Interplay of physicochemical and structural features in ionic compounds and melts

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Why lanthanide halides?

- Increasing technological importance
- Alloys production
- Lighting industry
- Nuclear waste processing
- Recycling of spent nuclear fuel
- Energy of future
- Electrodeposition of metals etc.

Outlines

- New experimental data on selected divalent and trivalent lanthanide halide mixtures with MX
- Topology of phase diagrams
- Modeling and processing by statistical techniques of large data sets where our original results have been incorporated

Experimental techniques

- High temperature calorimetry – *Calvet* Microcalorimetry
- Differential Scanning Calorimetry (DSC)
- Electrical conductivity measurements
- Reflectance and *Raman* spectroscopy

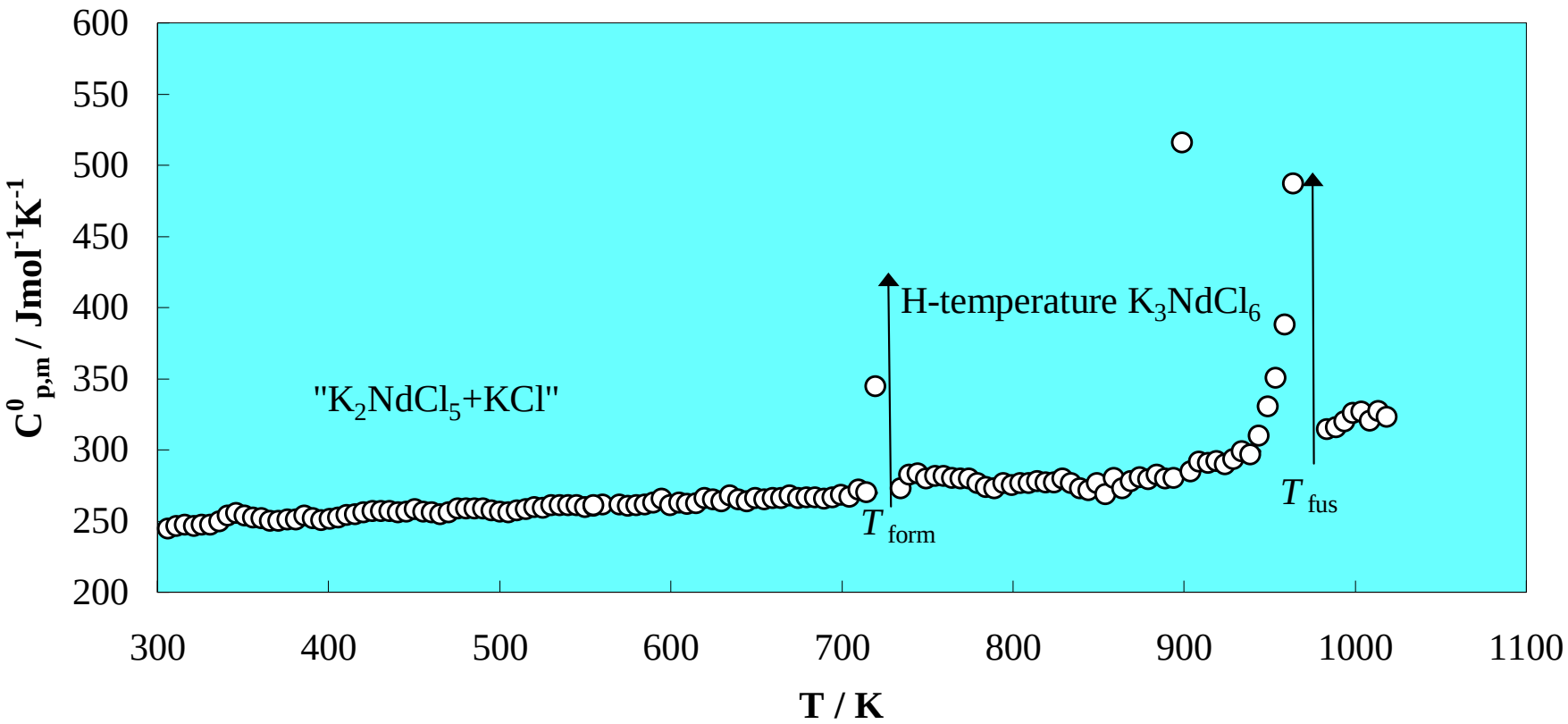
M_3LnX_6 compounds (3:1 compounds)

