Using containerless techniques to study materials in extreme and non-equilibrium conditions

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Containerless methods completely eliminate mechanical contact with a sample. This unique feature enables work on materials at extreme temperatures and in controlled atmospheres and often provides access to supercooled or supersaturated liquids and novel glasses. Containerless methods will be briefly described and surveyed. Aerodynamic and electrostatic levitation will be discussed in more detail and their applications illustrated with examples of processing, structure and property measurements on molten materials, hot crystals and glasses. Some practical issues such as non-contact temperature measurements will be briefly discussed. The use of containerless methods to study materials in extreme conditions will be summarized in the context of the current state of the art and potential opportunities for further development.

Deeply undercooled oxide melts

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Deep undercooling of molten Al_2O_3, Y_2O_3 and $Y_3Al_5O_{12}$ (YAG) was achieved with CO_2 laser beam heated and melted oxides in the aero-acoustic levitator (AAL)*. 1800 Hz video results will be shown that illustrate (i) stinger-induced crystallization of Al_2O_3 at various degrees of undercooling, (ii) recalescence and solid/solid phase transition of Y_2O_3 and of relatively slow crystallization of YAG undercooled by more than 1000 Celsius. Spontaneous nucleation and crystallization of undercooled Al_2O_3 occurred at a highly reproducible temperature. Molten YAG could be held at a deeply undercooled temperature for more than 30 minutes. Implications for further research on undercooled melts will be discussed.

* Nordine, P. C., D. Merkley, J. Sickel, S. Finkelman, R. Telle, A. Kaiser, and R. Prieler, “A levitation instrument for containerless study of molten materials,” Rev. Sci. Instrumen. 83,125107 (2012).

Stable and metastable liquid immiscibility in the ZrO_2-SiO_2 system observed by containerless aero-acoustic levitation

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In the technically important ZrO_2-SiO_2 phase system we studied liquid phase formation and solidification by means of the containerless aero acoustic levitation preventing contamination by contact to crucible material. The behavior of the melt was recorded by a high-speed camera allowing for direct observation of convection, formation of emulsified reams and solidification. For the first time since 1956, we re-treated the liquidus miscibility gap between 59.5 mol-% and 78 mol-% SiO_2 at 2250°C with the critical point at 2430°C and 70 mol%. Cooling down ZrO_2-rich liquids with 700-1000 K/s preserved equilibrium microstructures of the monotectic equilibrium with ZrO_2-dendrites in a matrix of silica glass and secondary ZrO_2. Quenching from inside the miscibility gap resulted in frozen-in Bénard-Marangoni cell patterns of metastably undercooled droplets of ZrO_2-rich and SiO_2-rich emulsions. Chemical analyses of these areas made the construction of the metastable continuation of the miscibility gap possible to temperatures as low as 1000°C. As ZrO_2 crystallizes without any solid solubility for SiO_2, further differentiation of emulsified droplets occurs by draining out SiO_2-rich glass into the matrix. Internal as well as external microstructures of the droplets remind to the partitioning and coagulation behavior of alkali-borosilicate glasses.

Literature: Telle, R., Greffrath, F., Prieler, R.: Direct observation of the liquid miscibility gap in the zirconia-silica system. J. Europ. Ceram. Soc. 35 (2015) 3995-4004

Atomic scale disorder in UO_2 at high temperatures

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Aerodynamic levitation enables experiments on ceramics at high temperatures in excess of 3000 degrees Kelvin eliminating any interactions with a container. This talk outlines a series of high-energy x-ray diffraction measurements that have been performed on nuclear materials at the Advanced Photon Source. The work can be grouped in to four main themes (i) High temperature crystallography: The pre-melting behavior of the oxygen sub-lattice in UO_2 is manifested by a second order λ-transition at 2670K and a crystallographic Rietveld refinement of our x-ray data show a slightly steeper trend of the thermal expansion compared to literature values, yet are in good agreement with existing isotropic thermal parameters (ii) Liquid state structure measurements: Following our initial pair distribution function measurements on the structure of liquid UO_2 we have modeled the results using classical molecular dynamics simulations. A small pre-peak observed in the number-number partial structure factor indicates topological ordering in the melt and it's origin analyzed using a Voronoi tessellation procedure (iii) Corium studies: Understanding the atomic scale interactions in corium or the Chernobyl “lavas” that form during core meltdown are important for modeling severe accident studies. One of the most important interactions in the lava is that of the molten fuel and its cladding material, which can be represented by the UO_2-ZrO_2 system. We find that the first metal-oxygen peak in the x-ray pair distribution function can be reasonably approximated by a linear combination of the UO_2 and ZrO_2 end-members suggesting that UO_2-ZrO_2 can be represented as an ideal associated solution (iv) Deviations from stoichiometry: Changing the levitation gas allows us to explore sample compositions other than stoichiometric UO_2. A preliminary analysis of the molten UO_{2-X} x-ray pair distribution functions have been analyzed and show only a slight lengthening of the average U-O bond length in more reducing atmospheres.

