

## DOE FINAL REPORT

### Thermochemical Studies of Nitrides, Oxynitride, and Oxide Ceramic Materials

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Work Done at Davis: 7/1/1997 – 6/30/03

#### Goals

- To develop high temperature oxide melt solution calorimetric techniques for a variety of nitrides and oxynitrides
- To determine thermodynamics of silicon nitride and of ternary phases in rare earth oxide- silica-alumina - nitrogen systems relevant to silicon nitride processing, thermal barrier coatings, and other applications
- To develop systematic understanding of the energetics of oxygen-nitrogen substitution, often coupled with altermultivalent cation substitution, in a variety of oxynitride systems
- To measure enthalpies of formation of a number of binary and ternary nitrides, often containing transition metals, and to begin to develop a systematic understanding of structure- energy relations analogous to that developed for oxide compounds.

#### Some highlights of accomplishments

##### *Technique development*

High temperature oxide melt solution calorimetry works by dissolving a small amount of sample in a large amount of oxide melt (Navrotsky 1997). Differences in heats of solution of reactants and products provide the enthalpy of reaction. When nitrides are involved, they are oxidized to the corresponding dissolved oxide species, with evolution of nitrogen into the gas phase (McHale et al. 1996, Navrotsky 2001). This “oxidative drop solution calorimetric technique” is now very well developed and virtually routine in our laboratory, the UC Davis Thermochemistry Facility. For silicon containing nitrides, an alkali borate melt near 800 °C must be used as solvent (Navrotsky et al. 1997, Liang et al. 1999a,b). A variety of nitrides and oxynitrides containing less acidic cations, sodium molybdate ( $3\text{Na}_2\text{O}-4\text{MoO}_3$ ) at 700 °C is an excellent solvent. In addition to being catalytic in the oxidation of nitrides (McHale et al. 1996, Navrotsky 2001), this solvent is extremely versatile in dissolving nitrides and oxides containing large and highly charged cations. Since these are not readily dissolved in the lead borate melt used for aluminosilicate minerals (Navrotsky 1997), other solvents must be used. The development of sodium molybdate solvent and the “bubbling gas drop solution techniques”(in which a gas, such as oxygen, is bubbled through as well as above the solvent), aids both nitride oxidation and rate of dissolution. These improved methods have greatly expanded the range of materials for which we can measure heats of formation. In particular, we now routinely perform solution calorimetry on samples containing high concentrations of Ti (Rane et al. 2001, Ranade et al. 2002, Helean and Navrotsky 2002), Zr (Molodetsky et al. 2000a, Rane et al. 2001, Helean and Navrotsky 2002), Ce (Putnam et al. 2000, Tessier et al. 2001), rare earths (Ushakov et al. 2002, Helean and Navrotsky 2002), Nb (Pozdnyakova et al. 2002, Xu et al. 2002), Ta (Elder et al. 1993).

These developments represent synergy among several projects. The developments for nitrides, of course, are the focus of the current DOE BES Materials grant. The work on zirconates, cerates, and titanates was also funded by a DOE EMSP grant (now expired) on oxide ceramic waste forms for Pu disposition. Current work on niobates is the focus of another EMSP on ion exchangers for tank wastes. The basic science questions and experimental techniques overlap substantially.

The UC Davis Thermochemistry Facility is running very smoothly after 5 years at Davis. We have a unique combination of custom built Calvet microcalorimeters, commercial Setaram reaction calorimeters, and differential scanning calorimeters and thermal analysis equipment. These instruments, and the techniques described above, enable us to tailor experiments to suit a particular problem. This concentration of equipment and expertise is unique in the U.S. and probably in the world.

### ***Silicon nitride, sialons, and related materials***

We determined the enthalpy of formation of  $\alpha$ - and  $\beta$ -silicon nitride (Liang et al. 1999a). The data show that, for pure  $\text{Si}_3\text{N}_4$ , the two polymorphs are essentially the same in enthalpy. Oxygen impurities, commonly present in the  $\alpha$  form, destabilize rather than stabilize it. These findings are important in understanding the synthesis, sintering, and mechanical properties of silicon nitride. We conclude that  $\alpha$ - $\text{Si}_3\text{N}_4$  is probably always a metastable phase, and its occurrence is kinetically controlled.

