

New Experimental Techniques to Study Oxides and Melts

S. K. Saxena,

Center for the Study of Matter at Extreme Conditions (CeSMEC)

Florida International University, University Park, Miami, FL 33199, USA.

Recent advances in laser-heating and temperature measurement techniques permit us to use micron-size samples to study phase transitions and melting in metals and oxides. One may use high power lasers based on Nd-YLF and CO₂ to heat materials to ultra-high temperatures without the container problem. Temperatures can be measured by use of spectroradiometry involving black/gray body radiation. Wavelengths over a wide range (400 to 900 nm) can be used lending a high degree of reliability to temperature measurements. Several experimental designs for the study of refractory materials at temperatures reaching 3000 K will be presented both for metals and oxides.

Introduction

The ultimate goal of the material sciences should be to understand the behavior of solids, melts and fluids over a range of pressures and temperatures, well enough to construct detailed, quantitative and predictive models of the physical and chemical processes operative in the industrial systems. In recent years, there has been significant technical improvement in generating and measuring high temperatures using lasers and spectroradiometry (multi wavelength pyrometry) and in-situ x-ray study of micrometer size heated samples using synchrotrons. These techniques permit us to extend the study of existing materials to higher temperatures and pressures than ever before and they will also inevitably help us in conceiving and producing a whole range of new materials.

While assessing thermodynamic data on binary and ternary phase diagrams for metals, inter-metallics and oxides, one is struck by the fact that there are very few modern experimental data available on most systems. One of the major problems has been the experimental limitation on achieving the appropriate temperatures for the study of refractory materials by use of thermocouples for temperature measurement. A second difficulty with the available data is lack of information on the in situ behavior of materials at the ambient pressure and temperature. For example, few phase diagrams are based on data with in situ determination of phase transitions. In many instances, the crystal structure is not quenchable.

The purpose of this paper is to describe certain techniques that have not been commonly adopted as yet in this field. In addition to providing new data on critical aspects of various phase diagrams, the techniques enable us to obtain physical data on refractory and super-hard materials, which include melting temperatures, thermal expansions and compressibility.

The systems that can be studied

There are many systems that require attention. We choose here certain systems for which the data at 1 bar is either uncertain or missing and for which high-pressure studies could help improve the current method of synthesis of a known material (e.g. diamonds) or help us synthesize a novel phase (carbide, nitride or oxide).

Carbon-metals

We may consider the carbon-metal (C, Fe-Co-C), and Fe-Co-W systems to illustrate our approach. Carbon phase diagram has never been resolved satisfactorily. The reason is obvious. There is the basic problem of reaching such high temperatures as 4000 K and above with conventional techniques. Additionally there are of course kinetic considerations. In binary and ternary systems, it has been feasible to work only with the carbon poor systems because of the high temperatures involved. Fernandez-Guillermot (1) assessed the thermodynamic data on the Co-C binary. He found that he was severely limited in this attempt because of lack of experimental data (see figure). Similar difficulties exist for all binaries where one of the components is high refractory e.g. C or W.

Carbon: The phase relations will be studied at 1 bar to a high pressure of 300 GPa using in situ techniques of heating and x-ray as discussed later. As the figure above shows there are many ill-defined parts of the phase diagram with little or no structural information on the carbon phases. Melt phase relations were recently computed by Glosli and Ree (AIRAPT-17,1999) which could be experimentally verified. The carbon phase diagram is fundamental to many important industrial substances. By doing these experiments, we will not only obtain x-ray information on the phases but also their thermal expansion and compressibility.

Cobalt-Carbon and Iron-Carbon: For the binary C-Co, the figure shows that experimental information is limited to the Co rich part as shown by the box. At 1 atm, there is limited solid solution of carbon in the fcc phase. This system will be studied from 1 bar to 10 GPa to study the effect of pressure on the solid solution. We will also obtain additional melting data above 2000 K both at 1 bar and at high pressures.

For the binary Fe-C, the calculated phase diagrams show a widening field of diamond stability at pressures starting at 5.7 to 6.5 GPa. In spite of the importance of these systems in synthesis of diamonds, experimental information on the pressure effect is rather limited. We will determine phase relations in the relevant part of the diagram from 1000 to liquidus temperatures. For both these binary systems, we will study the feasibility of doping of diamonds (semi-conductor) by dropping the temperature of the melt to the diamond stability field (2).

For both binary systems, thermal expansion and compressibility data (both as a function of pressure and temperature) will be provided.

Titanium-Carbon: The calculated phase diagram of TiC has a large stability field. Again due to difficulty in achieving the temperatures needed to study the phase diagram, the experimental information is meagre. We will study the system with in situ x-ray on heated and pressurized samples and obtain both phase relations and physical property data. We have recently determined the compressibility of TiC (3).

W-Carbon: The system needs to be studied in detail for pressure-volume-temperature properties of the carbides. There are very few experimental data either on in situ structures or on the liquidus.

Light Alloys

Binary alloys such as Fe-Al and Fe-Si have been experimentally and theoretically studied but again due to lack of suitable techniques, these studies are mostly confined to x-raying the quenched samples. In a study of Fe-Al binary (5), we found structural details through in situ studies at high temperature, which were not known before. The phase transformation from bcc to fcc in the Fe-5%Al alloy was observed between 1203 to 1238 K while the 10%Al alloy had a primitive cubic structure above 1300 K. We need similar data on several binaries such as Fe-Si and Ni-Al.

