Fully connected bulk $Pb_{1-x}Sn_xMo_6S_{7.6}$ samples made by hot isostatic pressing

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(Received 24 October 1991; accepted for publication 9 December 1991)

High-density bulk $Pb_{1-x}Sn_xMo_6S_{7.6}$ ($0 \leqslant x \leqslant 1$) samples have been made by hot isostatic pressing at the relatively low temperatures of 800 and 900 °C. Critical current densities, computed from magnetization data taken at various magnetic fields and temperatures, show excellent temperature scaling indicating that a single pinning mechanism is present. The magnetization of all samples scales with size, showing that full density samples are not granular. Samples sintered without pressure at higher temperatures did not achieve full density and did not exhibit good size scaling of the magnetization, thus indicating only percolation connections across the sample in this case. We conclude that there is no intrinsic granularity in these Chevrel phases even though their coherence length is short.

The high-critical-field Chevrel phase compounds, of which $PbMo_6S_8$ is the best example, remain promising candidates for generating magnetic fields above 20 T.[1] Up to now, however, transport current densities (J_c) in wires remain a little too low to make applications really attractive since the best values are in the range $1\text{–}2\times10^8$ A/m^2 at 20 T. Why the J_c values remain at this level[2–4] is not clear. It may be due to insufficient flux pinning, to an intrinsic granularity,[5] or to an essentially percolative connection between grains.[6] As observed in the high-temperature superconducting oxides,[7] intrinsic granularity may indeed be expected in these materials because of their short coherence length (about 3 nm).[8] Some evidence for this has recently been presented by Cattani *et al.*[5,9,10] In this letter we explicitly test the influence of contact quality between grains by comparing the properties of various $Pb_{1-x}Sn_xMo_6S_8$ bulk samples when sintered both by hot isostatic pressure (HIP) and by pressureless sintering.

Five samples having nominal compositions $Pb_{1-x}Sn_xMo_6S_{7.6}$ ($x = 0,0.1,0.5,1$) were prepared by a two-step process. This stoichiometry was chosen since this composition is found to be single phase in published phase diagrams.[11,12] A first heat treatment of the elements (Pb, Sn, Mo, S) was made at 800 or 900 °C for 20 h in a sealed evacuated quartz tube, followed by grinding and mixing. The subsequent HIP heat treatment was performed at the same temperature, under 2 kbars of argon pressure for 8 h, after the samples were wrapped in molybdenum sheets and sealed in evacuated stainless-steel tubes. All operations were carried out in inert atmosphere, in order to minimize oxygen contamination, although some did occur. Magnetization data were then taken on rectangular cross-section specimens in a vibrating sample magnetometer in magnetic fields up to 12 T and in the temperature range 2–12 K.

All samples had inductively measured critical temperatures (T_c) between 11.5 and 13 K, somewhat below the highest values of 15 K which have been reported.[9,13] We believe that these depressed T_c values represent some oxygen contamination introduced during processing.[13,14] Some of this enters in the HIP step, since non-HIP'ed samples had T_c values about 1 K higher. We computed the critical current densities (J_c) from the magnetization hysteresis using the equation $J_c = 3\Delta M/d$, where $d = 1.5l_1\ (1 - l_1/3l_2)$, $l_1 < l_2$, where l_1 and l_2 are the sample dimensions perpendicular to the magnetic field. This implicitly assumes that current circulates over the whole sample, an assumption that will be tested later. Typical J_c results (for a $Pb_{0.1}Sn_{0.9}Mo_6S_{7.6}$ sample HIP'ed at 800 °C) are shown in Fig. 1 at temperatures from 4.2 to 11 K. We found J_c values between 0.45 and 2.5×10^8 A/m^2 at 10 T and 4.2 K across the whole range of samples studied. Figure 2 shows the reduced pinning force ($F_p/F_{p_{max}}$) vs reduced field curve ($b = B/B^*$, where B^* is the field at which ΔM becomes zero) for the same sample as Fig. 1. We checked this relationship for three samples, two being HIP'ed at 800 °C

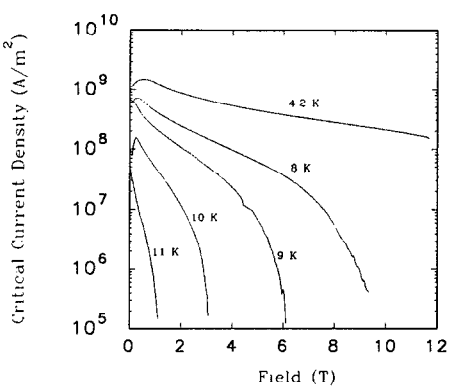

FIG. 1. Critical current density as a function of magnetic field at 4.2, 8, 9, 10, and 11 K for a $Pb_{0.1}Sn_{0.9}Mo_6S_{7.6}$ bulk sample HIP'ed at 800 °C.

