

Systematics in the formation of lanthanide halide compounds

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Abstract: The phase diagrams of trivalent lanthanide–alkali metal halide systems range from simple eutectic systems to systems with one (several) congruently or incongruently melting compounds.

Using both literature information and our extensive experimental results, the LnX_3 -MX binary mixtures phase diagrams were screened in terms of the $IP_{\text{M}^+}/IP_{\text{Ln}^{3+}}$ ratio ($IP_i = z_i/r_i$; z_i : ionic charge; r_i : ionic radius; Ln: lanthanide, X: halide and M: alkali metal).

A similar approach was conducted on the divalent LnX_2 -MX lanthanide-alkali halides phase diagrams ranging from simple eutectic to one or more congruently melting compounds.

Lanthanides being widely used as simulants of actinides, this classification can constitute a useful predictive tool for those still unexplored systems.

Keywords: Lanthanide, alkali metal, halide, mixture, phase diagram, topology, ionic potential, prediction

1. Introduction

The lanthanide trihalides have been the subject of investigations for many years. The physicochemical properties of the compounds they form, for instance with the alkali halides, can be examined and correlated in a way which is unique since the lanthanides regularly vary along the series they form in the periodic table. Lanthanide metal halides as also the systems they form with alkali metal halides were recently the subject of focused and renewed interest. While the lanthanide fluorides or chlorides and related systems have been investigated in the past in relation with different applications, mostly nuclear in the 1950s and 1960s, very little existed until recently on their bromide and iodide counterparts. These systems are of technological importance in several fields of which optical and scintillation devices, high-temperature energy-saving light sources (metal-halide lamps), etc., are just a few examples. They also characterize by several features making them challenging objects of fundamental interest.

Phase equilibrium in melts and also the topology of related binary phase diagrams strongly depend on the physicochemical properties of the ions in the mixture. The phase equilibria and hence the phase diagrams topology of binary mixtures are a function of the physico-chemical properties of components. There are many factors that influence these equilibria, but ionic charge (z_i) and radius (r_i) play the most important role [1]. The ratio of these two values gives the so-called ionic potential IP [2-3]

$$IP = z_i/r_i$$

In common anion systems, the cation with the higher ionic potential value may coordinate anions thus forming a complex ion. Conversely the other cation, that has a lower ionic potential, would not compete in the common anion coordination. Thus, the formation of compound(s) in binary molten salt systems depends on cation competition to coordinate the common anion. This competition can be expressed by the ratio of ionic potentials [5-6]. In the case of cations with the same charge, this ratio is that of ionic radii [8-9].

When screening a series of binary salt mixtures with one common component in terms of the cationic potential of the second component, one can observe a correlated change in the phase diagram topology (from solid solutions, through eutectic and incongruently melting/congruently melting compounds systems) [1, 9-10]. Gawel [10-12] investigated this correlation between the ionic potential ratio and topology of phase diagram on the example of $\text{MeCl}_n\text{-UCl}_4$ binary systems, evidencing that the IP_{M+n}/IP_{U4+} ratio for the multivalent and uranium cations is essential for a classification of phase diagrams, including the number of compounds formed, their existence range and (congruently or incongruently) melting mechanism. Depending on the values of ionic potentials ratio, they are simple eutectic systems, or systems with one or more congruently melting compounds.

From this perspective, using both literature information and our extensive experimental results, efforts were performed to characterize the $\text{LnX}_3\text{-MX}$ and $\text{LnX}_2\text{-MX}$ (trivalent and divalent) lanthanide–alkali halides binary mixtures phase diagrams in terms of the IP_{M+}/IP_{Ln3+} and IP_{M+}/IP_{Ln2+} ratio (Ln=lanthanide, X=halide and M = alkali metal).

2. Results and discussion

2.1 Lanthanide(III) halide systems

The whole information available on the $\text{LnX}_3\text{-MX}$ phase diagrams was used in analyzing the influence of cationic potentials ratio on the topology of phase diagrams. The ionic radii used in ionic potential calculation were taken from literature [13] while the phase diagrams results for chloride [14-32], bromides [7, 33-45] and iodide [43, 46-51] systems were exhaustively compiled from all existing sources, including our experimental investigations.

Indeed a clear correlation was evidenced between the ionic potentials ratio IP_{M+}/IP_{Ln3+} of the alkali and lanthanide cations, and the resulting phase diagram type for all $\text{LnCl}_3\text{-MCl}$, $\text{LnBr}_3\text{-MBr}$ and $\text{LnI}_3\text{-MI}$ binary systems.

The whole systems split into three groups:

- simple eutectic systems ($IP_{M+}/IP_{Ln3+} \geq 0.448$; 0.325 and 0.333 for chloride, bromide and iodide systems, respectively),
- systems including only incongruently melting compounds (ionic potential ratio within the range $0.416 \geq IP_{M+}/IP_{Ln3+} \geq 0.280$; $0.315 \geq IP_{M+}/IP_{Ln3+} \geq 0.284$ and $0.352 \geq IP_{M+}/IP_{Ln3+} \geq 0.306$ for chloride, bromide and iodide systems, respectively),
- systems including both incongruently and congruently melting compounds ($IP_{M+}/IP_{Ln3+} \leq 0.256$).

