SAND2011-4445C

I. Renewable Energy Challenges: the Role of Systems Analysis
II. System Analysis of Algae-based Biofuel Manufacturing
III. Design of Advanced Heat-transfer fluids for CSP

June 28, 2011

Amy Sun

Sandia National Laboratories

(505)284-5861 acsun@sandia.gov

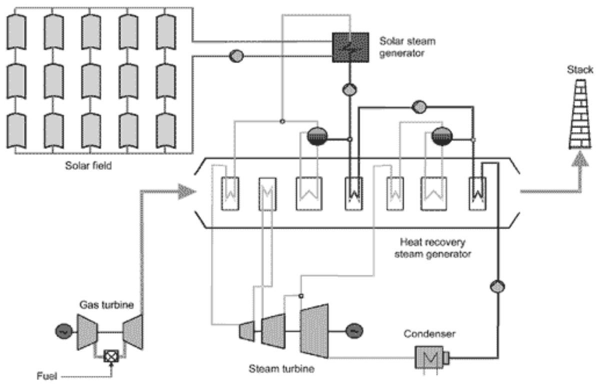
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Heat Transfer Fluids (HTF) for Solar Technology

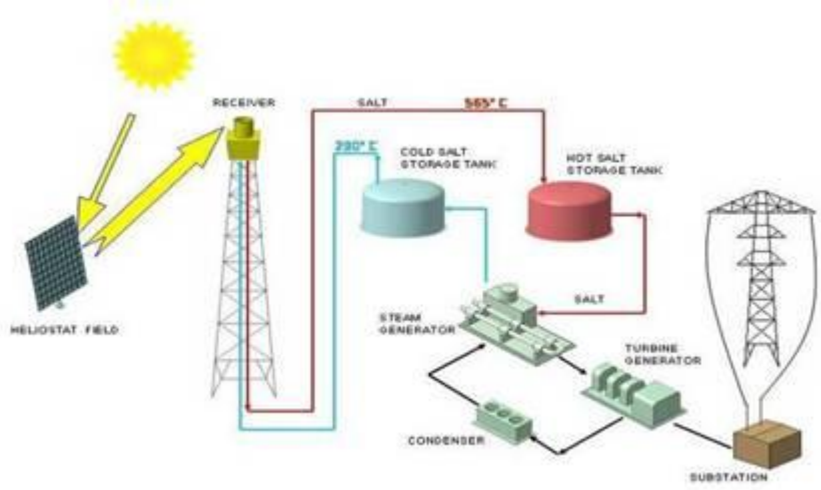
- Systems
  - –Parabolic trough
  - –Central Receiver
- Functions
  - –Energy storage
  - –Working fluids

Objective

Provide the lowest cost, hightest performing HTF for concentrated solar power.



parabolic trough



central receiver

HTF considerations are numerous

- Requirements
  - Operating range
  - Transport properties
  - Heat transfer characteristics
  - Corrosion
  - Decomposition
- Constraints
  - Equipment
  - Cost
  - Experimental data
  - Time
  - etc.

Sandia National Laboratories

Use of computation to resolve material properties for mixed salts

- Close data gaps
- Explore new candidates
- Expedite search space
- Develop new material models

Thermophysical properties:

T_{mp}, $C_p(T)$, k_t, ρ, η

Sandia National Laboratories

Multicomponent property predictions

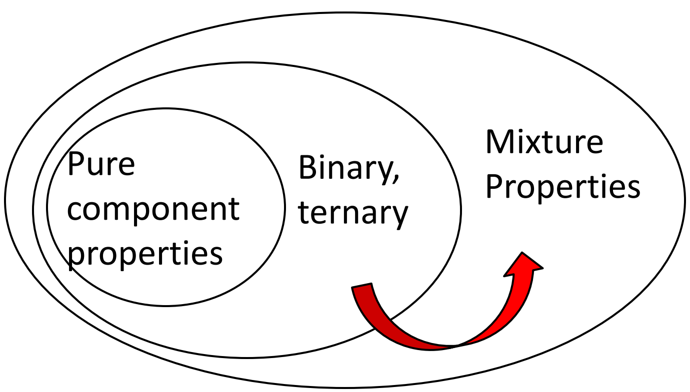
Property target

$\Delta T_{operation}$, $C_p(T)$, k_t, ρ

Possible
Candidate salts

Modeling

Experiments



- **Methods**
  - Classical thermodynamics
  - Atomistic simulations
  - etc.
- **Constraints**
  - Mass balance
  - Laws of thermodynamics

Chemical phase equilibria: liquid to solid

Equality of chemical potential.

$$\mu_i^{solid} = \mu_i^{liquid}$$

$$f_i^{solid} = f_i^{liquid}$$

$$f_i^{solid} = \gamma_i x_i f_i^{o}$$

f_i^{o} = *defined as pure solute i, subcooled liquid at T.*

γ_i = *activity coefficient of component i*

x_i = *solubility composition*

Free energy change upon melting.

$$\Delta g_i = RT \ln \frac{f_i^{o}}{f_i^{solid}} = RT \ln \frac{1}{\gamma_i x_i}$$

