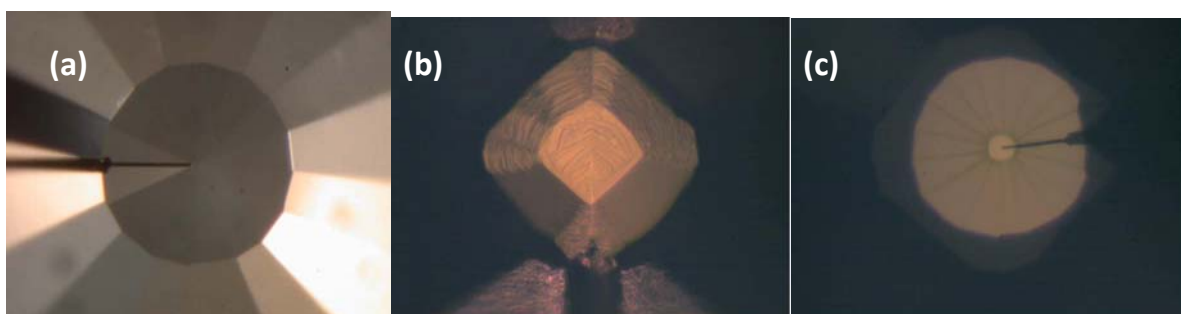


Final/Scientific Technical Report
DE-FG52-06NA26168, PI Yogesh K. Vohra
University of Alabama at Birmingham (UAB)

1. DOE Award Number: DE-FG52-06NA26168
Name of Recipient: University of Alabama at Birmingham (UAB)
Project Title: “Development of Designer Diamond Technology for High Pressure High Temperature Experiments in Support of Stockpile Stewardship Program”
Name of Project Director/Principal Investigator: Yogesh K. Vohra, PhD
2. Authorization Distribution Limitation Notices: None
3. Executive Summary:
The role of nitrogen in the fabrication of designer diamond was systematically investigated by adding controlled amount of nitrogen in hydrogen/methane/oxygen plasma. *This has led to a successful recipe for reproducible fabrication of designer diamond anvils for high-pressure high-temperature research in support of stockpile stewardship program.* In the three-year support period, several designer diamonds fabricated with this new growth chemistry were utilized in high-pressure experiments at UAB and Lawrence Livermore National Laboratory. The designer diamond anvils were utilized in high-pressure studies on heavy rare earth metals, high pressure melting studies on metals, and electrical resistance measurements on iron-based layered superconductors under high pressures. The growth chemistry developed under NNSA support can be adapted for commercial production of designer diamonds.
4. Comparison of the actual accomplishments with the goals and objectives of the project:
All the project goals in regard to fabrication of designer diamond anvils and high-pressure high-temperature research were achieved in this project period.
5. Summary of project activities:
5.1 Role of Nitrogen in the Homoepitaxial Growth on Diamond Anvils by Microwave Plasma Chemical Vapor Deposition:
The catalytic effect of nitrogen during the homoepitaxial diamond growth on a diamond anvil was investigated using isotopically enriched Carbon-13 methane in a feed-gas mixture in a microwave plasma chemical vapor deposition reactor. The use of isotopically enriched Carbon-13 allows us to precisely measure the film thickness in this homoepitaxial growth process by Raman Spectroscopy. It is found that the addition of 0.4 standard cubic centimeters per minute of nitrogen to a H₂/CH₄/O₂ gas phase mixture increases the growth rate by a factor of 2.3. This enhanced growth rate with the addition of trace amounts of nitrogen allows for a quick encapsulation of embedded sensors in the designer diamond anvils and is a key control parameter in the fabrication process. Photoluminescence spectroscopy reveals nitrogen-vacancy defect centers in the high growth rate diamonds. Atomic force microscopy reveals dramatic changes in the surface microstructure as is indicated by a total loss of step flow growth morphology on addition of nitrogen in the plasma. We have achieved a near 100 % success rate in the fabrication of designer diamonds with this growth chemistry developed under NNSA support.

