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NEW SYNTHESIS ROUTE OF PbM0₆S₈ SUPERCONDUCTING CHEVREL PHASE FROM ULTRAFINE PRECURSOR MIXTURES: II. PbS, M0₆S₈, AND M0 POWDERS

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ABSTRACT

We have used a new ultrafine precursor, the Mo_6S_8 binary sulfide, and ultrafine PbS and Mo powders (${\sim}0.05{-}0.5~\mu\text{m}$) to prepare an original mixture for PbMo_6S_8 synthesis. The reaction of PbMo_6S_8 formation occurs in a two-step process, at 600 and 800°C, leading to a ${\sim}0.5~\mu\text{m}$ grain size. χ_{ac} measurements exhibit good superconducting quality ($T_c \approx 14~K$) of the resulting PbMo_6S_8 phase. Additionally, we have perfected new synthesis processes of the $Ni_{\sim2}Mo_6S_8$ and $Li_{\sim3}Mo_6S_8$ ternary Chevrel phases, precursors of the Mo_6S_8 compound. These syntheses are carried out by H_2S gas sulfurization of the liquid or solid route and then reduction by H_2 gas over solid reaction. The $Li_{\sim3}Mo_6S_8$ phase was chosen because its cation deintercalation yields the smallest Mo_6S_8 grain size (${\sim}0.3~\mu\text{m}$). © 1998 Elsevier Science Ltd

KEYWORDS: A. chalcogenides, B. chemical synthesis, C. electron microscopy, D. superconductivity

INTRODUCTION

In Part I of our paper [1], we described the synthesis and the characterization of the superconducting $PbMo_6S_8$ lead Chevrel phase from PbS, MoS_2 , and Mo ultrafine precursors mixture (~0.05–0.5 µm) in comparison with the same precursors made by the conventional

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Chevrel Phase Sulfides [6,7]						
Phase	a _H (Å)	$\boldsymbol{c}_{\mathrm{H}}~(\mathrm{\AA})$	$V_{\rm H}~({\rm \AA}^3)$	a _R (Å)	α_{R} (°)	
Li~3Mo6S8	9.73	10.61	869.6	6.64	94.28	
Ni~2Mo6S8	9.51	10.24	801.0	6.46	94.70	
Mo _c S _o	9.20	10.88	797.5	6.43	91.34	

TABLE 1 Hexagonal and Rhombohedral Unit Cell Parameters of Chevrel Phase Sulfides [6,7]

route (1–15 μ m) [1]. From these new synthesis routes (coprecipitation, precipitation, and gaseous reaction) of precursors powders, we succeeded in making precursor grains with quasispherical morphology and very small grain size. The resulting PbMo₆S₈ material keeps the same morphology grain with ~0.5 μ m size and shows good superconducting qualities (~14 K). We have already pointed out [2–4] the significance of the Mo₆S₈ binary as a precursor in another new PbMo₆S₈ preparation.

In Part II, we report the synthesis and the characterization of the $PbMo_6S_8$ phase from a new original mixture of PbS, Mo_6S_8 , and Mo ultrafine precursors. This new synthesis route of $PbMo_6S_8$ from that mixture is like a combination of both previous syntheses: one with PbS, MoS_2 , and Mo ultrafine powders (route 1) [1] and the other one with the PbS and Mo_6S_8 compounds under gas flow (route 2) [2]. In the new method, we have substituted MoS_2 with Mo_6S_8 as the new sulfuring agent, with respect to route 1, and we have suppressed the H₂ gas flow with respect to route 2.

The new synthesis of fine $PbMo_6S_8$ powder arises from the following reaction:

$$PbS + 0.875Mo_6S_8 + 0.75Mo \rightarrow PbMo_6S_8.$$
(1)

The preparation of the PbS and Mo ultrafine powders has been presented in our previous paper [1]. Now, we describe the fabrication of the new ultrafine Mo_6S_8 powder.

