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Shock-induced changes in HgO powder

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Powder compacts of HgO were subjected to explosively-generated shock-wave loading in Sandia Bear fixtures and recovered for analysis. Although XRD powder spectra show only the orthorhombic form of HgO in both the as-received and recovered samples, XRD line profiles and TEM indicate up to an order of magnitude *increase* in crystallite size. Magnetic data reveal a superconducting transition below 4.2 K that is attributed to metallic α -Hg formed by a partial, shock-induced decomposition of the HgO, consistent with TEM identification of α -Hg particles using a cold stage. In addition, paramagnetic impurities present in the as-received HgO powder appear to be partially converted to a ferromagnetic or ferrimagnetic phase that dominates the magnetic properties of the recovered powder. The amounts of both the superconducting and ferromagnetic phases vary strongly with position within the shock recovery capsules.

1. INTRODUCTION

The discovery [1] of high-temperature superconductivity in the Hg-Ba-Ca-Cu-O compounds has attracted considerable interest since one structural phase, $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_y$, has the highest transition temperature reported to date, $T_c \approx 135$ K [2]. Initial syntheses were carried out in high pressure configurations because HgO decomposes near 500°C at ambient pressure [1]. However, successful low-pressure preparation of Hg-Ba-Ca-Cu-O superconductors via rapid heating of mixed oxides above 800°C suggested that HgO decomposition was not a problem in the presence of the other oxides [3]. This latter result prompted the present study of the stability of HgO powder subjected to the transient pressure and temperature excursions characteristic of high-pressure shock-wave loading.

An earlier shock compression study employed water or oil suspensions of the red and yellow forms of HgO [4-6]. Shock compression to 10-15 kbar produced a brown modification which exhibited no change in the x-ray diffraction pattern except for line broadening attributed to plastic deformation [5]. A shift in the x-ray absorption spectrum for the Hg L_{III} line suggested a shock-induced change in the local oxygen configuration surrounding the Hg. This was tentatively attributed to formation of a dispersed, metastable sphalerite (HgS) form of HgO in small quantities which appeared as an extra line in the neutron diffraction spectrum [6].

The experiments discussed here employed planar explosive loading of HgO compacts *with no additives* in the well-characterized Sandia Momma Bear and Papa Bear recovery fixtures

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[7-9]. The next section describes the experimental details, followed by a comparison of the structural and morphological changes in the HgO identified by x-ray diffraction (XRD) and transmission electron microscopy (TEM). Magnetic measurements are presented that indicate small quantities of both superconducting and ferromagnetic phases in the recovered HgO powder. The relative amount of these "impurity" phases exhibits a strong dependence on position within the recovery capsule. A summary and discussion of our results concludes the paper.

2. EXPERIMENTAL DETAILS

Commercial HgO powder from Alfa/Aesar (reagent grade, stock #12276, lot #b15e10) was loaded "as-received" into the copper recovery capsules for both the Sandia Momma Bear and Papa Bear fixtures [7-9] and pressed to a compact with ~ 55% of theoretical density. The powder was handled carefully both in preparing and loading the copper capsules and in the subsequent analysis because of environmental concerns. The samples analyzed in this paper were removed from the copper recovery capsule following two planar explosive loading experiments. The experiments, designated LE95-23 and LE95-50, utilized baratol explosive with conditions summarized in Table I.

Table 1
Schedule of shock experiments with baratol explosive

Experiment #	Fixture	Compact Density (Mg/m ³) (%)	Pressure ^a (GPa)	Temperature ^b (°C)
LE95-23	Momma Bear	6.03 (54%)	7.5	225
LE95-50	Papa Bear	5.90 (53%)	5.0	150

Notes: (a) Average peak shock pressure excluding center and front-outer edge [7].

(b) Mean bulk temperature for 55% powder density using full 2-D simulation [8].

Each loading experiment yielded four samples with three extracted from the "center", "bulk" and "edge" regions, respectively, of the two cylindrical recovery capsules. The recovered compact from both experiments was removed essentially whole, but was somewhat fragile, particularly for the extreme edge of experiment LE95-23. A separate powder sample obtained from this region was designated "extreme edge". A thin layer of powder adjacent to the top of the copper capsule in experiment LE95-50 stuck to the copper plug; this powder was gently scraped away, producing a sample designated "top plug". The edge samples from both experiments appeared slightly more reddish-brown than the original orange color of the as-received HgO powder while the "top plug" sample was more reddish.