5.2 Fabrication of a Single Probe Designer Diamond for Ultra High Pressure Electrical Resistance Measurements:

In ultra high-pressure diamond anvil cell research, there is a requirement that diamond central flat size has to be between 25 microns to 35 microns in diameter for attainment of 300 GPa pressure. It is difficult to fabricate four probe designer diamonds with a central flat of 25 microns in diameter with a probe spacing of 5 microns. However, if the primary interest is to detect an insulator to metal transition at extreme pressures then one could work with a single electrode on the diamond flat that can be exposed to make electrical contact with the sample and metallic gasket itself can be used as a second electrode. This way one can detect metallic behavior of sample under compression by monitoring the two probe electrical resistance under extreme compressions. Figure 1 shows a successful fabrication of a single probe designer diamond with the new growth chemistry that we have developed.



6.

Figure 1: Fabrication of a single probe designer diamond anvil. (a) Showing the lithographic patterning of a single tungsten probe on the diamond anvil. (b) Diamond surface after growth in the microwave plasma chemical vapor deposition chamber for three hours using a specially developed $H_2/CH_4/O_2/N_2$ chemistry. (c) Fully fabricated single probe designer diamond with central flat of 35 microns in diameter and culet size of 300 microns in diameter.

5.3 Electrical Resistance Measurements on Heavy Rare Earth Metals under High Pressures Using Designer Diamond Anvils

We report four probe electrical resistance measurements on heavy rare earth metals under high pressures using designer diamond anvils containing embedded electrical microprobes. As a validation of this technique for detecting semimetal to metal as well as metal-to-metal phase transitions, we have carried out four-probe electrical resistance measurements on semimetal Bismuth to 9 GPa (Figure 2). All three known phase transitions at 2.1 GPa, 2.5 GPa, and 7.5 GPa in Bismuth are clearly detected in our four-probe electrical resistance data using the designer diamond anvils as shown in Figure 1. This clearly demonstrates that the designer diamond technology is a valuable tool for detecting semimetal to metal as well as metal-metal phase transitions under high pressures. We also present electrical resistance data on heavy rare earth metal Dysprosium to 40 GPa (Figure 3), Holmium to 70 GPa (Figure 4) and Terbium to 100 GPa (Figure 5) at room temperature. The observed changes in the electrical resistance of the heavy rare earth metals are correlated with the structural phase transformations observed in x-ray diffraction studies at high pressures. Furthermore, in the electrical resistance data, we investigate a possible evidence of 4-f shell delocalization in heavy rare earth metals at high pressures

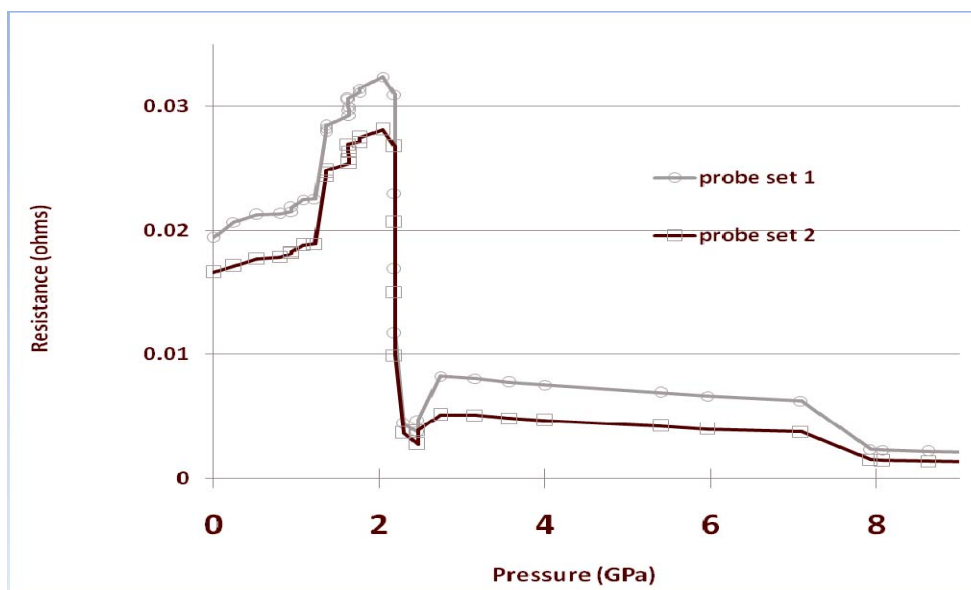


Figure 2: Four probe electrical resistance data on semimetal Bismuth to 9 GPa. All the three structural phase transitions at 2.1 GPa, 2.5 GPa, and 7.5 GPa were detected in the electrical resistance data. This experiment shows that the designer diamond technology has the necessary sensitivity to detect metal-metal phase transitions under high pressures.