Syntheses and Characterization of Mo_6S_8 Ultrafine Powder. Contrary to the other binary molybdenum chalcogenides Mo_6Se_8 and Mo_6Te_8 , the Mo_6S_8 binary sulfide cannot be prepared directly from the elements [5]. Therefore, this metastable phase is generally obtained from oxidation of the $A_xMo_6S_8$ ternary phase, where A is a small cation (e.g., Li, Ni, Cu), by the HCl leaching method, according to eq. 2:

$$A_{x}^{n+}Mo_{6}S_{8} + nx(H^{+}\cdot Cl^{-}) \rightarrow Mo_{6}S_{8} + x(A^{n+}\cdot nCl^{-}) + nx/2H_{2}\uparrow.$$
 (2)

In order to get single-phase Mo_6S_8 with homogeneous grains smaller than obtained before, we have looked for new routes in the synthesis of ternary $A_x^{n^+}Mo_6S_8$ compounds. We chose the $Ni_{2}Mo_6S_8$ and $Li_{3}Mo_6S_8$ phases as precursors of Mo_6S_8 because nickel and lithium ions are withdrawn easily and quickly in HCl solution. The deintercalation provides, by the exploding of grains, very small particles of Mo_6S_8 powder due to the large variations of the unit cell rhombohedral angle (~3°) between the binary and ternary phases (Table 1). The $Li_{3}Mo_6S_8$ ternary compound has one of the biggest hexagonal unit cell volumes of the Chevrel phase sulfides 869.6 Å³, ($\alpha_R = 94.28$) [6], whereas the $Ni_{2}Mo_6S_8$ phase has a hexagonal volume very close to that of the Mo_6S_8 binary phase, 801.0 Å³ ($\alpha_R = 94.70^\circ$) vs. 797.5 Å³ ($\alpha_R = 91.34^\circ$), respectively [7] (Table 1). The large difference in hexagonal volume

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XRD pattern indexed in the hexagonal system (space group $R\overline{3}$) of $Ni_{\sim 2}Mo_6S_8$ phase from the new synthesis process: coprecipitation of Ni and Mo sulfur compounds and reduction ($V_H = 804.5(2) \text{ Å}^3$).

between the $Li_{\sim 3}Mo_6S_8$ and Mo_6S_8 compounds is advantageous in that it allows an even greater decrease in the grain size of the end product.

New Synthesis Process of the Ni_{~2}Mo₆S₈ Ternary Phase. The ternary Ni_{~2}Mo₆S₈ (NMS) phase is generally synthesized by the classical ceramic route from a mixture of Ni, MoS₂, and Mo powders heated at 950°C for 48 h in a sealed evacuated silica tube. We call it the classical Ni_{~2}Mo₆S₈ phase. Several grindings and annealings are usually required to avoid the presence of MoS₂ and Ni₃Mo impurities.

Our new synthesis method of NMS phase consists of the coprecipitation of Ni and Mo sulfur complexes by sulfurization of a solution of nickel nitrate and ammonium heptamolybdate, followed by the reduction of the resulting precipitate [8]. For the first step, we chose as precursors the materials ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ (purity >99.0%) and nitrate nickel Ni(NO₃)₂·6H₂O (purity >99.0%) in atomic proportions Ni/Mo = 1/3. Both precursors are soluble in ammonia solution at room temperature and do not coprecipitate in the presence of each other.

The sulfurization is realized by bubbling H_2S gas in the solution. After 10–15 min, a precipitated mixture of sulfides $[(NH_4)_2MoS_4,NiS]$ forms. After filtration and drying, the powder is reduced under H_2 gas flow by a gas/solid reaction. From this new synthesis process, we obtained pure $Ni_{\sim 2}Mo_6S_8$ phase at only 675°C after 24 h of reaction; this is the minimum reaction temperature ever published for the formation of the Chevrel phase framework except for that obtained by the inorganic molecular process [9,10]. The lattice parameters are comparable to the parameters of the ternary phase prepared by the classical method in a sealed tube (Fig. 1). This new synthesis route of NMS, close to a preindustrial route, allows a decrease in the fabrication temperature of about 200°C in comparison with the classical process (laboratory method). This method could be improved by a one-step process with H_2S/H_2 gas with sulfurization and reduction occurring simultaneously.

Scanning electron microscopy (SEM) examinations of the Ni_{$\sim 2}Mo₆S₈ powders show that the classical phase contains particles of about 5 <math>\mu$ m in size, recalling the characteristic shape of Chevrel phase crystals (Fig. 2a). The new fine NMS powder has grains of about 0.5–1 μ m in size and a shape that is not well defined (Fig. 2b).</sub>



FIG. 2

SEM images of $Ni_{\sim 2}Mo_6S_8$ ternary phase from the (a) classical route (~5 µm) and (b) new synthesis route (~ 0.5-1 µm).

