Pb_xSr_{1.9}$-$Ca_{1-y}Y_yCu_2O_{8+x}$–$SrAO_3$ composites, $v_{cooling}$ = 2 K h^{-1}.

x	y	A = Zr		A = Hf		No additive
		Trapping ratio	τ	Trapping ratio	τ	
0	0	31	81	2	76	71
0.2	0	33	79	10	78	70
0.4	0	36	82	19	80	72
0^a	0	81	83	25	79	—
0	0.2	65	< 20	42	< 20	—

$^a v_{cooling}$ = 5 K h^{-1}.

Therefore, we can conclude that the composites have an additional number of pinning centres with high energy and increased pinning at elevated temperature. There is no clear correlation of the pinning parameters with the size of the dispersed phases and with the trapping ratio: other factors such as defect structure may play an important role. Note that a W-containing composite has the best pinning parameters.

Considering the $Bi_{2.1-x}Pb_xSr_{1.9}Ca_{1-y}Y_yCu_2O_{8+x}$–$SrAO_3$ composites, the trapping ratio of $SrHfO_3$ increases with Pb content, while the increase is small for $SrZrO_3$ (Table 2). This may be related to the better wetting of $SrHfO_3$ with the melt resulting in the partial decomposition of its aggregates. The addition of Y provides a significant increase of the trapping ratio in both cases. As it is expected from the above equation for v_{cr}, the increase in the melt cooling rate drastically improved the trapping of foreign particles.

The partial replacement of Bi by Pb and of Ca by Y results in a few degrees T_c decrease. In the case of the replacement of Bi by Pb, the τ parameter is considerably higher for the composites in comparison with the corresponding single-phase Bi-2212 samples. In addition, it does not appreciably depend on the Pb doping for both for the composites and the reference samples. Though an increase of τ takes place at high Pb doping (y = 0.4) and high cooling rates. In the case of the replacement of Ca by Y, the τ parameter is very low implying low J_c values, which can be connected with an increased electromagnetic anisotropy in Bi-2212 as a result of Y doping.

The described additives with the exception of $SrTiO_3$ provide the enhancement of the material superconducting characteristics or leave them unchanged. The best superconducting properties are obtained for the composite containing Sr_2CaWO_6. The $SrTiO_3$ addition deteriorate both T_c and pinning. The trapping of additive particles depends on the particle size and chemical composition of the matrix; coarse particles are trapped better. The best trapping is observed in Y-doped Bi-2212 composites, but the pinning parameters deteriorate due to the change of the Bi-2212 matrix superconducting properties.

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