Superconducting, microstructural, and grain boundary properties of hot-pressed $PbMo_6S_8$

Selvam, Parasuraman; Cattani, Daniel; Cors, Jorge; Decroux, Michel André; Junod, Alain; Niedermann, Philipp; Ritter, Sophie Stéphanie; Fischer, Oystein; Rabiller, P.; Chevrel, R.

How to cite

SELVAM, Parasuraman et al. Superconducting, microstructural, and grain boundary properties of hot-pressed $PbMo_6S_8$. In: Journal of Applied Physics, 1992, vol. 72, n° 9, p. 4232–4239. doi: 10.1063/1.352235

This publication URL: https://archive-ouverte.unige.ch/unige:114642

Publication DOI: 10.1063/1.352235

Superconducting, microstructural, and grain boundary properties of hot-pressed $PbMo_6S_8$

P. Selvam, D. Cattani, J. Cors, M. Decroux, A. Junod, Ph. Niedermann, S. Ritter, and Ø. Fischer
Département de Physique de la Matière Condensée, Université de Genève, 24, Quai E. Ansermet, CH-1211 Genève 4, Switzerland

P. Rabiller and R. Chevrel
Chimie Minérale B, U.A. CNRS 254, Université de Rennes, Rennes Cedex, F-35042, France

(Received 29 April 1992; accepted for publication 15 July 1992)

An alternative procedure is outlined for the synthesis of high quality, fine grained $PbMo_6S_8$. As the grain size plays an important role on the densification process, which in turn has an influence on the magnitude of J_c, an attempt has been made to produce dense samples from such powders by "Hot Pressing." The effect of the hot-pressing temperature on the superconducting, crystallographic, microstructural, and grain boundary characteristics of the ternary compound was evaluated. Scanning electron micrographs and *ac*-susceptibility measurements indicate that hot pressing (1000–1200 °C) improves the grain connection as a consequence of better densification. However, at higher temperatures (1250–1400 °C) it also precipitates MoS_2 as an additional phase. Calorimetric data indicate a continuous broadening, as a function of hot-pressing temperature, of the specific heat jump at T_c. Preliminary investigation on the T_c distribution of the samples shows a progressive degradation, as indicated by a smearing in T_c down at least to 8 K. The deterioration was examined using Auger electron spectroscopy and the results suggest possible compositional variations rather than oxygen defects in the phase. The origin of such behavior is examined on the basis of nonstoichiometry or chemical heterogeneity at the grain surface. In addition, grain boundary contaminants and their role on the superconducting properties are considered. Finally, the often encountered problem of transport J_c limitation in these materials is discussed in terms of interconnectivity of the grains, phases, the presence of secondary phases, impurities, inhomogeneities, and the grain boundary phases.

I. INTRODUCTION

The high critical field Chevrel-phase compound, $PbMo_6S_8$ has prompted a significant amount of work in order to understand its remarkable superconducting properties.[1,2] However, its progress towards major applications such as generating magnetic fields above 20 T has been hindered by the slow improvement in the transport critical current density J_c. Despite much work, J_c in the bulk samples is not as high as required for practical purposes. One of the reasons is the large grain size causing a low density and a highly porous microstructure of the sintered materials. As a consequence, they subdivide into superconducting regions separated by weak superconducting or normal interfaces at the grain boundaries.[3,4] Another one is the nonreproducibility of the materials properties and quality. This, however, has been identified in recent times and is in good control.[5]

For the development of superconductors with improved properties an understanding of the interplay between microstructure and critical current is of fundamental importance. As is known, the transport J_c of $PbMo_6S_8$ increases with a decreasing grain size and better intergrain connectivity.[6,7] Progress should be made in this direction for a further advancement. The present investigation is, therefore, an attempt to produce high quality, in terms of homogeneity and phase purity, and fine grained $PbMo_6S_8$ using a newly developed method, and eventually to densify the samples by hot pressing. The latter is essentially a sintering process with a simultaneous application of a high pressure to a uniaxially cold pressed mass enclosed in a die. The effects arising from microstructural, grain boundary, and crystallographic variations on superconducting properties are examined. A preliminary account of this work containing some of the measurements and a brief interpretation has appeared previously.[4]

II. EXPERIMENTAL PROCEDURE

A. Sample preparation

Ternary $PbMo_6S_8$ was prepared by optimized experimental conditions, in a three step process, as described below.

First, ternary $Ni_2Mo_6S_8$ was synthesized by a direct reaction of appropriate amounts of Ni, Mo, and MoS_2 powders in a Mo crucible sealed thermomechanically under vacuum. The mixture was heated to 1030 °C for 5 h. X-ray patterns of the resulting powder indicate a pure phase with the lattice constants, in the hexagonal cell, $a_h = 9.5091(3)$ Å; $c_h = 10.2201(5)$ Å; space group R-3. Next, Ni was disintercalated from the ternary phase to obtain binary Mo_6S_8 by acid leaching procedure. That is, the sample was immersed in dilute HCl (50% by volume) and stirred continuously at room temperature for 24 h. This enables us to remove all the Ni from the phase. It was washed and filtered with water and alcohol, and then dried

 0021-8979/92/214232-08$04.00

TABLE I. Density, crystallographic, and superconducting data of hot-pressed $PbMo_6S_8$. For a comparison the parameters of the starting powder (SP) are also included.