New Synthesis Process of $\text{Li}_{3}\text{Mo}_6\text{S}_8$ Phase. The first synthesis route of ultrafine $\text{Li}_{4}\text{Mo}_6\text{S}_8$ phase uses Li_2S and MoS_3 binary sulfides under hydrogen gas flow at 900°C for 72 h [2], but this process leads to a ternary compound that sometimes contains impurities such as MoS_2 . Therefore, we have looked for a new method of preparation for ultrafine ternary compound.

Our new $\text{Li}_{x}\text{Mo}_{6}\text{S}_{8}$ synthesis route, which was inspired by the thesis of Sergent [11] on alkaline thiomolybdates, is based on the preparation of the ternary compound, lithium tetramolybdate oxide, $\text{Li}_{2}\text{Mo}_{4}\text{O}_{13}$, followed by sulfurization and reduction of this compound [8]. The choice of this ternary oxide was motivated by the excellent homogeneity of the metallic mixture, i.e., the good atomic ratio of the lithium and molybdenum metals equivalent to the metallic proportions occurring in the ternary sulfide $\text{Li}_{3}\text{Mo}_{6}\text{S}_{8}$.

The Li₂Mo₄O₁₃ material is prepared from commercial Li₂CO₃ (>99.0%) and MoO₃ (purity >99.5%) powders under an air atmosphere at 450–500°C. Several grinding and annealing stages are required to homogenize the reaction. This ternary oxide is characterized by X-ray powder diffraction. The sulfurization of the oxide is carried out at 450°C for 1.5 h under H₂S gas flow by a gas/solid reaction process. A reactive mixture of Li₂S and MoS₂ sulfides is obtained. After the reduction of the powder mixture under hydrogen atmosphere at 850°C for 48 h, a pure Li_{~3}Mo₆S₈ phase is obtained (Fig. 3a). Flame spectrophotometry



XRD patterns (Cu K α_1) with hexagonal indexation (space group R $\overline{3}$) of (a) Li_{~3}Mo₆S₈ phase (V_H = 872.4(6) Å³); (b) Li_{~1}Mo₆S₈ phase (V_H = 813.3(7) Å³); and (c) Mo₆S₈ binary phase (V_H = 797.1(7) A³).

analysis shows effectively that the powder has the composition $\text{Li}_{3}\text{Mo}_6\text{S}_8$ (3Li for IMo_6S_8) as expected. This ternary material is very moisture sensitive as reported in the literature [6]. We have observed that a compound such as $\text{Li}_{3}\text{Mo}_6\text{S}_8$, after being exposed to air for only 15 min, displays the same lattice parameters as $\text{Li}_{1}\text{Mo}_6\text{S}_8$ (Fig. 3b), and after 1 h, the same parameters as Mo_6S_8 (Fig. 3c). This large variation in the crystalline parameters is easily observed in the (220) and (104) hexagonal *hkl* diffraction peaks. The explanation for this phenomena is that the mobility of lithium ions is rather high inside the Mo_6S_8 unit at room temperature [6,12] and the oxidation of the Mo_6S_8 unit takes place. The lithium atoms move and react at the surface of the channels with the air moisture.



FIG. 4 SEM image of $Li_{\sim 3}Mo_6S_8$ phase from the new synthesis process (~20-80 µm).

Figure 4 shows the particle morphology of the $Li_{\sim 3}Mo_6S_8$ phase from this new synthesis process. The powder grain dimensions of this ternary material are very large (~ 20-80 μ m).

 Mo_6S_8 Binary Sulfide Synthesis from Ni_{~2}Mo₆S₈ and Li_{~3}Mo₆S₈ Phases. We prepared Mo₆S₈ powder from different ternary phases: classical Ni_{~2}Mo₆S₈, fine Ni_{~2}Mo₆S₈, and Li_{~3}Mo₆S₈ powders according to eq. 2. The resulting powder was washed several times with distilled water to eliminate any trace of chloride and then dried under vacuum. The Mo₆S₈ binary phase obtained from the new fine ternary phases and the classical ternary phase displays the same X-ray diffraction (XRD) pattern with the same parameters, and no impurity is detected (Fig. 3c).

