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FY20 Status report on the Molten Salt Thermodynamic Database (MSTDB) development

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OAK RIDGE NATIONAL LABORATORY
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CONTENTS

ABSTRACT

The current status of the Molten Salt Thermodynamic Database (MSTDB) is reported. While a series of informational exchange meetings with Moten Salt Reactor (MSR) developers has given the NEAMS program insight into the systems of interest, the current effort is devoted to mining data already available in the literature for continued development of MSTDB. Many relevant systems have not been previously studied. Therefore, once the data from the literature is completely reviewed, curated, and used as inputs for MSTDB, new thermodynamic values will need to be generated using computational and experimental approaches.

1. INTRODUCTION

The Molten Salt Thermodynamic Database (*MSTDB*) consists of Gibbs energy models for fluoride and chloridebased systems of interest for molten salt reactor (MSR) technology and related heat transfer applications. It has been prepared for its initial public release through the code.ornl GitLab repository hosted by Oak Ridge National Laboratory (ORNL) and is available via request to an ORNL U. S. Department of Energy representative. The repository includes the following files for *MSTDB*:

- Data files in the ASC II .dat format for the full databases.
- Documentation Excel files (data packages) provided for each subsystem which are intended to make information easily traceable to original sources [1-25]. The data packages provide an account of all pure compounds, liquid solutions and solid solutions used in modeling the subsystems with linked references. Modeling parameters from newly performed work are also reported in the data package along with all applicable references.
- An Excel file containing the thermodynamic values used for all pure compounds of the *MSTDB* along with linked references.
- Readme files in the code.ornl format for each of the major directories of the repository. These files provide details and explanations for the files contained within each major directory.

Complete descriptions of the contents of the solution databases can also be found in the Appendix of this document. The following is a brief description of the database content:

- Liquid solutions are modeled with the Modified Quasi-chemical Model (SUBG[1]).
- Solid solutions are modeled by either the Compound Energy Formalism (SUBL[1]) or the one-lattice polynomial model (QKTO[1]).
- Values for 136 total pure compounds
- Fluoride-based salt systems (nicknamed MSAX):
    - Contains the following elements: Be-Ca-Ce-Cs-K-La-Li-Mg-Na-Nd-Ni-Pu-Rb-Th-U-F
    - 48 pseudo-binary subsystems (Fig. 1)
    - 28 pseudo-ternary subsystems
    - 3 higher order systems:
    - 23 solid solutions

[1] The four-letter codes reflect the type of solution thermodynamic model that is employed.