In this third group, *i.e.* in the systems including both congruently and incongruently melting compounds, one can find far-reaching similarities as well as differences between the chloride, iodide and bromide systems.

Table 1. Ionic potential ratio and type of phase diagram in the systems LnCl₃-MCl.

System	$IP_{M^+} / IP_{Ln^{3+}}$	System type	Reference
LaCl ₃ -LiCl	0.478	Eutectic	[14]
CeCl ₃ -LiCl	0.465	Eutectic	[15]
PrCl ₃ -LiCl	0.456	Eutectic	[16]
NdCl ₃ -LiCl	0.448	Eutectic	[17]
TbCl ₃ -LiCl	0.416	LiTb ₂ Cl ₇ (decomposition in solid state)	[18]
HoCl ₃ -LiCl	0.402	Li ₃ HoCl ₆ *	[19]
ErCl ₃ -LiCl	0.396	Li ₃ ErCl ₆ *	[20]
YbCl ₃ -LiCl	0.386	Li ₃ YbCl ₆ *	[21]
LaCl ₃ -NaCl	0.346	Na ₃ LaCl ₆ *	[22]
CeCl ₃ -NaCl	0.336	Na ₃ CeCl ₆ *	[23]
PrCl ₃ -NaCl	0.330	Na ₃ PrCl ₆ *	[24]
NdCl ₃ -NaCl	0.325	Na ₃ NdCl ₆ *	[25]
SmCl ₃ -NaCl	0.315	Na ₂ SmCl ₅ *, Na ₃ Sm ₅ Cl ₁₈	[26]
EuCl ₃ -NaCl	0.310	Na ₂ EuCl ₅ *, Na ₃ EuCl ₆ *, NaEuCl ₄ *	[27]
GdCl ₃ -NaCl	0.306	Na ₃ GdCl ₆ *, Na ₂ GdCl ₅ *, NaGdCl ₄	[28]
TbCl ₃ -NaCl	0.301	Na ₃ TbCl ₆ *, Na ₂ TbCl ₅ *, NaTbCl ₄ *, NaTb ₂ Cl ₇ *	[29]
YbCl ₃ -NaCl	0.280	Na ₃ YbCl ₆ , NaYbCl ₄ *	[21]
LaCl ₃ -KCl	0.256	K ₂ LaCl ₅	[22]
CeCl ₃ -KCl	0.249	K ₃ CeCl ₆ , K ₂ CeCl ₅ , K ₂ Ce ₅ Cl ₁₈ *	[23]
PrCl ₃ -KCl	0.244	K ₃ PrCl ₆ , K ₂ PrCl ₅ *	[24]
NdCl ₃ -KCl	0.240	K ₃ NdCl ₆ , K ₂ NdCl ₅ *, KNd ₂ Cl ₇ *	[25]
LaCl ₃ -RbCl	0.237	Rb ₃ LaCl ₆ , Rb ₂ LaCl ₅ *, RbLa ₂ Cl ₇ *	[22]
SmCl ₃ -KCl	0.231	K ₃ SmCl ₆ , K ₂ SmCl ₅ *, KSm ₂ Cl ₇	[26]
CeCl ₃ -RbCl	0.231	Rb ₃ CeCl ₆ , Rb ₂ CeCl ₅ *, RbCe ₂ Cl ₇ *	[23]
EuCl ₃ -KCl	0.229	K ₃ EuCl ₆ , K ₂ EuCl ₅ *, KEu ₂ Cl ₇	[27]
PrCl ₃ -RbCl	0.227	Rb ₃ PrCl ₆ , Rb ₂ PrCl ₅ *, RbPr ₂ Cl ₇ *	[24]
GdCl ₃ -KCl	0.226	K ₃ GdCl ₆ , K ₂ GdCl ₅ *, KGd ₂ Cl ₇	[28]
TbCl ₃ -KCl	0.222	K ₃ TbCl ₆ , K ₂ TbCl ₅ *, KTb ₂ Cl ₇	[30]
NdCl ₃ -RbCl	0.222	Rb ₃ NdCl ₆ , Rb ₂ NdCl ₅ *, RbNd ₂ Cl ₇ *	[25]
HoCl ₃ -KCl	0.216	K ₃ HoCl ₆ , K ₂ HoCl ₅ *, KHO ₂ Cl ₇	[31]
SmCl ₃ -RbCl	0.216	Rb ₃ SmCl ₆ , Rb ₂ SmCl ₅ *, RbSm ₂ Cl ₇	[26]
EuCl ₃ -RbCl	0.212	Rb ₃ EuCl ₆ , Rb ₂ EuCl ₅ *, RbEu ₂ Cl ₇	[27]
TmCl ₃ -KCl	0.209	K ₃ TmCl ₆ , K ₂ TmCl ₅ *, KTm ₂ Cl ₇ *	[32]
GdCl ₃ -RbCl	0.209	Rb ₃ GdCl ₆ , Rb ₂ GdCl ₅ *, RbGd ₂ Cl ₇	[28]
LaCl ₃ -CsCl	0.208	Cs ₃ LaCl ₆ , Cs ₂ LaCl ₅ *, CsLa ₂ Cl ₇ *	[22]
TbCl ₃ -RbCl	0.206	Rb ₃ TbCl ₆ , RbTb ₂ Cl ₇	[30]
CeCl ₃ -CsCl	0.202	Cs ₃ CeCl ₆ , Cs ₂ CeCl ₅ *, CsCe ₂ Cl ₇	[23]
HoCl ₃ -RbCl	0.200	Rb ₃ HoCl ₆ , Rb ₂ HoCl ₅ *, RbHo ₂ Cl ₇	[31]
PrCl ₃ -CsCl	0.198	Cs ₃ PrCl ₆ , Cs ₂ PrCl ₅ *, CsPr ₂ Cl ₇	[24]
NdCl ₃ -CsCl	0.195	Cs ₃ NdCl ₆ , Cs ₂ NdCl ₅ *, CsNd ₂ Cl ₇	[25]
TmCl ₃ -RbCl	0.194	Rb ₃ TmCl ₆ , Rb ₂ TmCl ₅ *, RbTm ₂ Cl ₇	[32]
SmCl ₃ -CsCl	0.189	Cs ₃ SmCl ₆ , Cs ₂ SmCl ₅ *, CsSm ₂ Cl ₇	[26]
EuCl ₃ -CsCl	0.186	Cs ₃ EuCl ₆ , Cs ₂ EuCl ₅ *, CsEu ₂ Cl ₇	[27]
GdCl ₃ -CsCl	0.183	Cs ₃ GdCl ₆ , Cs ₂ GdCl ₅ *, CsGd ₂ Cl ₇	[28]
TbCl ₃ -CsCl	0.181	Cs ₃ TbCl ₆ , Cs ₂ TbCl ₅ *, CsTb ₂ Cl ₇	[30]
HoCl ₃ -CsCl	0.175	Cs ₃ HoCl ₆ , Cs ₂ HoCl ₅ *, CsHo ₂ Cl ₇ , Cs ₃ Ho ₂ Cl ₉ *	[31]
TmCl ₃ -CsCl	0.170	Cs ₃ TmCl ₆ , Cs ₂ TmCl ₅ *, CsTm ₂ Cl ₇ , Cs ₃ Tm ₂ Cl ₉ *	[32]