- Compounds formed at higher temperatures in reaction between M_2LnX_5 and MX - (reconstructive phase transition)
- Compounds stable or metastable at low temperatures (non-reconstructive phase transition)

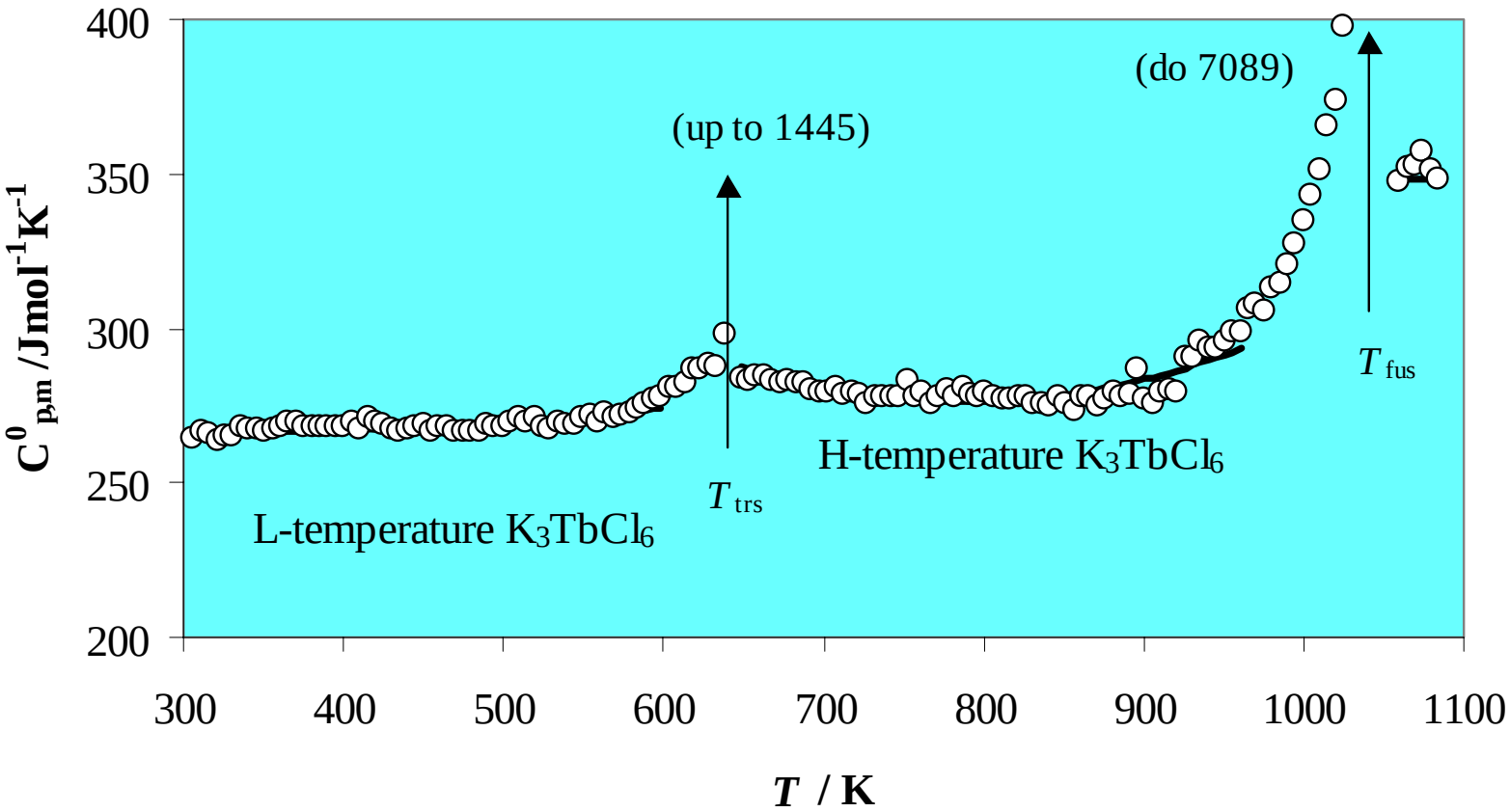
- Compounds formed at higher temperatures have only high-temperature crystal structure (cubic, elpasolite-type)
- Formation of compounds at higher temperatures (reconstructive phase transition) is followed by high molar enthalpy(~30-50 kJ mol^{-1})

