

**FIRST-PRINCIPLES THERMODYNAMICS OF ULTRA-REFRACTORY INCLUSIONS: CONDENSATION TEMPERATURE OF ALLENDEITE.** V.R.Manga<sup>1,2</sup>, T.J. Zega<sup>1,2</sup>. <sup>1</sup>Lunar and Planetary Laboratory, <sup>2</sup>Dept. of Materials Science and Engineering, University of Arizona, Tucson, AZ 85721, USA. (manga@arizona.edu).

**Introduction:** Ultra-refractory (UR) phases found within primitive meteorites can be composed of oxides of Sc, Zr, Y etc. [1,2]. Such oxides occur along with the most abundant phases in calcium-aluminum-rich inclusions (CAIs) and thought to have originated from condensation in the solar nebula. Their refractory compositions suggest that they could have condensed at temperatures above those of CAIs which themselves are composed of high-temperature refractory mineral phases [3] predicted by equilibrium thermodynamic calculations to condense from a gas of solar composition [4,5]. Isotopically age dated at 4.5673 Ga [6,7], CAIs mark the chronological origins of the solar protoplanetary disk. Thus, UR inclusions offer a tantalizing opportunity to investigate high-temperature processing in the inner and early solar protoplanetary disk.

The thermochemistry of mineral phases is crucial to model and calculate their condensation temperatures. In the case of UR phases, however, thermochemical data is scarce and no thermodynamic models are available. To fill this knowledge gap, we have undertaken a first-principles quantum-mechanics approach to model the thermochemistry of ultra-refractory phases. Here we report on allendeite  $\text{Sc}_4\text{Zr}_3\text{O}_{12}$ .

**Theoretical methods and modeling:** The finite temperature thermodynamic properties are obtained from first-principles with the Helmholtz free energy  $F(V, T)$  at volume  $V$  and temperature  $T$  via  $F(V, T) = E(V) + F_{el}(V, T) + F_{vib}(V, T)$  where  $E(V)$  is the static total energy at 0 K as a function volume.  $F_{el}(V, T)$  is the thermal electronic contribution to the Helmholtz free energy as a function of  $V$  and  $T$  and is important for metals owing to the non-zero electronic density at Fermi level.  $F_{vib}(V, T)$  is the vibrational contribution to the Helmholtz free energy as a function of  $V$  and  $T$  and is obtained within the quasiharmonic approximation. The Gibbs free energy as a function of  $P$  and  $T$  can be obtained via  $G(P, T) = F(V, T) + PV$ . The  $F_{vib}(V, T)$  can also be obtained from Debye-Grüneisen approach, which predicts the free energies from ground state equation of state (i.e. energy vs. volume) calculations. The vibrational contribution from phonons within the quasiharmonic approximation is obtained only for selected phases due to limited computational resources.

The first-principles quantum-mechanics calculations are performed employing Vienna *Ab initio* Simulation Package (VASP) [8,9] to calculate the thermochemical data of solid solutions of interest. Special quasirandom structures (SQS) predict enthalpies of mixing in solid solutions as a function of composition with respect to their end-members. The entropic contributions

to the free energy, as mentioned above, are obtained from phonons and Debye calculations [10]. The exchange correlation functional as described by Perdew-Burke-Ernzerhof (PBE) is used in the calculations [9].

Thermodynamic modeling is conducted within the CALculation of PHase Diagrams (CALPHAD) framework. Within the CALPHAD methodology, the condensation and stability of minerals can be modeled by combining the computed and available experimental thermochemical data with crystal structure-based models. Gibbs free energy descriptions of solution phases in their entire composition space are developed to calculate their crystal chemistry and precise thermochemical origins under nebular conditions in addition to predicting their post-formation histories. The modeling includes the common CAI phases with selected solutes in the solid solutions [11]. The gas phase is modeled by incorporating all the species ( $\text{O}_2, \text{O}_3, \text{Al}, \text{Mg}, \text{Ca}, \text{Ti}, \text{V}, \text{Zr}, \text{Zr}_2, \text{Sc}, \text{Al}_2\text{O}_3, \text{Al}_2\text{O}_2, \text{Al}_2, \text{Al}_2\text{O}_1, \text{Al}_2\text{O}_2, \text{Al}_2\text{O}_3, \text{Mg}_2\text{O}_1, \text{Ca}_2\text{O}_1, \text{Mg}_2, \text{Ca}_2, \text{H}, \text{H}_2, \text{H}_2\text{O}_1, \text{H}_1\text{O}_2, \text{H}_1\text{O}_1, \text{H}_2\text{O}_2, \text{C}, \text{C}_1\text{O}_2, \text{C}_1\text{O}_1, \text{Si}, \text{Ti}_1\text{O}_1, \text{Ti}_1\text{O}_2, \text{V}_1\text{O}_1, \text{V}_1\text{O}_2, \text{Si}_1\text{O}_1, \text{Si}_1\text{O}_2, \text{HZr}$ )

**Results and Discussion:** The calculated preliminary total phonon density of states of  $\text{Sc}_2\text{O}_3$  and  $\text{Sc}_4\text{Zr}_3\text{O}_{12}$ , within the harmonic approximation, are shown below (Fig. 1). The phonons obtained within the harmonic approximation are utilized to evaluate and benchmark the calculated Debye temperature and the scaling factor in the Debye-Grüneisen approach. The heat capacity ( $C_p$ ) of  $\text{Sc}_2\text{O}_3$  and  $\text{Sc}_4\text{Zr}_3\text{O}_{12}$  is obtained from the Debye-Grüneisen approach is shown in Figure 2. A good agreement between the experimental and predicted heat capacity (from this work) of  $\text{Sc}_2\text{O}_3$  demonstrates the accuracy of the DB approach.