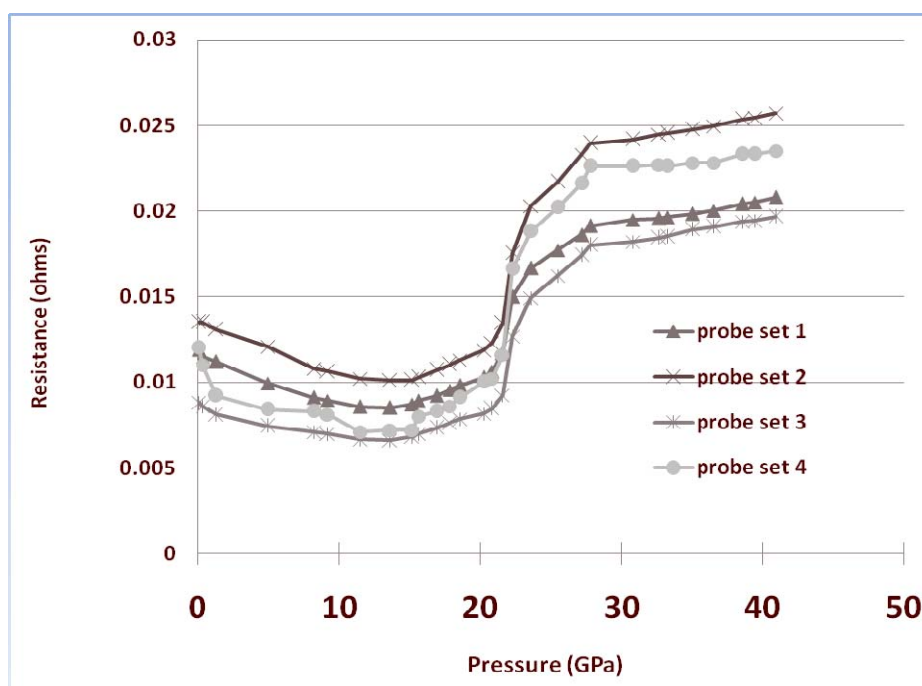


Figure 3: Four probe electrical resistance data on heavy rare earth metal Dysprosium (Dy) to 40 GPa. The resistance increase at 20 GPa is attributed to a phase transition from the samarium phase to the double hexagonal close packed phase in Dy.

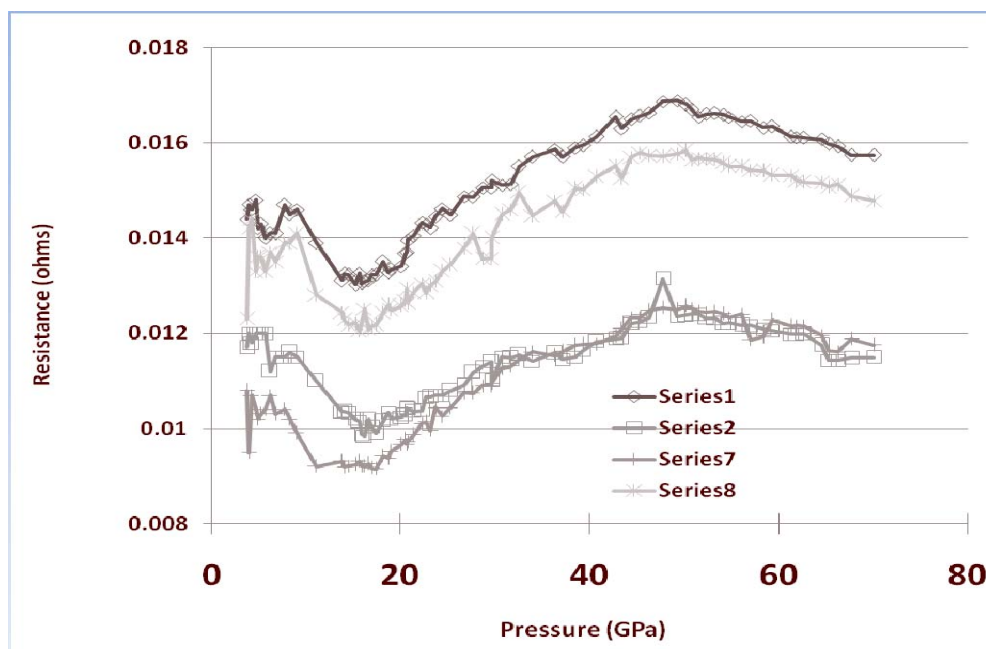


Figure 4: Four probe electrical resistance data on heavy rare earth metal Holmium (Ho) to 70 GPa. The increase near 20 GPa is attributed to a phase transition from the samarium phase to the double hexagonal close packed phase in Ho.