Synchrotron x-ray measurements of levitated liquids and glasses

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The combination of synchrotron x-ray measurements and levitation techniques is a powerful approach to reveal the structure of high-temperature liquids, as well as of glasses with limited glass forming ability. In particular, aerodynamic levitation is very useful to measure total scattering from oxide liquids, and to prepare bulk oxide glasses with low glass forming ability. The high-energy x-ray scattering technique, the element specific anomalous x-ray scattering method and recent developments of containerless processing techniques for extremely high-temperature liquids at SPring-8 are introduced. Furthermore, scientific investigations of oxide glasses and high-temperature liquids reported over the past five years are reviewed.

Investigation of some nuclear and refractory materials under extreme conditions

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A thorough assessment of refractory and ultra-refractory materials behavior under extreme conditions (of temperature, pressure and chemical environment)is paramount in sensitive fields like the choice of coatings for aerospace applications and the safety of nuclear plants, particularly under hypothetical accidental conditions. Recent studies are presented on different types of refractory and nuclear materials under extreme conditions. In particular, the European Commission‘s JRC-ITU in Karlsruhe (Germany) developed an innovative laser method to measure very high temperature ($1500\ K < T < 5000\ K$) properties based on quasi-containerless conditions with variable durations of the heating cycles (milliseconds to seconds). Example results are shown on the melting and vaporisation behavior of refractory oxides and ultra-refractory carbides (HfC, TaC, ZrC) and on laboratory simulations of severe accidents in nuclear power plants. Materials characterisation campaigns and thermodynamic calculations supporting the interpretation of data obtained under extreme conditions are also shown and discussed.

SiO_2 Scale Structure and Defects Formed during Oxidation of SiC in High Temperature Air and Steam

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The structure of the SiO_2 scale formed during high temperature oxidation of SiC fibers affects oxidation kinetics and the scale residual stress. This affects fiber properties and therefore the mechanical properties and environmental durability of SiC-SiC ceramic matrix composites used for high temperature structural applications. Several types of structures and defects will be discussed: **1.** Porosity that often, but not always, forms at the interface between inner scale that formed as cristobalite and outer scale that formed originally as glass and later crystallized. **2.** Heavily deformed, fine-grained cristobalite scale that forms as cristobalite and deforms to accommodate oxidation volume expansion. Dynamic recrystallization occurs during oxidation and forms subgrains that increase in size with oxidation temperature and time. Increased subgrain size in turn reduces the oxidation rate by enhanced O_2 transport through grain-boundary diffusion, causing anomalous time dependence for parabolic oxidation kinetics. **3.** Under some conditions tridymite forms instead of cristobalite, which has a large effect on scale thermal residual stress. **4.** During oxidation in steam, under some conditions glass scale dewets and spheroidizes on the SiC surface. This causes an unusual form of active oxidation where SiO_2 that rapidly forms on bare SiC surface wicks to the spheroids as fast as it forms. Scale crystallization increases scale viscosity and inhibits this process. **5.** Under some conditions carbon is incorporated in the scale, which in turn affects scale viscosity and O_2 permeability. Efforts to quantify, correlate, and explain the various phenomena will be discussed.

Thermodynamics of Oxides from Knudsen Effusion Mass Spectrometry

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Knudsen Effusion Mass Spectrometry (KEMS) is a powerful tool to study the vaporization of condensed phases. In equilibrium, the measured vapor pressures relate to the thermodynamic activities in the condensed phase and thus yield a variety of thermodynamic quantities. The NASA Glenn instrument is described in addition to a number of interesting challenges in oxide vapor measurement studies. These challenges include~~:~~ equilibration issues, reactivity with the cells, complex vaporization behavior, and the need for very high temperatures to attain measureable signals. Every material system requires a different approach due to these complexities. We present examples of our studies, which include B_2O_3, rare earth silicates, and the olivine system.