SEM images of Mo_6S_8 powder from these ternary phases show that the grain size decreases from 1–5 µm for classical NMS (Fig. 5a) to 0.5–1 µm for fine NMS (Fig. 5b). The large grains of the $Li_{\sim 4}Mo_6S_8$ phase provide, by deintercalation, very small grains of the Mo_6S_8 binary compound (~ 0.3–0.5 µm), as viewed in Figure 5c. This can be explained by a very strong reactivity of the lithium phase with HCl acid solution and by the large variation in hexagonal volume between the ternary and the binary sulfide that we have emphasized previously. Thus, the shape of the Mo_6S_8 particles recalls that of the ternary compound, except for the $Li_{\sim 3}Mo_6S_8$ phase.

Laser granulometry measurements were performed on Mo_6S_8 (from $Li_{3}Mo_6S_8$) powder, according to the dispersing conditions already reported [1]. The grain size distribution in volume percent vs. diameter of particle (µm) ranges mainly between 0.123 and 3.206 µm (% volume = 82.58%; mean diameter $d_m = 0.619$ µm). However, the result in percent number presents a grain size repartition ranging from 0.123 to 1.520 µm, corresponding to 99.92% of particles, with a mean diameter of 0.303 µm.

Synthesis and Characterization of PbMo₆S₈ Phase (PbS, Mo₆S₈, Mo Ultrafine Precursors). Until now, we have prepared fine PbMo₆S₈ powders by only two methods: from a mixture of PbS, MoS₂, and Mo ultrafine precursors, as described in Part I [1] and from a PbS and Mo₆S₈ mixture under H₂ gas flow [2]. Now we mainly use the new Mo₆S₈ ultrafine precursor in a new method of PbMo₆S₈ preparation. PbMo₆S₈ phase is prepared according to eq. 1,

LEAD MOLYBDENUM SULFIDE



FIG. 5

SEM images of Mo_6S_8 binary phase from the (a) classical $Ni_{\sim 2}Mo_6S_8$ phase (1–5 μ m), (b) new fine $Ni_{\sim 2}Mo_6S_8$ phase (0.5–1 μ m), and (c) new $Li_{\sim 3}Mo_6S_8$ compound (0.3–0.5 μ m).

from an original mixture of ultrafine precursors: lead sulfide PbS, molybdenum, and Mo_6S_8 (from $Li_{\sim 3}Mo_6S_8$) powders.

Synthesis of PbMo₆S₈ **Powder.** In order to understand the chemical reactions occurring during the PbMo₆S₈ phase fabrication from the mixture of PbS, Mo_6S_8 , and Mo powders, calorimetric measurements were performed from 200 to 900°C at a heating rate of 3°C/h. About 3 g of mixed precursor powders were introduced into a silica tube sealed under argon partial pressure.



FIG. 6

Calorimetry study of PbMo₆S₈ formation from a mixture of PbS, Mo, and Mo₆S₈ ultrafine precursors (heating rate 3° C/h).

Calorimetric analysis of the thermal reaction shows three exothermic peaks with only two thermal effects (Fig. 6). The first effect between initial temperature $T_i = 410^{\circ}$ C and final temperature $T_f = 570^{\circ}$ C shows a dissipated energy about -60 J/g with two maxima at $T_p = 475^{\circ}$ C and $T_p = 540^{\circ}$ C. The last anomaly at $T_p = 630^{\circ}$ C from $T_i = 600^{\circ}$ C to $T_f = 645^{\circ}$ C has a very weak intensity. Based on these calorimetric results, we used X-ray powder diffraction to investigate the chemical reactions in a sealed evacuated silica tube at different temperatures (i.e., 500, 600, 650, 800, and 850^{\circ}C) with a ramp of 9 h from room temperature to stop temperature followed by a 12 h stage duration (Fig. 7). The initial mixture consisted of PbS + $0.875Mo_6S_8 + 0.75Mo_6S_8$, and Mo powders) remain. At 500°C, we observe the presence of PbMo₆S₈, Mo₆S₈, PbS, MoS₂, and Mo compounds (Fig. 7a).