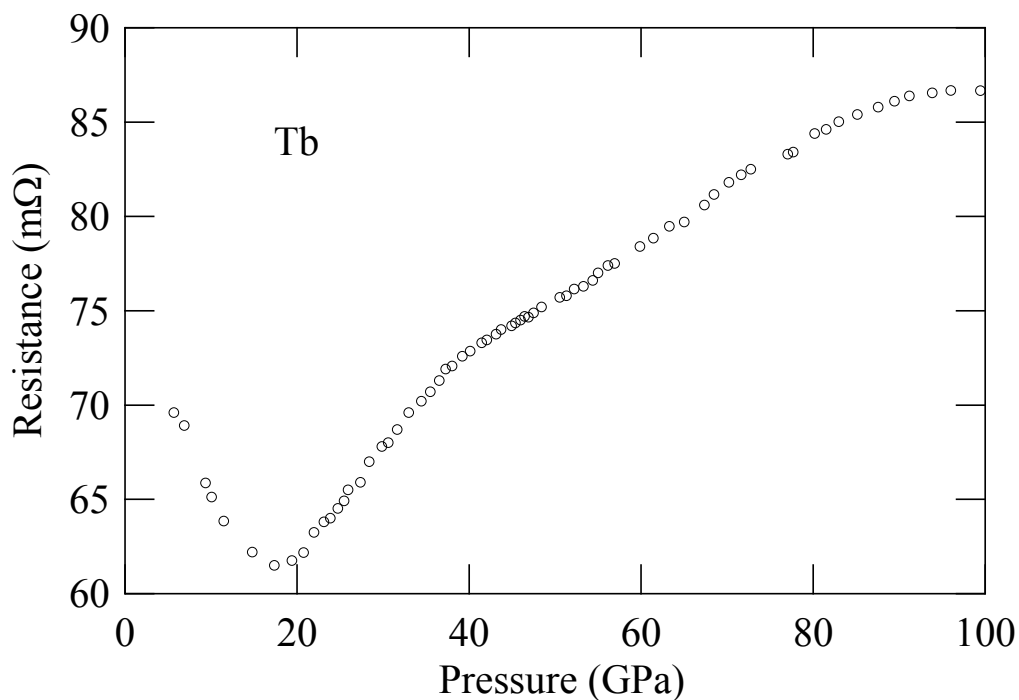


Figure 5: Four probe electrical resistance data on heavy rare earth metal Terbium (Tb) to 100 GPa. The increase near 20 GPa is attributed to a phase transition from the samarium phase to double hexagonal close packed phase in Tb. The anomaly at 50 GPa is due to a phase transition to a monoclinic phase that is associated with 4-f shell delocalization in Tb under high pressure.

5.4 Nanostructured Diamond Deposition on a Copper-Beryllium Alloy

Microwave plasma chemical vapor deposition (CVD) was used to coat nanostructured diamond onto a copper-beryllium alloy (~1.7 wt% Be) commonly used as a non-magnetic gasket material in diamond anvil cell devices. Adhered diamond coatings up to 12.5 μm thickness were obtained with a root-mean-squared surface roughness of 15 nm. The coatings were characterized by Raman spectroscopy, glancing-angle x-ray diffraction, atomic force microscopy, and nanoindentation. CVD diamond deposition on copper-based substrates has historically resulted in poor coating adhesion due to the very large thermal expansion mismatch between the substrate and coating as well as the inability of copper to form a carbide phase at the interface. Despite these challenges and previous shortcomings, we have successfully deposited a thick, adhered diamond coating on a copper-beryllium alloy. The nanostructured diamond coating exhibit surface hardness of up to 84 GPa and resist the delamination and brittle fracture characteristic of conventional CVD diamond. Such coatings are useful in preventing plastic flow of Cu-Be gaskets in diamond anvil cells, and thus increasing the sample volume at high pressures thereby improving the sensitivity of magnetic measurements.