Activity coefficient represented
By Wilson Equation

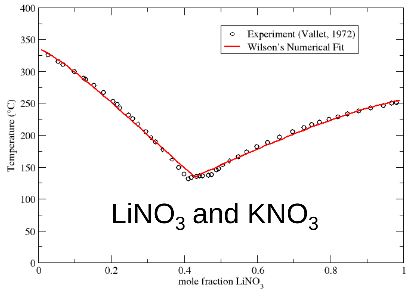
Λ_{ij}

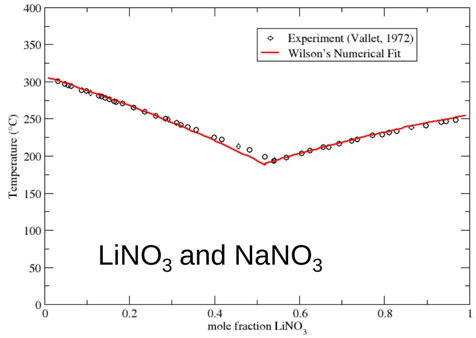
$$\ln \gamma_k = -\ln\left(\sum_{j=1}^{NC} x_j \Lambda_{jk}\right) + 1 - \sum_{i=1}^{NC} \frac{x_i \Lambda_{ik}}{\sum_{j=1}^{NC} x_j \Lambda_{ij}}$$

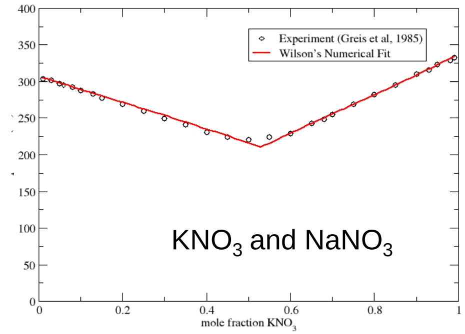
$$\Lambda_{ij} = \frac{v_j}{v_i} \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right)$$

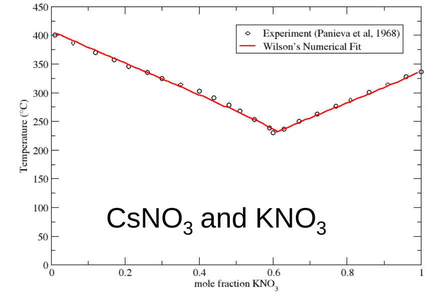
$$\Lambda_{ji} = \frac{v_i}{v_j} \exp\left(-\frac{\lambda_{ji} - \lambda_{jj}}{RT}\right)$$

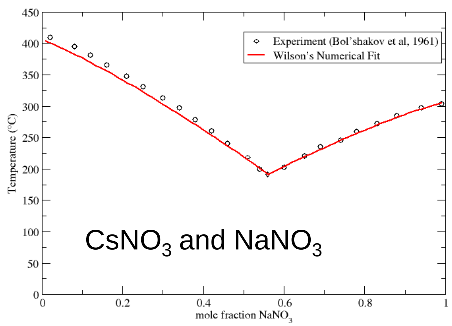
Tracking liquidus lines based on Wilson Equation

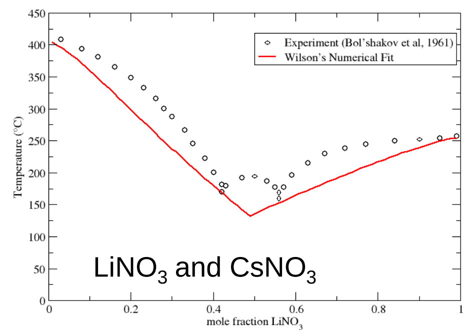












1) Use of binary data to fit binary interaction parameters

2) Extrapolate to ternary and quaternary phase diagrams.

	Λ_{ij}	Λ_{ji}
$LiNO_3$-KNO_3 (1-2)	3.157	2.363
$LiNO_3$-$NaNO_3$ (1-3)	2.221	0.5753
KNO_3-$NaNO_3$ (2-3)	1.021	0.5931
$CsNO_3$-KNO_3 (4-2)	0.5010	1.211
$CsNO_3$-$NaNO_3$ (4-3)	1.278	1.906
$CsNO_3$-$LiNO_3$ (4-1)	4.438	4.281

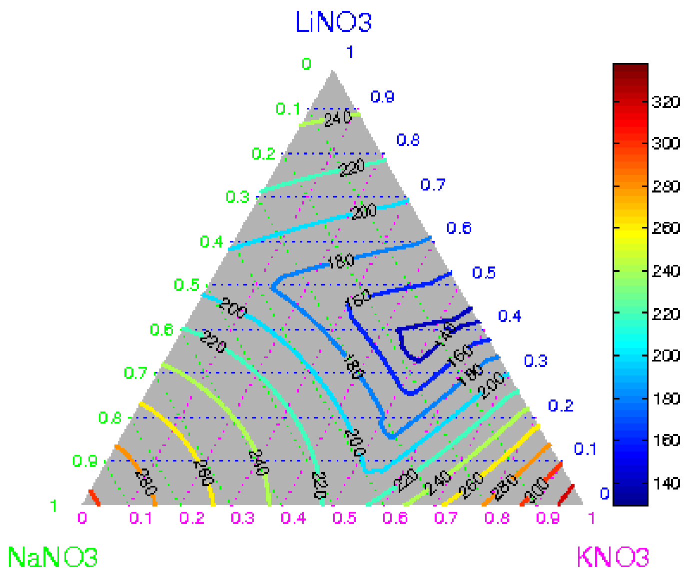
(Sun et al., SAND2011-1703)