Table 1. shows the calculated condensation temperatures of  $\text{Sc}_4\text{Zr}_3\text{O}_{12}$  as a function of pressure. The solar gas composition as reported in [5] is employed in the calculations. The preliminary results from modeling show that Zr- and Sc-based allendeite clearly condense at temperatures higher than those of the widely reported minerals in CAIs, e.g., perovskite, hibonite and melilite. These results have important implications for the thermochemistry and dynamics of dust in the early solar protoplanetary disk.

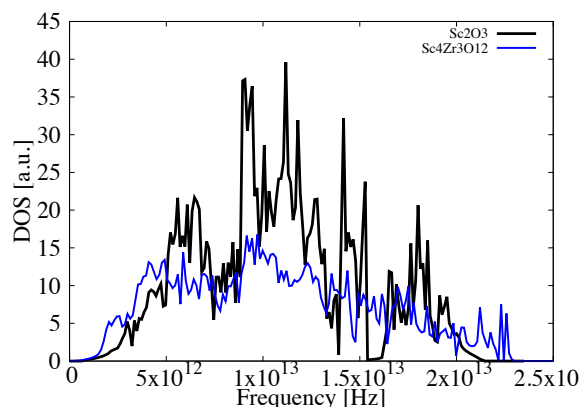


Fig. 1. DOS for  $\text{Sc}_2\text{O}_3$  and  $\text{Sc}_4\text{Zr}_3\text{O}_{12}$  (the non-analytical term correction to be incorporated).

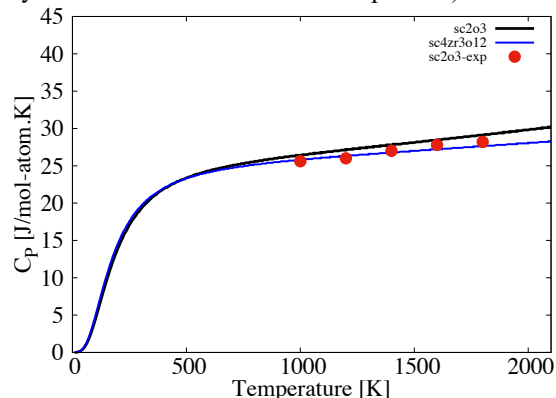


Fig. 2. Heat capacity of  $\text{Sc}_2\text{O}_3$  and  $\text{Sc}_4\text{Zr}_3\text{O}_{12}$  as a function of temperature.

Table 1: Condensation temperatures.

	$10^{-3}$ bar	$10^{-4}$ bar	$10^{-5}$ bar
$\text{Sc}_4\text{Zr}_3\text{O}_{12}$	1925 K	1830 K	1730 K

That URs occur within CAIs suggest that they could have formed prior to their host inclusions [1]. Our thermodynamic modeling appears to support such a scenario. We hypothesize that UR dust such as allendeite, when transported from the high-temperature region ( $>1700$  K) of the disk due to gas-and-dust dynamics [11], can induce heterogeneous nucleation sites for minerals phases that commonly occur in CAIs. Their nano-to atomic-scale structure should help test such a hypothesis. Further, we propose that astrophysical models aimed at describing the dust-and-gas dynamics especially in the inner region of the solar protoplanetary disk consider the high-temperature limits predicted in this work.

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**References:** [1] Rubin et al. (2021) *Meteorite Mineralogy*. Cambridge University Press. [2] Genzel et al. (2020) *Goldschmidt abstract*. [3] MacPherson G.J. (2014) *Treatise on Geochemistry*. Oxford:Elsevier. [4] Ebel D.S. and Grossman L. (2000) *Geochimica et Cosmochimica Acta* 64:339-366. [5] Lodders K. (2003) *The Astrophysical Journal* 591:1220-1247. [6] Amelin Y. et al. (2002) *Science* 297:1678-1683. [7] Connolly J. N. et al. (2012) *Science* 338: 651-655. [8] Kresse G. and Joubert J. (1999) *Phys. Rev. B* 59: 1758-1775. [9] Perdew J.P. et al. (1996) *Phys. Rev. Lett.*, 77, 3865-3868. [10] Anderson O.L. (1995) *Equations of state of solids for geophysics and ceramic science*. New York: Oxford university press. [11] Zega et al. (2021) *Planetary Science Journal*, 2:115