Sample No.	Hot-pressing temp. (°C)	Density		Structural parameters				T_c onset (K)	
		exp. ($g\,cm^{-3}$)	cal. ($g\,cm^{-3}$)	a (Å)	c (Å)	v (Å^3)	c/a ratio	Specific heat	ac susceptibility
1	SP	···	6.15	9.1992(6)	11.489(1)	842.0(1)	1.2489(2)	14.9	···
2	1000	4.45	6.15	9.1961(7)	11.494(1)	841.8(1)	1.2499(2)	14.9	14.7
3	1100	4.87	6.16	9.1964(7)	11.485(1)	841.2(1)	1.2489(2)	14.8	14.5
4	1200	5.78	6.16	9.1948(7)	11.485(1)	840.9(1)	1.2491(2)	···	14.65
5	1250	6.15	6.15	9.1948(9)	11.495(2)	842.3(2)	1.2502(3)	15.0	···
6	1300	6.17	6.15	9.1983(9)	11.494(2)	842.2(2)	1.2496(3)	14.8	14.6
7	1400	6.18	6.15	9.1991(6)	11.489(1)	842.0(1)	1.2489(2)	···	14.7

in air at 100 °C for 2 h. X-ray powder diffraction analysis showed a single phase. The lattice parameters were determined from the extracted line positions [a_h=9.1912(2) Å; c_h=10.8900(4) Å; space group R-3].

Subsequently, the synthesis of $PbMo_6S_8$ was carried out in a sealed molybdenum crucible, as before, at 1180 °C for about 2 h with appropriate amounts of Pb ingot, and ultrafine Mo, MoS_2, and/or Mo_2S_3 precursors obtained from *in situ* decomposition of Mo_6S_8. Note that it is not an intercalation process.[5,8] It is, however, to be noted that the distribution of the decomposition products of Mo_6S_8 depends mainly on the reaction temperature. The overall processes and the corresponding reactions can be written as follows:

$$2Ni+4MoS_2+2Mo \xrightarrow{1030\,^\circ C} Ni_2Mo_6S_8, \quad (1)$$

$$Ni_2Mo_6S_8+4HCl \xrightarrow{20\,^\circ C} 2NiCl_2+Mo_6S_8+2H_2, \quad (2)$$

$$Pb+Mo_6S_8 \xrightarrow{1180\,^\circ C} Pb+[Mo_2S_3+MoS_2+Mo] \rightarrow PbMo_6S_8. \quad (3)$$

The resulting product, $PbMo_6S_8$ was of high quality in terms of crystallographic and superconducting properties. The typical grain size was about 0.5–2 μm. It contains, however, a small amount of Mo_2S_3 as an impurity phase. Observations of increases in the cell constants, particularly the "c" parameter or the c/a ratio (1.249–1.250) and the T_c of $\approx$15 K, indicate the absence of oxygen defects.[5] The precursors and the reacted powder were, all the time, handled in a high purity argon filled glove box. The final powder, $PbMo_6S_8$ was divided into several parts and was used for the hot-pressing process.

B. Hot pressing

In order to achieve higher densities, $PbMo_6S_8$ was hot-pressed at different temperatures as per the following procedure. Dense bulk samples were first prepared by uniaxial cold pressing into powder compacts (at 50 bar) in the glove box using a graphite matrix reinforced with molybdenum. They were then transferred to the hot-pressing furnace and pressed at 2 kbar pressure in the temperature range from 1000 to 1400 °C under 5×10^{-2} mbar vacuum for 1 h. The long cylindrical pellets of 6 mm in length and 3.5 mm in diameter were used, as fabricated, for further measurements. However, attempts to prepare longer samples were unsuccessful.

C. Characterization

The densities of samples were measured with a picnometer using alcohol as the fluid. Ten measurements were carried out on each sample and the mean value was deduced. These samples were then sliced to final dimensions with a diamond saw. The small disks thus obtained were subjected to a systematic study by x-ray diffraction (XRD), scanning electron microscopy (SEM), Auger electron spectroscopy (AES), specific heat, ac-susceptibility, and resistivity measurements. The experimental details were given elsewhere.[5] The essential and relevant data are summarized in Table I.