* incongruent melting

The common features are as follows:

- in all systems - the identical value of the ionic potential ratio at which the congruently melting compounds occur ($IP_{M^+}/IP_{Ln^{3+}} = 0.256$),
- the first congruently melting compound that occurs at $IP_{M^+}/IP_{Ln^{3+}} = 0.256$ is K_2LnX_5 ($X = Cl, Br, I$),
- the congruently melting M_2LnX_5 compounds exist within a very narrow ionic potential ratio range ($0.256 \geq IP_{M^+}/IP_{Ln^{3+}} \geq 0.249$),
- at smaller ionic potential ratio ($IP_{M^+}/IP_{Ln^{3+}} < 0.249$), the M_2LnX_5 compounds melt incongruently,

- the congruently melting compounds M_3LnX_6 form at smaller $IP_{M^+}/IP_{Ln^{3+}}$ values (≤ 0.249).
- The common characteristics of chloride and bromide systems is also the occurrence of MLn_2X_7 compounds ($X = Cl, Br; M = K, Rb, Cs$) that melt congruently or incongruently, and form in the systems where $IP_{M^+}/IP_{Ln^{3+}} \leq 0.244$.

Table 2. Ionic potential ratio and type of phase diagram in the systems $LnBr_3$ -MBr

System	$IP_{M^+} / IP_{Ln^{3+}}$	System type	Reference
LaBr ₃ -LiBr	0.478	Eutectic	[33]
CeBr ₃ -LiBr	0.465	Eutectic	[34]
PrBr ₃ -LiBr	0.456	Eutectic	[35]
NdBr ₃ -LiBr	0.448	Eutectic	[36]
LaBr ₃ -NaBr	0.346	Eutectic	[37]
CeBr ₃ -NaBr	0.336	Eutectic	[34]
PrBr ₃ -NaBr	0.330	Eutectic	[37]
NdBr ₃ -NaBr	0.325	Eutectic	[37]
SmBr ₃ -NaBr	0.315	Na ₇ SmBr ₁₀ *	[37]
GdBr ₃ -NaBr	0.306	Na ₃ GdBr ₆ *	[37]
HoBr ₃ -NaBr	0.292	Na ₃ HoBr ₆ *	[38]
TmBr ₃ -NaBr	0.284	Na ₃ TmBr ₆ *	[39]
LaBr ₃ -KBr	0.256	K ₂ LaBr ₅	[40]
CeBr ₃ -KBr	0.249	K ₃ CeBr ₆ , K ₂ CeBr ₅ *	[41]
PrBr ₃ -KBr	0.244	K ₃ PrBr ₆ , K ₂ PrBr ₅ *, KPr ₂ Br ₇ *	[7]
NdBr ₃ -KBr	0.240	K ₃ NdBr ₆ , K ₂ NdBr ₅ *, KNd ₂ Br ₇	[7]
LaBr ₃ -RbBr	0.237	Rb ₃ LaBr ₆ , Rb ₂ LaBr ₅ *	[40]
SmBr ₃ -KBr	0.231	K ₃ SmBr ₆ , K ₂ SmBr ₅ *, KSm ₂ Br ₇	[7]
CeBr ₃ -RbBr	0.231	Rb ₃ CeBr ₆ , Rb ₂ CeBr ₅ *, RbCe ₂ Br ₇ *	[42]
PrBr ₃ -RbBr	0.227	Rb ₃ PrBr ₆ , Rb ₂ PrBr ₅ *, RbPr ₂ Br ₇ *	[7]
GdBr ₃ -KBr	0.226	K ₃ GdBr ₆ , K ₂ GdBr ₅ *, KGd ₂ Br ₇	[7]