Ceramics

As for the refractory metals, the data on many single or binary phases for refractory oxides are missing particularly at high temperatures. We will present here a few examples of what could be good starting studies under this project.

The binaries in the FeO-MnO-MgO-NiO system: The binaries generally miscible systems with moderately high liquidus temperatures and yet the data are mostly missing. For CaO-MnO and MgO-MnO, only the solidus points are available, while for FeO-MnO the solidus is missing. For CaO-NiO, all data above the eutectic temperature is missing and the eutectic composition is calculated by “petrographic” approximation. There are no experimental data on the MnO-NiO binary.

Zirconia-FeO and Zirconia-MnO: For ZrO_2 -FeO, there are no experimental data above 2000 K and no structural data. Similarly for the second binary, there are very few data available from one report.

Melting temperatures of several refractory oxides: The melting temperatures of practically all oxides melting above 2500 K, particularly those that sublime (e.g. CaO), require a re-determination. Such oxides include MgO, CaO (T_m given between 2800 to 3200 K in different measurements), BeO and SrO. We may add to this list a number of other oxides of rare-earth elements. H. Seifert (pers. Comm.) finds that all the melting temperatures of the following silicates Yb_2SiO_5 , $\text{Yb}_2\text{Si}_2\text{O}_7$, Y_2SiO_5 and $\text{Er}_2\text{Si}_2\text{O}_7$ need to be determined.

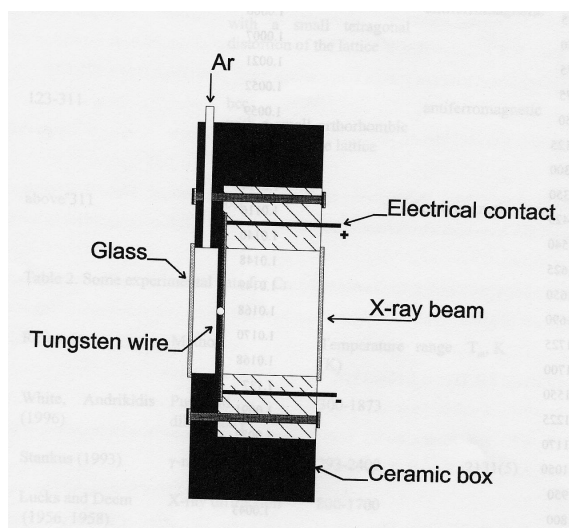
Melting temperatures of carbides and nitrides: A similar difficulty as for refractory oxides discussed above exists in determining the melting temperatures of carbides and nitrides. An example may be given of Si_3N_4 where the problem of sublimation becomes very difficult to control as one approached the melting temperature. This problem was solved by determining the temperature of melting at moderate pressures and then extrapolating the melting curve to zero pressure (Y. Ceranius, Master's thesis, Uppsala University, 1996). Another example is that of GaN. The calculated phase diagram predicts incongruent sublimation (26).

General Experimental Techniques

The emphasis in this type of research is to heat and pressurize solids and fluids and measure the changes in the material properties as they happen. Employing in situ x-ray and spectroscopic techniques does this. In most cases visual observation of the process is possible. We use various types of diamond and sapphire cells depending on the physical conditions of measurement to contain the samples.

Heating the sample

Heating at 1 atm:



Electrical : For measurement of thermal expansion to melting temperatures as high as melting temperature of tungsten, we have used metal wires with a 100 to 200 micron hole in the center for placing the sample. Fig. 1 shows the device, which is used with a continuous flow of argon preventing any oxidation of the metal wire or the sample (6,7). The temperature is determined by using an internal standard with known cell constants.

Using lasers: The laboratory contains lasers (CO_2 - and Nd-YLF) to heat solids to several thousand degrees. This can be done at 1 atmosphere in inert gas. Temperature is determined by using either internal standard if x-ray is used or by spectroradiometry as discussed later.

We use the scientific grade lasers in continuous wave mode. These lasers are power stabilized by the makers and we add further stability by using feed back loops monitoring either the power fluctuation or the thermal radiation. We use liquid-crystal-based stabilizer (Cambridge Research Inc.) with feedback what results in intensity stabilization within 0.05% peak-to-peak.

To maintain a homogeneous temperature, we use double side laser heating as discussed in the next section.

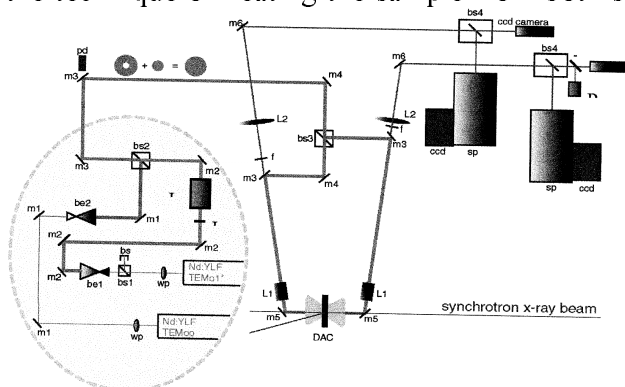
Heating at high pressures: Heating at any pressure up to several million bars in a diamond-anvil or other high-pressure cells may be done both by electrical resistance or using lasers in a diamond-anvil cell.