III. RESULTS AND DISCUSSION

A. Structural parameters

The unit cell parameters, in the hexagonal cell, of the samples at different hot-pressing temperatures were determined with the data obtained on a Philips diffractometer using Cu $K\alpha$ radiation. Silicon powder was used as internal standard. All measurements were carried out at room temperature. The samples show consistently high c/a ratio (Table I), a factor which determines the phase purity with respect to a possible oxygen contamination. However, as can be seen from this table, a slight variation in the unit cell volume can be noticed as a result of hot pressing. The value decreases up to 1200 °C, then starts to increase at 1250 °C, and thereafter levels off. It has to be noted that the increase in volume at higher temperatures is associated with a precipitation of MoS_2.[4]

B. Microstructural analysis

Figure 1 shows SEM pictures of the fractured surface of $PbMo_6S_8$ samples hot pressed at different temperatures. The morphology of the material is altered as the hot-pressing temperature increases. However, the individual grains remain distinct at lower temperatures. The grains are approximately rectangular. Typical grain size of the cold-pressed sample is in the range 0.5–2 μm. The average

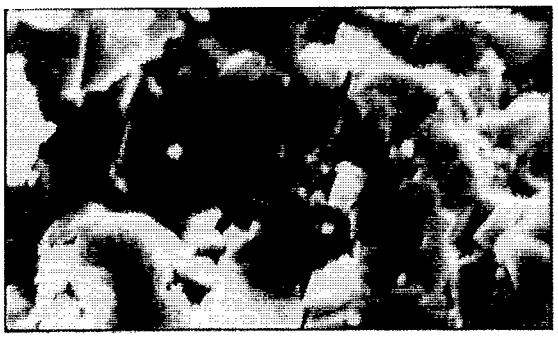

FIG. 1. SEM showing the morphology of hot-pressed (HP) $PbMo_6S_8$.

size of the hot-pressed samples is approximately 2 μm. The sample hot-pressed at 1000 °C appears as an agglomerate consisting of small grains. It contains many pores and voids [Fig. 1(a)] and the grains appear somewhat randomly stacked and poorly connected. At 1100 °C [Fig. 1(b)] the grains are closely packed with fine interconnected porosity and full face-on-face connections between grains. In the temperature range from 1200–1400 °C, the micrographs indicate a highly dense, fully connected matrix with some isolated pores. They show some evidence of partial melting that could occur at the interface [Figs. 1(c) and 1(d)]. We do find some voids or gas pockets or some amount of gas trapped in the interior. It may probably arise from the cold pressing of the samples in the argon-filled glove box. The SEM pictures also show some microcracks and the presence of a secondary phase, namely MoS_2 as precipitate at the grain surface [Fig. 1(d)]. This latter observation is in accordance with XRD results.[4] Additionally, the low-density specimens fracture almost exclusively between the grains (intergranular), while the high-density samples show considerable intragranular cleavage.

C. Density measurements

The experimental densities for the hot-pressed $PbMo_6S_8$ are presented in Table I. They are compared with the theoretical densities of each sample, calculated in the hexagonal cell. Contrary to the samples hot-pressed at higher temperatures (1200–1400 °C), the lower temperature (1000 and 1100 °C) hot-pressed samples do not achieve full density. This is very clear from the SEM, as they show, respectively highly dense and porous microstructures (see Fig. 1). The density for hot-pressed ($\geqslant$1200 °C) samples is high, $>95\%$ of the theoretical value. For the low temperature (1000 and 1100 °C) hot-pressed samples the density is low, only about 70%–85% of the theoretical density. As described in Sec. II B, the SEM pictures show distinct morphologies for these different density regimes.

D. Superconducting properties

1. ac susceptibility

The *ac*-susceptibility measurements indicate that all samples have high T_c-onset values close to 15 K (Table I and Fig. 2). The transitions are generally sharp with ΔT_c less than 0.5 K. One exception is the sample hot-pressed at 1000 °C, which shows a transition width of about 5 K; this indicates a typical granular behavior in agreement with the SEM results. Sample hot-pressed at this temperature shows a multistep transition (see Fig. 2) in a similar way to that of the earlier observations.[9] The part of the transition around 13 K which depends strongly on the amplitude of the *ac* field, not shown in the figure, is attributed to the onset of coherence between grains. The *ac*-field independent transition above 14.5 K, also not shown here, comes from individual grains or a group of well connected grains. Additionally, the specific heat data rule out any possibility of large T_c distribution in this sample. For hot pressing at