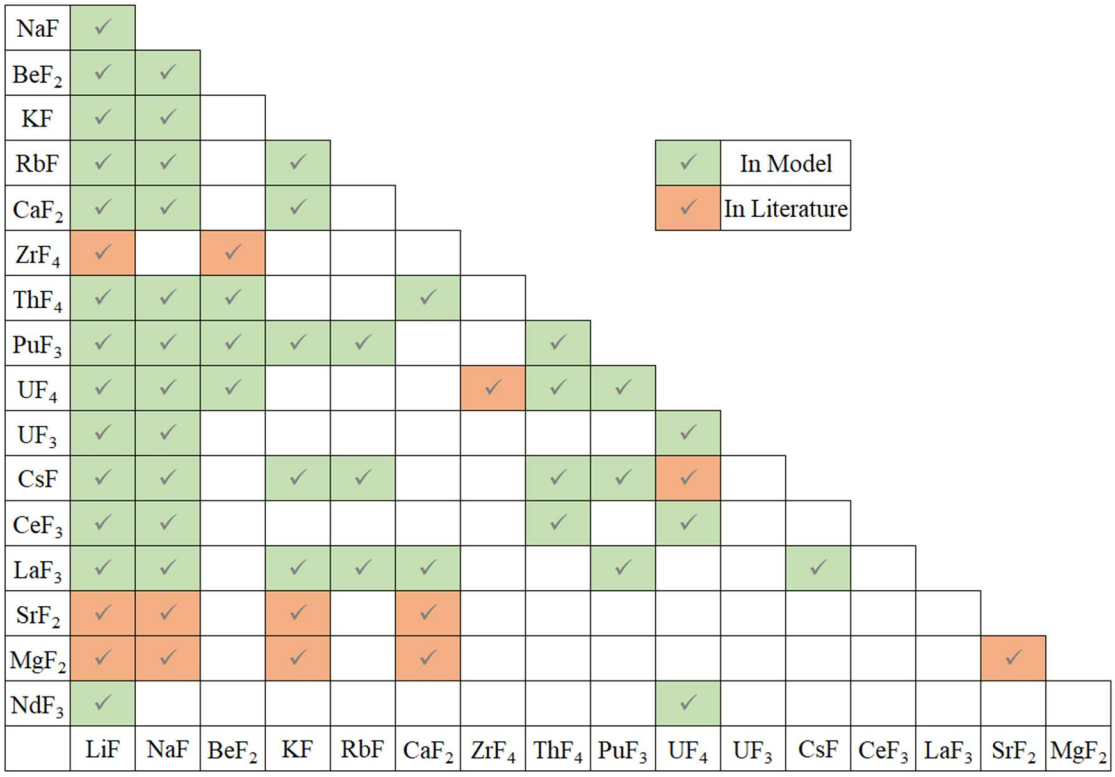

Figure 1 – Fluoride-based pseudo-binary assessment status.

- Chloride-based salt system (nicknamed CLAK):
  - Contains the following elements: Cs-K-Li-Mg-Na-Pu-U-Cl
  - 12 pseudo-binary subsystems (Fig. 2)
  - 1 pseudo-ternary subsystem
  - 3 solid solutions
  - Models for excess K and Mg in solution

Future updates to the *MSTDB* will continue to increase the overall capability of the database by incorporating additional published systems as well as newly assessed systems.