In-Situ High Temperature Synchrotron Diffraction Studies of Oxide Ceramics

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A four lamp furnace capable of 2,000°C in air coupled with a rapid image plate detector for use at the APS and NSLS synchrotron sources was developed in our lab. Coupled with Rietveld and PDF analyses we have shown the way to (i) measure thermal expansion coefficients in 3D (ii) determine the principal axes of thermal expansion and their orientation wrt crystal axes (iii) present the thermal expansion tensor quantitatively in orthonormal space via a PROGRAM CTEAS algorithm (iv) use these principal thermal expansion strain axes to indicate likely orientation relations in phase transformation (v) measure the lattice parameters, hysteresis, kinetics and activation energies for phase transformations in situ on heating and cooling (vi) quantitatively determined phase equilibria in a ternary phase diagram (vii) follow in situ chemical reactions. Accuracies of ± 4 °C in temperature to 1840 °C and lattice parameters to fifth decimal places in nm are achieved.

Precise Structure Analysis of Oxide Materials through Neutron and Synchrotron Powder Diffractometry up to 1830 K

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We review our recent works on the precise crystal structure analysis of oxides including the visualization of diffusional pathway of mobile ions and chemical bonding in ceramic materials through neutron and synchrotron X-ray powder diffraction experiments up to 1830 K. Our group has developed new high-temperature neutron and high-resolution synchrotron diffraction techniques to study the precise crystal structures, nuclear and electron density in inorganic materials up to 1900 K. These techniques enabled precise structural analysis leading to diffusion path and structural disorder in ionic conductors. Here we review our works on the positional disorder and diffusion path of oxide ions in Bi_2O_3, $(La_{0.8}Sr_{0.2})(Ga_{0.8}Mg_{0.15}Co_{0.05})O_{2.8}$, CeO_2, $Bi_{1.4}Yb_{0.6}O_3$, $Ce_{0.93}Y_{0.07}O_{1.96}$, and $La_{0.64}(Ti_{0.92}Nb_{0.08})O_3$ at high temperatures. We also describe the diffusion path of Li cations in Li-doped lanthanum titanate perovskite $La_{0.62}Li_{0.16}TiO_3$ and of Cu cations in copper iodide CuI. These were studied through the nuclear/electron density distribution obtained by a combined technique including a Rietveld refinement and a maximum-entropy method (MEM)-based pattern fitting of the neutron-powder-diffraction data. We found that the mobile ions in fluorite-type ionic conductors have a complicated disorder spreading over a wide area and shift to the <111> directions from the ideal fluorite site at high temperatures. The fast oxide-ion conductors $Bi_{1.4}Yb_{0.6}O_3$ and $Ce_{0.93}Y_{0.07}O_{1.96}$ exhibited a curved diffusion pathway along the <100> direction. The Cu cation conductor has also a fluorite-type structure and curved diffusion pathway along the <100> direction. The curve feature would be common for various ionic conductors. We have demonstrated that the diffusion path of mobile oxide ions in the lanthanum gallate-based compound was not along the straight line between the ideal positions, but exhibited an arc shape away from the B-site cation $(Ga_{0.8}Mg_{0.15}Co_{0.05})$. The diffusion pathway forms a three-dimensional network. The double perovskite-type $La_{0.64}(Ti_{0.92}Nb_{0.08})O_3$ exhibits a curved diffusion pathway at high temperatures. The diffusion pathway in the $La_{0.64}(Ti_{0.92}Nb_{0.08})O_3$ forms a two-dimensional network. We also reported for the first time the diffusional path of oxide ions in a K_2NiF_4-type mixed conductor $(Pr_{0.9}La_{0.1})_2(Ni_{0.74}Cu_{0.21}Ga_{0.05})O_{4+\delta}$, through a high-temperature neutron powder diffraction study. We also present in situ studies of the phase transitions in ceria-zirconia, calcium titanate perovskite, hydroxyapatite and so on.

Fe and Ti K-edge x-ray absorption near-edge structure spectroscopy of aerodynamically levitated oxide melts and glasses

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The local structure about Ti^{4+}, Fe^{3+} and Fe^{2+} cations in oxide melts and glasses has been studied using both high-energy x-ray diffraction (APS, 6-ID-D) and x-ray absorption near edge structure (XANES) spectroscopy (APS, 20-BM-B). *In-situ* measurements on melts were enabled by the use of an aerodynamic levitation system combined with CO_2 laser heating. Oxygen partial pressure was controlled using an environmental chamber and by varying the levitation gas composition, allowing various Fe^{3+}/Fe^{2+} ratios to be accessed. The results show that both ferric and ferrous iron and titanium typically have average coordination numbers close to 5, or less, in the molten state. Furthermore, changes in the XANES spectra and diffraction patterns upon melt quenching to form glasses imply that Ti^{4+} coordination to oxygen *increases* during cooling, but remains smaller than the octahedral value of 6 found in most of the corresponding crystalline materials. Changes in iron environment on glass formation are also evident, but interpretation is complicated by possible oxidation during quenching and the presence of both Fe^{3+} and Fe^{2+} which may display differential changes. Compositions were chosen from the FeO-Fe_2O_3-TiO_2-MgO-CaO-Al_2O_3-SiO_2 system, including various endmembers, as well as the binary alkaline-earth and rare-earth titanates. Future work should include the study of redox kinetics in the context of aerodynamically levitated melts.