Diamond-anvil cell: In recent years, the diamond-anvil cell (8) has become firmly established in materials science as a research tool. Pressures from a few GPa (gigapascal) to several hundred GPa are generated routinely. The advantage of the diamond-anvil cell as containers for high temperature-high-pressure research is the ease with which samples can be prepared and squeezed to desired pressures and heated at the same time as you study them optically or using x-ray and a variety of spectroscopic techniques. This is due to the transparency of diamonds as well as their hardness and high thermal conductivity. The disadvantages are that the sample size is small and the pressure is uniaxial which may result in large pressure gradients at very high pressures. Both these disadvantages are largely overcome by using high intensity sources such as synchrotron x-ray and releasing the stress by using heated cells (4). In a typical setup for low to moderate pressure studies, a stainless steel T301 gasket with the thickness of 400 micron is indented between diamonds having culet size 450

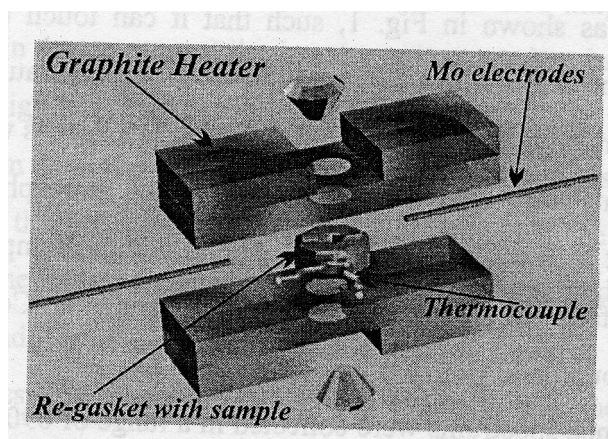
micron and a hole with the diameter of 200 micron drilled in the center of indentation. A metal or oxide sample in the form of a flattened disk 20-30 micron thick is placed between dry compressed discs of insulators in the sample chamber. Several small ruby chips may be placed across this assemblage if needed for pressure determination by the standard ruby fluorescence technique (8). The sample preparation depends on the purpose of study. If the cell is to be heated externally, internal standards (e.g. non-reacting substance with known x-ray data) are to be preferred.

Laser-heating: Pressurized sample in a DAC may be heated by stabilized Nd:YLF laser (Photonics, 50 Watts CW at 1064 nm, TEM₀₀ mode). Temperatures are determined from the thermal radiation of hot sample using spectroradiometry as described below. The use of 2-dimensional CCD detector and imaging spectrograph with entrance slit give possibility to measure temperatures along narrow vertical strip in one single measurement with spatial resolution of about 3 micron. The detailed description of the laser heating system is given in Ref. (9).

In laser heating from one side of the sample, there is a large temperature gradient from the front to back. While this is not a problem for some studies e.g. melting where only surface reaction is involved, it is a definite draw back for determining physical properties of solids where the x-ray samples the whole thickness. Therefore, we use the technique of heating the sample from both sides as developed by Shen et al. (10).



External heating: We use a flexible graphite foil for external electric heating. In such a design, both the diamonds and gasket can be heated homogeneously to over a temperature of about 1200°C. We use two rectangular flexible graphite slabs (~23*10mm²) of 1mm thickness. Small pieces (~8*10mm²) of the graphite foil of 0.5 mm thickness are glued at the edges of these slabs along their lengths using high temperature graphite glue. These small pieces at the edge of the slabs make the furnace stable and direct the heat to the sample and the diamond tips. The slabs are indented simultaneously and the Re-gasket is placed in between them.



The whole furnace is then isolated from the cell using thin sheets of mica (~50 micron) above and below the slabs and screwed together using a thin molybdenum sheet. Two molybdenum electrodes (thickness 4mm) are inserted between the two slabs of graphite foils and finally glued using high temperature ceramic glue. The sample is heated using a DC power supply, with an operating range between 13A/10V-150A/26V. For measuring the temperature, a Pt/Pt13%Rh precision thin micro-thermocouple with a junction diameter around 25 micron is used. The junction of thermocouple is inserted between the two parts of the graphite heater foils as shown in figure, such that it can touch the gasket sitting between them. The reproducibility of

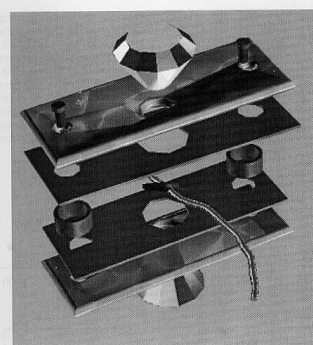
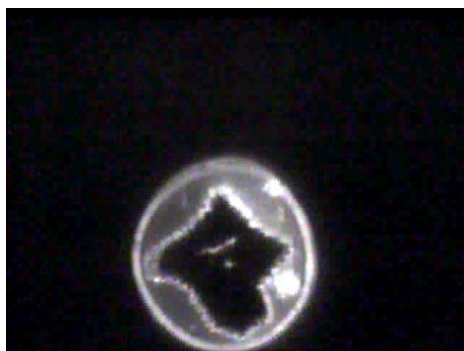