XRD data were recorded using a commercial Rigaku Θ - Θ automated powder diffractometer equipped with a monochromator on the detector set so that both Cu K α_1 and K α_2 radiation were obtained. The as-received powder is orange in color and was shown by XRD to be the usual orthorhombic form of HgO (space group Pnma, unit cell dimensions $6.6121 \times 5.5201 \times 3.5213$ Å³). The orthorhombic structure is characterized by infinitely long zigzag but planar

chains of mercury and oxygen atoms. XRD line profiles for this powder were slightly broadened, consistent with an average crystallite domain size near 140 nm.

TEM specimens were prepared by dispersing the HgO powders onto holey carbon film supported on a copper grid. Measurements were obtained with a JEOL model 1200EX TEM operated at 120 keV. Both bright-field imaging and electron diffraction were conducted on selected grains for all samples. Bright-field imaging blocks out the diffracted beams, thus providing more contrast in the area of observation. Bright-field TEM on as-received HgO powder showed individual grains between 50 and 150 nm with many single crystal faceted grains; electron diffraction confirmed the orthorhombic Pnma phase.

The magnetic properties of the HgO powders were determined as a function of temperature and applied magnetic field using a commercial SQUID magnetometer (Quantum Design model MPMS). Typical samples were 300 mg of powder loaded into closed, kel-F plastic cylindrical holders approximately 0.8 cm long $\times$ 0.5 cm diameter. All data were corrected for the diamagnetic signal from the empty plastic container. Surprisingly, the as-received HgO powder contains a significant paramagnetic impurity phase as discussed below.

3. STRUCTURAL AND MORPHOLOGICAL CHANGES

3.1. X-ray Diffraction

XRD spectra showed only the orthorhombic form of HgO in the recovered powder samples with no detectable traces of any other compound. The presence of well-dispersed liquid Hg metal droplets, suggested by the magnetic data below, would not be detected at low concentration by the usual XRD measurement. There were no discernible differences in XRD between either the more reddish "top plug" sample from experiment LE95-50 or the reddish-brown "extreme edge" sample from experiment LE95-23. With the exception of the LE95-50 "center" sample, the XRD line profiles for all shock-loaded samples were slightly narrower than those for the as-received HgO powder. The line widths for most of the recovered samples are consistent with those for well-annealed material with a crystallite domain size of $\sim$ 200 nm or larger.

The copper top plug of experiment LE95-23 exhibited a dull silver-colored interface. XRD measurements on a specimen of this interface showed that it was the intermetallic compound $\text{Cu}_{15}\text{Hg}_{11}$ (space group R3m with $a = 13.351$ and $c = 16.175$ Å). This intermetallic has been confirmed by energy-dispersive x-ray analysis on a scanning electron microscopy specimen.

3.2. Transmission Electron Microscopy

TEM bright-field imaging was used to determine the size and microstructure of the shock-loaded and as-received HgO grains. HgO proved to be very sensitive to the electron beam. All of the HgO grains studied by TEM break up into a fibrous morphology when exposed to heating by a focused electron beam. Because of this sensitivity, detailed microstructural characterization is difficult; however, changes attributed to explosive loading were observed.

Grains in the as-received HgO powder were between 100 and 300 nm in size; all samples from loading experiment LE95-23 had larger grains. Sizes ranged from 300-1000 nm for the center sample to 500-1500 nm for the edge sample where the peak shock temperature is higher [8]. Note that the observed grain growth may occur after the shock event. In the LE95-23 extreme edge sample a second phase was identified as a HgCu alloy; pieces of this alloy were

intergrown with HgO.

The LE95-50 experiment generated lower peak shock temperatures at all sample locations and the samples showed a smaller amount of grain growth. The largest grains, 200-700 nm, were found in the LE95-50 edge sample. In addition, some fine grains of fibrous-like clusters, less than 50 nm in size, were identified between the larger HgO grains. The LE95-50 center sample showed no grain growth. A second phase was observed among these fibrous clusters which appeared to move under the electron beam, consistent with small droplets of liquid, metallic α -Hg.