- Compounds stable or metastable at low temperatures have low-temperature (monoclinic, Cs_3BiCl_6 - type) and high-temperature (cubic, elpasolite-type) crystal structures
- Transition from low- to high-temperature modification (non-reconstructive phase transition) is followed by significantly lower molar enthalpy (6-10 kJ mol^{-1})

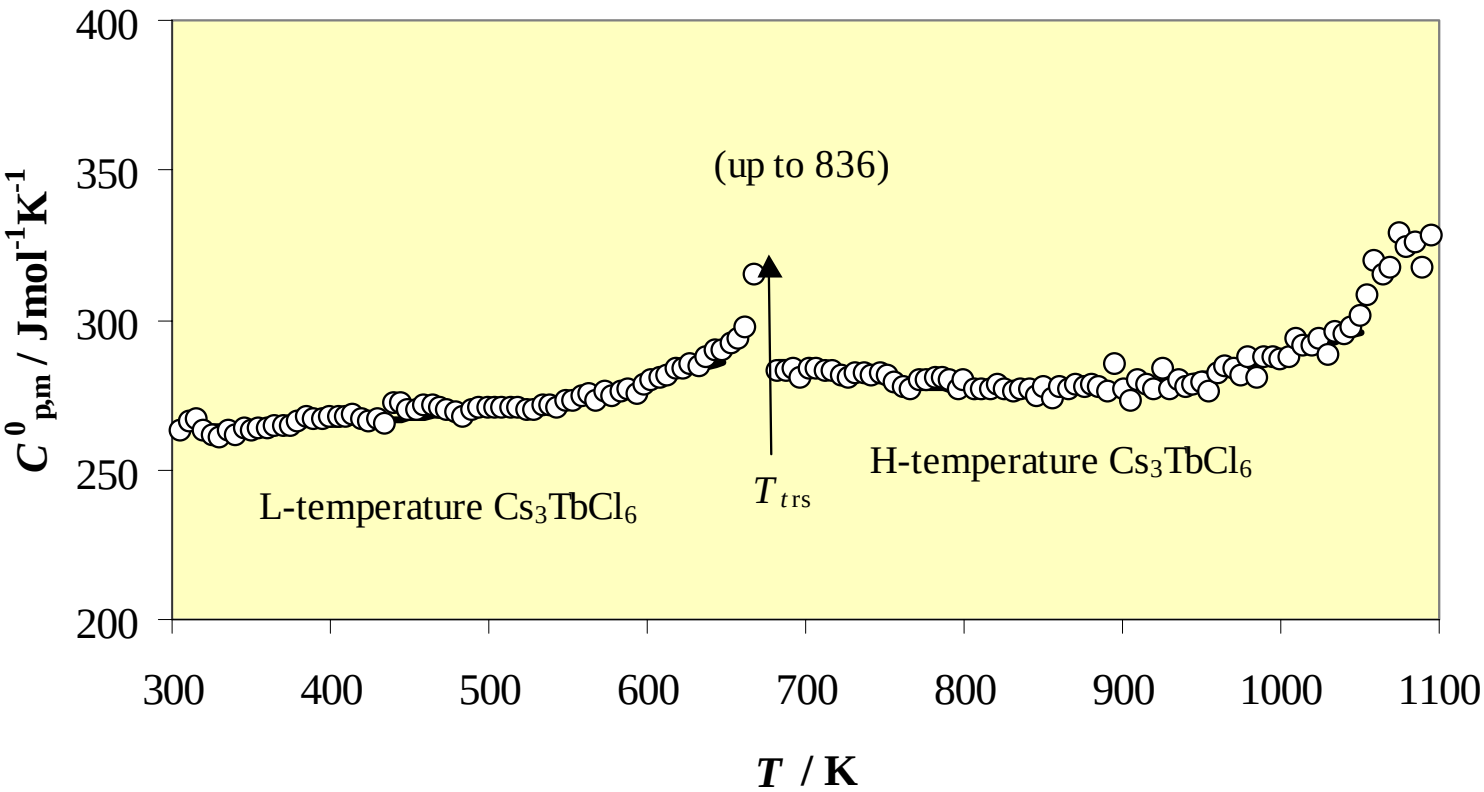
Heat capacity of K_3NdCl_6



Heat capacity of K_3TbCl_6



Heat capacity of Cs_3TbCl_6