TbBr ₃ -KBr	0.222	K ₃ TbBr ₆ , K ₂ TbBr ₅ *, KTb ₂ Br ₇ *	[43]
NdBr ₃ -RbBr	0.222	Rb ₃ NdBr ₆ , Rb ₂ NdBr ₅ *, RbNd ₂ Br ₇	[7]
DyBr ₃ -KBr	0.219	K ₃ DyBr ₆ , K ₂ DyBr ₅ *	[7]
SmBr ₃ -RbBr	0.216	Rb ₃ SmBr ₆ , Rb ₂ SmBr ₅ *, RbSm ₂ Br ₇	[7]
ErBr ₃ -KBr	0.212	K ₃ ErBr ₆ , K ₂ ErBr ₅ *	[7]
GdBr ₃ -RbBr	0.209	Rb ₃ GdBr ₆ , Rb ₂ GdBr ₅ *, RbGd ₂ Br ₇	[7]
LaBr ₃ -CsBr	0.208	Cs ₃ LaBr ₆ , Cs ₂ LaBr ₅ *, CsLa ₂ Br ₇ *	[40]
YbBr ₃ -KBr	0.207	K ₃ YbBr ₆ , K ₂ YbBr ₅ *	[7]
TbBr ₃ -RbBr	0.206	Rb ₃ TbBr ₆ , RbTb ₂ Br ₇ *	[43]
DyBr ₃ -RbBr	0.203	Rb ₃ DyBr ₆ , Rb ₂ DyBr ₅ *, RbDy ₂ Br ₇ *	[7]
CeBr ₃ -CsBr	0.202	Cs ₃ CeBr ₆ , Cs ₂ CeBr ₅ *, CsCe ₂ Br ₇	[44]
PrBr ₃ -CsBr	0.198	Cs ₃ PrBr ₆ , CsPr ₂ Br ₇	[37]
ErBr ₃ -RbBr	0.197	Rb ₃ ErBr ₆ , Rb ₂ ErBr ₅ *	[7]
NdBr ₃ -CsBr	0.195	Cs ₃ NdBr ₆ , CsNd ₂ Br ₇	[37]
YbBr ₃ -RbBr	0.192	Rb ₃ YbBr ₆ , Rb ₂ YbBr ₅ *	[7]
SmBr ₃ -CsBr	0.189	Cs ₃ SmBr ₆ , Cs ₂ SmBr ₅ *, CsSm ₂ Br ₇	[7]
GdBr ₃ -CsBr	0.183	Cs ₃ GdBr ₆ , Cs ₂ GdBr ₅ *, CsGd ₂ Br ₇	[7]
TbBr ₃ -CsBr	0.181	Cs ₃ TbBr ₆ , CsTb ₂ Br ₇ *	[43]
DyBr ₃ -CsBr	0.178	Cs ₃ DyBr ₆ , CsDy ₂ Cl ₇ *, Cs ₃ Dy ₂ Br ₉ *	[45]
HoBr ₃ -CsBr	0.175	Cs ₃ HoBr ₆ , CsHo ₂ Br ₇ *	[38]
ErBr ₃ -CsBr	0.173	Cs ₃ ErBr ₆ , Cs ₂ ErCl ₅ *	[7]
YbBr ₃ -CsBr	0.168	Cs ₃ YbBr ₆ , Cs ₂ YbBr ₅ *	[7]

However, some differences can be noted between the chloride, bromide and iodide systems within this classification:

- M_2LnI_5 compounds occur within a narrow range of ionic potential ratio values (0.256–0.222), while the M_2LnCl_5 and M_2LnBr_5 occur in all chloride and bromide systems with ratio $IP_{M^+}/IP_{Ln^{3+}} \leq 0.256$,
- MLn_2X_7 compounds, present in chloride and bromide systems at $IP_{M^+}/IP_{Ln^{3+}} \leq 0.244$, practically do not occur in iodide systems (with the exception of RbNd₂I₇),
- $M_3Ln_2X_9$ compounds that exist in chloride ($IP_{M^+}/IP_{Ln^{3+}} \leq 0.175$) and iodide ($IP_{M^+}/IP_{Ln^{3+}} \leq 0.198$, systems practically do not occur in bromide systems (excepted for Cs₃Dy₂Br₉).