As individual grains were studied at high magnification with the electron beam focused to a small area, the grains transformed immediately to a fibrous morphology. This was mitigated by using a cold stage which held the TEM sample at -48°C , allowing observation with the electron beam in one spot for up to 5 seconds. Electron diffraction for a cooled extreme edge sample from experiment LE95-23 was inconclusive in directly determining the presence of α -Hg because the d-spacing intensities for HgO and α -Hg overlap within the resolution of the diffraction. However, one isolated particle was studied with selected-area diffraction and the pattern contained a single pair of spots with a d-spacing which matched that of rhombohedral α -Hg.

4. MAGNETIC CHARACTERIZATION

4.1. Magnetization versus Temperature

Figures 1(a) and 1(b) compare the magnetic moment per gram of sample versus decreasing temperature for all HgO powders. Note that all data were corrected for the magnetic response of the plastic cylinder used as a sample holder. The as-received HgO powder (solid diamonds) has a small negative (diamagnetic) moment at room temperature and a distinct increase with decreasing temperature, resulting in a larger positive (paramagnetic) moment at liquid helium temperatures. In contrast, the four shock-loaded samples in Figure 1(a), removed from distinct positions within the Momma Bear copper recovery capsule after shock experiment LE95-23 five powders, have a large positive magnetic moment at all temperatures that increases nearly linearly with decreasing temperature. This response is attributed to the presence of a small ferromagnetic impurity phase as discussed below. Similarly, the four shock-loaded samples in Figure 1(b), removed from the Papa Bear recovery capsule after shock experiment LE95-50, have a positive magnetic moment with a linear temperature dependence. However, the magnitude of the magnetic response is small, except for the edge sample which has a large, nearly temperature-independent magnetic moment.

Since pure HgO is diamagnetic at all temperatures with a mass magnetic susceptibility of $-2 \times 10^{-7} \text{ cm}^3/\text{g}$ at room temperature [10], the magnetic response of the as-received powder (Figure 1) indicates a significant paramagnetic impurity phase. Converted to a magnetic mass susceptibility $\chi_g = (\text{magnetic moment})/(\text{applied field})$, the as-received data are well fit by a combined temperature-independent diamagnetism χ_d plus a Curie-Weiss temperature-dependent paramagnetism [11]: $\chi_g(T) = \chi_d + N(p_{\text{eff}}\mu_B)^2/[3k_B(T-\theta)]$ where N is the number of magnetic impurity ions per gram of sample with an effective moment p_{eff} per ion, μ_B is the Bohr magneton, k_B is Boltzmann's constant, T is the absolute temperature and θ is a phenomenological Weiss temperature arising from magnetic interactions between the impurity ions.

Figure 1. Temperature dependence of the magnetic moment of HgO powders in a field of 0.1 tesla: (a) as-received and four LE95-23 samples; (b) as-received and four LE95-50 samples. All data were corrected for the signal from the kel-F plastic sample holder.

The parameters from a least-squares fit of $\chi_g(T)$ to the as-received HgO data are $\chi_d = -4 \times 10^{-8} \text{ cm}^3/\text{g}$ and $\theta = -16 \text{ K}$ (the negative sign implies antiferromagnetic interactions); p_{eff} and N cannot be determined separately. The XRD data show only orthorhombic HgO while the measured diamagnetism is significantly smaller in magnitude than the reported value for HgO. This suggests a small ferromagnetic impurity as well as the paramagnetic impurity phase. This ferromagnetic impurity is greatly enhanced in all shock-loaded samples as evident in Figure 1 and discussed below. A plausible contaminant in HgO is divalent Fe with $p_{\text{eff}} \sim 5.4$ [12]. If the contaminant is divalent Fe, the paramagnetic impurity component in the as-received HgO data in Figure 1 corresponds to 4×10^{-4} Fe ions per Hg ion.

4.2. Magnetization versus Applied Field

The ferromagnetism suggested by the shock-loaded sample data in Figures 1(a) and 1(b) is confirmed in Figures 2(a) and 2(b) where we compare the magnetic moment versus applied field at 5 K for all samples from the two loading experiments. To emphasize the "impurity" signal, the data in Figure 2 were corrected for the magnetic signals from both the plastic sample container *and* the HgO reference powder (scaled for the appropriate shock-loaded sample weight). This correction assumes that the majority of the recovered material is unchanged HgO as indicated by XRD and TEM studies. The nonlinear shape of these response curves is characteristic of "hard" ferromagnetic materials where the moment "saturates" in large applied magnetic fields.