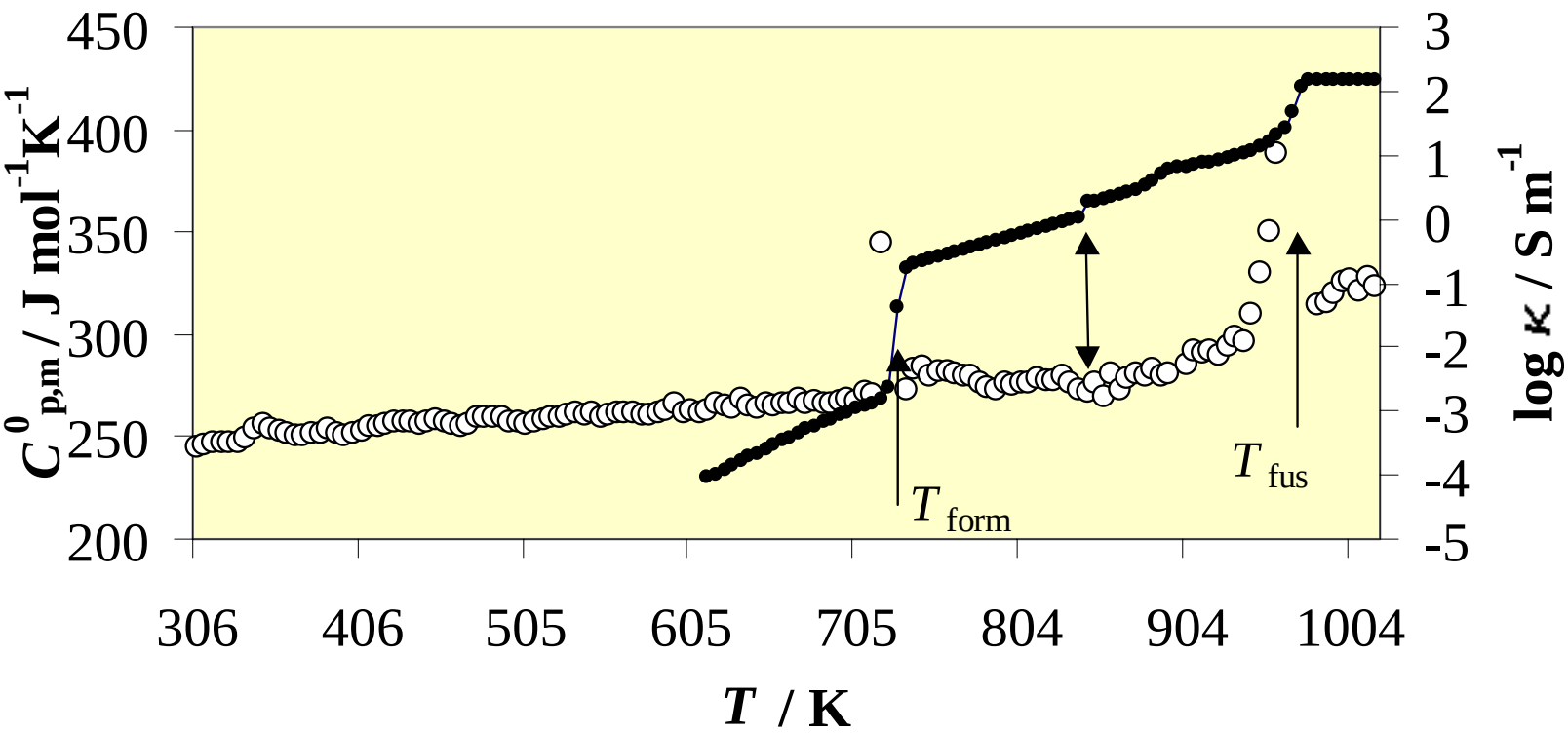
O ’Keeffe and Hyde «The Solid Electrolyte Transition and Melting in Salts»

- Simple, quantitative model of solid electrolyte - electrolyte properties are the result of existing of disordered phase with ionic conductivity
- Crystals with solid electrolyte phases pass, either gradually, or through a series of phase transitions, from normal ionic conductivity (0.1 Sm^{-1}) to liquidlike values while still solid.