Table 3. Ionic potential ratio and type of phase diagram in the systems LnI₃-MI

System	$IP_{M^{+}} / IP_{Ln^{3+}}$	System type	Reference
Lal ₃ -Lil	0.478	Eutectic	[46]
Ndl ₃ -Lil	0.465	Eutectic	[46]
Lal ₃ -Nal	0.346	Eutectic	[47]
Prl ₃ -Nal	0.330	Eutectic	[47]
Ndl ₃ -Nal	0.325	Na ₇ Ndl ₁₀ *	[47]
Sml ₃ -Nal	0.315	Na ₃ Sml ₆ *	[47]
Gdl ₃ -Nal	0.306	Na ₃ Gdl ₆ *	[47]
Lal ₃ -Kl	0.256	K ₂ Lal ₅	[47]
Prl ₃ -Kl	0.244	K ₃ Prl ₆ , K ₂ Prl ₅ *	[47]
Ndl ₃ -Kl	0.240	K ₃ Ndl ₆ , K ₂ Ndl ₅ *	[47]
Lal ₃ -Rbl	0.237	Rb ₃ Lal ₆ , Rb ₂ Lal ₅ *	[43]
Sml ₃ -Kl	0.231	K ₃ Sml ₆	[47]
Gdl ₃ -Kl	0.226	K ₃ Gdl ₆	[47]
Ndl ₃ -Rbl	0.222	Rb ₃ Ndl ₆ , Rb ₂ Ndl ₅ *, RbNd ₂ l ₇ *	[43]
Dyl ₃ -Kl	0.219	K ₃ Dyl ₆	[47]
Erl ₃ -Kl	0.212	K ₃ Erl ₆	[47]
Lal ₃ -Csl	0.208	Cs ₃ Lal ₆ , CsLa ₉ l ₂₈ *	[47]
Prl ₃ -Csl	0.198	Cs ₃ Prl ₆ , Cs ₃ Pr ₂ l ₉ *, CsPr ₉ l ₂₈ *	[47]
Ndl ₃ -Csl	0.195	Cs ₃ Ndl ₆ , Cs ₃ Nd ₂ l ₉ *, CsNd ₄ l ₁₃ *	[47]
Sml ₃ -Csl	0.189	Cs ₃ Sml ₆ , Cs ₃ Sm ₂ l ₉ *	[47]
Gdl ₃ -Csl	0.183	Cs ₃ Gdl ₆ , Cs ₃ Gd ₂ l ₉	[47]
Tbl ₃ -Csl	0.181	Cs ₃ Tbl ₆ , Cs ₃ Tb ₂ l ₉	[48]
Dyl ₃ -Csl	0.178	Cs ₃ Dyl ₆ , Cs ₃ Dy ₂ l ₉	[49]
Hol ₃ -Csl	0.175	Cs ₃ Hol ₆ , Cs ₃ Ho ₂ l ₉	[50-51]
Erl ₃ -Csl	0.173	Cs ₃ Erl ₆ , Cs ₃ Er ₂ l ₉	[47]
Tml ₃ -Csl	0.170	Cs ₃ Tml ₆ , Cs ₃ Tm ₂ l ₉	[48]

* incongruent melting

This classification was tested on the CeBr₃-MBr binary systems (M=Li, Na, K, Rb, Cs), still unknown at the time it was established. Further experimental investigations validated that CeBr₃-LiBr and CeBr₃-NaBr are simple eutectic systems [34] ($IP_{M^{+}}/IP_{Ce^{3+}}=0.465$ and 0.366 , respectively), while two congruently melting compounds, namely K₃CeBr₆ and K₂CeBr₅ exist in the CeBr₃-KBr system [41] as expected from the corresponding ionic potential ratio ($IP_{K^{+}}/IP_{Ce^{3+}} = 0.249$). The CeBr₃-RbBr [42] and CeBr₃-CsBr [44] systems ($IP_{Rb^{+}}/IP_{Ce^{3+}} = 0.231$ and $IP_{Cs^{+}}/IP_{Ce^{3+}} = 0.202$, respectively) follow the predicted pattern. The former system is characterized by the existence of three compounds, namely Rb₃CeBr₆, Rb₂CeBr₅ and RbCe₂Br₇. Rb₃CeBr₆ melts congruently whereas Rb₂CeBr₅ and RbCe₂Br₇ melt incongruently. The CeBr₃-CsBr system includes three compounds: the congruently melting Cs₃CeBr₆ and CsCe₂Br₇ together with Cs₂CeBr₅, which decomposes in the solid state.

Other tests were performed more recently on the PrBr₃-based bromide systems that also follow this trend. The binary systems with LiBr and NaBr are of simple eutectic-type [35] ($IP_{M^{+}}/IP_{Pr^{3+}} = 0.456$ and 0.330 , respectively) (Figs.1-2). In the system with KBr [52], the congruently melting compound, K₃PrBr₆ and two incongruently melting compounds (K₂PrBr₅ and KPr₂Br₇) were found ($IP_{K^{+}}/IP_{Pr^{3+}} = 0.244$) (Fig.3). The system with rubidium bromide ($IP_{Rb^{+}}/IP_{Pr^{3+}} = 0.227$) [53] was also characterized by two congruently (Rb₃PrBr₆ and RbPr₂Br₇) and one incongruently melting (Rb₂PrBr₅) compounds (Fig.4).

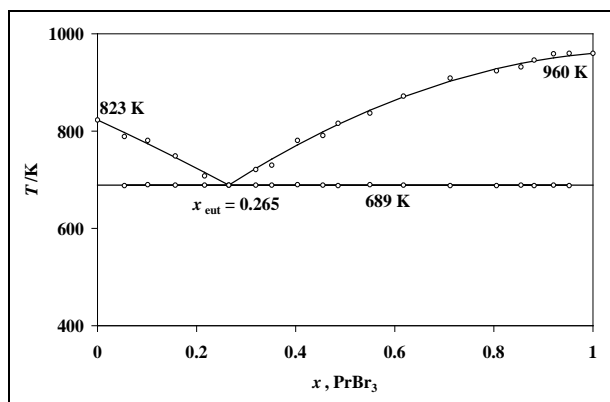


Figure 1. Phase diagram of the PrBr_3 -LiBr binary system.