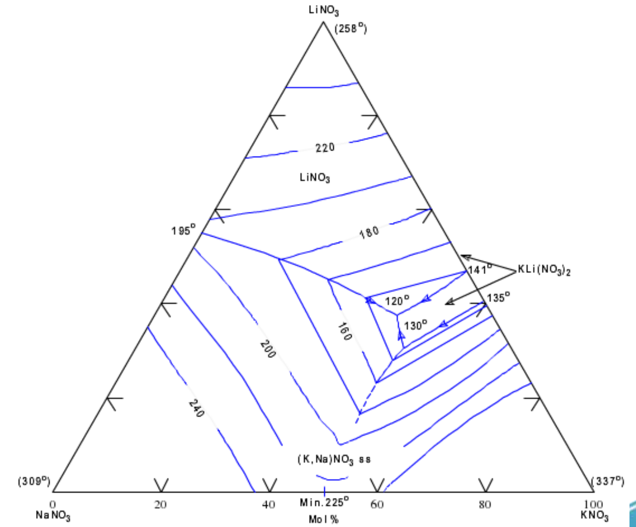
Sandia National Laboratories

Ternary phase diagrams

	Calculated $T_{eutectic}$(C°)	Experimental $T_{eutectic}$(C°)	Reference	Error (%)
$LiNO_3$-KNO_3-$NaNO_3$ (1-2-3)	129	120	27	7.5
$LiNO_3$-$NaNO_3$-$CsNO_3$(1-3-4)	133	130	28	2.3
KNO_3-$NaNO_3$-$CsNO_3$(2-3-4)	153	154	29	0.60
$LiNO_3$-KNO_3-$CsNO_3$(1-2-4)	115	N/A	N/A	N/A

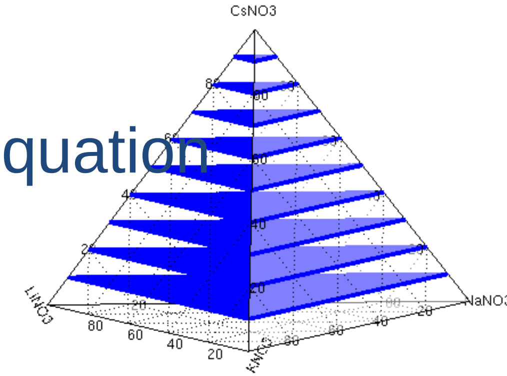
	$LiNO_3$	KNO_3	$NaNO_3$	$CsNO_3$	Error (%)
$LiNO_3$-KNO_3-$NaNO_3$ (1-2-3)	0.360	0.481	0.160	0.00	8,10,4
$LiNO_3$-$NaNO_3$-$CsNO_3$ (1-3-4)	0.375	0.00	0.211	0.414	20,21,15
KNO_3-$NaNO_3$-$CsNO_3$ (2-3-4)	0.00	0.340	0.364	0.296	7,16,8
$LiNO_3$-KNO_3-$CsNO_3$ (1-2-4)	0.373	0.356	0.00	0.272	N/A

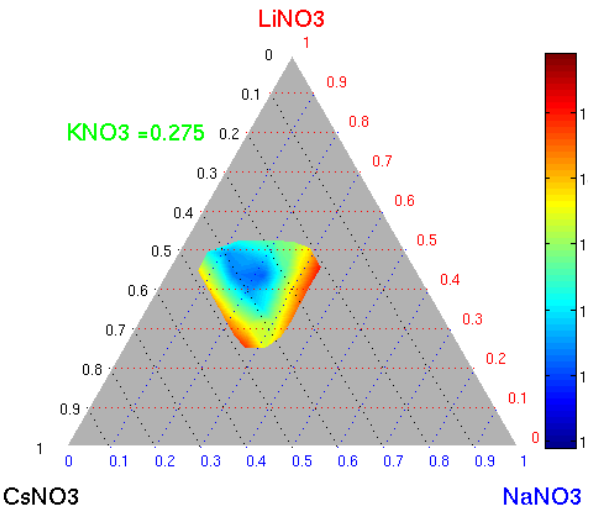


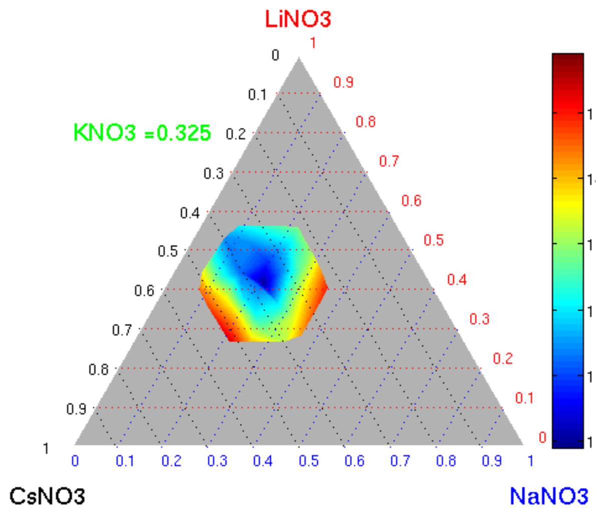


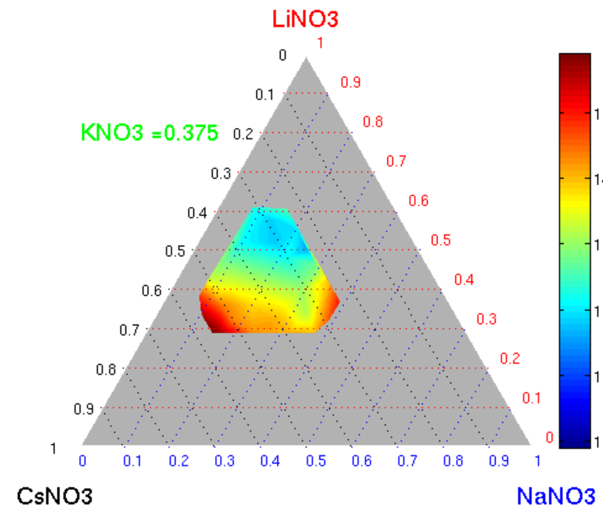
Prediction of melting points of quaternary mixtures of nitrate salts using the Wilson Equation

(Davison & Sun, in review, I&EC research, 2011)