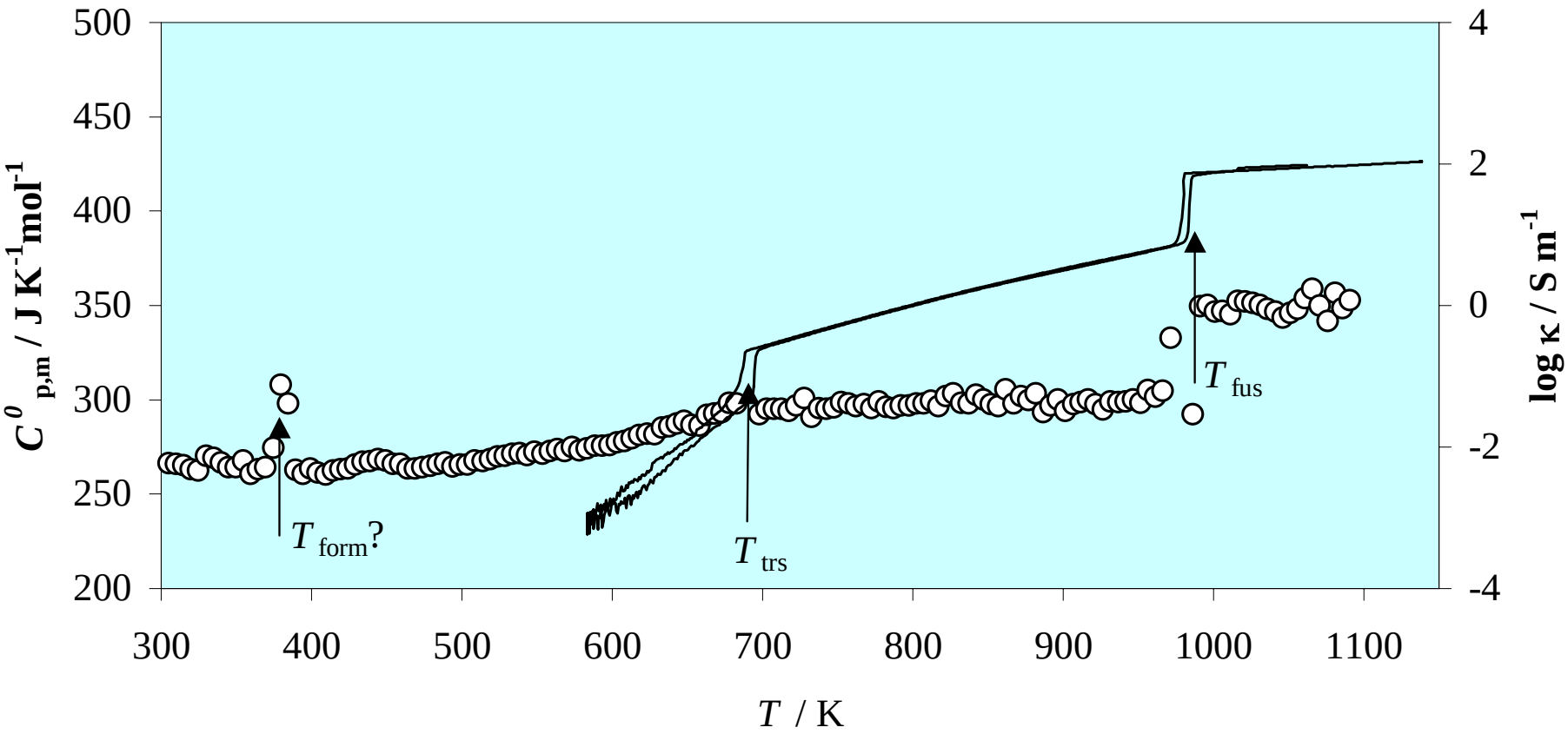
O ’Keeffe and Hyde «The Solid Electrolyte Transition and Melting in Salts»

- Superionic phase is a result of sublattice « melting », that is, atoms on a certain set of lattice positions become mobile, almost liquidlike, while the remaining atoms retain their normal lattice positions