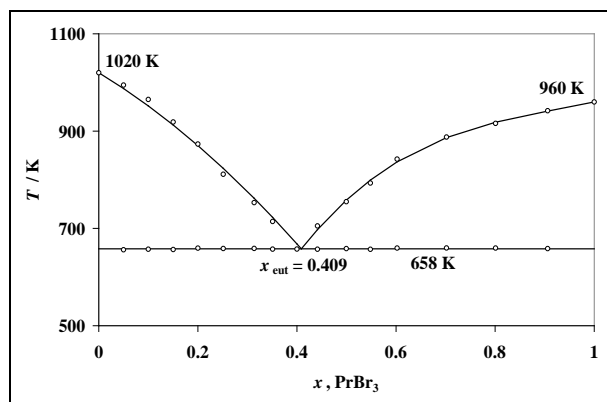


Figure 2. Phase diagram of the PrBr_3 -NaBr binary system.

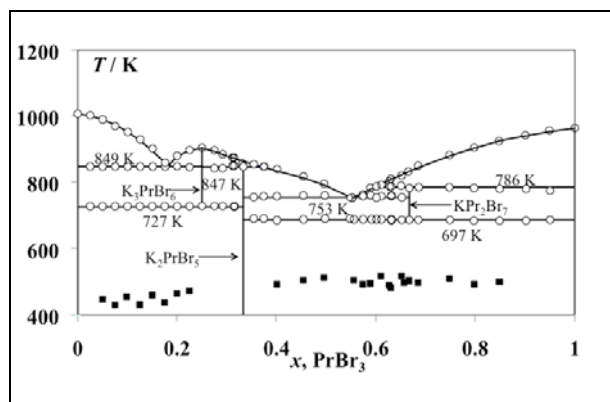


Figure 3. Phase diagram of the PrBr_3 -KBr binary system.

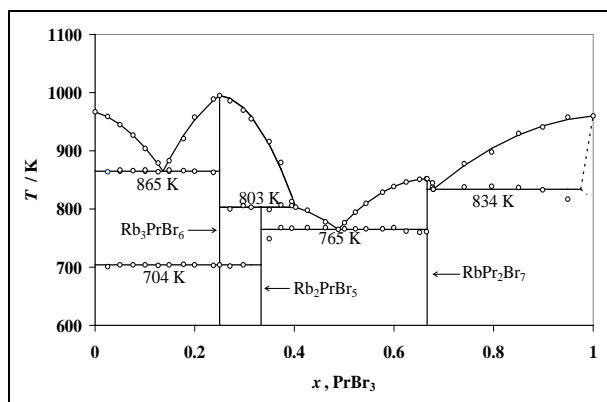


Figure 4. Phase diagram of the PrBr_3 -RbBr binary system.

Ongoing thermodynamic investigations on the DyBr_3 -MBr systems validated both early experimental results and the reliability of the ionic potential predictive tool for phase diagram topology.

2.2 Lanthanide(II) halide systems

For the lanthanide(II) halide systems, information was less but is building up through the experimental research being carried out.

Phase equilibrium data are rather scarce for the systems with divalent lanthanide halides and, most of the time, not confirmed by structural measurements. However, a number of ternary alkali-metal/rare-earth metal iodide compounds were reported in a detailed review article [53].

In Tables 4-5 we gathered the whole information on 60 binary lanthanide(II) halide systems (fluoride melts were not considered in this work).

The overall information is being complemented through investigations carried out by several research groups, including ours, some of it not published yet.

We applied to all divalent systems the same approach of correlating the main features in the corresponding phase diagrams, highlighting how this ionic potential criterion could make it possible to predict *a priori* the general features of still unexplored systems. Special attention has been paid to the intermediate compounds formed in these LnX₂-MX binary mixtures because they have specific properties suitable for a number of technological applications (halide lamps, digital radiography,...).

Table 4. Ionic potential ratio and type of phase diagram in the systems LnX₂-MX (X= Cl, Br)