The formation of $PbMo_6S_8$ phase required elemental lead, which is not present in the mixture. Therefore, we have studied, by calorimetry, the PbS decomposition in the presence of molybdenum:

$$2PbS + Mo \rightarrow 2Pb + MoS_2$$

This reaction in a sealed evacuated silica tube takes place at 650°C. In the case of these experiments, however, we think that this reaction was catalyzed at about 500°C by the presence of the Mo_6S_8 binary.

In summary, the PbS transforms largely into lead (87.5%) and sulfur elements; therefore, the very reactive Pb inserts immediately into Mo_6S_8 channels to form $PbMo_6S_8$. The excess of sulfur reacts with molybdenum, leading to MoS_2 sulfide.

The following reaction occurs in the temperature range of $\sim 500-600^{\circ}$ C:

 $0.875PbS + 0.875Mo_6S_8 + 0.437Mo \rightarrow 0.875PbMo_6S_8 + 0.437MoS_2.$ (3)

Our results show definitively that it is the Mo_6S_8 compound that governs the reaction, considering the quantities of the constituents. At 600°C, we see the disappearance of Mo_6S_8



XRD investigations of $PbMo_6S_8$ formation from a mixture of PbS, Mo_6S_8 , and Mo ultrafine precursors at different temperatures (a) 500°C), (b) 600°C, (c) 650°C, (d) 800°C, and (e) 850°C. XRD patterns are indexed in the hexagonal system (R3 space group).



FIG. 8 SEM images of PbMo₆S₈ phase samples (a) S1 (800°C, 48 h) and (b) S3 (1050°C, 48 h).

phase and the presence of $PbMo_6S_8$, PbS, MoS_2 , and Mo compounds (Fig. 7b). Therefore, the overall reaction is

$$1PbS + 0.875Mo_6S_8 + 0.75Mo \rightarrow 0.875PbMo_6S_8 + 0.437MoS_2 + 0.125PbS + 0.313Mo.$$
(4)

Calorimetric results show two exothermic peaks in the range $400-570^{\circ}$ C (Fig. 6). We know that the insertion of lead into the Mo₆S₈ compound leads to exothermic behavior [2] as well as the reaction between PbS and Mo [1]. Hence, beginning at 410°C, we see the decomposition of PbS, accompanied by the insertion of lead into the Mo₆S₈ phase. But, during the decomposition of PbS, the sulfur atoms attack the surface of Mo grains, and a thin film of MoS₂ sulfide is formed. This MoS₂ thin film in turn protects against a new attack of sulfur atoms and prevents further decomposition of PbS [1]. The reaction kinetics of PbS decomposition decreases, and we are obliged to increase the temperature to again effect decomposition of PbS and lead intercalation (second peak).

At 650° C (Fig. 7c), we observe the presence of lead due to the decomposition of all the remaining PbS (eq. 4) and the decreasing amount of Mo. The reaction between the resulting PbS and Mo is

$$0.125Pb + 0.0625Mo \rightarrow 0.125Pb + 0.0625MoS_2.$$
 (5)

Thus, the components of the mixture are



FIG. 9

Grain size distribution of $PbMo_6S_8$ S3 powder (1050°C, 48 h) from laser granulometer (a) in % volume and (b) in % number.

$$0.875PbMo_6S_8 + 0.5MoS_2 + 0.125Pb + 0.25Mo.$$

We have detected elemental lead because all of the Mo_6S_8 phase has already reacted. Furthermore, we have confirmation of the reaction (eq. 5) by calorimetry (Fig. 6). Indeed, a third thermal effect is shown in the range of 600–650°C. This effect is exothermic, as observed from classical powders [1]. The intensity of the peak is very weak in comparison with the peak intensities exhibited from classical precursors, due to the very low molar coefficients of the constituents of the reaction (eq. 5).

At 800°C, we observe the lowering of Pb, MoS_2 , and Mo peak intensities (Fig. 7d). At 850°C, the PbMo₆S₈ formation is complete. Thus, between 650 and 850°C, the last reaction of the mixture is

$$0.125Pb + 0.5MoS_2 + 0.25Mo \rightarrow 0.125PbMo_6S_8.$$
 (6)

In the calorimetric pattern, we notice that above 800° C we do not detect the endothermic peak for the PbMo₆S₈ formation (eq. 6) due to the very small proportions of reagents. The endothermic peak with a molar composition is already extremely weak, 4 J/g [1].