Experimental phase diagram determination and Thermodynamic optimization and of Li_2O-Na_2O-MgO-CaO-Al_2O_3-SiO_2 system

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A self-consistent thermodynamic database for the Li_2O-Na_2O-CaO-MgO-Al_2O_3-SiO_2 system was developed based on existing and new experimental phase diagram and thermodynamic data. The new experiments were conducted between 800 and 1550 °C using sealed Pt and Au_{75}-Pd_{25} crucibles to hinder any mass loss from the volatile alkali-rich starting materials. Differential Scanning Calorimetry (DSC) and Thermo-Gravimetric Analysis (TGA) were employed together with the quenching method to investigate phase stabilities and transitions. Phase characterization was performed using X-ray diffraction (XRD), back-scattered electron (BSE) imaging and Electron Probe Micro Analysis (EPMA). The DSC/TGA and quenching experiments produced both the same results. Numerous phases, like Li_2MgSiO_4 and Li_2CaSiO_4, with little information about polymorphs and stability, were synthesized. The new experimental information allowed us to resolve inconsistencies in previous experimental data and to constrain our thermodynamic assessments. Several complex solid solutions like Li-spinel, ^{2}-eucryptite, and ^{2}-spodumene were modeled for the first time by considering their lattice structure and crystal chemistry. Our new thermodynamic database reproduces all the reliable phase assemblages in the Li_2O-Na_2O-CaO-MgO-Al_2O_3-SiO_2 system and has a high predictive ability for the other unknown isopleths. This thermochemical knowledge can be used for process and material design in applications for steelmaking, glassmaking, ceramic engineering, solid-state ionic, and fuel cells; it will be also useful in understanding phase relations of geological materials.

Calculations of heat of fusion and melting temperature via an automated *ab initio* tool

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Computational methods nowadays complement and help corroborate experimental measurements, especially in situations with challenging experimental conditions. Here we demonstrate how key material properties that provide guidance in the design of refractory materials can be accurately determined via ab initio thermodynamic calculations. In particular, we introduce our recently developed computer code, SLUSCHI, for automated *ab initio* calculations of heat of fusion and melting temperature. The SLUSCHI code automates the whole complex and time-consuming procedures of setting up these calculations, and drastically simplifies them into several easy computer commands. Various examples of its application in refractory oxides are given, including Al_2O_3, Y_2O_3 and $La_2Zr_2O_7$. The capability of automated and accurate calculations of thermodynamic properties also opens the way to *ab initio* screening and discovery of refractory materials.

Charge distribution in nano-scale grains of magnesium aluminate spinel

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Charge distribution in magnesium aluminate spinel (MAS) results in the formation of a space-charge region that plays a critical role in assigning functional properties. Significant theoretical advances explaining this phenomenon have been accomplished, even though quantitative experimental support from nano-scale granular MAS is only indirect. In this work, the electrostatic potential distribution in nano-scale grains of non-stoichiometric MAS ($MgO_{0.95}Al_2O_3$ and $MgO_{1.07}Al_2O_3$) was measured by off-axis electron holography and compared to the distribution of cations and defects in this material as measured by electron energy-loss spectroscopy. In this manner, we studied the roles of composition, grain size and applied electric field on the formation of a space-charge region. We quantitatively demonstrated that regardless of grain size, the vicinity of $MgO_{0.95}Al_2O_3$ grain boundaries presented an excess of Mg^{+2} cations, whereas the vicinity of $MgO_{1.07}Al_2O_3$ grain boundaries included an excess of Al^{+3} cations. The degree of structural disorder (i.e., the inversion parameter), indicated that as-synthesized MAS were significantly disordered (between 0.37 and 0.41), with values decreasing toward equilibrium ordering values following annealing (between 0.27 and 0.31). The application of an external 150 Vcm^{-1} electric field during annealing further enhanced lattice ordering (between 0.16 and 0.19). Such variations in the distribution of cations and defects should determine the space-charged potential (SCP). However, using these measurements to calculate the SCP was not possible due to the wide range of values reported for formation energies of defects (0.82-8.78 eV). Consequently, we correlated local ionic ordering with electrostatic potential in non-stoichiometric MAS. The magnitudes of the SCP in both $MgO_{0.95}Al_2O_3$ and $MgO_{1.07}Al_2O_3$ decreased following annealing from -3.4 ±0.3V and +2.0 ±0.2 V to -2.0 ±0.2 V and +1.6 ±0.1 V, respectively.