We have just completed calorimetry on the high pressure spinel form of silicon nitride and germanium nitride ( $\gamma$ ) (Zhang et al. in prep.) provided by T. Sekine in Japan.  $\gamma$ - $\text{Si}_3\text{N}_4$ , a proposed ultra hard material, is  $80.4 \pm 9.6$  kJ/mol less stable in enthalpy than  $\beta$ - $\text{Si}_3\text{N}_4$  and we are analyzing the implications for its thermodynamic P–T field of stability.

Enthalpies of formation were determined for  $\beta$ -sialon phases ( $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ ,  $z = 0.46$  to  $3.6$ ) by high-temperature oxidative drop solution calorimetry using an alkali borate (52 wt%  $\text{LiBO}_2$ ; 48 wt%  $\text{NaBO}_2$ ) solvent (Liang et al. 1999b). Sialons near  $z = 2$  appear less stable energetically than ones with higher or lower nitrogen content. A large configurational entropy contribution for sialons with  $z > 2$  may further stabilize these materials. This larger free energy driving force may be the reason for success in pulse-activated processing of these materials. The enthalpies of formation further suggest that greater driving force for oxynitride formation exists in batch synthesis using  $\text{SiO}_2$  rather than  $\text{Al}_2\text{O}_3$ .

### ***Phosphorus oxynitrides***

A number of new materials contain both phosphorus and nitrogen, often following the charge balanced substitution

$$(\text{Si}^{4+})_{\text{T}} + (\text{O}^{2-})_{\text{O}} = (\text{P}^{5+})_{\text{T}} + (\text{N}^{3-})_{\text{O}} \quad (1)$$

where the subscripts T and O refer to the tetrahedral silicon sites and the oxygen sublattice, respectively. The crystalline PON materials are thus silica analogues, while oxide glasses containing both P and N are more refractory than phosphate glasses and can provide reducing environments to form metal nanoclusters.

We measured the energetics of formation of phosphorus oxynitride PON samples and of a series of LiNaPON oxynitride glasses (Tessier et al. 2000a). Enthalpies of formation from the elements at 298 K are  $-371.71 \pm 4.45$  and  $-356.14 \pm 3.98$  kJ mol<sup>-1</sup> for  $\exists$ -cristobalite and amorphous PON, respectively, and  $-961.88 \pm 3.86$  kJ mol<sup>-1</sup> for a 9 wt% nitrogen-containing LiNaPON glass. The  $\beta$ -cristobalite energy of amorphization is  $-15.57 \pm 5.97$  kJ mol<sup>-1</sup>. A linear relation,  $\Delta H_{\text{f}}^0(\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_{(3-3x/2)}\text{N}_x) = \Delta H_{\text{f}}^0(\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_3) + 441.7x$ , was found between the enthalpies of formation of the glasses and their atomic nitrogen content,  $x$  ( $0 \leq x \leq 0.57$ ). The magnitude of the energetics of nitrogen/oxygen substitution with PON and LiNaPON glasses has been correctly evaluated by using N–N, O–O, P–N, and P–O bond strengths. The in-situ precipitation of metallic particles from corresponding oxides in LiNaPON glasses can be predicted from high-temperature solution calorimetry results and are in good agreement with the observations that Pd, Cu, Pb, Ce, and Ni oxides are easily reduced, CdO and FeO are at the edge of reducibility, and  $\text{MoO}_2$ ,  $\text{WO}_2$ , ZnO, MnO,  $\text{Ti}_2\text{O}_3$  are not reducible. These results constitute the first set of energetic data on nitridophosphates.

### ***Doped zirconia and zirconium oxynitrides***

Zirconia can accommodate oxygen vacancies and stabilize the cubic fluorite structure by two types of charge balanced substitution. The first involves a cation of lower valence, such as yttrium or calcium and can be written as

$$2(\text{Zr}^{4+})_{\text{Zr}} + (\text{O}^{2-})_{\text{O}} = 2(\text{M}^{3+})_{\text{Zr}} + (\text{Vacancy})_{\text{O}} \quad (2)$$

or



The second is substitution of oxygen by nitrogen



These substitutions can occur simultaneously, giving rise to a complex series of oxynitride phases with different symmetries and/or ordering schemes.