Heat capacity and electrical conductivity of K_3NdCl_6



Heat capacity and electrical conductivity of K_3TbBr_6



- Characteristic dependence of heat capacity and electrical conductivity of solid phase of M_3LnX_6 compounds on temperature is a result of disordering of cationic sublattice formed by alkali metal cations
- Disordering of cationic sublattice in compounds that have only high-temperature modification takes place in a discontinuous way at compound formation temperature
- Disordering of cationic sublattice of compounds that have low- and high-temperature modifications takes place in a continuous way

Phase diagram topology

- Ionic potential (IP): IP = *z*/*r* - for the systems with common anion
- IP_M/IP_{Ln} essential for classification
- Approach valid for trivalent Ln halides
- Divalent Ln halides – less investigated – approach gives only general trends
- Influence of common ion?
- $EuBr_2$-MBr compared with $SrBr_2$-MBr binaries

Ionic potential ratio and $CeBr_3$-MBr phase diagrams (r_{Ce}=103 pm)

	r_M	IP_M/IP_{Ce}	Type of system
$CeBr_3$-LiBr	74	0.464	Eutectic
$CeBr_3$-NaBr	102	0.336	Eutectic
$CeBr_3$-KBr	138	0.249	K_3CeBr_6, K_2CeBr_5
$CeBr_3$-RbBr	149	0.230	Rb_3CeBr_6, Rb_2CeBr_5, *$RbCe_2Br_7$**

* Incongruently melting compound (in italic)

$SrBr_2$-MBr and $EuBr_2$-MBr phase diagrams (r_{Sr}=140 pm; r_{Eu}=139 pm)

System	$IP_M/IP_{Eu, Sr}$	Type of system	References
$SrBr_2$-LiBr	0.946	$LiSr_2Br_5$	Belyaev1962
$SrBr_2$-NaBr	0.686	Eutectic	Belyaev1962
$SrBr_2$-KBr	0.507	K_2SrBr_4, $KSrBr_3$, KSr_2Br_5	Bukhalov1966
$SrBr_2$-RbBr	0.470	Rb_2SrBr_4, $RbSrBr_3$, $RbSr_2Br_5$	Shurginov1969
$SrBr_2$-CsBr	0.412	$CsSrBr_3$	Riccardi1970
$EuBr_2$-LiBr	0.939	$EuSr_2Br_5$	This work
$EuBr_2$-NaBr	0.681	Eutectic	This work
$EuBr_2$-KBr	0.504	K_2EuBr_4, $KEuBr_3$, KEu_2Br_5	This work
$EuBr_2$-RbBr	0.466	Rb_2EuBr_4, $RbEuBr_3$, $RbEu_2Br_5$	This work
$EuBr_2$-CsBr	0.408	$CsEuBr_3$	Unpublished
$SrCl_2$-LiCl	0.946	Eutectic	Belyaev1962
$SrCl_2$-NaCl	0.686	Eutectic	Tokarev1956
$SrCl_2$-KCl	0.507	K_2SrCl_4, KSr_2Cl_5	Belyaev1962
$SrCl_2$-RbCl	0.470	$RbSrCl_3$, $RbSr_2Cl_5$	Bukhalova1967
$SrCl_2$-CsCl	0.412	$CsSrCl_3$	Bergman1965
$EuCl_2$-LiCl	0.939	Eutectic	Sun2002
$EuCl_2$-NaCl	0.681	Eutectic	Rycerz2004c
$EuCl_2$-KCl	0.504	K_2EuCl_4, KEu_2Cl_5	Fink1980
$EuCl_2$-RbCl	0.466	$RbEuCl_3$, $RbEu_2Cl_5$	Fink1980
$EuCl_2$-CsCl	0.408	$CsEuCl_3$	Fink1980

- The complete experimental investigation of all properties for the whole lanthanide series of bromides, either in the (III) and (II) valence state would be of course of unrealistic duration.