IP _{M+} / IP _{Ln2+(Sr+2)}	System	System type	Ref.	System	System type	Ref.
0.953	SmCl ₂ -LiCl	---	----	SmBr ₂ -LiBr	---	----
0.946	SrCl ₂ -LiCl	Eutectic	[57]	SrBr ₂ -LiBr	LiSr ₂ Br ₅	[59-67]
0.939	EuCl ₂ -LiCl	Eutectic	[54]	EuBr ₂ -LiBr	LiEu ₂ Br ₅	[68]
0.865	YbCl ₂ -LiCl	---	----	YbBr ₂ -LiBr	---	----
0.691	SmCl ₂ -NaCl	---	----	SmBr ₂ -NaBr	---	----
0.686	SrCl ₂ -NaCl	Eutectic	[60]	SrBr ₂ -NaBr	Eutectic	[59]
0.681	EuCl ₂ -NaCl	Eutectic	[61], [62]	EuBr ₂ -NaBr	Eutectic	[56]
0.627	YbCl ₂ -NaCl	---	----	YbBr ₂ -NaBr	---	----
0.511	SmCl ₂ -KCl	---	----	SmBr ₂ -KBr	---	----
0.507	SrCl ₂ -KCl	K ₂ SrCl ₄ , K ₂ Sr ₂ Cl ₅	[59-63]	SrBr ₂ -KBr	K ₂ SrBr ₄ , K ₂ SrBr ₃ , K ₂ Sr ₂ Br ₅	[65]
0.504	EuCl ₂ -KCl	K ₂ EuCl ₄ , KEu ₂ Cl ₅	[64]	EuBr ₂ -KBr	K ₂ EuBr ₄ , KEuBr ₃ , KEu ₂ Br ₅	[69]
0.464	YbCl ₂ -KCl	---	----	YbBr ₂ -KBr	---	----
0.473	SmCl ₂ -RbCl	---	----	SmBr ₂ -RbBr	---	----
0.470	SrCl ₂ -RbCl	RbSrCl ₃ , RbSr ₂ I ₅	[65]	SrBr ₂ -RbBr	Rb ₂ SrBr ₄ , RbSrBr ₃ , RbSr ₂ Br ₅	[70]
0.466	EuCl ₂ -RbCl	RbEuCl ₃ , RbEu ₂ Cl ₅	[64]	EuBr ₂ -RbBr	Rb ₂ EuBr ₄ , RbEuBr ₃ , RbEu ₂ Br ₅	[71]
0.430	YbCl ₂ -RbCl	---	----	YbBr ₂ -RbBr	---	----
0.415	SmCl ₂ -CsCl	---	----	SmBr ₂ -CsBr	---	----
0.412	SrCl ₂ -CsCl	CsSrCl ₃	[66]	SrBr ₂ -CsBr	CsSrBr ₃	[72]
0.408	EuCl ₂ -CsCl	CsEuCl ₃	[64]	EuBr ₂ -CsBr	CsEuBr ₃	[73]
0.376	YbCl ₂ -CsCl	---	----	YbBr ₂ -CsBr	---	----

* incongruent melting

As reported in literature, mostly Sm, Eu and Yb can form stable divalent halides.

The systems in Tables 4-5 were analyzed in terms of the IP_{M+}/IP_{Ln2+} ionic potential ratio.

It is clear that in some systems with IP_{M+}/IP_{Ln2+} > 0.850 we can find either a eutectic or a compound corresponding to the stoichiometry LiLn₂X₅. In the 0.627 < IP_{M+}/IP_{Ln2+} < 0.691 range, only eutectic mixtures are present (NaX-LnX₂). It is possible to expect that systems in the 0.627 < IP_{M+}/IP_{Ln2+} < 0.691 range, where experimental measurements were not performed yet, would be of the simple eutectic type (SmCl₂-NaCl or SmBr₂-NaBr).

All the phase diagrams characterized so far, except those with NaX, are not of this simple eutectic type. In the case of the systems formed by the LnX₂'s with KX and RbX, (0.430 < IP_{M+}/IP_{Ln2+} < 0.511 range), the phase diagrams are more complex and they include several either congruently or incongruently melting stoichiometric compounds. The analogous CsCl and CsBr systems are simpler than we expected, only one congruently melting compound (CsLnX₃) was found. This is not the case for SmI₂-CsI and YbI₂-CsI systems, where several congruently and incongruently stoichiometric compounds were reported [53-54].

All literature information together with our recent experimental data on the $\text{EuBr}_2\text{-MBr}$ binary mixtures [55-57] is presented in Table 4 for comparison with the $\text{SrX}_2\text{-MX}$ systems.

Strontium was selected for the purpose of comparison since its ionic radius is very similar to that of the Eu^{2+} ion with $\text{SrBr}_2/\text{EuBr}_2$ being isostructural.

Table 4 evidences identical features in all those $\text{EuX}_2\text{-MX}$ and $\text{SrX}_2\text{-MX}$ that had been characterized so far. An analogous compound was observed in all LiX systems; no compound in the NaX mixtures and compounds of the same stoichiometry were found in the KX- , RbX- and CsX- based binaries.

It should be stressed that while no compound had been reported in all Li- based lanthanide(III) halide systems, and the LiLn_2Br_5 compound is present in the Ln(II)-LiX systems ($\text{Ln(II)= Eu, Yb ; X= Br, I}$) as also LiSr_2Br_5 in the $\text{SrBr}_2\text{-LiBr}$ system.

The reason might be related to the fact that all these systems correspond to a high and identical ionic potential ratio ($\text{IP}_{\text{Li}^+}/\text{IP}_{\text{Eu}^{2+}(\text{Sr}^{2+})} \approx 1$). This indicates that the contribution of ionic potentials, both of lithium and europium(II) or strontium, is almost identical and both cations are attracted by the common anion in the same way. In other words, both the alkali and divalent cations contribute equally to compound formation.