Fig. 1. The double-gasket pressure assemblage for heating a sample electrically in DAC. The wire with a hole is connected to electrical leads isolated from the gaskets with mica plates. See text for a full discussion

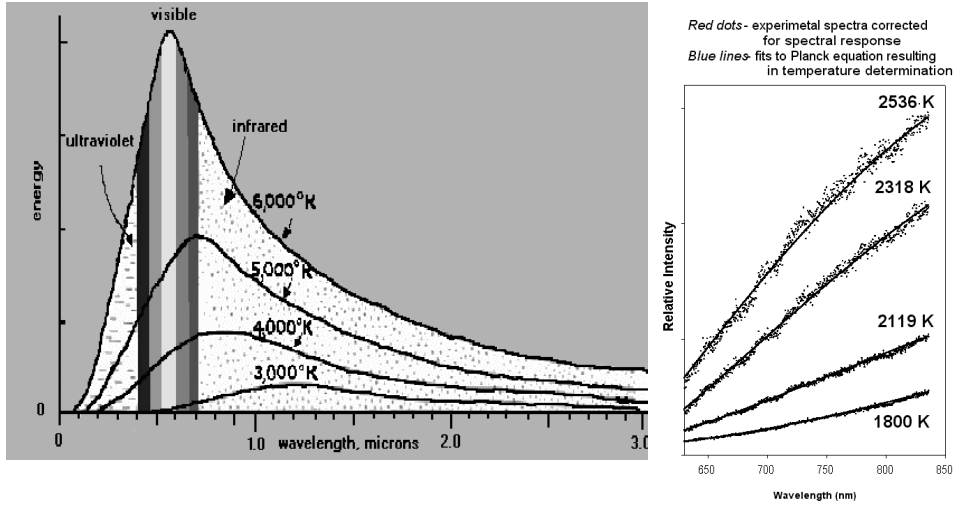
temperature with such type of attachment of thermocouple near the diamond-gasket interface is within 10 K (13). All experiments are carried out with flowing argon, which creates an inert ambient condition and acts as a coolant to the cell. Figure above shows another arrangement of heating cell externally. Another figure shows heating of iron with a laser.

Multiwavelength Spectral Radiometry: The temperature is measured using the method of spectroradiometry (12-14) for heated metals and silicates.

For correct temperature determination wavelength dependent emissivity has to be considered when fitting the spectra to the Planck radiation function. After major advances in instrumentation during the last decade, a poor knowledge of high pressure and temperature emissivities became the main source of systematic errors in temperature measurements in high pressure studies. These errors may range from few tens to several hundreds of degrees depending on the actual emissivity variation with wavelength and the temperature range of a study. Thermal radiation is collected over a range of wavelengths and the resulting spectrum is fitted with Planck's function. The accuracy of measured temperature requires data on emissivity of a sample as a function of pressure, temperature and wavelength (15). In multiwavelength thermometry the

spectral radiance of the target at several wavelengths is curve fitted to Planck's or Wien's equation.

A spectrum of the black body radiation can be described by Planck equation



$$b^0(\lambda, T) = \frac{2\pi hc^2 \lambda^{-5}}{\exp\left(\frac{hc}{\lambda kT}\right) - 1}, \quad (1)$$

where $b^0(\lambda, T)$ is the spectral intensity of the black body radiation at wavelength λ and temperature T , h Planck constant, c light velocity, and k Boltzman constant.

For real (gray) body we can write

$$b(\lambda, T) = \varepsilon(\lambda, T) \frac{2\pi hc^2 \lambda^{-5}}{\exp\left(\frac{hc}{\lambda kT}\right) - 1}, \quad (2)$$

where $\varepsilon(\lambda, T)$ is the body emissivity at given λ and T .

If $hc/\lambda \gg kT$ (valid up to 5000 K at $\lambda < 0.9 \mu\text{m}$), we can use Wien's approximation

$$b^0(\lambda, T) = \frac{2\pi hc^2 \lambda^{-5}}{\exp\left(\frac{hc}{\lambda kT}\right)}, \quad (1a)$$

$$b(\lambda, T) = \varepsilon(\lambda, T) \frac{2\pi hc^2 \lambda^{-5}}{\exp\left(\frac{hc}{\lambda kT}\right)}. \quad (2a)$$

Experimental set up for collecting spectra is described elsewhere (16, 18). Experimentally measured spectrum cannot be described by eq. (2) or (2a) because it includes effects due to geometry of collecting optics, absorption in lenses, sensitivity of spectrometer etc., which can affect spectral intensity. To solve this problem, a calibration function from quartz halogen tungsten lamp (QHTL) is usually used. In addition to the available data on emissivity which many times lacks the dependence

Table 1. Emissivity some metals and oxides at melting temperature.

Compounds	Emissivity*		Melting temperature, K
	ϵ_{800}	Δ	
W	0.34	-72100	3685
Pt	0.44	-241000	2045
Fe	0.28	-782000	1808
Al ₂ O ₃	0.40	-151000	2288
ZrO ₂	0.29	101000	2988
Na ₂ SiO ₃	0.21	-102000	1361

*Emissivity at wavelength λ (in nm) is $\epsilon_{\lambda} = \epsilon_{800} + \Delta(\lambda - 800)/10^9$

on wave-length we also determine a temperature calibration using melting temperatures of a series of metals and oxides as shown in Table 1 (23).