- Need for such data was claimed in a number of modern technologies

- This context was the trigger of the second part of this work, with the ultimate goal of predictions being the global properties of these materials

- Several informatic and statistical techniques play a significant role in data analysis and estimation of missing properties
- *Chemometrics* (data-based sub-discipline of chemistry)
- Molten salt systems are multivariate – data collected by *Janz* can be transformed by multivariate analysis into dynamic dataset for analysis and intercorrelation of the properties

- Two techniques:
  - Principal Component Analysis (PCA) and
  - Partial Least Squares (PLS)

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Principal Component Analysis (PCA)

- Useful tool for data compression
- Data compressed into more compact space
- To identify patterns among the data and connections between variables

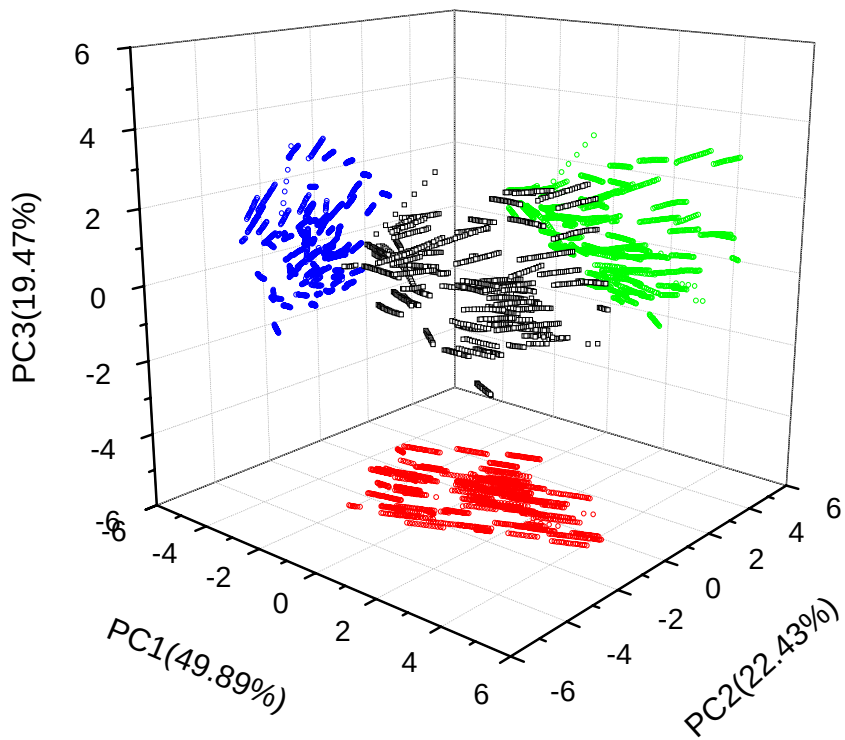
Partial Least Squares (PLS)

- Recent technique that generalizes and combines features from PCA
- Useful to make predictions
- In this work, two essential thermodynamic properties were predicted for the set of 14 lanthanide halides