5.5 Finite Element Modeling of Stresses and Strains in a Diamond Anvil Cell Device: Case of a Diamond Coated Rhenium Gasket

The stresses and strains in a diamond anvil cell device were investigated using a finite element code NIKE2D for the case of an ultra-hard composite gasket material. The pressure distribution in a diamond coated rhenium gasket was measured by the energy dispersive diffraction technique to 213 GPa and compared with the finite element modeling results. We examine various models for the mechanical properties of diamond coated rhenium gasket as well as for diamond failure for shear stresses exceeding 100 GPa. The elastic and plastic properties of gasket were varied such that a good agreement between the experimentally measured pressure distribution and the computational pressure profiles were obtained. As a result, we obtained the effective Young's modulus, Poisson's ratio, yield stress for indented gasket, linear hardening modulus, and hardening parameter value for this layered ultra-hard composite gasket material. Future diamond design strategies for attainment of extreme high pressures using ultra-hard gasket materials are also discussed.

5.6: High Pressure Superconductivity in Iron Based Layered Compounds Studied using Designer Diamonds:

The pressure variable has always played a pivotal role in the discovery and optimization of novel superconducting materials. The high temperature superconductivity in a new class of iron-based layered compounds has received extensive attention recently because of the diversity of systems in which this phenomenon has been documented. Iron-based layered compounds like REOFeAs (RE= trivalent rare earth metal), AFe_2Se_2 (A = divalent alkaline earth metal), BFeSe (B= alkali metal), and simple $\text{FeSe}(\text{Te})$ materials have exhibited superconductivity with transition temperature (T_c) in the range of 0-55 K. In this broad range of iron-based layered compounds, the basic system FeSe remains of considerable interest, as it is the foundation on which more complicated layered structures are built. The superconductivity in the PbO-type structure $\alpha\text{-FeSe}$ was discovered recently at 8 K in samples prepared with Se deficiency. The occurrence of superconductivity in this simple layered FeSe compound with edge-sharing FeSe_4 tetrahedron has created tremendous interest

in the effects of chemical substitution and high pressure on this material system. In particular, Tellurium (Te) substitution has been studied and a maximum superconducting transition temperature of 15.2 K was measured for $\text{FeSe}_{0.5}\text{Te}_{0.5}$. Additionally, pressure induced enhancement of superconducting transition temperature of $\text{FeSe}_{0.5}\text{Te}_{0.5}$ has been reported that warrant further high-pressure structural and superconducting properties investigations. Figure 6 shows an eight-probe designer diamond anvil employed in high-pressure superconductivity measurements on the layered iron based compounds. The eight tungsten microprobes are encapsulated in a homoepitaxial diamond film and are exposed only near the tip of the diamond to make contact with the $\text{FeSe}_{0.5}\text{Te}_{0.5}$ sample at high pressure (Figure 6-insert). Two electrical leads are used to set constant current through the sample and the two additional leads are used to monitor the voltage across the sample (Figure 6). The following equation describes the reference value for R_1 that is utilized in the pressure measurement at low temperature using the ruby fluorescence technique,

$$R_1(T) = R_1(0) + \alpha \left(\frac{T}{\theta} \right)^4 \int_0^{\theta/T} \frac{x^3 dx}{e^x - 1},$$

where $R_1(T)$ is the wave number of the R_1 band at temperature T and ambient pressure; $R_1(0)$ is the wave number of the R_1 band at 0 K and ambient pressure; θ and α are the effective Debye temperature and an electron-phonon coupling parameter. We used the following fit parameters based on our measurements: $\alpha = -440 \text{ cm}^{-1}$; $\theta = 760 \text{ K}$; $R_1(0) = 14423.2 \text{ cm}^{-1}$. The high-pressure x-ray diffraction experiments were carried out at the beam-line 16-BM-D, HPCAT, Advanced Photon Source, Argonne National Laboratory. An angle dispersive technique with an image-plate area detector was employed using an x-ray wavelength $\lambda = 0.3875 \text{ \AA}$ and sample detector distance of 555.5 mm. An internal copper pressure marker with a known equation of state was utilized in our high-pressure x-ray diffraction experiments.