Table 5. Ionic potential ratio and type of phase diagram in the systems $\text{LnI}_2\text{-MI}$

$\text{IP}_{\text{M}^+}/\text{IP}_{\text{Ln}^{2+}(\text{Sr}^{2+})}$	System	System type	Ref.
0.953	$\text{SmI}_2\text{-LiI}$	---	----
0.946	$\text{SrI}_2\text{-LiI}$	---	----
0.939	$\text{EuI}_2\text{-LiI}$	---	----
0.865	$\text{YbI}_2\text{-LiI}$	$\text{Li}_3\text{YbI}_5, \text{LiYb}_2\text{I}_5$	[54]
0.691	$\text{SmI}_2\text{-NaI}$	Eutectic	[79]
0.686	$\text{SrI}_2\text{-NaI}$	---	----
0.681	$\text{EuI}_2\text{-NaI}$	Eutectic	[54]
0.627	$\text{YbI}_2\text{-NaI}$	$\text{NaYb}_2\text{I}_5^*$	[74]
0.511	$\text{SmI}_2\text{-KI}$	$\text{KSm}_2\text{I}_5, \text{K}_2\text{SmI}_4^*$	[54], [79]
0.507	$\text{SrI}_2\text{-KI}$	---	----
0.504	$\text{EuI}_2\text{-KI}$	$\text{KEu}_2\text{I}_5, \text{K}_4\text{EuI}_6$	[54]
0.464	$\text{YbI}_2\text{-KI}$	KYbI_3	[74], [78]
0.473	$\text{SmI}_2\text{-RbI}$	$\text{Rb}_2\text{SmI}_4, \text{RbSm}_2\text{I}_5, \text{Rb}_4\text{SmI}_6$	[54,71]
0.470	$\text{SrI}_2\text{-RbI}$	---	----
0.466	$\text{EuI}_2\text{-RbI}$	$\text{RbEu}_2\text{I}_5, \text{RbEuI}_3, \text{Rb}_3\text{EuI}_5^*, \text{Rb}_4\text{EuI}_6^*$	[77-79]
0.430	$\text{YbI}_2\text{-RbI}$	$\text{RbYbI}_3, \text{Rb}_4\text{YbI}_6^*, \text{Rb}_4\text{YbI}_6$	[71], [80]
0.415	$\text{SmI}_2\text{-CsI}$	$\text{Cs}_2\text{SmI}_4^*, \text{CsSmI}_3, \text{Cs}_3\text{SmI}_5^*, \text{CsSm}_2\text{I}_5^*, \text{Cs}_4\text{SmI}_6$	[79-82]
0.412	$\text{SrI}_2\text{-CsI}$	---	----
0.408	$\text{EuI}_2\text{-CsI}$	$\text{CsEuI}_3, \text{Cs}_4\text{EuI}_6$	[54,77, 80-82]
0.376	$\text{YbI}_2\text{-CsI}$	$\text{CsYbI}_3, \text{Cs}_2\text{YbI}_4^*, \text{Cs}_6\text{YbI}_8, \text{Cs}_4\text{YbI}_6$	[80-83]

* incongruent melting

3. Conclusion

The whole information available on the $\text{LnX}_3\text{-MX}$ phase diagrams was used in analyzing the influence of cationic potentials ratio on the topology of phase diagrams. Indeed we found that the topology of $\text{LnX}_3\text{-MX}$ binary phase diagrams depends on the cationic potentials ratio. The trend to compound formation increases if $\text{IP}_{\text{M}^+}/\text{IP}_{\text{Ln}}$ decreases, resulting in

more and more complex phase diagrams. This tendency is related to the stronger interactions between lanthanide and halide ions, compared to those between alkali and halide ions. These lanthanide-halide interactions increase with the atomic number of lanthanide. It was also found that this trend increases in the sequence from LiX to CsX in the binary LnX_3 -MX systems. This approach constitutes a valuable tool for the prediction of the still unexplored lanthanide-alkali metal halide phase diagrams.

In addition, lanthanides being widely used as simulants of actinides (Ac), this classification would be of major interest for those AcX_3 -MX systems that cannot be investigated experimentally. It is well-accepted indeed that the chemistry of uranium(III), plutonium(III) and a trivalent transplutonium element directly under each lanthanide element in the periodic classification is similar to that of the lanthanide element in its trivalent state. This correlation holds especially well for those elements that occur later in the series. For example, the chemistry of americium(III) is similar to that of europium(III). Hence the interest of the same ionic potential-based approach for the AcX_3 -MX systems.

One may conclude that in the case of the Ln(II)-based binary systems, ion size and possibly common halide features have also influence on compound formation, as suggested by the more complex phase equilibria from the chloride to iodide series. It is clear from Table 4-5 that the IP parameter only is not sufficient for a more detailed classification of the LnX_2 -MX binary systems. However, it is difficult to go beyond this general observation since, as already stressed, experimental data are scanty and in addition may be questionable. For lanthanide(II) iodides, which are extremely reactive compounds, chemical synthesis is crucial and it was impossible to check for it in the corresponding papers [77-78, 82, 83-87].

Because of the lesser data available on the divalent lanthanide series, compared to those in the Ln(III)-based systems, only general trends could be observed for the former. This highlights the need of further experimental determinations for the still unexplored systems. This would make possible the validation of this ionic potential approach for the Ln(II)-based systems and its capability for predicting phase topology in those systems that cannot be investigated experimentally.

The investigation of LnX_n -MX system opened a fascinating route from multitechnique data acquisition to data prediction [88] and coupling the present approach will make it still more stimulating.

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