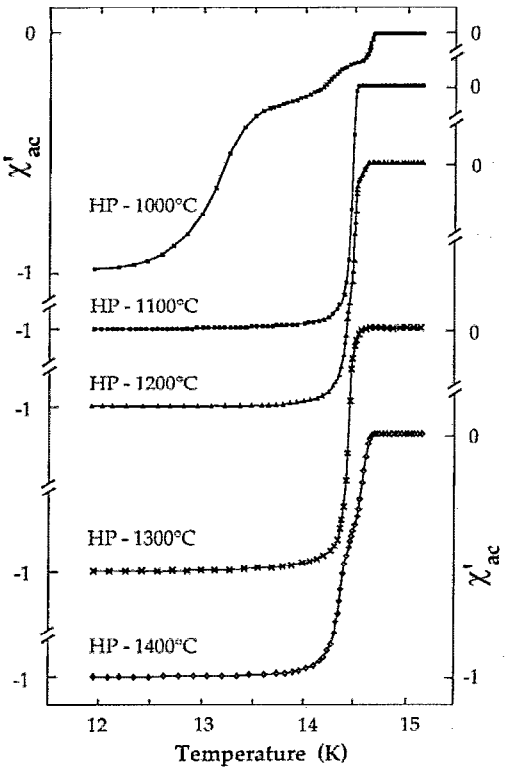

FIG. 2. *ac*-susceptibility transitions of hot-pressed (HP) $PbMo_6S_8$ with an excitation field of 6 mG and a frequency of 87 Hz.

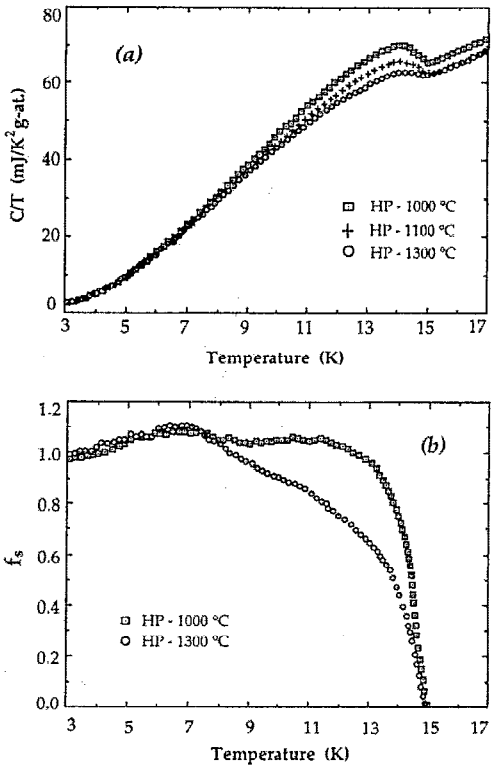

FIG. 3. (a) Specific heat jumps and (b) superconducting volume fraction, f_s of hot-pressed (HP) $PbMo_6S_8$.

1100 °C or above, only a single transition is observed. It still depends on the *ac* field, indicating that grain interconnection is not perfect. However, the sample hot-pressed at 1400 °C shows a multistep response and the origin of this feature is not clear.

2. Specific heat

The homogeneity with respect to T_c is deduced from the specific heat data. A well-defined sharp jump indicates that the samples are highly homogeneous.[10] As can be seen from Fig. 3(a), the calorimetric measurements show a progressive broadening, with increasing hot-pressing temperature, of the specific heat anomaly at T_c.[4] The magnitude of the jump shows the fraction that undergoes a sharp transition. Although the samples are single phase, inhomogeneities may cause an appreciable width in the superconducting transitions. Deconvolution of these data, in terms of superconducting volume fraction,[11,12] indicates clearly a distribution of T_c in the range 8–15 K [see Fig. 3(b)]. It is to be noted that the continuous distribution of T_c over several Kelvin will not give rise to any appreciable anomaly in the specific heat jump. Interestingly, as-prepared samples (before hot-pressing) or the samples hot-pressed at lower temperatures (for example at 1000 and 1100 °C) are fully superconducting within 1–2 K whereas the samples hot-pressed at higher temperatures (for example at 1250 and 1300 °C) have a T_c smearing up to 8 K.

3. Electrical resistivity

All samples show a sharp resistive transition around 14.5 K with a typical width of 0.2 K. In general, there are two distinct features of the resistivity data depending on the T_c range of the samples.[5] First, there is a correlation between the residual resistivity and T_c: the lower the value, the higher the T_c. Second, the temperature dependence of the normal state resistivity, which shows a curvature for the optimal T_c samples, tends to become linear as T_c is reduced. The nonlinear behavior is characteristic of the pure phase. The same has also been observed for the isoelectronic $EuMo_6S_8$ under pressure.[13] The room temperature resistivity of the hot-pressed $PbMo_6S_8$ samples are presented in Fig. 4. The two first large values can be understood by the fact that the grains are poorly connected (see Fig. 1). However, it is interesting to note that the room temperature resistivity values for the dense samples are in the same range (500–700 $\mu\Omega$ cm) as that reported for $EuMo_6S_8$[13] and $PbMo_{6.2}S_8$.[14] The very small differences in the resistivity values possibly reflects some intrinsic transport properties of the phase. On the other hand, the best resistivity ratio, $R(293\ \text{K})/R(16\ \text{K})$ of the bulk $PbMo_6S_8$ is far from that measured on $EuMo_6S_8$ crystal[13] or on bulk $SnMo_6S_8$.[15] The lower values of our samples can be correlated to the observed decrease in T_c. This, we believe to occur at the interface and hence contribute to an increase in the residual resistivity of the samples. Therefore, we propose that the residual resistivity or the resistivity ratio is also a convenient way to characterize Chevrel phases at the grain boundaries.