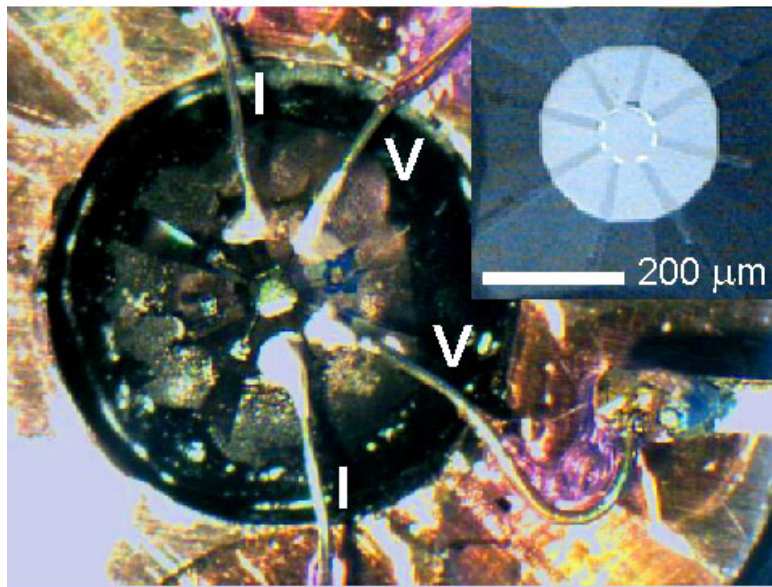


Figure 6: Eight-probe designer diamond anvil used in high-pressure superconductivity measurements. The current and voltage contacts in the four probe electrical measurements are indicated. The insert is the close-up of the diamond culet showing the eight shiny tungsten metal probes emerging near the center to make contact with the sample at high pressures.

Powder materials of Fe (3N purity), Se (3N purity), and Te (5N purity) with appropriate stoichiometry ($\text{FeSe}_{0.5}\text{Te}_{0.5}$) were mixed in a ball mill for duration of one hour. The well mixed powders were cold-pressed into discs under 400 kg/cm^2 uniaxial pressure, and then sealed in an evacuated quartz tube with pressure less than 10^{-4} torr and heat treated at 600°-C for 20 hours. The reacted bulk sample was reground into fine powders repressed, sealed, and subsequently sintered at 650°-C for 20 hours. The sample for high-pressure studies was cut from the sintered pellet and loaded in a gas membrane diamond anvil cell for both structural and superconducting property investigations. The $\text{FeSe}_{0.5}\text{Te}_{0.5}$ compound belongs to the PbO type structure (Space Group P4/nmm), tetragonal with 4 atoms/cell. Fe atoms occupy the 2a positions (0, 0, 0) and $(1/2, 1/2, 0)$ and Se and Te atoms at random occupy 2c positions $(0, 1/2, z)$, and $(1/2, 0, -z)$. The parameter z has been determined to be 0.2715 based on earlier work on $\text{Fe}_{1+y}\text{Se}_x\text{Te}_{1-x}$ compounds [7]. The measured lattice parameters for the tetragonal phase of $\text{FeSe}_{0.5}\text{Te}_{0.5}$ sample at ambient conditions are $a = 3.7924 \text{ \AA}$ and $c = 6.0112 \text{ \AA}$ with volume (V_0) = $21.614 \text{ \AA}^3/\text{atom}$. It is to be noted that our materials synthesis method resulted in a phase pure sample with a well crystallized PbO-type tetragonal phase and no detectable contamination of any impurity phases were observed in x-ray diffraction studies in the diamond anvil cell.