The enthalpies of oxidation,  $\Delta H_{\text{ox}}$ , of oxynitrides  $\text{Y}_y\text{Zr}_{1-y}\text{O}_{2x-0.5y-2/3x}\text{N}_x$  ( $0.016 < x < 0.2$ ),  $\text{Ca}_y\text{Zr}_{1-y}\text{O}_{2x-y-2/3x}\text{N}_x$  ( $0.03 < x < 0.14$ ),  $\text{Mg}_y\text{Zr}_{1-y}\text{O}_{2x-y-2/3x}\text{N}_x$  ( $0.146 < x < 0.28$ ), and  $\text{Zr-O-N}$  ( $\exists$ -type and  $\gamma$ -phases) were measured using drop solution calorimetry in molten sodium molybdate ( $3\text{Na}_2\text{O} \cdot 4\text{MoO}_3$ ) at 973 K (Molodetsky et al. 2000a). Linear relations between the enthalpy  $\Delta H_{\text{ox}}^{\text{n}}$  and nitrogen content were found in all oxynitrides. They indicate that, within the experimental range of nitrogen concentrations, sites occupied by nitrogen ions are energetically equivalent in a given substitutional series. The enthalpies normalized per mole of nitrogen,  $\Delta H_{\text{ox}}^{\text{n}}$ , for compounds of  $\text{Y-Zr-N-O}$ ,  $\text{Ca-Zr-N-O}$ , and  $\text{Zr-O}$  are similar, about  $-500$  kJ/(mol of N). A more exothermic value of  $\Delta H_{\text{ox}}^{\text{n}}$ , of about  $-950$  kJ/(mol of N), is seen in  $\text{Mg-Zr-N-O}$  compounds. The energetics of vacancy formation in zirconium oxynitrides was determined and compared to the energetics of vacancy formation in yttria- and calcia-stabilized zirconia. The enthalpy of vacancy formation (enthalpy of formation relative to end members normalized per vacancy) in zirconium oxynitrides ( $-190.5 \pm 27.0$  kJ/mol of oxygen vacancies) is more exothermic than that in yttria- and calcia-stabilized zirconia ( $-105 \pm 7.2$  and  $-91.4 \pm 3.8$  kJ/mol, respectively). This is consistent with the higher tendency for long-range ordering in zirconium oxynitrides compared to stabilized zirconia.

The enthalpy of oxidation of the mixed  $\text{M-Zr-O-N}$  oxynitride depends on the ionic radius of the substituting cation, see Fig 1.

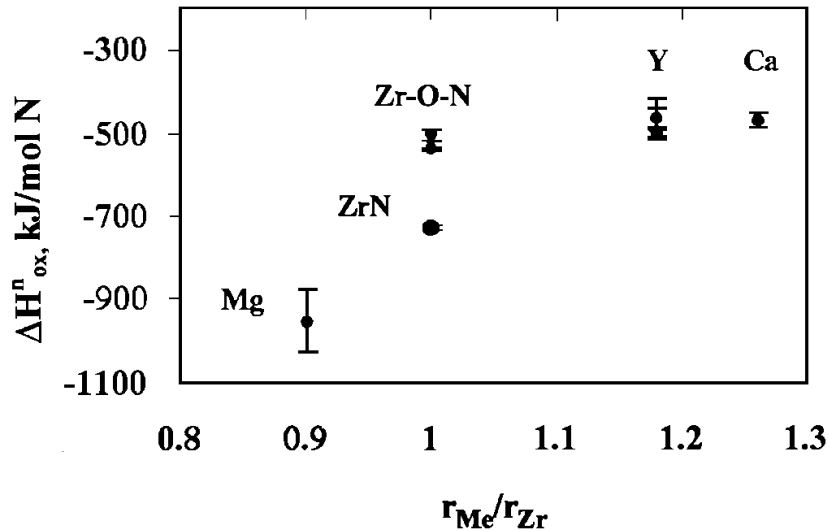


Figure 1. Enthalpy of oxidation (per mol N) of a series of oxynitrides (Me = Mg, Zr, Y, Ca) as a function of ratio of ionic radius of dopant and of zirconium (Molodetsky et al. 2000a).