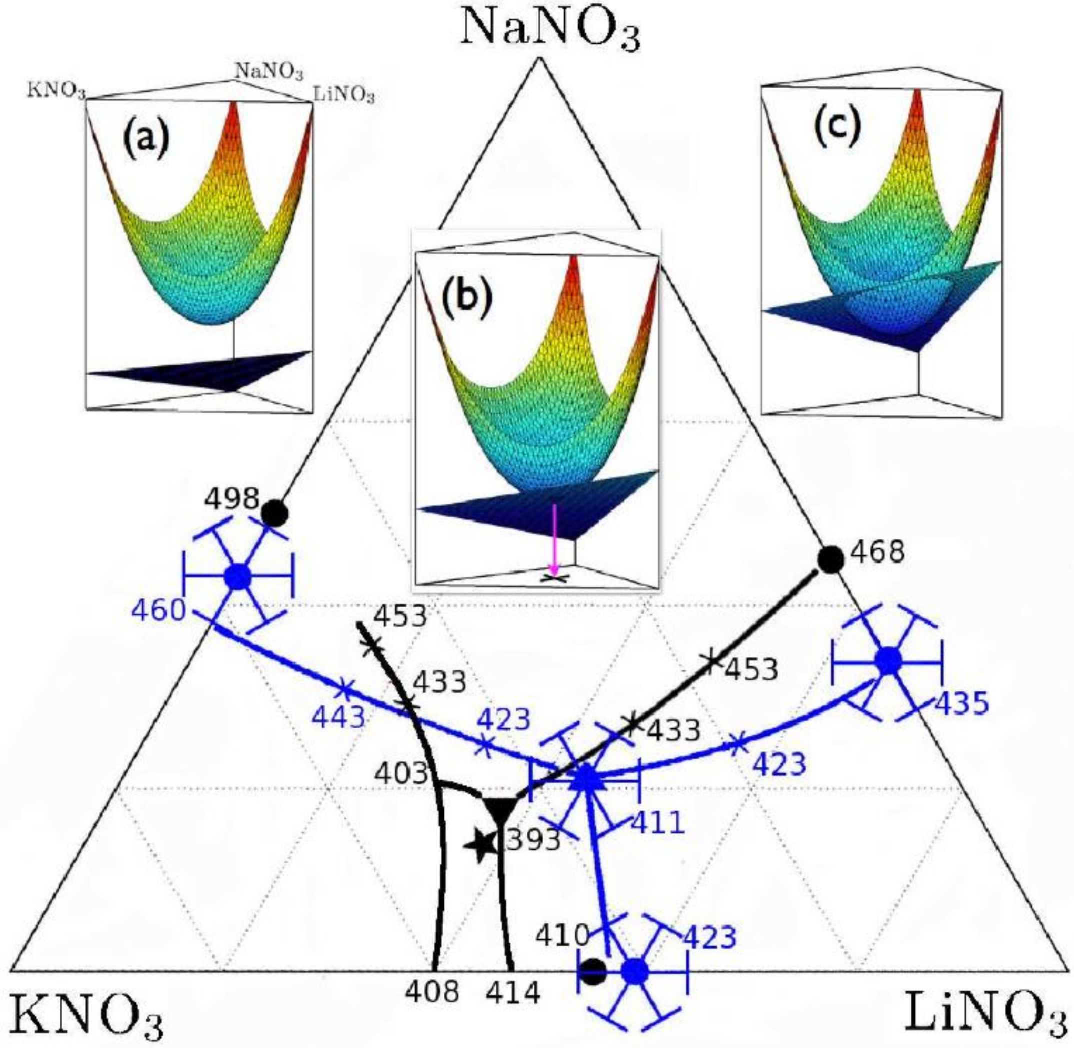




Mixture of 0.28 $LiNO_3$, 0.14 $NaNO_3$, 0.33 KNO_3, 0.25 $CsNO_3$ predicted to melt at 100°C

Phase Diagram based on Molecular Dynamics

1. Constructing a continuous path that gradually transforms the liquid in to the solid at one temperature to get
2. $\Delta G_{solid\text{->}liquid}$
3. $G_{liquid}(T,x)$, $G_{solid}(T)$



