

LiCl-KCl-NaCl working title...

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Abstract

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1. Introduction

Due to the favorable properties, such as the wide range of thermal stability and chemical and radio-chemical stability, molten halides are widely used in electro refining, nuclear waste recycling, and aluminum production applications [1]. Alkali halides are not only widely used in the electrolysis process, but also in solar storage [2] and as nuclear coolants [3].

Some intro about molten salts/reactors

Info about experimental data for salts

Some intro about computational methods into salts

What work has been done in these systems?

What we will do?

2. Computational Methods

The AIMD simulations were performed with the VASP code [4]. All simulations used the Γ point for integration in reciprocal space. The plane wave cut-off energy was increased above the standard setting to 500 eV, which is 200 eV above the recommended value. Gaussian smearing with a smearing parameter of 0.02 eV was used for the partial occupancies of the wave functions. The convergence criteria for the electronic minimization was at most 10^{-4} eV. The Projector Augmented Wave (PAW) method was used to describe the core electrons [5, 6]. It is well-established in the literature that Van der Waals (vdW), or dispersion, interactions are critical for reproducing the density of molten salts by DFT methods [7, 8, 9]. In general, density functional theory methods are unable to describe Van der Waals dispersion forces. A pragmatic method to work around this problem is to add a correction to the conventional Kohn-Sham DFT energy. This is performed through the addition of a vdW correction, or a replacement of the exchange-correlation functional to account for dispersion interactions. Previous simulations have used both the DFT-D3 [7, 10] and the Langreth & Lundqvist (vdW-DF2) [9, 11, 12] methodologies for various molten chloride salts. In this

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Compositions including the three molecular species, pseudo-binary eutectics, and various ternary compositions are investigated in this work, shown in fig. 1.



2

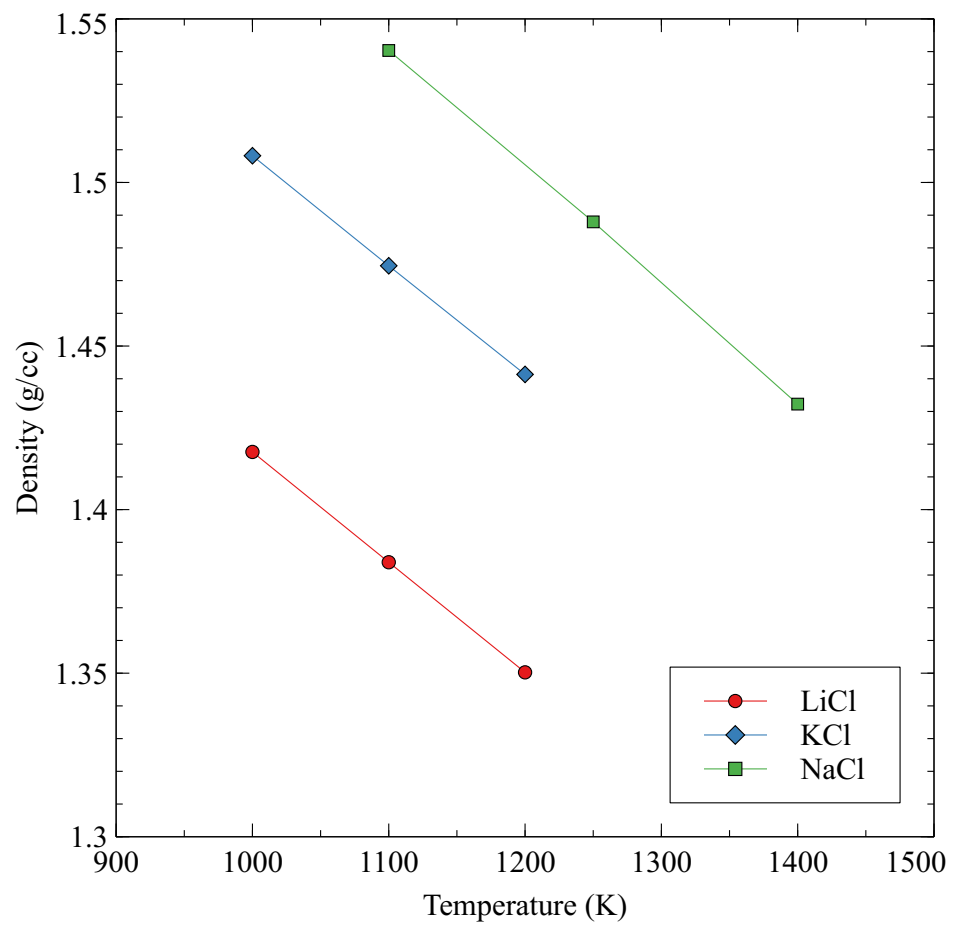


Figure 2: Densities of LiCl, KCl, and NaCl as a function of temperature.