Table 2. Measured melting temperatures of solids using YAG laser at 1 atm. Large errors are shown here from the work in 1993. Since then, we have improved the system such that errors in temperature measurement could be as little as 1%.

Solid	T (K)	T(K), This study
Copper	1356.4	1350 (50)
Fe-Wustite	1642	1620 (30)
Nickel	1726	1745 (35)
Cobalt	1768	1756 (15)
Iron	1808	1800 (30)
Platinum	2045	2043 (35)
Rhenium	3453	3450 (40)
Tungsten	3683	3671 (40)
Diopside	1665	1650 (40)
Corundum	2345	2340 (50)
Enstatite	1830	1840 (50)

Note: The silicates were heated in contact with rhenium.

We use Pt and Re as reference metals (19-22) among others. Fig.2 shows a schematic representation of thermal radiation spectra which when corrected for the optical path using calibration may be fitted with the Wien's approximation of Planck's theory (Fig.above).

Melting criteria: The common criterion in determining melting is the visual observation of motion on the sample surface. In our experiments, we combine this method with the recording of a laser power – sample temperature dependence. We believe this represents a significant improvement in reliability and objectivity of melting determination. In addition to detecting a melting transition, even solid-solid structural and electronic transformations accompanied by no apparent visual change (no motion on the surface) may be recorded due to changed optical and/or transport (conductivity) properties of a sample (23). Moreover, at ultrahigh pressures of several hundreds of GPa, melting detection by visual observation only may become problematic due to the very small size of a sample; it is not even certain that there is any clear convection

during the melting in a DAC at these pressures. The melting criterion by the laser power – sample temperature function requires very stable intensity of a laser beam.

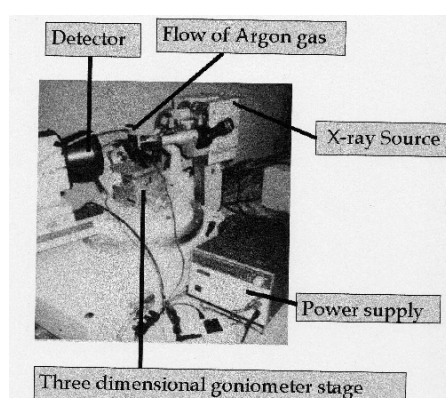
Pressure measurement

Pressure is determined from ruby fluorescence. An important issue in laser heating experiments in DAC is the magnitude of thermal pressure and volume relaxation during a laser heating. When determined by the ruby fluorescence technique, pressures reported in melting experiments are cold pressures as measured at 300 K. These may not be identical to actual melting pressures. In double-side laser heated sample with in situ x-ray, one may use an internal standard with a known equation of state.

The hot sample while under pressure can be studied either by micro-Raman spectroscopy for phase transformation and vibrational spectroscopic data and by x-ray (rotating anode with Siemens new smart CCD). The in-situ x-ray studies permit the determination of phase structures, thermal expansion, compressibility and generally equations of state of solids.

X-ray study

We use both local x-ray facilities as well as the synchrotron facilities at BNL, ESRF and APS. Until we build the FIU x-ray facility, we will use the laboratory at Uppsala. We obtain powder X-ray diffraction data with a Siemens X-ray system consisting of a Smart CCD Area Detector and a direct-drive rotating anode as x-ray generator (18 kW). MoK_α radiation (tube voltage 50 kV, tube current 24 mA, cathode gun 0.1×1 mm) monochromatized by using an incident beam graphite monochromator is passed through a collimator of diameter 200 μm to the sample. The diffracted x-ray is collected on a 512×512 pixels area detector. Data are acquired for different experiments at different fixed 2θ settings of 20 and 30° (corresponding to fixed



positions of the detector) and by varying the sample-to-detector distance (120-260 mm). Settings of the detector are carefully calibrated using three independent standards (Pt, NaCl, Al_2O_3) at each position of the detector. Since a large portion of the Debye ring is measured on the detector surface, it reduces the counting time by the solid angle covered. This angular range also helps in collecting data that might be missed if linear detectors were used, because the area under investigation may have substantial preferred orientation or may recrystallize in experiments with heating (the sample cannot be rotated during heating). Usually data collection time is 10-30 s, but due to small size of our samples (see below), time of collection was 120 s.

For thermal expansion measurement of alloys, we use the *in situ* diffraction patterns recorded on heating and cooling. The specimen is heated by passing an electrical current from 0-20V/0-20A power supply through the sample placed into a versatile pyrophyllite heating cell (as shown in a figure before). The sample consists of a flexible carbon strip (thickness of 0.3 mm) as a heater and scales of the alloy pressed onto its surface with Perkin-Elmer (5 ton/cm²) press. After pressing, the thickness of the carbon strip may decrease to 0.1 mm with a width equal to 2 mm. We carry out several experiments on heating before we find the optimal size of a heater corresponding to the voltage-current characteristics of the power supply (Thunder, 18A-20V) and reach the initial resistivity of the heater of approximately 1 Ohm.