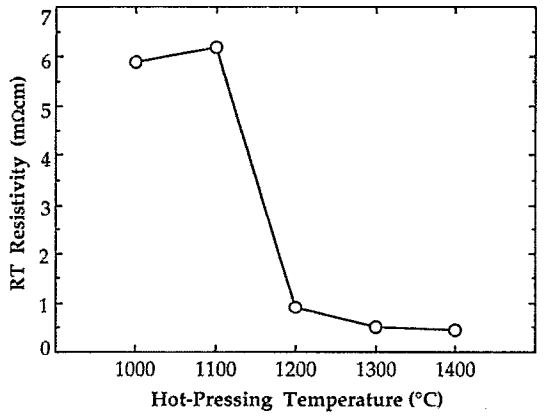

FIG. 4. Room temperature (RT) resistivity data of hot-pressed (HP) $PbMo_6S_8$.

E. Grain surface behavior

1. Fractured surface

Figure 5 shows the Auger spectra of $PbMo_6S_8$ samples fractured in an ultrahigh vacuum chamber. The low density sample shows a significant amount of carbon and a small amount of oxygen [Fig. 5(a)]. The presence of carbon and oxygen is probably caused by the contamination of adsorbed gases, during sample handling in the atmosphere, in the low density pellets as they are porous enough to accommodate such impurities. Compositional analysis indicate a sulphur enrichment by a factor of about two at the surface. This excess shows a tendency to increase further with hot-pressing temperature [Fig. 6(a)]. This deviation from the ideal bulk composition (S/Mo=1.33) suggests a change in the chemical composition from the surface to the bulk of the grains.

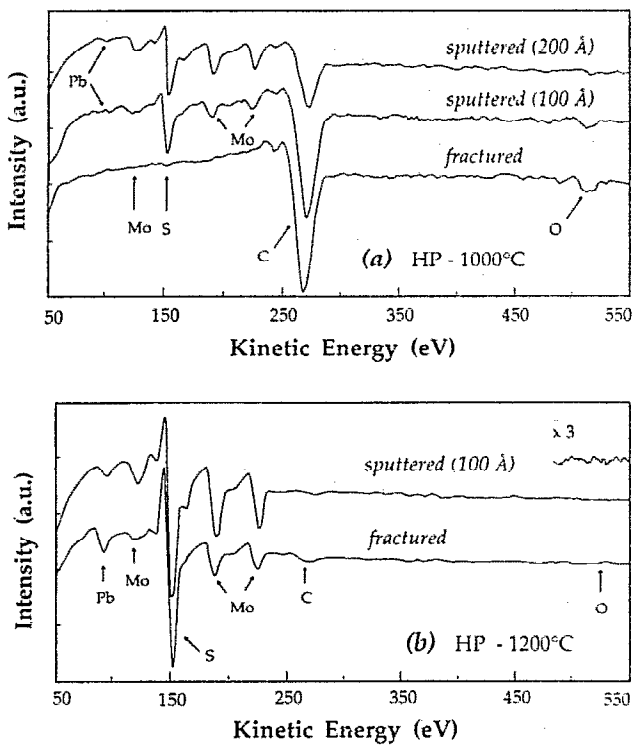

FIG. 5. Auger spectra of *in situ* fractured and sputtered surfaces of *hot*-pressed (HP) $PbMo_6S_8$.

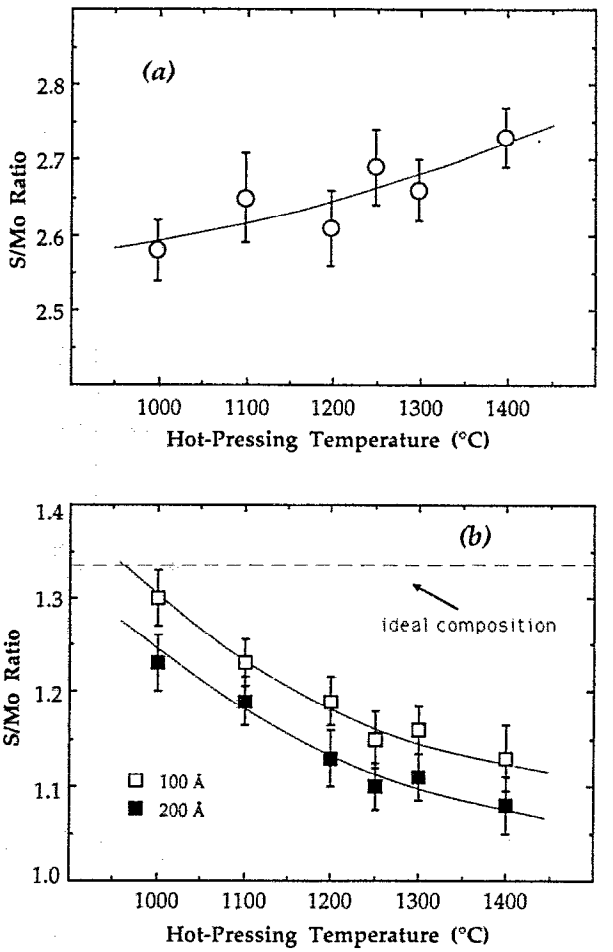

FIG. 6. Surface compositions of (a) fractured and (b) sputtered specimens of hot-pressed (HP) $PbMo_6S_8$.