International Research Conference on
Structure and Thermodynamics of Oxides at High Temperature
October 20 – 22, 2016 |University of California, Davis

Themochemical measurements for alkaline-earth molybdates as a part of the OECD NEA TDB Mo project

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The OECD/NEA Thermochemical Database (TDB) Project (www.oecd-nea.org/dbtdb/) provides a database of chemical thermodynamic values treating the elements related to nuclear waste management. The present investigation was carried out as a part of the TDB Mo project. Molybdenum is generated as fission product from uranium in the operating nuclear reactor. It is a harmful element as it forms hygroscopic crystals, known as "yellow phases" in borosilicate nuclear waste glasses. The host crystals of the yellow phases are Na_2MoO_4 and $CaMoO_4$ depending on the composition and process for making nuclear waste glasses. In order to understand the phase stability of the yellow phases, the thermodynamic properties for the end members should be inevitably necessary. In the present study, the $C^{\circ}_{p,\mathrm{m}}$ data for $CaMoO_4$ [1], $SrMoO_4$ [2] and $BaMoO_4$ [3] were measured from 2 K to high temperatures. Thier standard Gibbs energies of formation, $\Delta_\mathrm{f}G^{\circ}_\mathrm{m}$ (T K), were determined by combining the $C^{\circ}_{p,\mathrm{m}}$ data with the standard enthalpies of formation, $\Delta_\mathrm{f}H^{\circ}_\mathrm{m}$ (298.15 K).

Figure 1 shows the $\Delta_\mathrm{f}G^{\circ}_\mathrm{m}$ (T K) data for $CaMoO_4$ [1], $SrMoO_4$ [2] and $BaMoO_4$ [3]. Although they were close toghether, their phase stabilities were found to be increased as the atomic numbers of alkaline-earth components increased. The $\Delta_\mathrm{f}G^{\circ}_\mathrm{m}$ (T K) data for the related molybdates of Ag_2MoO_4, $NiMoO_4$ [4], $FeMoO_4$, $ZrMo_2O_8$, $UMoO_6$, and $ThMo_2O_8$ were revived by Morishita as a reviwer of the TDB Mo project [1]. They were summarised in **Fig.2**. The most stable molybdate was found to be $BaMoO_4$. Enough cooling rate should be kept for depressing crystallization of the yellow phases during waste glass making.

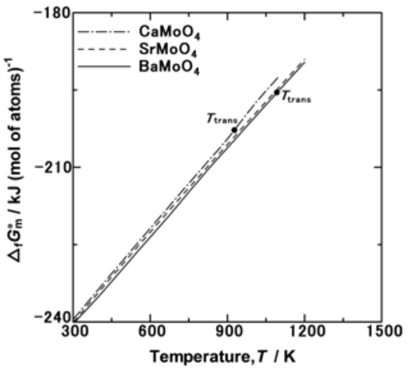

Fig. 1 The present obtained $\Delta_\mathrm{f}G^{\circ}_\mathrm{m}$ (T K) for $CaMoO_4$, $SrMoO_4$ and $BaMoO_4$.

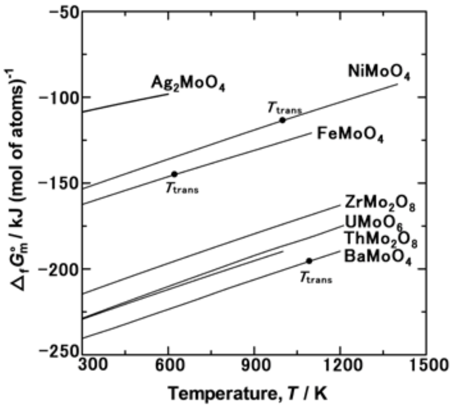

Fig. 2 The $\Delta_\mathrm{f}G^{\circ}_\mathrm{m}$ (T K) for molybdates [1].