Characterization of PbMo₆**S**₈ **Powders.** Three PbMo₆**S**₈ samples (S1, S2, and S3) were prepared. Pellets of the ultrafine PbS, Mo, and Mo₆**S**₈ powders mixture were placed in alumina crucibles in a quartz tube, which was then sealed under vacuum. The syntheses were carried out at 800°C (S1), 900°C (S2), and 1050°C (S3) for 48 h. XRD patterns of these three samples revealed pure PbMo₆**S**₈ phase in all cases, including at 800°C. The hexagonal volumes have been determined from these patterns and all are close to 840 Å³.

From SEM observations, the micrographs of samples S1 (800°C, 48 h; see Fig. 8a) and S3 (1050°C, 48 h) (Fig. 8b) are very different. Sample S3 shows grains (\sim 0.5–1 µm) with the



 χ_{ac} vs. T under 3 mGauss of three fine PbMo₆S₈ samples.

characteristic shape of Chevrel phase. Indeed, we know that the $PbMo_6S_8$ formation results from the addition of two reactions, at 600°C and then at 800°C. We note that the behavior at these temperatures is very different from that at 1050°C. For the S3 sample, we see the formation of small grains at 600° and 800°C, followed by the growth of particles with well defined shapes; this behavior is opposite that of sample S1 (800°C). At 800°C, we see only the formation of PbMo₆S₈ grains but no increase in the grain size.

Laser granulometry measurements on PbMo₆S₈ powder synthesized at 1050°C for 48 h exhibit two maxima in the grain size repartition histogram (% volume) (Fig. 9a): the first between 0.195 and 1.149 μ m (63.87%; d_m = 0.490 μ m) and the second between 1.149 and 4.656 μ m (36.13%; d_m = 2.508 μ m). In % number result (Fig. 9b), the second peak disappears (0.41%), corresponding to few large particles, and the remaining peak (0.105–1.149 μ m) represents the real distribution of the grain size (99.59%; d_m = 0.416 μ m).

The critical temperature, $T_{c(onset)}$, was determined from ac susceptibility measurements under a 3 mGauss field (Fig. 10 and Table 2). We see that the T_c of sample S2 (14 K) is higher than that of sample S1 (13.2 K) due to the increasing temperature, from 800 to 900°C, which allows maximum homogenization and a growth of grains. On the other hand, the lowering of T_c for sample S3 (13.6 K) already indicates incipient contamination at the temperature of 1050°C under our experimental conditions. Furthermore, this lower T_c (13.6 K) corresponds to a minimum hexagonal volume for the three samples (838 Å³).

TABLE	E 2				
Superconducting Critical					
Temperature, $T_{c(onset)}$,					
of three PMS Samples					
Heat treatment	T _{c(onset)} (K)				
800°C, 48 h	13.2				
900°, 48 h	14.0				
1050°C, 48 h	13.6				

CONCLUSION

We have perfected a new mixture of ultrafine precursors for PbMo₆S₈ synthesis (eq. 1). In comparison with the mixture of PbS, Mo, and MoS₂ constituents [1], we use the metastable Mo_6S_8 binary phase in the new mixture instead of MoS_2 sulfide (eq. 6). This choice allows a decrease in the proportion of molybdenum in the new mixture; it changes from 2.5 (ref. [1]; eq. 1) to 0.75 (eq. 1). This is an advantage because of the extreme hardness of elemental Mo, especially during the drawing of superconducting wire containing the precursor mixture. The additional significance of this choice is that the reaction with Mo_6S_8 is exothermic.

Ultrafine PbS, Mo, and Mo_6S_8 precursors, with their quasispherical morphology and small grain size, increase the reactivity of the mixture and thus decrease the fabrication temperature of PbMo₆S₈ phase. The PbMo₆S₈ compound is obtained from a two-step process at 600 and 800°C, the limit in temperature for industrial wire insulation.

The ac susceptibility results show a $T_{c(onset)}$ equal to 14 K for sample S2 heated at 900°C for 48 h, indicating a high superconducting quality of PbMo₆S₈ grains with a diameter of about 0.5–1 µm.

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