2. Sputtered surface

Figure 5 also shows the Auger spectra of *in situ* sputtered $PbMo_6S_8$ samples. An important point is that no evidence for carbon and/or oxygen (within the detection limit of our system) is noticed for the high density samples [Fig. 5(b)]. The oxygen disappears completely and carbon is reduced greatly with sputtering in the low density samples. However, even after prolonged sputtering, a considerable amount of carbon is still present, thus indicating the adsorption of carbon on the walls of the pores in the samples. Although the carbon signal drops noticeably after sputtering [Fig. 5(a)], it tends to recover the original amplitude with time.[16] At 1000 °C, the S/Mo ratio is comparable with the bulk composition and the slightly lower value can be understood by considering preferential sputtering of sulfur. However, an unexpected feature is the progressive decrease in this ratio with the increase of hot-pressing temperature [Fig. 6(b)].

F. Issues in the processing of $PbMo_6S_8$

1. Macroscopic problems

a. Stoichiometry. One striking feature of the majority of the phase diagram and homogeneity range studies is that the observed T_cs are well below 15 K. Although some of these investigations[17] have shown an effect of sulfur nonstoichiometry upon T_c, our studies[5] clearly demonstrated that there is still substantial oxygen substitution in some of these samples. This could account for the apparent sulfur deficiencies reported earlier. One of the important and interesting questions in the investigation of the $PbMo_6S_8$ system is the determination of the correlation between structural parameters and superconducting properties. A correlation was found between T_c and the hexagonal lattice constant ratio, c/a.[5] That is, T_c varies continuously as a function of the c/a ratio, which in turn can be related to a possible oxygen content in the ternary phase.[5,18] Based on this relationship, one can conclude that in order to obtain the maximum T_c one should consider the strictly stoichiometric composition. This progress was obtained as a consequence of careful preparation and characterization processes, which eventually yield high quality samples with highly reproducible results.

b. Secondary phases. Binary phases, such as MoS_2, Mo_2S_3 and/or PbS, and the elements, namely Pb and/or Mo, are often observed along with the ternary phase, $PbMo_6S_8$. They are equally important with respect to J_c degradation. That is, they act as barriers and hence lower the transport J_c. Even if one avoids such secondary phases during the formation of the ternary compound, the subsequent densification process, for instance in the present case the hot-pressing process, precipitates some MoS_2, particularly at higher temperatures.[4] This may possibly alter the true composition of the phase and may also further restrict the current carrying capacity.

c. Impurity phases. Impurities, such as carbon and silicon oxide, SiO_x are known to diffuse at the grain boundaries.[5,16,19] SiO_x appears, in some of the samples, as a result of the reaction between the reactants/products and the quartz (SiO_2) tube used for the preparation, with a simultaneous production of $PbMo_6S_{8-x}O_x$. The latter eventually alters the superconducting properties to a considerable extent. Using the same starting powder, grain boundary contamination by carbon was observed on the low density samples. It predominates at lower hot-pressing temperatures (Fig. 6). Even after sputtering, a considerable amount of carbon remains on the surface, indicating a rapid diffusion to the surface. The incorporation of carbon results from external contamination, organic matter as an inclusion during sample handling, due to the presence of microcracks, pores, and voids. These impurities are also expected to affect the J_c values.[20]

2. Microscopic difficulties

a. Phase stability. Although the present data are not extensive enough to permit an accurate determination of the relative importance of hot-pressing temperature versus composition, the influence of the former is evident. Specific heat data show considerable broadening of the sharp distribution of T_c down to 8 K[4,10] with the increase of hot-pressing temperature. That is, $PbMo_6S_8$ starts to decompose and the composition is altered near the grain boundaries as it is apparent in the analysis of Auger data. A monotonic decrease of the S/Mo ratio on the sputtered surface, with increasing hot-pressing temperature, suggests a plausible compositional variation or nonstoichiometry at the interface with possible degradation of the current carrying capacity of the ternary compound. Additionally, precipitates of MoS_2 start to appear at higher temperatures, as observed from XRD patterns,[4] and a simultaneous increase of S/Mo ratio occurs at the interface on the fractured surface, as judged from AES studies. It should also be recalled here that the hot pressing was carried out in vacuum, which may have some influence on the phase. It is, however, to be noted that there is no considerable difference in the structural parameters except for a slight change in the unit cell volume (see Table I).