Figure 7 shows the integrated x-ray diffraction profile (Intensity versus 2θ) for a $\text{FeSe}_{0.5}\text{Te}_{0.5}$ sample at various pressures. Figure 7(a) shows the tetragonal phase at ambient condition after pressure cycling to 27.2 GPa and this x-ray spectrum is identical to that of the starting tetragonal sample. The spectrum in Figure 7(a) at ambient pressure was measured outside the high-pressure cell with sample contained in the metallic gasket after the high-pressure experiment. All ten observed diffraction peaks in Figure 7(a) can be assigned to a tetragonal phase. Figure 7(b) shows the onset of transformation at 11.5 GPa where a broad peak characteristic of amorphous phase marked by an “asterisk” is beginning to appear along with the tetragonal phase. The phase transformation in $\text{FeSe}_{0.5}\text{Te}_{0.5}$ sample to an amorphous phase is completed under a high pressure of 15.2 GPa. The amorphous phase was found to be stable to the highest pressure of 27.2 GPa. The measured spectrum for the amorphous phase at 25.3 GPa is shown in Figure 7(c) and is dominated by a strong band of the amorphous phase at an interplanar spacing of 2.644 \AA . The tetragonal to amorphous phase transformation is reversible on decreasing pressure and a back-transformation is observed to start at 2.8 GPa and a pure tetragonal phase is recovered at ambient condition as shown in Figure 7(a). The measured superconducting transition temperature T_c for a $\text{FeSe}_{0.5}\text{Te}_{0.5}$ sample using a designer diamond anvil cell is shown in Figure 8. Our measured value of dT_c/dP at ambient pressure ($P \approx 0$) is 2.86 GPa/K. This is lower than the value of dT_c/dP of 4.87/GPa reported earlier in measurements confined to lower pressures region between 1-2 GPa. The maximum T_c value from the parabolic fit to the data is 19.1 K and occurs at a pressure of 3.6 GPa. The extrapolation of the parabolic fit to the T_c data predicts that material will be non-superconducting above a pressure of 10 GPa. This prediction coincides with the observations in our x-ray diffraction studies that the $\text{FeSe}_{0.5}\text{Te}_{0.5}$ sample becomes amorphous under high pressures above $11.5 \pm 1 \text{ GPa}$ at ambient temperature. We also show this amorphization pressure range in Figure 8.

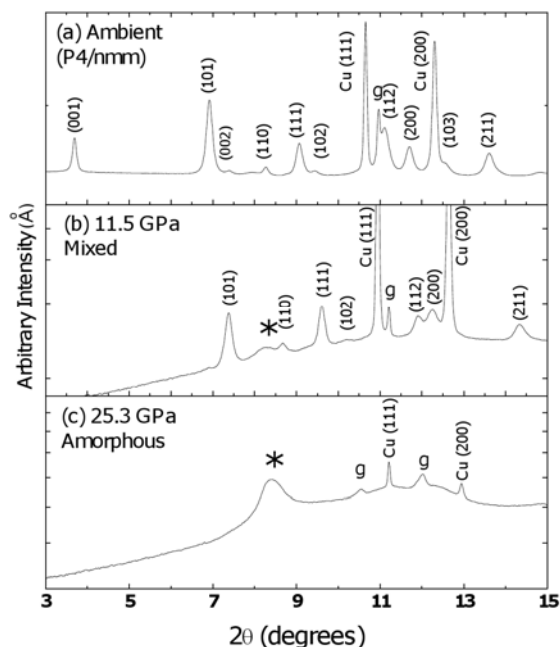


Figure 7: Pressure-induced amorphization in $\text{FeSe}_{0.5}\text{Te}_{0.5}$ sample. The diffraction patterns are shown for $\text{FeSe}_{0.5}\text{Te}_{0.5}$ sample and a copper (Cu) pressure marker at various pressures. All spectra have been collected at a synchrotron source using a x-ray wavelength $\lambda = 0.3875 \text{ \AA}$. (a) Sample in the tetragonal phase at ambient pressure after pressure release from 27.2 GPa, (b) Sample at 11.5 GPa at the onset of transition to amorphous phase, and (c) sample in pure amorphous phase showing a broad peak denoted by an “asterisk”. The diffraction peaks from Cu pressure marker are also indicated and “g” represents weak peaks from the spring steel gasket.

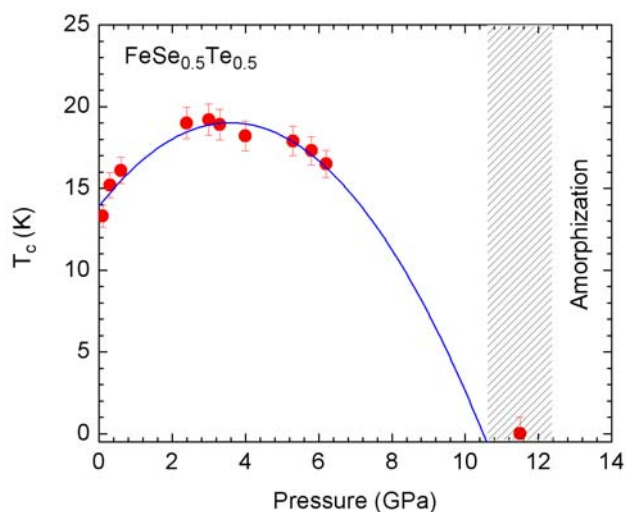


Figure 4: The measured superconducting transition temperature for $\text{FeSe}_{0.5}\text{Te}_{0.5}$ as a function of pressure to 14 GPa. The solid curve is a quadratic fit to the data. The amorphization pressure range of $11.5 \pm 1 \text{ GPa}$ at room temperature is also indicated.