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Mechanical Damping and Polarization of 8 mol% YSZ

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8 mol% Yittria Stabilized Zirconia (YSZ) with high ionic conductivity is currently essential material for highly-efficient and environmentally-friendly energy technologies, such as solid oxide fuel cells (SOFCs). Mechanical properties, as well as electrochemical properties, of 8YSZ are significant to reliability and durability of SOFCs which work under harsh environment including high temperature, mechanical stress, electrical field, etc. In this study, mechanical behaviors of 8YSZ were studied by cycling compression testing and Dynamic Mechanical Analysis (DMA) in the 25 °C – 600 °C temperature range. Both testing methods demonstrate significant frequency dependent damping in the 50 °C - 500 °C temperature range that can be attributed to reorientation of oxygen vacancy-dopant clusters. In-situ neutron diffraction test was used to verify the change of oxygen vacancy complexes under stress. In addition, electro-mechanical coupling tests were carried on in the same temperature range. The coupling between electrical and mechanical behavior of 8YSZ in 25 °C - 600 °C temperature range is discussed in details in this paper

In-situ Phase Diagram Determination of the HfO_2-Ta_2O_5 Binary up to 3000 °C

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Ceramic equilibrium phase diagrams have proved to be difficult to produce for materials above 1500 °C. We demonstrate that in-situ X-ray diffraction of laser heated levitated samples can be used to elucidate phase fields. In these experiments, solid spherical samples are suspended and rotated in plane by an air stream through a conical nozzle, heated by 400 W CO^2 laser at Argonne National Labs beamline 6-ID-D. X-ray diffraction patterns suitable for Rietveld refinement can be collected at 100 °C temperature intervals and can be used to determine the phase fraction of phases present. The temperature of each sample was determined based on crystallographic thermal expansion data collected by using powder diffraction in conjunction with the Quadrupole Lamp Furnace (QLF) at beamline 33-BM-C. HfO_2-Ta_2O_5 was used as an example system.

Thermochemistry of $CaO-MgO-Al_2O_3-SiO_2$ (CMAS) and Advanced Thermal and Environmental Barrier Coating Systems

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$CaO-MgO-Al_2O_3-SiO_2$ (CMAS) oxides are constituents in a broad number of materials and minerals which have recently inferred to discussions in materials science, planetary science, geochemistry and cosmochemistry communities. In materials science, there is increasing interest in the degradation studies of thermal (TBC) and environmental (EBC) barrier coatings of gas turbines by molten CMAS. CMAS minerals usually are carried by the intake air into gas turbines, e.g. in aircraft engines, and their deposits react at high temperatures (>1000 °C) with the coating materials. This causes degradation and accelerated failure of the static and rotating components of the turbine engines. We discuss some preliminary results of the reactions between CMAS and Rare-Earth (RE = Y, Yb, Dy, Gd, Nd and Sm) oxide stabilized ZrO_2 or HfO_2 systems, and the stability of the resulting oxides and silicates. Plasma sprayed hollow tube samples (2.2 mm diameter and 26 mm height) were half filled with CMAS powder, wrapped and sealed with platinum foil, and heat treated at 1310 °C for 5h. Samples were characterized by differential scanning calorimetry, X-ray diffraction and cross section electron microscopy analysis.

Calorimetric Measurement of Interface Enthalpy of Nanocrystalline Silver(I) Oxide (Ag_2O)

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The interface enthalpy of nanocrystalline silver(I) oxide ($Ag_2O{\cdot}nH_2O$) was measured. $Ag_2O.nH_2O$ nanocrystalline samples of varying surface areas and degrees of agglomeration were synthesized by wet chemical technique. Interface areas were estimated by comparing the surface areas measured by N_2 adsorption to the crystallite sizes refined from X-ray diffraction data. The interface enthalpy was verified by utilizing thermodynamic cycle, using enthalpy of solution measurements in 25% HNO_3 at room temperature solution calorimetry. The interface enthalpy of the nanocrystalline $Ag_2O{\cdot}nH_2O$ is (0.842 ± 0.508 J/m^2). This work provides the first calorimetric measurement of the interface enthalpy of nanocrystalline silver(I) oxide ($Ag_2O.nH_2O$).

Calorimetric Measurements of Surface Energy of Amorphous HfO_2 Nanoparticles from Gas Phase Condensation

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Measuring the surface energy of nanomaterials is essential for calculating and predicting their thermodynamic stabilities. In the present work, surface energy of amorphous hafnium oxide (am-HfO_2) nanoparticles was measured using various calorimetric techniques. Am-HfO_2 nanoparticles were synthesized by condensation from gas phase generated through laser evaporation of bulk HfO_2 targets in a controlled oxygen environment. Absence of water on the surface of am-HfO_2 nanoparticles was confirmed by zero weight loss on heating the sample to 400 ^oC under Ar atmosphere inside the glovebox. The surface energy of the am-HfO_2 was assessed using high temperature oxide melt solution calorimetry, differential scanning calorimetry and water adsorption calorimetry. The measured surface energies were 0.79 ± 0.12 J/m^2, 0.47 J/ m^2 and 0.59 J/ m^2, obtained by high temperature oxide melt solution calorimetry, differential scanning calorimetry and water adsorption calorimetry, respectively. The difference between the surface energy values is about 0.3 J/m^2 which is within the experimental uncertainties and different assumptions for each technique.