### 2.2.5 Glasses containing rare earths and/or nitrogen

Aluminosilicate and borosilicate glasses containing rare earths and/or nitrogen are important in several contexts. Glasses in the  $\text{RE}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2\text{-Si}_3\text{N}_4\text{-AlN}$  system occur when rare earth additives are

used as sintering aids in the processing of silicon nitride and sialons. Rare earth containing aluminate and aluminosilicate glasses and crystals are important laser hosts; a classic example is Nd-doped YAG. Rare earth aluminate glass fibers are promising new materials. Multicomponent borosilicate glass containing lanthanides and actinides is a primary nuclear waste containment material; vitrification has been going on for several years now at the DOE Savannah River Site. For these reasons, Yahong Zhang, supported by the current grant, is completing her doctorate on thermochemical studies of this class of materials. The following are highlights of her work.

- Enthalpies of formation were measured for  $\text{RE}_{1.1}\text{Si}_{1.7}\text{Al}_{0.6}\text{O}_{6-1.5x}\text{N}_x$  (RE = Y, Nd, Gd, Dy, Er;  $x = 0 - 0.82$ ) glasses. The enthalpies of formation from elements become linearly more endothermic with increasing nitrogen content. These oxynitride glasses are energetically more stable with increasing atomic number (decreasing radius) of the rare earth substituent. The onset glass transition temperature shows a linear increase with increasing nitrogen content and decreasing ionic radius of rare earth cations. All RESiAlON glasses contain a small extent of N-rich, RE-poor micro-heterogeneity, which might be incipient phase separation.
- $\text{REAlO}_3$  (RE = La, Pr, Nd, Sm, Gd) glasses were successfully synthesized for the first time by levitation melting in collaboration with Containerless Research, Inc. These glasses are extremely fragile and crystallize into single phase perovskite when heated. The enthalpy of vitrification for  $\text{NdAlO}_3$  was measured to be  $277.9 \pm 3.5$  kJ/mol (12 oxygen basis), comparable to that of  $\text{Y}_3\text{Al}_5\text{O}_{12}$  determined by Lin et al. (1999).
- The effects of  $\text{SiO}_2$  content, RE/Al ratio and different rare earth element addition was investigated by synthesis, characterization and thermochemical study of  $\text{RESiAlO}$  (RE = Y, Nd, Gd, Dy, Er) glasses. These findings are important to optimize the microstructure of ceramic bodies, synthesize new compounds and establish theoretical models for relevant multi-component system. These glasses are energetically stabilized with increasing RE/Al ratio and increasing ionic radius. For glasses along  $2\text{REAlO}_3 - 3\text{SiO}_2$  joins, there is an energetic stabilization around  $\text{Al/Si} = 1$ , which might be related to the reaction  $\text{Al-O-Al} + \text{Si-OSi} = 2\text{SiOAl}$  (Navrotsky et al. 1985). Enthalpies of mixing are negative, indicating the absence of immiscibility in the composition range studied. Onset glass transition temperatures are insensitive to the content of a given rare earth, while they increase with decreasing ionic radius. This indicates rare earth cations might play an intermediate role between those of conventional network modifiers and network formers. Structure-property correlation is difficult due to the coexistence of Al in three coordination states (IV, V and VI), actual distribution of RE and NBOs between the postulated tetrahedra and non-tetrahedral volumes, and the composition of such volumes across the system. Neutron diffraction and small angle X-ray scattering are being carried out for further understanding of the structure of rare earth containing aluminosilicate glasses.
- The enthalpies of solution of  $\text{HfO}_2$  and of  $\text{Gd}_2\text{O}_3$  in a simulated nuclear waste glass were measured (Zhang et al. 2001). Direct energetic evidence for clustering and a change in thermodynamic behavior at dopant contents of 1-2 mol% was seen (see Fig 2). This work represents a collaboration with Dennis Strachan's group at PNNL.