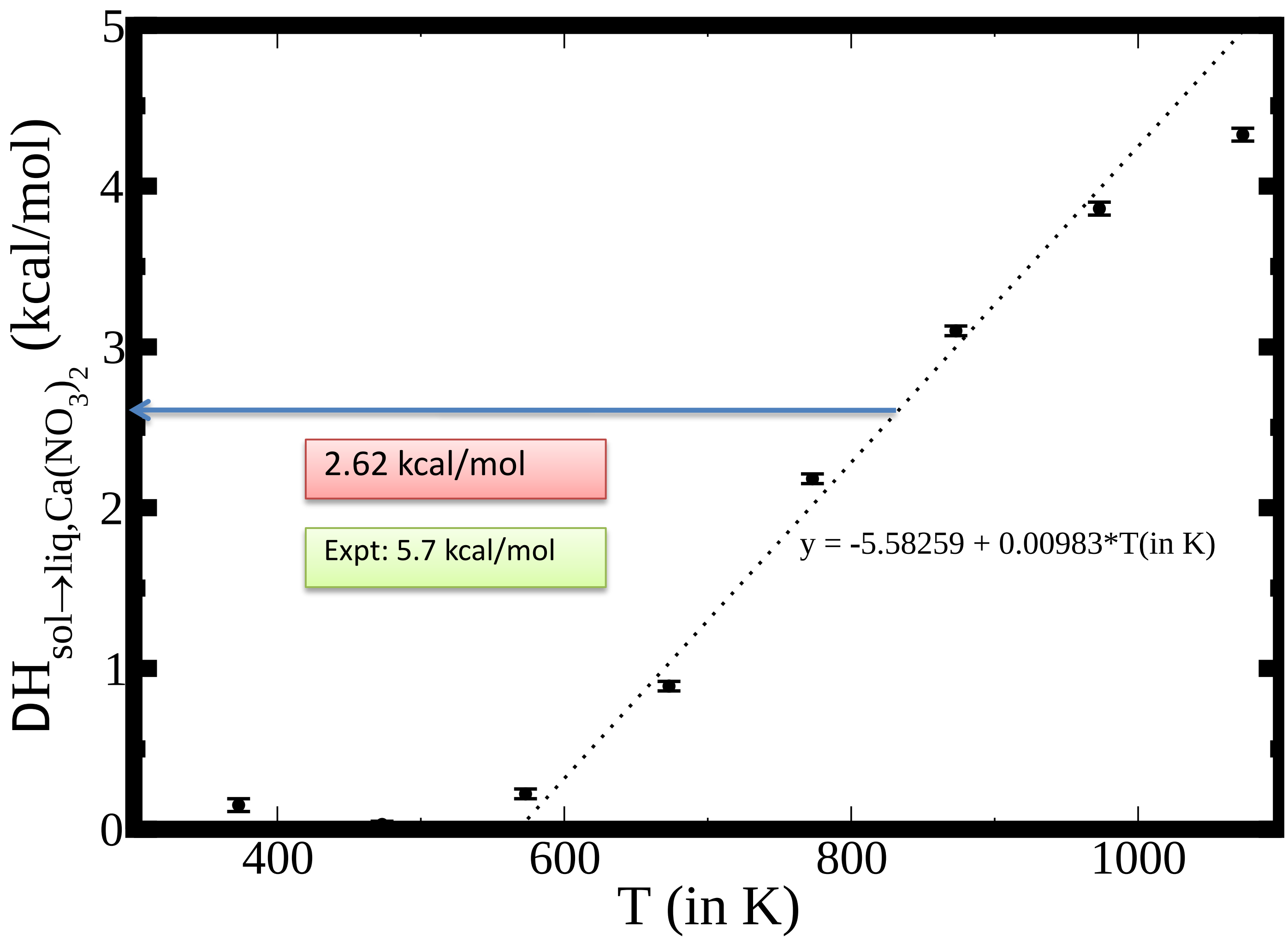
S Jayaraman, A. P. Thompson and O. A. von Lilienfeld, accepted, *Phys. Review E.*

A.G. Bergman and K. Nogoev, Zh. Neorg. Khim., **9** 1423 (1964) - Ternary

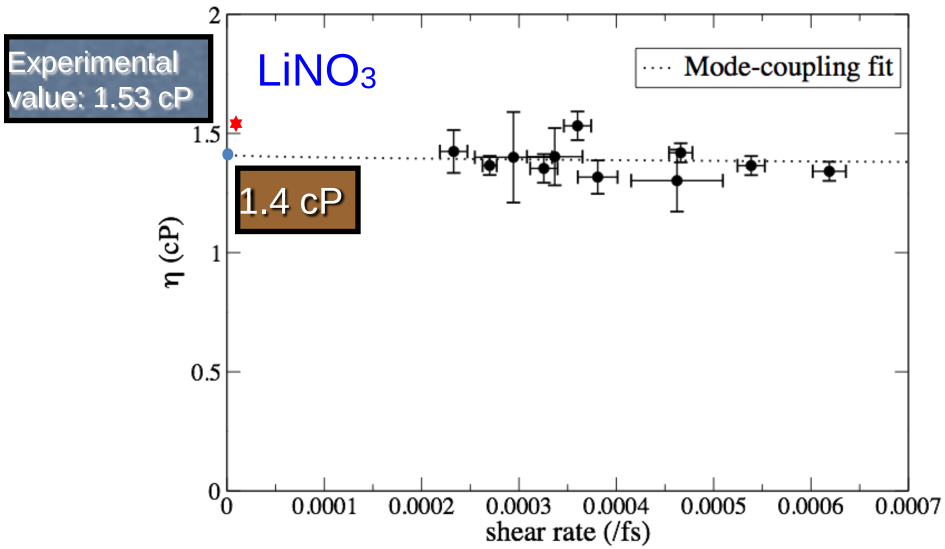
H. R. Carveth, J. Phys. Chem., **2**, 209 (1898) - ★