In order to prevent the specimen from oxidation, the experiments must be carried out in an argon-hydrogen flow. A carbon strip is a good heater and which prevents the alloy from oxidation. It is also safe to use carbon in our experiments because carbon does not react with many alloys. Pt-13% Rh microthermocouple with a junction size of 25 μ (Omega Inc.) attached to the graphite strip in contact with heated sample is used for temperature determination.

Synchrotron x-ray

The third generation synchrotrons permit the use of samples of much smaller size that can be heated thoroughly with little thermal gradient. Using the double-side laser heating technique as shown before minimizes the axial thermal gradient. At APS, the x-ray data are collected in energy dispersive mode but it will be soon possible to use monochromatic light and CCD or imaging plates permitting us to obtain a full high resolution powder diffraction pattern from a small and thin sample. For our *in situ* studies, we will combine the electrical heating which is very stable, homogeneous and easy to regulate with laser heating; laser heating in the diamond-anvil cell (DAC) allows us to routinely reach temperatures as high as 4000 K at megabar pressure range. However, combination of laser heating and x-ray require special sample preparation. First of all, sample has to be thin (3-4 μ m) to avoid significant temperature gradients in the axial (loading) direction in the metal. The problem is less severe with double laser-heating. Second, for the same reason, it should be perfectly isolated from diamonds requiring 20-25 μ m thick layers of an insulator. As a result, reflections due to the pressure medium will have a much higher intensity than that of the reflections due to metal. Therefore it is crucial that we use high intensity x-ray source such as the third generation synchrotron x-ray facilities.

In all those cases where evaporation becomes a significant problem due to high temperatures involved and the nature of the solids, it may be necessary to conduct experiments at low to moderate pressures. Such is the case, for example, in melting temperature determination of CaO or silicon nitride. As discussed in the previous section, if an insulator material has to be used in the diamond-anvil cell, it must be non-reactive. We have used various fluids such argon or xenon. The use of salts such as NaCl or CsI has also been made. Nitrides can be heated under nitrogen pressure. All melting temperatures are best determined by observation of the first visible sign of melting. This may be confirmed by *in situ* x-ray or Raman studies.

Application

As emphasized above, practically all high temperature data on phase diagrams, which was difficult to obtain before due to technical difficulties both in containing the heated sample and in measuring the high temperatures above the thermocouple limits can now be attempted with an excellent chance of success. Such data are crucial to the creation of thermodynamic databases and in our modelling the industrial processes and our search for new materials.

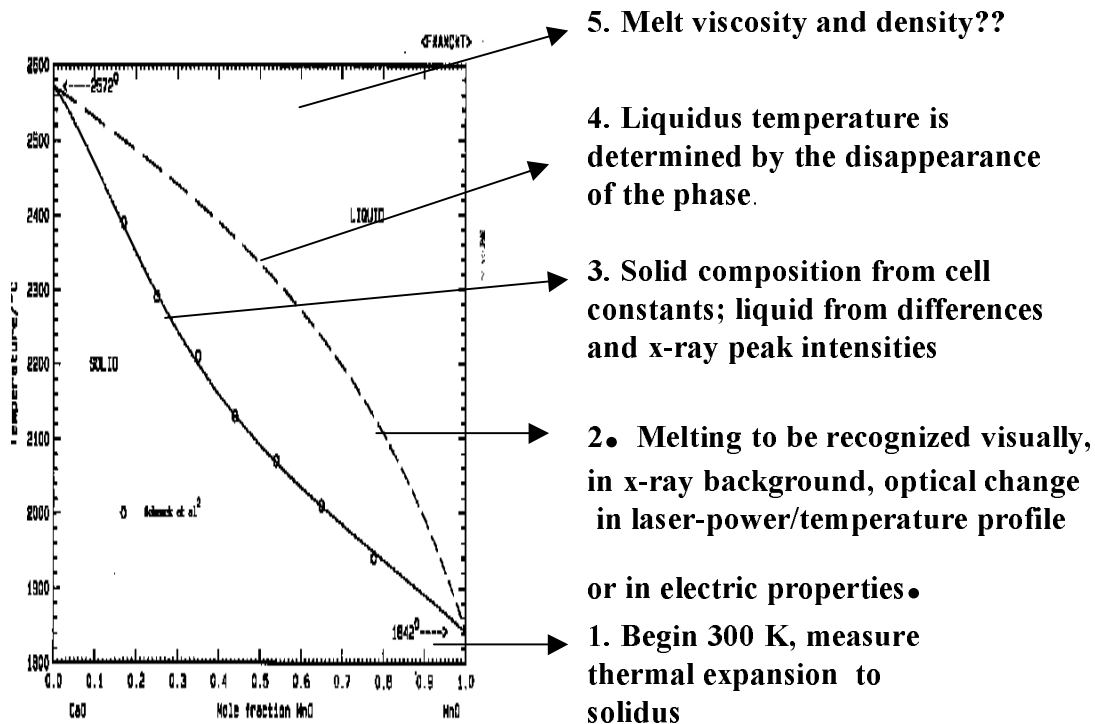


Figure above illustrates the approach to be adopted for experimentally determining the phase diagram data for a series of compositions for a binary solid solution. Similar considerations are applied to other types of phase diagrams.

There are many systems that require attention. We choose here certain systems for which the data at 1 bar is either uncertain or missing and for which high-pressure studies could help improve the current method of synthesis of a known material (e.g. diamonds) or help us synthesize a novel phase (carbide, nitride or oxide).