The work was supported by the National Science Foundation Award DMR-1506229.

"Drop-n-catch" approach to calorimetry of laser heated levitated alumina and yttria above 2000 °C

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Design and processing of ultra-high-temperature materials (aerospace and nuclear applications) demand detailed understanding of thermodynamic properties of their constituents. Nevertheless there is a lack of experimental thermodynamic data above 2000 °C. Even for La_2O_3, Y_2O_3, HfO_2, and ZrO_2 binary oxides, high temperature data are often missing and evaluated with a number of assumptions. Among the rare earth oxides, fusion enthalpy data are largely missing.

A recently modified commercial Setaram Setsys DTA instrument working up to 2500 °C allows observation of phase transitions but the lack of reliable enthalpy standards above the melting temperature of Al_2O_3 (2054 °C) has posed a major problem caused by the absence of reliable sensitivity calibration in the 2100–2500 ^{o}C range.

A newly designed “drop-n-catch” (DnC) calorimeter utilizing laser heated levitated samples significantly complement thermal analysis above 2000 °C and makes it possible to measure enthalpies of phase transitions and fusion in variable atmospheres at temperatures limited by the sample only.

Enthalpy increments measured on DnC experiments give the fusion enthalpy in Al_2O_3 as 119 ± 10 kJ/mol, compared to 120 kJ/mol from FactSage database. The sum of premelting phase transition (cubic-to-hexagonal) and fusion enthalpies in Y_2O_3 has been estimated as 120 ± 10 kJ/mol. These first results open the door to measurements previously inaccessible in terms of temperature range, controllable atmosphere, and lack of sample-container interactions. The instrument and future directions will be discussed.

The work was supported by the National Science Foundation Award DMR-1506229.

Drop and catch calorimetry on Lu_2O_3 and Yb_2O_3

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The enthalpies of fusion of most rare earth sesquioxides have not been measured experimentally and are required for calculations of phase diagrams with rare earths oxides. The "Drop and Catch" (DnC) calorimetry technique was developed to enable such measurements. In this method, aerodynamically levitated laser heated samples are dropped by splitting the nozzle and caught by calorimeter plates held at room temperature. The step in heat effect measured upon cooling samples to room temperature prior and after melting gives enthalpy of fusion. In this work we report drop and catch calorimetry experiments performed in air on lutetium and ytterbium sesquioxides. Enthalpy of fusion was measured as 97 kJ/mol for Yb_2O_3 and 92 kJ/mol for Lu_2O_3 compared with previous estimates 107 kJ/mol for Yb_2O_3 and 81 kJ/mol for Lu_2O_3 from thermodynamic assessment.[1] The estimated uncertainty in DnC measurements of fusion enthalpies is ±5%. Possible improvements of drop and catch calorimeter system will be presented.

[1] M. Zinkevich, " Thermodynamics of rare earth sesquioxides," Prog. Mater. Sci., 52(4) , 597-647 (2007)

The work was supported by the National Science Foundation Award DMR-1506229.

International Research Conference on
Structure and Thermodynamics of Oxides at High Temperature
October 20 – 22, 2016 |University of California, Davis

High Temperature X-ray diffraction of Lu, Yb, Ho and Er sesquioxides

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Development of new nuclear reactors, fuels and actinide transmutation matrices requires high temperature data. We demonstrated that X-ray and neutron diffraction on solid laser heated levitated samples can be used on many refractory oxide compounds to obtain thermal expansion, refine high temperature crystal structure and for in situ study of phase transitions and melting in variable atmosphere. Aerodynamic levitators with laser heating are accessible as sample environment for X-ray diffraction experiments at beamline 6-ID-D at Advanced Photon Source at Argonne National Laboratory and for neutron diffraction experiments on NOMAD BL1B instrument at Spallation Neutron Source at Oak Ridge National Laboratory. In these instruments, solid spherical sample is suspended and rotated by a gas stream through a conical nozzle, heated by 400 W CO_2 laser and temperature is monitored by pyrometer. X-ray diffraction pattern suitable for Rietveld refinement can be collected in less than 10 seconds and neutron diffraction pattern in ~10 minutes. The maximum temperature is inherently limited only by the sample and its amenability to laser heating. The method was successfully used to collect diffraction data up to the melting temperature on Hf, Zr, La, Nd, Sm, Eu, Gd, Ho, Er, Yb and Lu oxides and on La, Sm and Nd zirconates and hafnates. Due to fast equilibration at high temperature, in-situ determination of phase diagrams is possible. The challenges lie in improvement of accuracy of temperature measurement, thermal gradient reduction and reproducible sample rotation to assure random orientation.