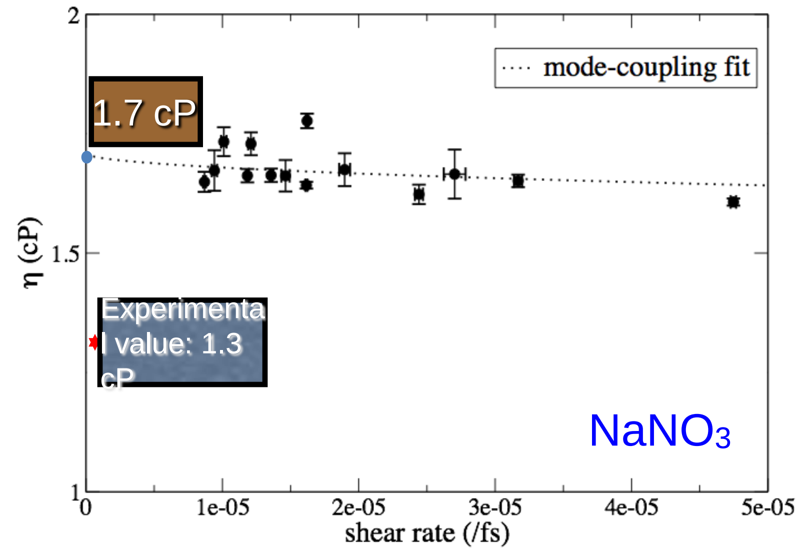
Sandia National Laboratories

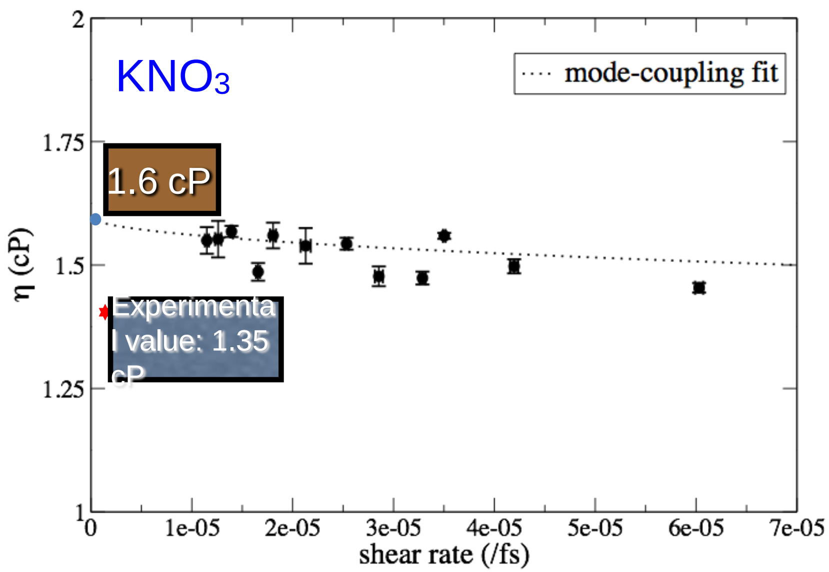
Change in Helmholtz Energy between solid and liquid, MD simulations



Transport Properties based on Molecular Dynamics



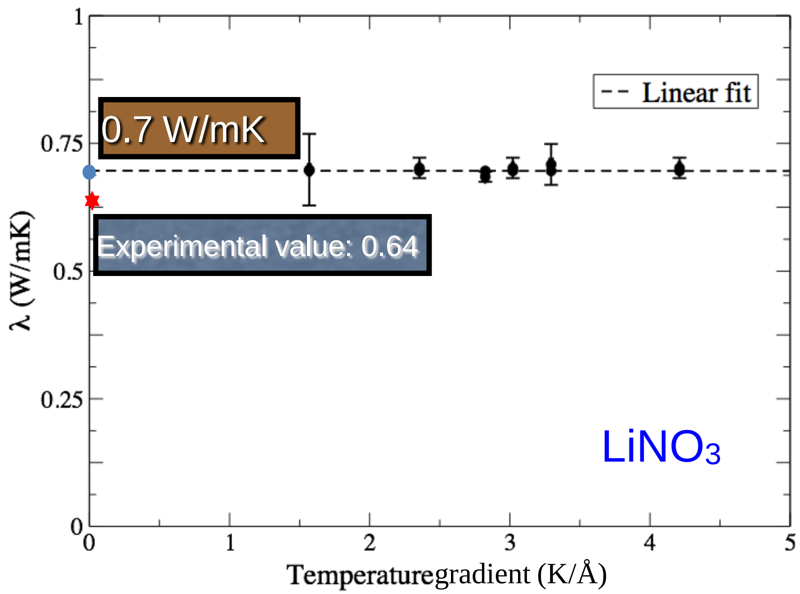


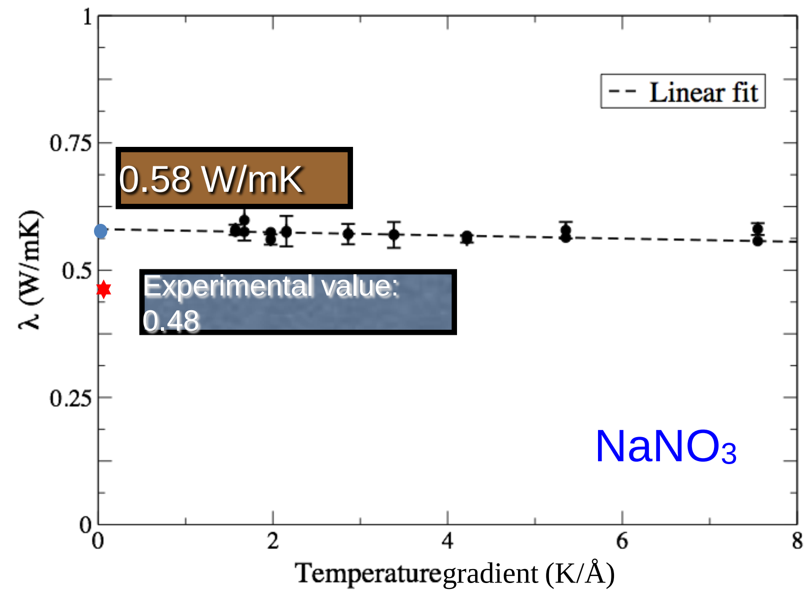


S Jayaraman, A. P. Thompson , O. A. von Lilienfeld and E. J. Maginn, I&EC Res, **49**, 559-571 (2010)