Carbon-metals

We may consider the carbon-metal (C, Fe-Co-C), and Fe-Co-W systems to illustrate our approach. Carbon phase diagram has never been resolved satisfactorily. The reason is obvious. There is the basic problem of reaching such high temperatures as 4000 K and above with conventional techniques. Additionally there are of course kinetic considerations. In binary and ternary systems, it has been feasible to work only with the carbon poor systems because of the high temperatures involved. Fernandez-Guillermet (1) assessed the thermodynamic data on the Co-C binary. He found that he was severely limited in this attempt because of lack of experimental data (see figure). Similar difficulties exist for all binaries where one of the components is high refractory e.g. C or W.

Carbon: The phase relations will be studied at 1 bar to a high pressure of 300 GPa using in situ techniques of heating and x-ray as discussed later. As the figure above shows there are many ill-defined parts of the phase diagram with little or no structural information on the carbon phases. Melt phase relations were recently computed by Glosli and Ree (AIRAPT-17,1999) which could be experimentally verified. The carbon phase diagram is fundamental to many important industrial substances. By doing these experiments, we will not only obtain x-ray information on the phases but also their thermal expansion and compressibility.

Cobalt-Carbon and Iron-Carbon: For the binary C-Co, the figure shows that experimental information is limited to the Co rich part as shown by the box. At 1 atm, there is limited solid solution of carbon in the fcc phase. This system will be studied from 1 bar to 10 GPa to study the effect of pressure on the solid solution. We will also obtain additional melting data above 2000 K both at 1 bar and at high pressures. For the binary Fe-C, the calculated phase diagrams show a widening field of diamond stability at pressures starting at 5.7 to 6.5 GPa. In spite of the importance of these systems in synthesis of diamonds, experimental information on the pressure effect is rather limited. We will determine phase relations in the relevant part of the diagram from 1000 to liquidus temperatures. For both these binary systems, we will study the feasibility of doping of diamonds (semi-conductor) by dropping the temperature of the melt to the diamond stability field (2).

For both binary systems, thermal expansion and compressibility data (both as a function of pressure and temperature) will be provided.

Titanium-Carbon: The calculated phase diagram of TiC has a large stability field. Again due to difficulty in achieving the temperatures needed to study the phase diagram, the experimental information is meagre. We will study the system with in situ x-ray on heated and pressurized samples and obtain both phase relations and physical property data. We have recently determined the compressibility of TiC (3).

W-Carbon: The system needs to be studied in detail for pressure-volume-temperature properties of the carbides. There are very few experimental data either on in situ structures or on the liquidus.

Light Alloys

Binary alloys such as Fe-Al and Fe-Si have been experimentally and theoretically studied but again due to lack of suitable techniques, these studies are mostly confined to x-raying the quenched samples. In a study of Fe-Al binary (5), we found structural details through in situ studies at high temperature, which were not known before. The phase transformation from bcc to fcc in the Fe-5%Al alloy was observed between 1203 to 1238 K while the 10%Al alloy had a primitive cubic structure above 1300 K. We need similar data on several binaries such as Fe-Si and Ni-Al.

Ceramics

As for the refractory metals, the data on many single or binary phases for refractory oxides are missing particularly at high temperatures.

The binaries in the FeO-MnO-MgO-NiO system: The binaries generally miscible systems with moderately high liquidus temperatures and yet the data are mostly missing. For CaO-MnO and MgO-MnO, only the solidus points are available, while for FeO-MnO the solidus is missing. For CaO-NiO, all data above the eutectic temperature is missing and the eutectic composition is calculated by “petrographic” approximation. There are no experimental data on the MnO-NiO binary.

Zirconia-FeO and Zirconia-MnO: For ZrO_2 -FeO, there are no experimental data above 2000 K and no structural data. Similarly for the second binary, there are very few data available from one report.

Melting temperatures of several refractory oxides: The melting temperatures of practically all oxides melting above 2500 K, particularly those that sublime (e.g. CaO), require a re-determination. Such oxides include MgO, CaO (T given between 2800 to 3200 K in different measurements), BeO and SrO. We may add to this list a number of other oxides of rare-earth elements. H. Seifert (pers. Comm.) finds that all the melting temperatures of the following silicates Yb_2SiO_5 , $\text{Yb}_2\text{Si}_2\text{O}_7$, Y_2SiO_5 and $\text{Er}_2\text{Si}_2\text{O}_7$ need to be determined.

Melting temperatures of carbides and nitrides: A similar difficulty as for refractory oxides discussed above exists in determining the melting temperatures of carbides and nitrides. An example may be given of Si_3N_4 where the problem of sublimation becomes very difficult to control as one approached the melting temperature. This problem was solved by determining the temperature of melting at moderate pressures and then extrapolating the melting curve to zero pressure (Y. Ceranius, Master's thesis, Uppsala University, 1996). Another example is that of GaN. The calculated phase diagram predicts incongruent sublimation (26).