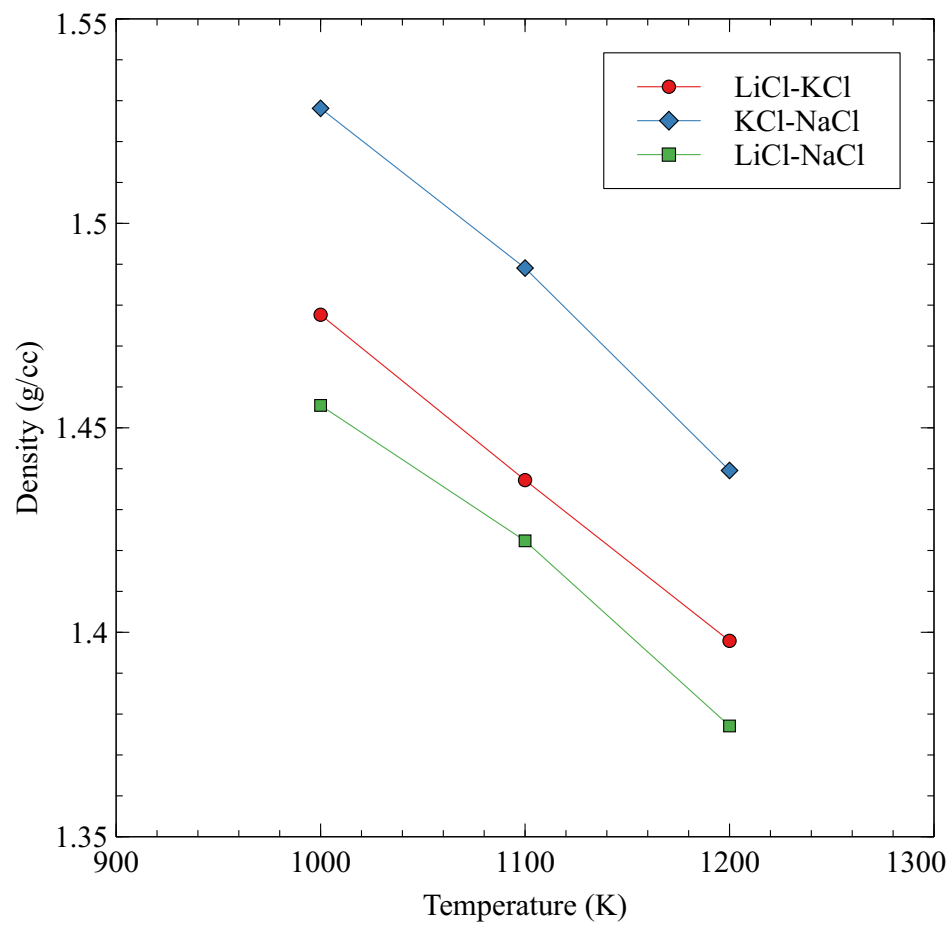


Figure 3: Densities of the eutectic compositions of LiCl-KCl, KCl-NaCl, and LiCl-NaCl as a function of temperature.