b. Surface heterogeneity. Of the various properties of the surface, perhaps, one of the most important that must be known in order to determine any other surface phenomena is the chemical composition. Often, the surface is passivated by protective coatings of the various oxidation products. Simple thermodynamic arguments, based on the enthalpy of formation of sulfides, convincingly demonstrate that the surface may be very different from the bulk of the sample. Small grains are unlikely to be completely homogeneous, especially near the surface where elemental disproportionation is thermodynamically favorable. It is evident from the present Auger experiments that the composition of grain boundaries differs from the bulk. Many grain boundaries are found to be enriched in sulfur and deficient in molybdenum. This deviation from the ideal composition could be attributed to the presence of sulfur-rich phases, like MoS_2, Mo_2S_3, etc. Sometimes, the sulfur enrichment is high enough to suggest that the near boundary phase comprises PbS, as identified from a simultaneous enrichment of lead on the fractured samples. That is, the majority of the grain boundaries present in our samples are not free of second phases, at least to a microscopic level. However, they can be improved to a considerable extent by the addition of metals such as Sn[21] or Ag[15] in the ternary phase.

3. Morphology

Well connected grains are an important requirement for high J_c in bulk samples. Smaller grains are preferred for densification at lower temperatures. One of the explanations for the low J_c values is the poor connectivity due to a bad densification. The transport current flows percolatively for the poorly connected or less dense samples, as in the case of a conventional sintering process, and it flows homogeneously for the fully connected or highly dense samples, as in the case of a hot isostatically pressing process.[7] As the internal stress limits the homogeneous growth of larger grain $PbMo_6S_8$, the most convenient morphology is that of a fine grained sample and hence the production of small grains is yet another criterion. The small dimensions

of fine grains reduce the buildup of internal stress to a considerable extent.[22–24] Previous works have shown a clear relation between J_c and grain size.[6,25] However, the grain size was too large (2-3 orders of magnitude higher than the coherence length) to attribute the increase of J_c solely to an increase of pinning force density. We believe the enhancement in J_c originates mainly from an improved grain connection which, however, can be achieved better with finer powders. It is noteworthy that good metallurgical connections are obtained for the samples with fourth elements like Sn[21] or Ag.[15]

4. J_c limiting regions

Measurement of intergrain and intragrain J_c of $PbMo_6S_8$[3] substantiate the idea that J_c decreases across the grain boundaries at least to an order of magnitude. It should be noted that the sulfur-rich regions at the interface are nonsuperconducting, and if sufficiently thick they would limit electron transport across the boundaries. Apart from these contaminants at the interface, the most critical issue that further limits the J_c across the sample is the tendency of materials to be weakly linked by the off-stoichiometry phases at the grain boundaries. This is clearly demonstrated by both Auger and specific heat experiments. As discussed earlier, such phases only could account for the observed T_c distributions in these samples which we believe to occur at the grain boundaries. This certainly influences the electronic structure which in turn alters the superconducting properties of the compound. In this state, J_c is much smaller than the intragrain J_c. A similar situation arises, in most cases, for lower temperature (well below 1200 °C) as prepared samples. The calorimetric transition in the superconducting state is extremely broad. This, in terms of superconducting volume fraction, indicates a T_c distribution tail extending well below 10 K.[12] Such an observation can be accounted for by the inhomogeneous phase formation due to an incomplete reaction. This means that some regions of the samples may have a lower critical field, B_{c2}. The same has earlier been related to the field dependence of the critical current densities.[3] While these grain boundary composition changes probably contribute to the weak-link behavior, other factors such as intrinsic structural disorder, phase transition, dislocations, defects, etc., may equally be important. The weak superconducting regions may also be caused by the small coherence length, or the misalignment of neighboring grains, or microcracking, or a disturbance of the structure at the grain surface.

IV. CONCLUSION

A new procedure is demonstrated for the production of high quality, homogeneous, and fine grained $PbMo_6S_8$. A few important issues in the processing of dense, fully superconducting bulk samples are also addressed. Among the points that must be considered for optimizing J_c, are the control of grain size, composition, secondary, and impurity phases, and more specifically the absence of the widespread oxygen contamination in the ternary phase. Additional requirements include the necessity to ensure complete reaction throughout the microstructure, stability towards the processing temperatures and the prevention of microcracks. In our opinion, the effect of intergrain connection predominates in accounting for the J_c enhancement over many other parameters, like moderate deviations from stoichiometry, impurity content, phase purity, etc. Therefore, it is plausible that mulitphase samples with moderate T_c but possibly with better intergrain connections exhibit higher J_c than single phase, high T_c samples with bad connections. On the other hand, even when the grains are well connected, the inhomogeneities, namely Pb and/or S deficiencies at the interface act as barriers and hence limit the J_c. Auger and specific heat studies give a stronger evidence pointing to the presence of such nonstoichiometric phases. On the basis of the results described here, it may be concluded that further optimization of the process should be carried out, with a hope to achieve better J_c values, namely by producing very fine starting powders, reducing the grain boundary contaminants, and lowering the heat treatment temperature in order to decrease the inhomogeneities and/or secondary phases at the interface.