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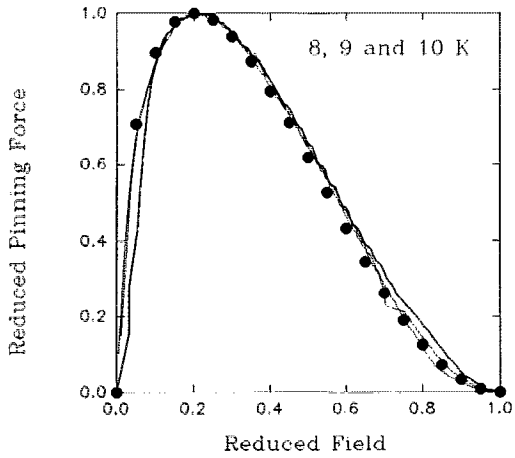

FIG. 2. Reduced pinning force as a function of reduced critical field for a $Pb_{0.1}Sn_{0.9}Mo_6S_{7.6}$ bulk sample HIP'ed at 800 °C. ● Calculated points for $F_p/F_{p_{max}} = C[b^{1/2}(1-b)^2]$.

and one at 900°C. They all displayed excellent temperature scaling with maxima in $F_p/F_{p_{max}}$ between 0.15 and 0.20b. The scaling law is close to $F_p/F_{p_{max}} = Cb^{1/2}(1-b)^2$, where C is a constant (see Fig. 2).

Figure 3 shows magnetization hysteresis (ΔM) versus sample size (d) plots for pure Pb and Sn and mixed composition HIP- and non-HIP-processed samples. All HIP'ed samples show an excellent proportionality between magnetization and size, as expected if the dimensions l_1 and l_2 used in the expression for J_c are indeed the dimensions over which the induced currents circulate. Scanning electron microscopy on the samples shows their grain size to lie in the general range 0.5–5 μm (see Fig. 4). Thus the sample size is of order 10^3–10^4 times the grain size. However, a sample of $Pb_{0.5}Sn_{0.5}Mo_6S_{7.6}$ which was sintered without pressure at 1100 °C exhibited a very flat characteristic which does not extrapolate to the origin. Given that the grain size is so much smaller than the sample size there is no reason to suppose that J_c is size dependent in this non-HIP'ed sample: therefore, the weak dependence of the

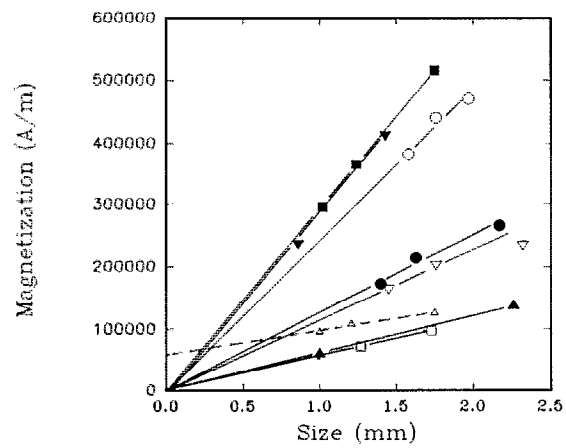

FIG. 3. Magnetization as a function of sample size for various $Pb_xSn_{1-x}Mo_6S_{7.6}$ samples at 4.2 K. (—) HIP'ed at 800 °C: ▽ $x = 1$; □ $x = 0.5$; □ $x = 0.1$; ▽ $x = 0$. (—) HIP'ed at 900 °C: ○ $x = 1$; △ $x = 0.1$; ● $x = 0$. (- -) Non-HIP'ed at 1100 °C: △ $x = 0.5$. *Note:* all magnetizations have been measured at 2 T, except for one 800 °C sample ($x = 1$) (6 T) and all three 900 °C samples (4 T) which all showed flux jumping at low fields, a further indication of good connectivity.