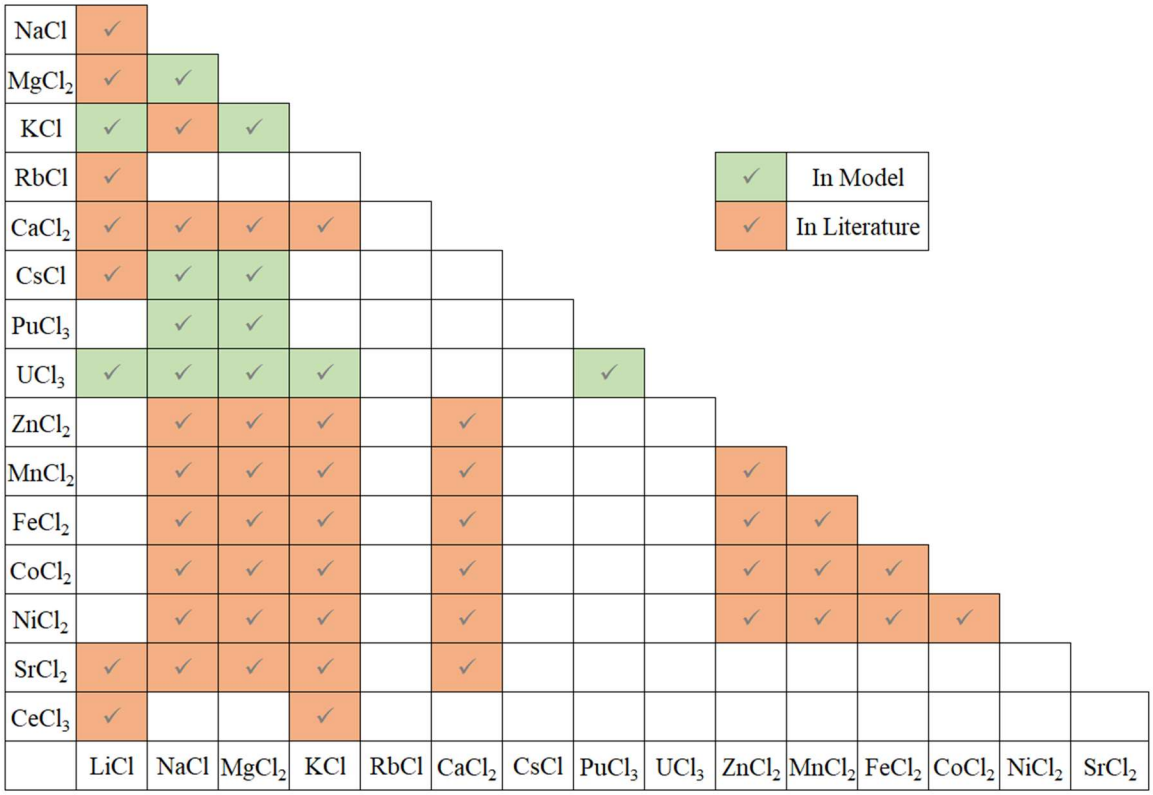

Figure 2 – Chloride-based Pseudo-binary Assessment Status

Note on naming conventions: Versions of the *MSTDB* databases are identified by four-letter names assigned to files where the first two letters, either MS or CL, designate whether it is fluoride- or chloride-based, respectively. The last two letters are used to increment the version of the database; following the pattern AA, AB, AC, … , AZ, BA, … , etc. The current datafiles are named MSAX and CLAK, respectively. Similarly, the solid solutions of the *MSTDB* are assigned four-letter names in where the first two letters are always SS. Each solid solution is assigned an individual pair of last two letters. Currently, aa-bz are reserved for fluoride-based solid solutions, and ca-dz are reserved for chloride-based solid solutions. SSaa-SSay and SSca-SScc are currently in use for the fluoride-based and chloride-based solid solutions, respectively. This may be changed in the future as the number of solid solutions grows.

2. DEVELOPMENT

The *MSTDB* is intended to include both fueled and un-fueled molten salt systems, consequential fission product and transuranic elements, contaminants such as air and moisture, and likely corrosion product elements such as nickel and chromium. Phases include the ideal gas, liquids (e.g., molten salts, noble metals), and solid compounds. Solutions include the fluoride- and chloride-based molten salts as well as a number of solid solutions. The database is provided in the Chemsage ASC II format accessible with the FactSage® commercial thermodynamic software suite and compatible with the open source equilibrium code Thermochimica (i.e., in the .dat format).

The models and values within *MSTDB* are obtained through combinations of literature-reported information, first principles calculations, and experimental measurements for performing pseudo-binary, pseudo-ternary, and higher order system assessments. A system is said to be assessed when sufficient

experimental and theoretical data are available to optimize adjustable thermochemical values and parameters for each phase in the system. A system is sufficiently assessed when models and values allow accurate computing of the phase equilibria (e.g. phase diagrams) and attendant values such as heat capacity and vapor pressures.

Maintaining consistency among unary, binary, and other stoichiometric compound thermodynamic values throughout the database is vital as these form the basis on which solution models are developed. As each component in the solution can appear in multiple subsystems, these fundamental values need to be consistent across all solutions. In order to accomplish this, a single set of thermodynamic values must be selected for each compound and used for all solutions. An effort was made to select the most widely accepted thermodynamic values for pure compounds, as any need to change the values in the future could require re-assessment of all affected systems. Due to differences in pure compound values between data sources, development of the current *MSTDB* required a number of re-assessments of published solution models to allow inclusion in the database.

The following is the list of systems for which published thermodynamic values were re-assessed to allow the database to be consistent across all the components.

Re-assessed systems:

- NaF-LaF3
- KF-RbF
- KF-CsF
- KF-CaF2
- LaF3-CaF2
- ThF4-CsF
- LiF-NaF
- LiF-CeF3
- NaF-CeF3
- NaCl-MgCl2
- MgCl2-CsCl
- MgCl2-UCl3
- LiF-ThF4-CaF2
- LiF-NaF-CeF3
- LiF-NaF-ThF4

A conversion issue between FactSage® and Thermochimica was discovered early in *MSTDB* development in collaboration with Dr. M.H.A Piro at Ontario Tech University. The presence of any two-lattice polynomial (SUBM) solid solutions caused Thermochimica to be unable to import the solution database. As compatibility of the database with Thermochimica is a project goal, it was necessary to re-assess all published models using the SUBM solid solutions so as to utilize one-lattice polynomial (QKTO) models, which could be imported to Thermochimica. Full details of the re-assessed values can be found directly in the systems' data package Excel files available on code.ornl. Below is the list of solid solutions for which this was necessary.