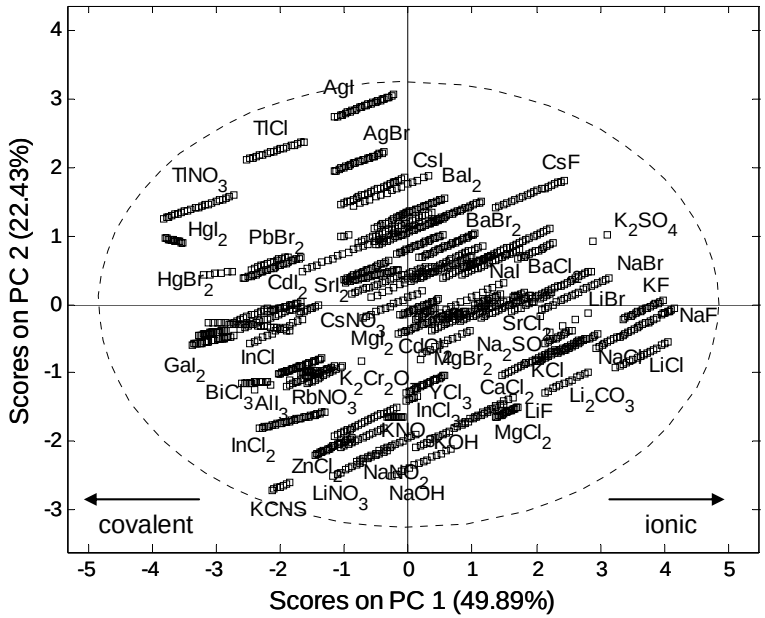
PCA results

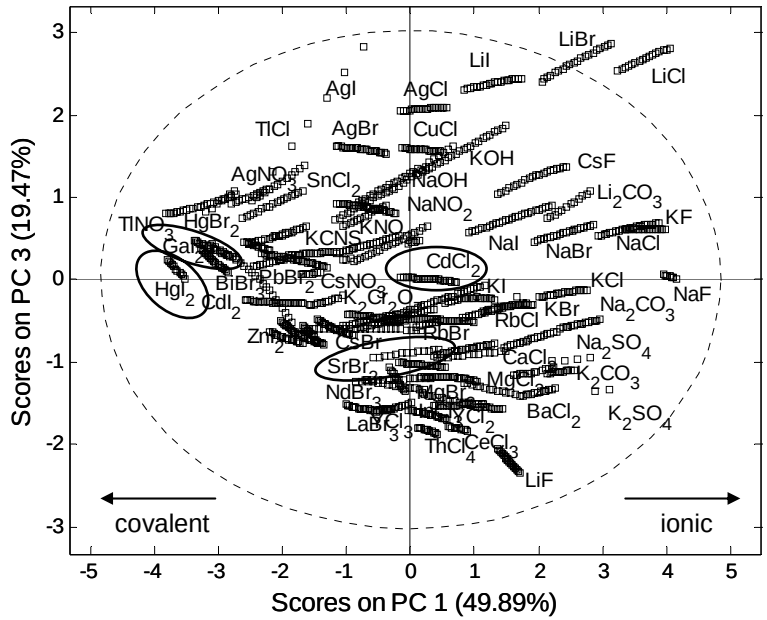
- Used data set derived from Janz, composed of seven variables for 1658 samples
- Results are PCs – linear combination of 7 descriptors (Equivalent weight, melting point, temperature, equivalent conductivity, specific conductivity, density and viscosity)
- Data from the matrix are compressed and visualized in three dimensional space
- This helps to identify compound/property relationship in a dataset of molten salts

The 3 dimensional score plots for complete data



Two interesting projections





PLS results

- Data set for 19 different lanthanide halides obtained during our thermodynamic investigations was used for a multivariate analysis on ΔH^0_{form} and ΔG^0_{form} behavior

- Descriptors: equivalent weight, atomic number, electronegativity difference, cationic charge/radius ratio, melting temperature, ΔH^0_{form} and ΔG^0_{form}

- In other words, without any information on ΔH^0_{form} and ΔG^0_{form} in the test set, it was possible to predict these quantities using the prediction model for training set

- The large R^2 values 90.26% and 77.83% were obtained, indicating a high level of confidence for these predictions

- Experimental ΔH_{form} values -856 and -811 kJ/mol for $CeBr_3$ and $GdBr_3$ were obtained. They are in good agreement with those obtained using the predictive model (-834.49 and -831.07 kJ/mol respectively)

Results

Compound	Eq. weight	Atomic number	ΔE	Z_c/r_c	T_{melt} (K)	Temp. range (K)
$YbBr_2$	166	70	1.75	0.0172	1050	1100-1300
YbI_2	213	70	1.49	0.0172	1053	1100-1300
EuI_2	203	63	1.58	0.0153	853	900-1300
$SmCl_2$	111	62	1.99	0.0142	1132	1150-1300
$SmBr_2$	155	62	1.79	0.0142	973	1000-1300
SmI_2	202	62	1.53	0.0142	793	900-1300
$CeBr_3$	127	58	1.84	0.0261	995	1000-1300
$PrBr_3$	127	59	1.83	0.0267	966	1000-1300
$SmBr_3$	130	62	1.79	0.0273	937	1000-1300
$EuBr_3$	131	63	1.84	0.0276	975	1000-1300
$GdBr_3$	132	64	1.79	0.0278	1058	1100-1300
$DyBr_3$	134	66	1.76	0.0285	1152	1180-1300
$TmBr_3$	136	69	1.71	0.0285	1227	1240-1300
$YbBr_3$	138	70	1.75	0.0298	1229	1240-1300

Conclusion

- Statistical approaches for identifying chemistry-property relationships in a classic materials database (molten salts) have been provided
- Results show that the original molten salts database is a good partial template for a modern data-mining base to be used for virtual materials design and analysis
- To complete this transformation, it is necessary to include structural and thermodynamical data in this database or closely relate it to other databases through well-designed linkages