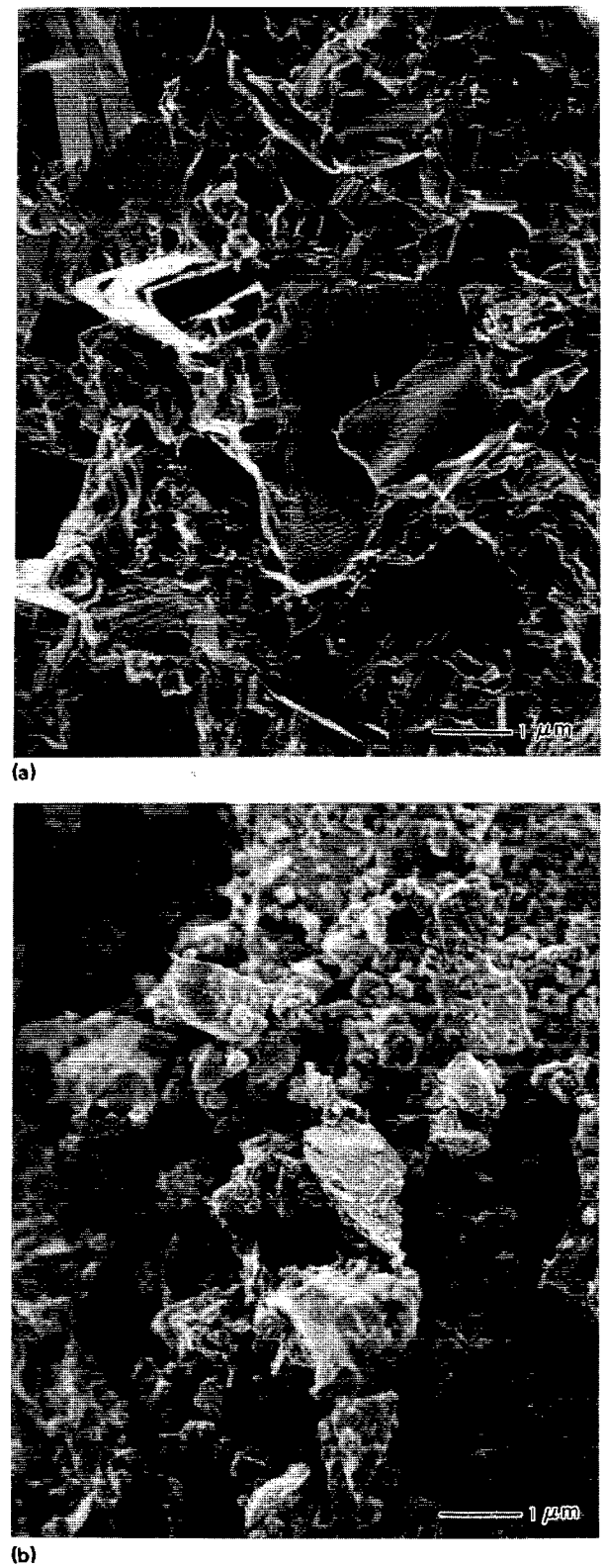

FIG. 4. High-resolution scanning electron microscope micrographs of (a) a $Sn_1Mo_6S_{7.6}$ HIP'ed bulk sample made at 800 °C and (b) a $Pb_{0.1}Sn_{0.9}Mo_6S_{7.6}$ non-HIP'ed bulk sample made at 800 °C.

magnetization hysteresis most reasonably arises from the fact that l_1 and l_2 overestimate the correct scaling lengths for the induced currents. This is consistent with the much smaller ΔM values seen for the non-HIP'ed sample. The difficulty of connections seems to be tied to the poor percolation connectivity of a low-density sample, as was seen earlier in Mo-sheathed wires of low density.[15]

It should first be stressed that the J_c values (Fig. 1) are in the same general range as the transport current densities observed in HIP-treated wires[2,3,6] and are only slightly lower than the best ones. These bulk samples thus appear comparable in quality to wires. We may ascribe the lower J_c values, as well as their lowered critical temperatures, to oxygen contamination arising from the fabrication process. In spite of this they exhibit good temperature scaling, as shown in Fig. 2. Such scaling is generally taken as evidence for a single pinning mechanism. We also point out that the same shape of pinning curves is observed for thin films[16] and bulk samples[17] prepared by different methods, where T_c values vary from 11 to 15 K. This supports the hypothesis that the same pinning mechanism is common to many Chevrel phase samples, including the present ones. Grain-boundary pinning, as proposed by Rickel *et al.* for bulk samples,[18] seems the most likely pinning mechanism.

Crucial for determining whether good connections exist between grains is the size scaling experiment. The good scaling found in all our HIP-processed samples is strong evidence that screening currents flow around the whole specimens rather than around any smaller agglomerates. By contrast, the non-HIP sample does not exhibit good size scaling behavior, thereby emphasizing the important role of pressure in producing a well-connected compact. It is interesting that this good connection is obtained at comparatively low temperatures for Chevrel phases (800 and 900 °C) and exists even when there is evidence for some oxygen contamination. There thus seems little reason to fear that granularity is an intrinsic problem for Chevrel phases, even though their coherence lengths are sufficiently short that this might be considered to be a reasonable possibility.[8]

Although it is agreed that the best J_c values are obtained for a Pb/Sn atomic ratio of about 8/2,[18–21] our results do not show any strong trend regarding this point. Further optimization of the process should be carried out to address this aspect as well as to investigate lowering the HIP treatment temperature in order to reduce the grain size and thus raise the critical current densities.

We thank N. Ingle for experimental assistance and the U.S. Department of Energy–Division of High Energy Physics and Office of Fusion Energy for support. The SEM micrographs were taken at the University of Wisconsin Integrated Microscopy Resource (IMR). The IMR in Madison is funded as an NIH Biomedical Research and Technology Resource (RR 570).

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