SUBM to QKTO converted solid solutions:

- SSab = (Pu, Th)Fx
- SSat = (U, Pu)Fx
- SSau = (U, Th)Fx
- SSam = (Li, Na, K, Rb,Cs)F
- SSan = (Ce, Th)F
- SSao = (Ca, Th)F
- SSap/SSaq = (Ca, La)F

A number of original assessments have been performed by the Besmann group at University of South Carolina. These utilized published phase equilibria data, thermodynamic values, assessments of proxy systems, and/or reassessments from an original solution model to one preferred for *MSTDB*, following the CALPHAD method. Full details of the newly assessed systems can be found directly in the system data package Excel files available on code.ornl. Below is the list of newly assessed systems.
Newly assessed systems:

- NaF-CeF3
- CeF3-UF4
- LiF-NdF3
- NdF3-UF4
- LiCl-KCl-UCl3
- UF3-UF4

3. AVAILABILITY

The *MSTDB* is hosted on the Oak Ridge National Laboratory code.ornl GitLab repository where the full fluoride- and chloride-based salt solution and compound databases are available in the .dat format readable by both FactSage® and Thermochimica. In addition to the full databases, individual .dat files are available for all modeled pseudo-binary and pseudo-ternary subsystems. An Excel file containing the thermodynamic values used for all pure compounds in the *MSTDB* along with linked references is also available in the mstdb/models/Data_Packages directory of the repository.

To ensure ease of traceability for all database systems, data packages have been generated for each *MSTDB* subsystem. The data packages are Excel files with multiple sheets which list the compounds, liquid interactions, and solid solutions alongside links to their references. All references used in creating the *MSTDB* have been assigned an internal reference number, which is consistent across all *MSTDB* documentation files. Quality assurance testing was performed independently by Oak Ridge National Laboratory where all systems were evaluated against the open literature.

Readme files are included for each of the major directories of the repository that provide up-to-date details and explanation of the contained files. A readme file which contains a full change log for new updates can be found in the main *MSTDB* directory.

Access to the code.ornl GitLab repository and downloading of the database can be obtained by request to Dr. J. W. McMurray (mcmurrayjw1@ornl.gov).

4. FUTURE WORK

The initial release of the *MSTDB* contains nearly half of publicly available assessed fluoride- and chloride-based salt systems as well as systems newly assessed in the current work. Future updates to the *MSTDB* are intended to be released as the following tasks are completed:

- The addition of the remaining published systems (Figs. 1 and 2) as well as potentially newly published systems, with re-assessments performed as necessary.
- New system assessments performed at the University of South Carolina, Oak Ridge National Laboratory, and collaborators.
- As needed re-assessments and/or corrections to systems already included in the *MSTDB*

5. ACKNOWLEDGEMENTS

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REFERENCES

[1] E. Capelli, O. Benes, R. J. M. Konings, *Journal of Nuclear Materials*, 449 (1-3) (2014) 111-21.
[2] O. Benes, R. J. M. Konings, *CALPHAD*, 32 (1) (2008) 121-8.
[3] O. Benes, R. J. M. Konings, *Journal of Nuclear Materials*, 377 (3) (2008) 449-57.
[4] P. Chartrand, A. D. Pelton, *Metallurgical and Materials Transactions a-Physical Metallurgy and Materials Science*, 32 (6) (2001) 1385-96.
[5] O. Benes, J. P. M. van der Meer, R. J. M. Konings, *Calphad-Computer Coupling of Phase Diagrams and Thermochemistry*, 31 (2) (2007) 209-16.
[6] O. Benes, R. J. M. Konings, *Journal of Nuclear Materials*, 435 (1-3) (2013) 164-71.
[7] J. P. M. van der Meer, R. J. M. Konings, K. Hack, H. A. J. Oonk, *Chem. Mater.*, 18 (2) (2006) 510-7.
[8] E. Capelli, O. Benes, P. E. Raison, M. Beilmann, C. Kunzel, R. J. M. Konings, *Journal of Chemical and Engineering Data*, 60 (11) (2015) 3166-74.
[9] N. Vozarova, A. L. Smith, J. Y. Colle, P. E. Raison, D. Bouexiere, R. J. M. Konings, O. Benes, *Journal of Chemical Thermodynamics*, 114 (2017) 71-82.
[10] X. Li, K. Wang, M. Y. Xie, Z. Wu, L. D. Xie, *Chemical Research in Chinese Universities*, 33 (3) (2017) 454-9.
[11] O. Benes, R. J. M. Konings, *Journal of Chemical Thermodynamics*, 41 (10) (2009) 1086-95.
[12] E. Capelli, O. Benes, R. J. M. Konings, *Journal of Nuclear Materials*, 462 (2015) 43-53.
[13] R. Thoma, Phase Diagrams of Nuclear Reactor Materials, Oak Ridge National Laboratory: ORNL-2548; 1959.
[14] R. Thoma, Rare Earth Halides, Oak Ridge National Laboratory: ORNL-3804; 1965.
[15] R. E. Thoma, H. Insley, G. D. Brunton, *Journal of Inorganic & Nuclear Chemistry*, 36 (5) (1974) 1095-8.
[16] J. A. Ocadiz-Flores, E. Capelli, P. E. Raison, R. J. M. Konings, A. L. Smith, *J. Chem. Thermodyn.*, 121 (2018) 17-26.
[17] M. Beilmann, O. Benes, R. J. M. Konings, T. Fanghanel, *Journal of Chemical Thermodynamics*, 57 (2013) 22-31.
[18] P. Chartrand, A. D. Pelton, *Metallurgical and Materials Transactions a-Physical Metallurgy and Materials Science*, 32 (6) (2001) 1361-83.
[19] O. Benes, R. J. M. Konings, *Journal of Nuclear Materials*, 375 (2) (2008) 202-8.
[20] M. Beilmann, O. Benes, R. J. M. Konings, T. Fanghanel, *J. Chem. Thermodyn.*, 43 (10) (2011) 1515-24.
[21] O. Benes, M. Beilmann, R. J. M. Konings, *Journal of Nuclear Materials*, 405 (2) (2010) 186-98.
[22] J. W. McMurray, S. S. Raiman, *Solar Energy*, 170 (2018) 1039-42.
[23] J. Sangster, A. D. Pelton, *Journal of Physical and Chemical Reference Data*, 16 (3) (1987) 509-61.
[24] C. Robelin, P. Chartrand, A. D. Pelton, *Journal of Chemical Thermodynamics*, 36 (8) (2004) 683-99.
[25] S. Ghosh, B. P. Reddy, K. Nagarajan, K. C. H. Kumar, *Calphad-Computer Coupling of Phase Diagrams and Thermochemistry*, 45 (2014) 11-26.