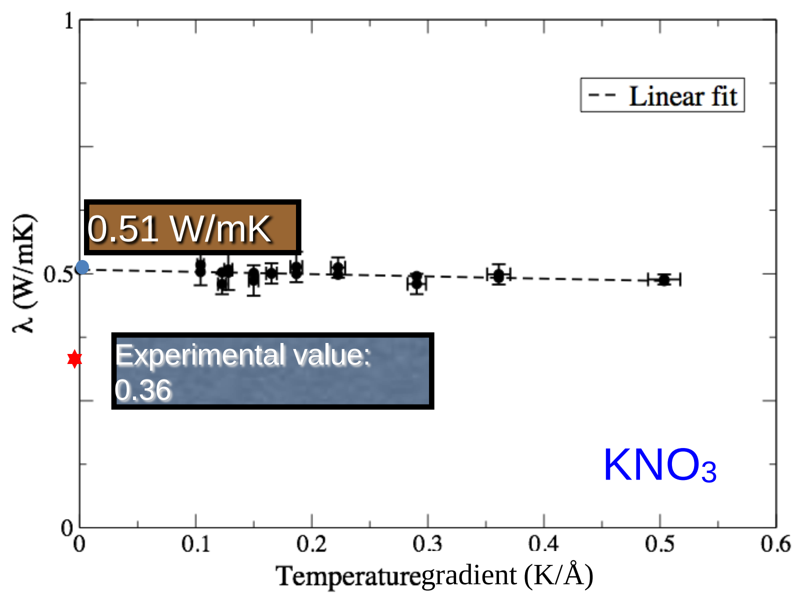
Sandia National Laboratories

Transport Properties based on Molecular Dynamics

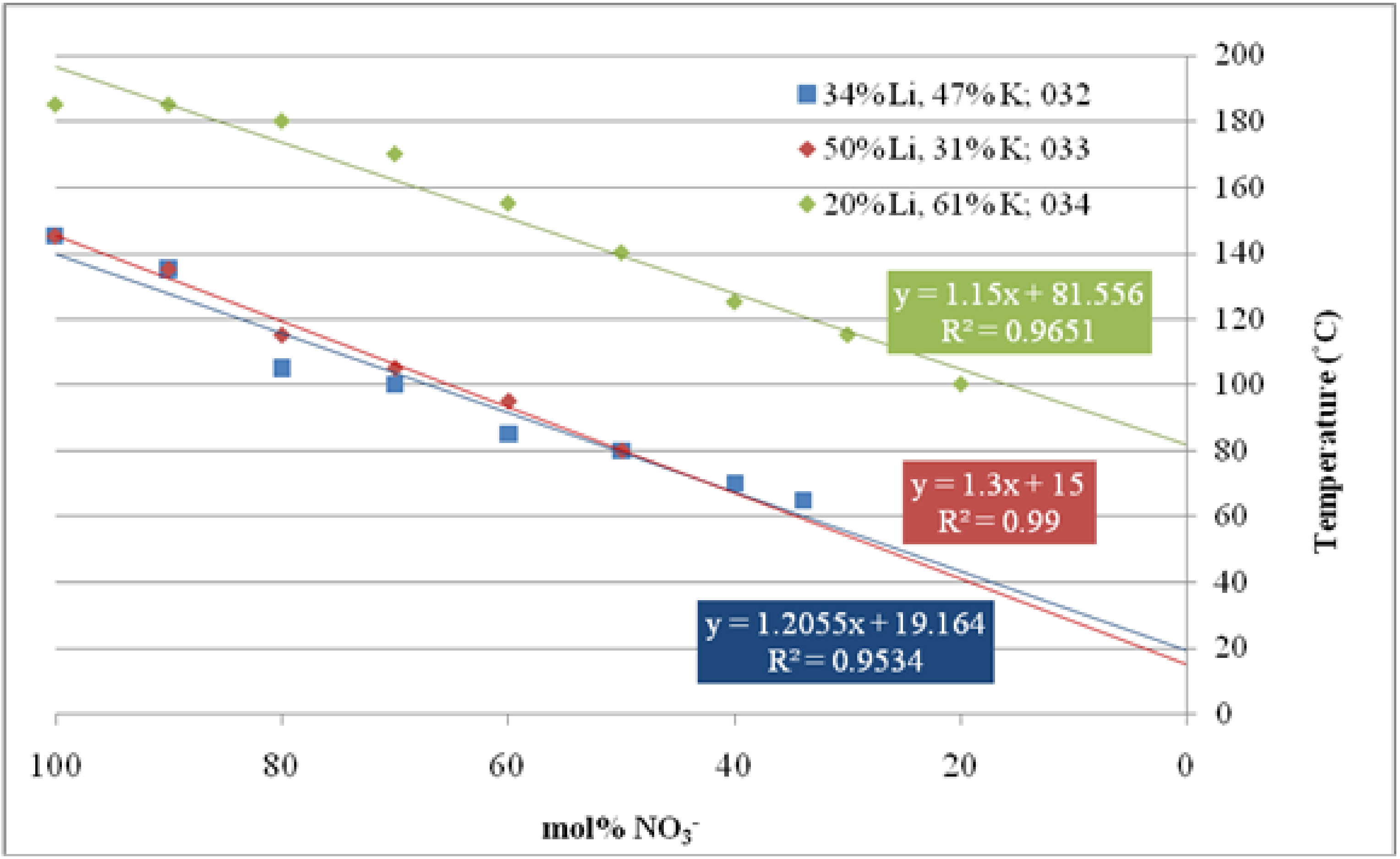




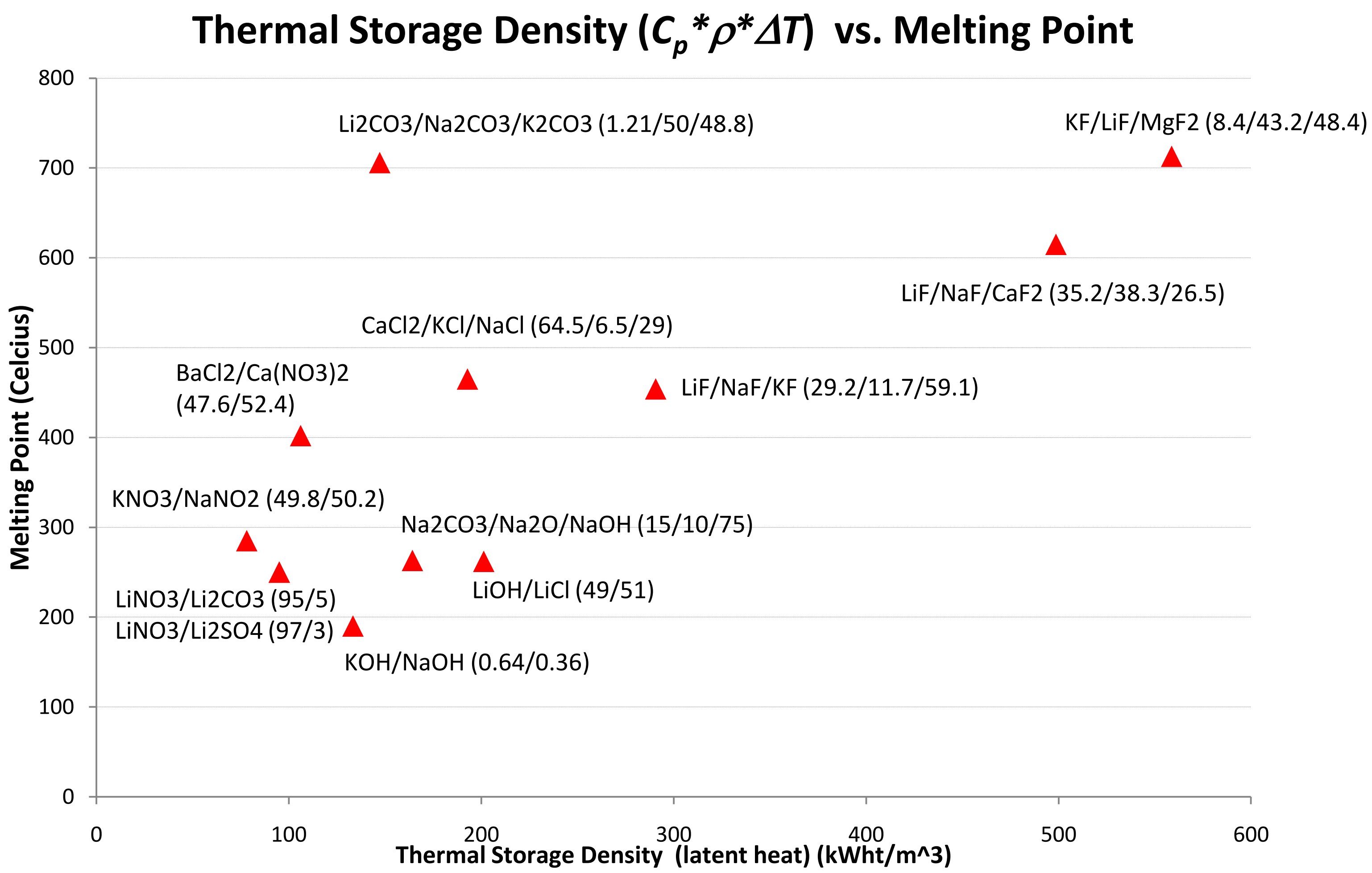
S Jayaraman, A. P. Thompson , O. A. von Lilienfeld and E. J. Maginn, I&EC Res, **49**, 559-571 (2010)



Experimental effort
(J. Cordaro & R. Bradshaw, 2010)



Past energy storage studies*



Sandia National Laboratories

Current effort

–Generalize and optimize methodology for the routine exploration of composition space in multi-component systems.
–Search through historical studies for overlap.
–Reconcile concurrent effort with other institutions (NREL, UAlabama, UWisconsin, Halotecnics)
–High temperature property estimations and decomposition chemistry
–Use of atomistic simulation for pure component data not available experimentally.

*References

Author(s)	Title	Date	Publisher	ID
Ferrara, Angelo, George Yenetchi, Robert Haslett, Robert Kosson	Thermal Energy Storage Heat Transfer	Oct-77	NASA	NASA CR 135244
Ferrara, Angelo	Thermal Energy Storage Heat Exchanger	Sep-77	ORNL	CONF-770955