References

1. A. Fernandez Guillermet : Study of the thermodynamic properties of the Co-Fe-Ni-W-C system using CALPHAD technique. Ph. D. Thesis, Royal Inst. Technology, Stockholm, Sweden, (1988).
2. M. I. Eremets, Semi-conducting diamond. *Semicond. Sci. Technol.* 6, (1991) 439-444.
3. N. A. Dubrovinskaia, L. S. Dubrovinsky, S. K. Saxena, R. Ahuja and B. Johansson, High-pressure study of titanium carbide. *J. Alloys & Comp.* 289 (1999) 24-27.
4. N. A. Dubrovinskaia, L. S. Dubrovinsky, S. K. Saxena, M. Selleby and B. Sundman, Thermal expansion and compressibility of $\text{Co}_6\text{W}_6\text{C}$. *J. Alloys & Comp.* 285, (1999) 242-245.
5. N. A. Dubrovinskaia, L. S. Dubrovinsky, A. Karlsson, S. K. Saxena and B. Sundman, Experimental study of thermal expansion and phase transformations in iron-rich Fe-Al alloys. *Calphad* 23, 69-84 (1999).
6. Dubrovinskaia N. A., Dubrovinsky, L.S. and Saxena S. K. Thermal expansion of chromium (Cr) to melting temperature. *Calphad* 21, 497-508.
7. S. K. Saxena and L. S. Dubrovinsky (1996) Nd-YAG laser heating temperature measurements in diamond-anvil cell. In: *Advanced Materials '96, Proceedings of the 3rd NIRIM International Symposium on Advanced Materials*, Tsukuba, Japan, March 4-8, 1996, 137-142.
8. Mao, H. K., Xu, J. and Bell, P.M. Calibration of the ruby pressure gauge to 800 kbar under quasihydrostatic conditions. *J. Geophysical Res.* 91, 1986, 4673-4676.

9. Leonid S Dubrovinsky, Surendra K Saxena, Peter Lazor, High-pressure and high-temperature *in situ* x-ray diffraction study of iron and corundum to 68 GPa using internally heated diamond anvil cell. *Phys. Chem. Minerals*, 1998, 434-441.
10. P. Lazor, G. Shen, S.K. Saxena, Laser-Heated Diamond Anvil Cell Experiments at High Pressure: Melting Curve of Nickel to 700 kbar. *Phys. Chem. Minerals*, **20**: 86-90, 1993.
11. G. Shen, H. K. Mao, R. J. Hemley, T. S. Duffy and M.L.Rivers, Melting and crystal structure of iron at high pressures and temperatures. *Geophys. Res. Letters* 25, 373-376, 1998.
12. S. Rekhi, L. S. Dubrovinsky and S. K. Saxena, Study of temperature-induced ruby fluorescence shifts upto a pressure of 15 GPa in an externally heated diamond-anvil cell. *High Temperatures-High Pressures*(in press).
13. Jeanloz, R. and A. Kavner, Melting criteria and imaging spectroradiometry in laser-heated diamond-cell experiments, *Trans. Royal Soc. London*. Lazor, P. and Saxena, S.K. (1996) Discussion comment on melting criteria and imaging spectroradiometry in laser-heated diamond-cell experiments (by R. Jeanloz & A. Kavner), *Phil. Trans. R. Soc. Lond. A* **354**, 1307-1313.
14. Bohler, R., Temperature in the Earth's core from melting-point measurements of iron at high pressures, *Nature*, 363, 534-536, 1993.
15. Lazor, P., G. Shen, and S. K. Saxena, Laser-heated diamond anvil cell experiments at high pressure: melting curve of nickel up to 700 kbar, *Phys. Chem. Minerals*, 20, 86-90, 1993.
16. Corwin, R. R. and A. Rodenburgh, Temperature error in radiation thermometry caused by emissivity and reflectance measurement error, *Applied Optics*, 33, 1950-1957, 1994.
17. Saxena, S. K. and L. S. Dubrovinsky, Nd-YAG laser heating temperature measurements in diamond-anvil cell. In: *Advanced Materials '96, Proceedings of the 3rd NIRIM International Symposium on Advanced Materials*, Tsukuba, Japan, March 4-8, 1996, 137-142, 1996.
18. Coates, P. B., Multi-wavelength pyrometry, *Metrologia*, 17, 103-109, 1981.
19. Andreic, Z., Distribution temperature calculations by fitting the Planck radiation curve to a measured spectrum, *Appl. Opt.*, 31, 126-130, 1992.
20. Cabannes, P. F., Facturs de reflexion et d'emission des metaux, *J. de Physique*, 28, 235-248, 1967.
21. Hiernaut, J.-P., F. Sakuma, and C. Ronchi, Determination of melting point and the emissivity of refractory metals with a six-wavelength pyrometry, *High Pressure - High Temperature*, 21, 139-148, 1989.
22. Wall, R. N., D. R. Basch, and D. L. Jacobson, High-temperature spectral emissivity of several refractory elements and alloys, *J. Materials Engineering and Performance*, 1, 679-684, 1992.
23. S. K. Saxena, G. Shen, P. Lazor, Experimental evidence for a new iron phase and implications for Earth's core. *Science*, 260, 1312-1314, 1993.
24. Davydov, A. and anderson, T.J. Thermodynamic analysis of the Ga-N system. III-V Nitride Materials and Processes III, Eds T.D. Moustakas, S.E. Mohny and S. J. Pearton, ECS (Boston, M.A., 1998), PV 98-18, pp. 38-49.