APPENDIX A. LIST OF PHASES IN MSTDB

APPENDIX A. LIST OF PHASES IN MSTDB

Full lists of all compounds, pseudo-binary systems, pseudo-ternary systems, and solid solutions included in the initial release of the *MSTDB* (MSAX and CLAK) are given below. This information can also be found in the code.ornl readme files as well as the MSTDB_Compounds_with_Refs.xlsx file in the mstdb/models/Data_Packages directory.

Pure Compounds (136):

(KCl)2	K2	MgCl	PuF
Be	K2F2	MgCl2	PuF2
BeF2	K2MgCl4	Na	PuF3
Ca	K2MgF4	Na2BeF4	PuF6
CaF2	K2NiF4	Na2MgCl4	Rb
CaThF6	K3LaF6	Na2ThF6	Rb2LaF5
Ce	K3Mg2Cl7	Na2UF6	Rb2PuF5
CeF3	K3PuF6	Na3BeTh10F45	Rb3LaF6
CeTh2F11	KCaF3	Na3Th2F11	Rb3PuF6
CeThF7	KCl	Na3UF7	RbF
Cr	KF	Na4ThF8	RbLa2F7
CrCl2	KLaF4	Na5U3F17	RbLaF4
CrCl3	KMgCl3	Na7Th2F15	RbPuF4
CrCl4	KMgF3	Na7Th6F31	Sr
CrCl5	KNiF3	Na7U6F31	Th
CrCl6	KPuF4	NaBeF3	Th2F9Li
Cs	La	NaCeF4	Th2PuF11
Cs2MgCl4	LaF3	NaCl	Th4F17Li
Cs2Th3F14	Li	NaF	ThF4
Cs2ThF6	Li2BeF4	NaLaF4	ThF5Li
Cs3LaF6	Li2CaThF8	NaMgCl3	ThF7Li3
Cs3MgCl5	Li2NiF4	NaNiF3	U
Cs3PuF6	LiBeF3	NaPuF4	U2PuF11
Cs3ThF7	LiCl	NaTh2F9	U4F17Li
CsCaCl3	LiCs2Cl3	NaThF5	U6F31Li7
CsCl	LiCsF2	NaU2F9	UCl2
CsF	LiF	NaU4F17	UCl3
CsMg3Cl7	LiNa2Be2F7	NaUF4	UCl5
CsMgCl3	LiNa5Be3F12	Nd	UCl6
CsTh2F9	LiNaBeF4	NdF3	UF3
CsTh3F13	LiRbF2	Ni	UF4
CsTh6F25	LiU2F9	NiF2	UF8Li4
CsThF5	Mg	Pu	Zn
K	Mg2	PuCl3	Zr