Haslett, R., J. Alario, and G. Yenetchi	Active Heat Exchanger System Development for Latent Heat Thermal Energy Storage System	Dec-78	SNL/CA	CONF-781231
LeFrois, R.T., G.R. Knowles, A.K. Mathur, and J. Budimir	Active Heat Exchange System Development for Latent Heat Thermal Energy Storage	Feb-79	Honeywell/NASA/DOE	DOE/NASA/0038-79/1
Alario, Joseph, Robert Kosson, and Robert Haslett	Active Heat Exchange System Development for Latent Heat Thermal Energy Storage	Jan-80	Grumman/NASA/DOE	DOE/NASA/0039-79/1
Petri, Randy.J., Terry D. Claar, and Estela T. Ong	High-Temperature Molten Salt Thermal Energy Storage Systems for Solar Applications	Jul-83	IGT/NASA/DOE	DOE/NASA/0156-83/1
	Survey and Selection of Inorganic Salts for Application to Thermal Energy Storage	Jun-75	USRDA	ERDA-59
Heine, D., F. Heess, and M. Groll	Physical and Chemical Properties of Phase Change Materials for Application in Solar Tower and Solar Farm Plants	Aug-90		SOEMDH 24(1-4) 1-782(1991)

Sandia National Laboratories

Acknowledgement

Scott Davison

Sai Jayaraman

Joe Cordaro

Nate Siegel