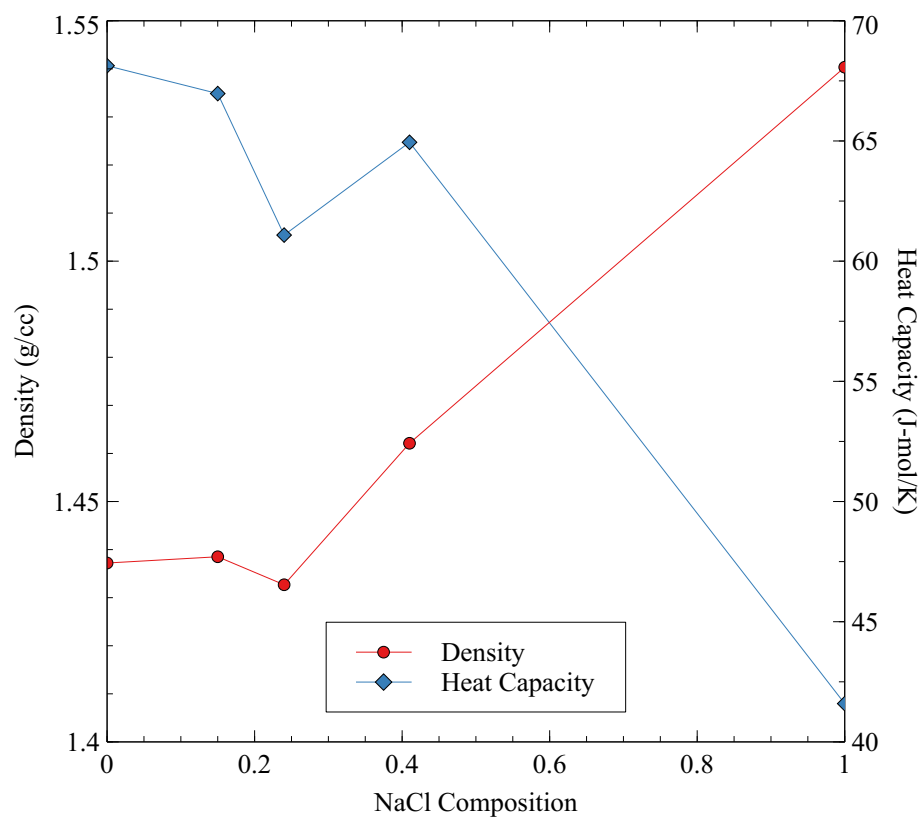


Figure 4: Density and heat capacity of the LiCl-KCl-NaCl system at 1100 K as a function of NaCl composition.

4. Conclusions

5. Acknowledgements

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References

- [1] A.-L. Rollet, M. Salanne, Studies of the local structures of molten metal halides, *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* 107 (2011) 88–123. doi:[10.1039/C1PC90003J](https://doi.org/10.1039/C1PC90003J).
URL <http://dx.doi.org/10.1039/C1PC90003J>
- [2] J. Ding, G. Pan, L. Du, J. Lu, X. Wei, J. Li, W. Wang, J. Yan, Theoretical prediction of the local structures and transport properties of binary alkali chloride salts for concentrating solar power, *Nano Energy* 39 (2017) 380–389. doi:<https://doi.org/10.1016/j.nanoen.2017.07.020>.
URL <https://www.sciencedirect.com/science/article/pii/S2211285517304330>
- [3] X. Li, J. Song, S. Shi, L. Yan, Z. Zhang, T. Jiang, S. Peng, Dynamic fluctuation of u^{3+} coordination structure in the molten $liCl$ – kCl eutectic via first principles molecular dynamics simulations, *The Journal of Physical Chemistry A* 121 (3) (2017) 571–578, PMID: 28045530. arXiv:<https://doi.org/10.1021/acs.jpca.6b10193>, doi:[10.1021/acs.jpca.6b10193](https://doi.org/10.1021/acs.jpca.6b10193).
URL <https://doi.org/10.1021/acs.jpca.6b10193>
- [4] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Computational Materials Science* 6 (1) (1996) 15–50. doi:[https://doi.org/10.1016/0927-0256\(96\)00008-0](https://doi.org/10.1016/0927-0256(96)00008-0).
URL <http://www.sciencedirect.com/science/article/pii/0927025696000080>
- [5] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B* 59 (1999) 1758–1775.
- [6] P. E. Blöchl, Projector augmented-wave method, *Phys. Rev. B* 50 (1994) 17953–17979.
- [7] B. Li, S. Dai, D.-e. Jiang, First-Principles Molecular Dynamics Simulations of UCl_n - $NaCl$ ($n = 3, 4$) Molten Salts, *ACS Appl. Energy Mater.* 2 (2019) 2122–2128.
- [8] H. O. Nam, A. Bengtson, K. Vörtler, S. Saha, R. Sakidja, D. Morgan, First-principles molecular dynamics modeling of the molten fluoride salt with Cr solute, *J. Nucl. Mater.* 449 (2014) 148.

- [9] H. O. Nam, D. Morgan, Redox condition in molten salts and solute behavior: A first-principles molecular dynamics study, *J. Nucl. Mater.* 465 (2015) 224.
- [10] S. Grimme, S. Ehrlich, L. Goerigk, Effect of the damping function in dispersion corrected density functional theory, *J. Comp. Chem.* 32 (7) (2011) 1456–1465.
- [11] M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, B. I. Lundqvist, Van der Waals Density Functional for General Geometries, *Phys. Rev. Lett.* 92 (2004) 246401.
- [12] J. Klimeš, D. R. Bowler, A. Michaelides, Van der Waals density functionals applied to solids, *Phys. Rev. B* 83 (2011) 195131.
- [13] K. Duemmler, Y. Lin, M. Woods, T. Karlsson, R. Gakhar, B. Beeler, Evaluation of thermophysical properties of the licl-kcl system via ab initio and experimental methods, *Journal of Nuclear Materials* (2021) 153414doi:<https://doi.org/10.1016/j.jnucmat.2021.153414>.
URL <https://www.sciencedirect.com/science/article/pii/S0022311521006346>