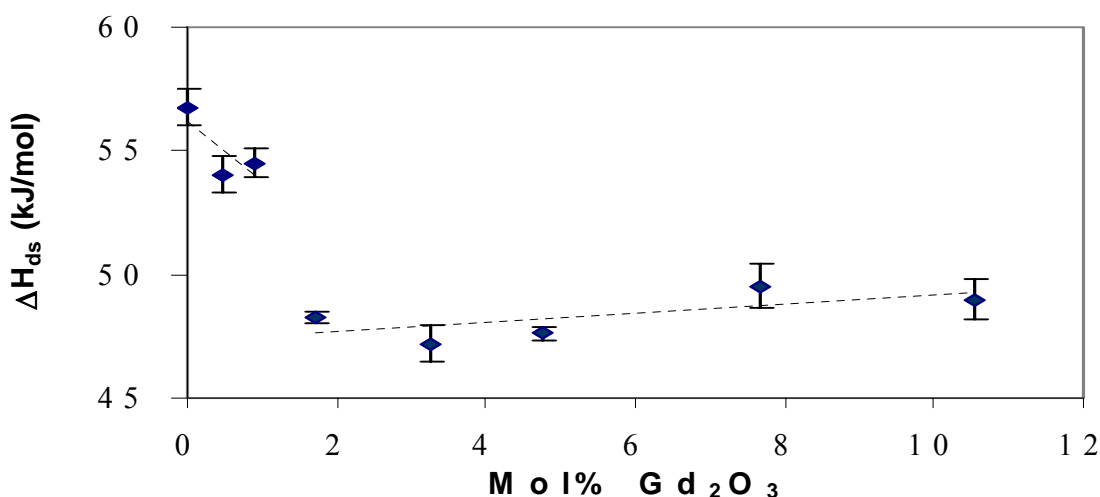


Figure 2. Enthalpy of drop solution of a complex borosilicoaluminate glass containing  $Gd_2O_3$  into molten lead borate solvent. The break in the trend between 1 and 2 % is consistent with the onset of clustering seen by other methods (Zhang et al. 2001).

***Crystalline rare earth aluminates and silicates and CALPHAD calculations of phase equilibria pertinent to silicon nitride processing***

In collaboration with Hans Seifert of the Max Planck Institute, Stuttgart, Germany, we determined the enthalpies of formation of several rare earth silicates and his group has incorporated our data on nitrides and rare earth silicates and aluminates into the CALPHAD database for these materials (Fabrichnaya et al. 2001a,b, Degterov et al. 2001). The calorimetry done at Davis was supported by the current DOE grant; the travel by an NSF International Programs grant.

***Other nitrides***

As part of Mandar Ranade's thesis, the heats of formation of indium and gallium nitride, important materials in the semiconductor industry, were redetermined and serious discrepancies in the literature resolved (Ranade et al. 2000, 2001). Iron nitrides (Tessier et al. 2000b) and cerium manganese nitrides (Tessier et al. 2001) were also studied.

**Ph.D. dissertations supported, at least in part, by the current grant (*names of women italicized*)**

***Irina Molodetsky***, Princeton University 1999, "Energetics of Zirconia Stabilized by Cation and Nitrogen Substitution".

**Mandar Ranade**, University of California at Davis 2000 "Thermodynamic Properties of Bulk and Nanocrystalline Materials: A Comparative Study".

***Yahong Zhang***, University of California at Davis, anticipated Feb. 2003, "Thermochemistry of Rare Earth Sialon Glasses".

**Placement of Students and Postdocs 1999-2001**

***Irina Molodetsky*** (Ph.D. 1999) is at Schlumberger Inc., Princeton NJ.

**Mandar Ranade** (Ph.D. 2001) is at Intel, Inc. Portland OR.

**Franck Tessier** (postdoc) is at the Univ. of Rennes, France in a permanent position.

**Jianjie Liang** (postdoc) is at Accelrys Inc (Formerly MSI), CA.

**Aditi Risbud** (B.S. 2000) is in a PhD program in materials science at UC Santa Barbara.

**Peter Lu** (BS 1999) is in a PhD program in physics at Harvard Univ.

## Publications

"Energetics of ternary nitride formation in the (Li, Ca) – (B, Al) – N system", J. M. McHale, A. Navrotsky, and F. J. DiSalvo, Chem. Materials 11, 1148-1152 (1999).

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"Energetics of nitridophosphates PON and LiNaPON glasses", F. Tessier, A. Le Sauze, R. Marchand, and A. Navrotsky, Mat. Res. Soc. Symp. Proc. 547, 389-394 (1999).

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"Thermochemistry of  $\text{Si}_{6-z}\text{Al}_z\text{N}_{8-z}$  ( $z = 0$  to 3.6) materials", J. - J. Liang, A. Navrotsky, V. J. Leppert, M. J. Paskowitz, S. H. Risbud, T. Ludwig, H. J. Seifert, F. Aldinger, and M. Mitomo, J. Mater. Res. 14, 4630-4636 (1999).

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