High temperature X-ray diffraction of Lu, Yb, Er and Ho sesquioxides in Oxygen and Argon showed that Lu_2O_3 and Yb_2O_3 maintain C-type bixbyite structure to the melting temperature with a mean linear thermal expansion $(7 \pm 2) \cdot 10^{-6}$/K. This is in a contrast with fluorite and defect fluorite structures known to exhibit anomalously high thermal expansion before melting due to disorder on Oxygen sublattice (Bredig transition).[1]

Er_2O_3 on melting in Ar and O_2 exhibits reversible phase transformation from C to hexagonal H-phase with volume decrease ~3.5%. Melting Ho_2O_3 in Ar demonstrated previously reported transformation sequence from C-type to monoclinic (B-type) phase to H-type structure in a narrow temperature range (~200 °C). No transitions were observed on melting of Ho_2O_3 in O_2.

[1] SV Ushakov, A Navrotsky, RJK Weber, JC Neuefeind "Structure and Thermal Expansion of YSZ and $La_2Zr_2O_7$ Above 1500° C from Neutron Diffraction on Levitated Samples" Journal of the American Ceramic Society 98 (10), 3381-8 (2015)

The work was supported by the National Science Foundation Award DMR-1506229.

In situ synchrotron diffraction from levitated solids under extreme conditions –Phase transition and thermal expansion studies of rare earth pyrochlores

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Rare earth pyrochlores are materials of high scientific and technological importance[1]. Many undergo an order-disorder phase transformations (pyrochlore (P) ” defect fluorite (F)) at elevated temperatures[2] (1500 – 2400 °C), which can affect their thermophysical properties such as for example structure stability, thermal conductivity, and ionic conductivity. The disordering process usually occurs via. anti-site cation exchange and anion Frankel defect formation. Also, the pyrochlore disordering is an inevitable consequence of a displacive radiation environment[3], and it is very important to understand the energy scales involved in these phase transitions. Thus, this study shows one such quantitative calculation of defect-formation energies using site occupancies derived from *in situ* high temperature synchrotron diffraction data obtained using aerodynamic levitation and laser heating on levitated solids[4]. Rare earth pyrochlores $RE_2M_2O_7$ [RE: Eu, Sm; M = Zr, Hf] were investigated and demonstrated the ability to reliably refine the structure, anti-site occupanices both cation and anion and linear thermal expansion coefficients at temperatures to 2500 °C. These high temperature structural studies open the door for further work on complex structural transitions, including non-quenchable disordering phenomena at temperatures to 2500 °C. In situ high temperature synchrotron diffraction was performed at the Advanced Photon Source and structure refinement was carried by Rietveld method using Fullprof.

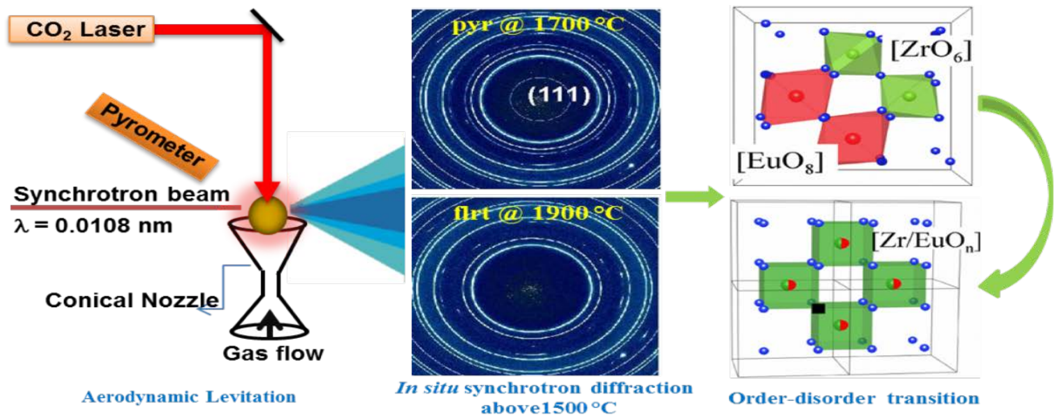

Figure: Showing order-disorder phase transitions in $Eu_2Zr_2O_7$ at high temperatures ranging from 1700-1900°C and the schematics for aerodynamic levitation setup.

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