ACKNOWLEDGMENT

This work is supported by CERS (Commission Suisse pour l'Encouragement de la Researche Scientifique) within EUREKA'96. The authors thank A. Stettler for the technical assistance.

[1] For recent developments, see Proceedings of the International Workshop on Chevrel-phase Superconductors, Chavannes de Bogis, Switzerland, September 10-12, 1991.
[2] For extensive reviews, see *Superconductivity in Ternary Compounds I & II, Topics in Current Physics*, edited by Ø. Fischer and M. B. Maple (Springer, Berlin, 1982), Vols. 32 and 34.
[3] D. Cattani, J. Cors, M. Decroux, and Ø. Fischer, IEEE Trans. Magn. **27**, 950 (1991).
[4] P. Selvam, D. Cattani, J. Cors, M. Decroux, Ph. Niedermann, S. Ritter, Ø. Fischer, L. Burel, R. Chevrel, P. Rabiller, and M. Sergent, *Proceedings of the 3rd International Conference on Superconductivity Materials, Physics and Applications* (ICMAS-91), edited by B. Raveau, K. Wasa, and R. Suryanarayanan, Technology Transfer Series, edited by A. Niku-Lari (IITT-International, Paris, 1991), p. 156.
[5] P. Selvam, D. Cattani, J. Cors, M. Decroux, Ph. Niedermann, S. Ritter, Ø. Fischer, P. Rabiller, R. Chevrel, L. Burel, and M. Sergent, Mater. Res. Bull. **26**, 1151 (1991).
[6] D. Cattani, Diploma thesis, University of Geneva, 1984.
[7] H. Yamasaki, M. Umeda, S. Kosaka, Y. Kimura, T. C. Willis, and D. C. Larbalestier, J. Appl. Phys. **70**, 1606 (1991).
[8] M. Decroux, J. Cors, D. Cattani, S. Ritter, P. Selvam, Ø. Fischer, P. Rabiller, R. Chevrel, L. Burel, and M. Sergent, in Ref. 1.
[9] M. Decroux, D. Cattani, J. Cors, S. Ritter, and Ø. Fischer, Physica B **165 & 166**, 1395 (1990).
[10] J. Cors, D. Cattani, M. Decroux, M. Stettler, and Ø. Fischer, Physica B **165 & 166**, 1521 (1990).
[11] A. Junod, T. Jarlborg, and J. Muller, Phys. Rev. B **27**, 1568 (1983).
[12] J. Cors, Ph. D. thesis, University of Geneva, 1990.
[13] M. Decroux, M. S. Torikachvili, M. B. Maple, R. Baillif, Ø. Fischer, and J. Muller, Phys. Rev. B **28**, 6270 (1983).
[14] R. Flükiger, R. Baillif, and E. Walker, Mater. Res. Bull. **13**, 743 (1988).
[15] P. Selvam, J. Cors, M. Decroux, and Ø. Fischer (unpublished).
[16] P. Selvam, J. Cors, M. Decroux, Ph. Niedermann, and Ø. Fischer (unpublished).
[17] See for example: H. Yamasaki, Y. Yamaguchi, and Y. Kimura, Mater. Res. Bull. **23**, 23 (1988).

[18] D. G. Hinks, J. D. Jorgensen, and H. -C. Li, Phys. Rev. Lett. **51**, 1911 (1983).
[19] P. Selvam, D. Cattani, J. Cors, M. Decroux, Ph. Niedermann, and Ø. Fischer, in Ref. 1.
[20] W. Goldaker, E. Seibt, G. Rimikis, and R. Flükiger, *Proceedings of the International Conference from Modern Superconductivity Towards Applications (ICMAS-90)*, edited by R. Tournier and R. Suryanarayanan, Technology Transfer Series, edited by A. Niku-Lari (IITT-International, Paris 1990), p. 99.
[21] P. Selvam, D. Cattani, J. Cors, M. Decroux, Ph. Niedermann, Ø. Fischer, R. Chevrel, and T. Pech, Applied Superconductivity Conference, Chicago, August 23–28, 1992 (to be published in IEEE Trans. Superconductivity, 1993).
[22] J. W. Ekin, T. Yamashita, and K. Hamasaki, IEEE Trans. Magn. **21**, 474 (1985).
[23] B. Seeber, W. Glaetzle, D. Cattani, R. Baillif, and Ø. Fischer, IEEE Trans. Magn. **23**, 1740 (1987).
[24] D. W. Capone II, D. G. Hinks, and D. C. Brewe, IEEE Trans. Magn. **23**, 1752 (1991).
[25] K. Hamasaki, Y. Shimizu, and K. Watanabe, Adv. Cryog. Eng. A **36**, 335 (1990).