7. Products developed:

a. List of Publications:

- 1) Wei Qiu, Yogesh K. Vohra, and Samuel T. Weir, "Role of Nitrogen in the Homoepitaxial Growth on Diamond Anvils by Microwave Plasma Chemical Vapor Deposition", *J. Mater. Res.* **22**, 1112 (2007).
- 2) D. D. Jackson, J. R. Jeffries, Wei Qiu, Joel D. Griffith, S. McCall, C. Aracne, M. Fluss, M. B. Maple, S. T. Weir, Y. K. Vohra, "Structure-Dependent Ferromagnetism in Au_4V Studied under High Pressure", *Phys. Rev. B* **74**, 174401-1 (2006).
- 3) D. D. Jackson, S. K. McCall, S. T. Weir, A. B. Karki, D. P. Young, W. Qiu, Y. K. Vohra, "Cubic Laves Ferromagnet $TbNi_2Mn$ Investigated through Ambient Pressure Magnetization and Specific Heat and High Pressure AC Magnetic Susceptibility", *Phys. Rev.* **B75**, 224422 (2007).
- 4) Andreiy Kondratyev and Yogesh K. Vohra, "Finite Element Modeling of Stresses and Strains in a Diamond Anvil Cell Device: Case of a Diamond-Coated Rhenium Gasket", *High Pressure Research* **27**, 321 (2007).
- 5) D. A. Zocco, J. J. Hamlin, R. E. Baumbach, M. B. Maple, M. A. McGuire, A. S. Sefat, B. C. Sales, R. Jin, D. Mandrus, J. R. Jeffries, S. T. Weir, Y. K. Vohra, "Effect of pressure on the superconducting critical temperature of $La[O_{0.89}F_{0.11}]FeAs$ and $Ce[O_{0.88}F_{0.12}]FeAs$ ", *Physica C* **468**, 2229 (2008).
- 6) Yogesh K. Vohra, Bagvanth Reddy Sangala, Andrew K. Stemshorn, and Kevin M. Hope "High Pressure Phase Transformations in Heavy Rare Earth Metals and Connections to Actinide Crystal Structures", *Mater. Res. Soc. Symp. Proc. Vol.* **1104**, 1104-NN01-04 (2008).
- 7) Shane A. Catledge, Yogesh K. Vohra, Damon D. Jackson, and Samuel T. Weir, "Adhesion of nanostructured diamond film on a copper-beryllium alloy", *J. Mater. Res.* **23**, 2373 (2008)
- 8) Gopi K. Samudrala and Yogesh K. Vohra, "Multivariable Study on Homoepitaxial Diamond Growth using Isotopically Enriched Carbon-13 Gas Mixtures", *J. Mater. Res.* **24**, 493 (2009).
- 9) Georgiy Tsoi, Andrew Stemshorn, Yogesh K. Vohra, Phillip M. Wu, F. C. Hsu, Y. L. Huang, M. K. Wu, K. W. Yeh, and Samuel T. Weir, "High Pressure Superconductivity in Iron Based Layered Compounds Studied using Designer Diamonds" *J. Phys.: Condens. Matter* **21**, 232201 (2009).
- 10) Andrew K. Stemshorn, Georgiy Tsoi, Yogesh K. Vohra, Stanislav Sinogeiken, Phillip M. Wu, Y. L. Huang, S.M. Rao, M.K. Wu, K.W. Yeh, and Samuel T. Weir, "Low Temperature Amorphization and Superconductivity in $FeSe$ Single Crystals at High Pressures", *Journal of Materials Research*, accepted for publication (2009).

b. Web-site: <http://www.phy.uab.edu/research/DOE/Index.htm>

c. Networks or collaborations fostered

We have an ongoing collaboration with Dr. Samuel T. Weir from H-Division, Lawrence Livermore National Laboratory under the sponsorship of this SSAA program.

e. Invention/Patent Application

Provisional Patent Application Serial No. 60/756,085

“High Growth Rate Methods of Producing High Quality Diamonds”

Filing Date: January 4, 2006

Inventors: Dr. Yogesh K. Vohra and Dr. Paul A. Baker