Solid Solutions (26):

- SSaa = (Li, Na)7Th6F31
- SSab = (Pu, Th)Fx
- SSac = Li(Th, U)4F17
- SSad = Li(Th, U)2F9
- SSae = Li7(Th, U)6F31
- SSaf = Li3(Th, U)F7
- SSag = Na2(Th, U)F6
- SSah = Na7(Th, U)6F31
- SSai = Na(Th, U)2F9
- SSam = (Li, Na, K, Rb, Cs)F
- SSan = (Ce, Th)Fx
- SSao = (Ca, Th)Fx
- SSap = (Ca, La)Fx
(LaF3 destabilized)
- SSaq = (Ca, La)Fx
(CaF2 destabilized)
- SSar = (La, Pu)Fx
- SSas = (Na, Th)Fx
- SSat = (U, Pu)Fx
- SSau = (U, Th)Fx
- SSav = Li3ThF7-BeF2-LiBeThF7
- SSaw = (Li, Na)7U6F31
- SSax = Na7(Th, U)2F15
- SSay = Na3Th2F11-Na5U3F17
- UF34 = UF(3+x)
- SSca = (U, Pu)Cl3
- SScb = (Li, K)Cl
- SScc = (Li, K)Cl

Fluoride-based System (MSAX):

MSAX solution database contains Be-Ca-Ce-Cs-K-La-Li-Na-Nd-Pu-Rb-Th-U-F

Pseudo-binary systems (48):

- LiF-BeF2
- LiF-UF4
- BeF2-UF4
- LiF-ThF4
- BeF2-ThF4
- LiF-UF3
- NaF-UF3
- LiF-NaF
- BeF2-NaF
- NaF-ThF4
- NaF-UF4
- UF4-PuF3
- LiF-PuF3
- NaF-PuF3
- LiF-RbF
- LiF-LaF3
- NaF-RbF
- NaF-LaF3
- RbF-LaF3
- LiF-CsF
- NaF-CsF
- LaF3-CsF
- ThF4-CsF
- PuF3-CsF
- PuF3-RbF
- LiF-KF
- NaF-KF
- RbF-KF
- LaF3-KF
- CsF-KF
- PuF3-KF
- LiF-CaF2
- NaF-CaF2
- KF-CaF2
- ThF4-CaF2
- LaF3-CaF2
- LiF-CeF3
- ThF4-CeF3
- ThF4-UF4
- ThF4-PuF3
- UF3-UF4
- CeF3-UF4
- CeF3-NaF
- LiF-NdF3
- NdF3-UF4
- NaF-CsF

Pseudo-ternary systems (28):

- LiF-BeF2-UF4
- LiF-BeF2-ThF4
- BeF2-UF4-ThF4
- BeF2-NaF-ThF4
- BeF2-NaF-UF4
- LiF-BeF2-NaF
- LiF-NaF-UF4
- NaF-UF4-ThF4
- LiF-ThF4-PuF3
- LiF-UF4-PuF3
- LiF-BeF3-PuF3
- BeF2-NaF-PuF3
- LiF-NaF-LaF3
- LiF-NaF-RbF
- LiF-LaF3-CsF
- LiF-NaF-PuF3
- LiF-PuF3-CsF
- LiF-NaF-KF
- LiF-KF-CsF
- LiF-KF-RbF
- LiF-KF-CaF2
- NaF-KF-CaF2
- LiF-ThF4-CaF2
- LiF-LaF3-CaF2
- NaF-LaF3-CaF2
- LiF-ThF4-CeF3
- LiF-NaF-CeF3

Chloride-based System Solutions (CLAK):

CLAK solution database contains Cr-Cs-K-Li-Mg-Na-Pu-U-Cl

Pseudo-binary systems (12):
- NaCl-MgCl2
- NaCl-CsCl
- NaCl-PuCl3
- NaCl-UCl3
- MgCl2-CsCl
- MgCl2-PuCl3
- MgCl2-UCl3
- MgCl2-KCl
- PuCl3-UCl3
- LiCl-KCl
- LiCl-UCl3
- KCl-UCl3
- K-KCl
- Mg-MgCl2

Pseudo-ternary systems (1 Total):
- KCl-LiCl-UCl3