Note that the amount of ferromagnetic impurity phase (size of the saturation value) is similar in magnitude for three of the four samples from each loading experiment. The extreme edge sample from experiment LE95-23 has a saturation value of $1.2(1) \times 10^{-2}$ emu per gram of recovered powder; the edge sample from experiment LE95-50 has a saturation value of $6.1(3) \times 10^{-2}$ emu per gram of recovered powder or $5 \times$ larger. A typical ferromagnetic (actually ferrimagnetic) oxide consistent with the oxidizing environment (due to partial HgO decomposition) in the sealed recovery capsule is magnetite, Fe_3O_4 , with a saturation moment

Figure 2. Magnetic moment versus applied field at 5 K: (a) four LE95-23 samples; (b) four LE95-50 samples. All data were corrected for the as-received HgO signal (see text).

of 97 emu/g at low temperatures. Assuming the ferromagnetic signal in the shock-loaded powders arises from magnetite contamination, the LE95-23 extreme edge sample would contain approximately 0.01% by weight while the LE95-50 edge sample would contain 0.06% by weight. This explanation requires that the loading and/or post-shock annealing process converts a large fraction of the paramagnetic impurities identified in the as-received HgO into a ferromagnetic phase.

4.3. Superconducting Phase

Figure 3 shows evidence for a superconducting component in the shock-loaded HgO powders. The data were measured versus decreasing temperature from 5 to 2 K in a very small applied magnetic field of 0.5 millitesla, four orders of magnitude smaller than the maximum field in Figure 2. The onset of superconductivity is indicated by the appearance of a negative magnetic moment below a transition temperature; the negative moment arises from the Meissner effect (expulsion of the applied field from the superconducting grains) [13]. All four shocked samples show a superconducting transition just below 4.2 K, consistent with metallic α -Hg with a transition temperature of 4.154 K [14].

Apparently, shock loading converts a small quantity of the HgO to Hg (the as-received HgO powder showed no evidence for superconductivity). If the superconducting Meissner signal at 2 K for the LE95-23 extreme edge sample, $-3.1(3) \times 10^{-3}$ emu/g in 0.5 millitesla, arises from Hg metal, approximately 10% of the sample by weight is α -Hg; for the LE95-50 sample, approximately 6% by weight.

5. CONCLUDING REMARKS

Powder compacts of HgO exhibited substantial grain growth and partial decomposition to metallic α -Hg following explosively-generated shock-wave loading to a mean bulk temperature of 225°C and a pressure of 7.5 GPa. While there was no change in the orthorhombic

Figure 3. Magnetic moment versus low temperature in a field of 0.5 millitesla indicates superconductivity in the four shock-loaded HgO powders from (a) LE95-23 and (b) LE95-50.

structural phase of the starting powder, XRD line profiles and TEM bright-field imaging indicate an *increase* in grain size by up to an order of magnitude in the recovered samples; the largest grain growth occurs where the peak shock pressure and temperature are greatest. However, the observed growth may occur after the shock event. TEM also shows fine grains of fibrous-like clusters plus a second phase of small liquid-like droplets which appear to move in the electron beam. These particles are tentatively identified as metallic α -Hg. Selected-area electron diffraction using a TEM cold stage shows sharp rings due to HgO plus smeared broad rings which are consistent with the d-spacing for α -Hg. One isolated particle had a diffraction pattern matching that for rhombohedral α -Hg.

Magnetic data show a superconducting transition occurring just below 4.2 K in the recovered samples; this transition is not present in the as-received HgO powder. The superconductivity is consistent with metallic α -Hg which forms through a shock-induced partial decomposition of the HgO compact. The magnitude of the superconducting signal is a maximum for the extreme edge sample from Momma Bear experiment LE95-23 and corresponds to $\sim 10\%$ by weight if due to α -Hg.

The recovered powder contains a ferromagnetic or ferrimagnetic phase with a magnetic ordering temperature above 300 K. This can be attributed to a shock-induced conversion of the paramagnetic impurity ions present in the commercial HgO starting powder to a ferromagnetic phase. The largest amount of ferromagnetism was observed in the edge sample from Papa Bear experiment LE95-50. It is interesting that this sample experienced a lower peak shock pressure and temperature than the sample exhibiting the most superconductivity. Both the superconductivity and ferromagnetism levels were strongly dependent on the position of the samples within the shock recovery capsules.

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