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_{M+}/IP_{Ln3+} 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 $MeCl_n$-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 LnX_3-MX and LnX_2-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 LnX_3-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 $LnCl_3$-MCl, $LnBr_3$-MBr and LnI_3-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 $LnCl_3$-MCl.

System	IP_{M+} / IP_{Ln3+}	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	$LiTb_2Cl_7$ (decomposition in solid state)	[18]
$HoCl_3$-$LiCl$	0.402	Li_3HoCl_6 *	[19]
$ErCl_3$-$LiCl$	0.396	Li_3ErCl_6 *	[20]
$YbCl_3$-$LiCl$	0.386	Li_3YbCl_6 *	[21]
$LaCl_3$-$NaCl$	0.346	Na_3LaCl_6 *	[22]
$CeCl_3$-$NaCl$	0.336	Na_3CeCl_6 *	[23]
$PrCl_3$-$NaCl$	0.330	Na_3PrCl_6 *	[24]
$NdCl_3$-$NaCl$	0.325	Na_3NdCl_6 *	[25]
$SmCl_3$-$NaCl$	0.315	Na_2SmCl_5 *, $Na_3Sm_5Cl_{18}$	[26]
$EuCl_3$-$NaCl$	0.310	Na_2EuCl_5 *, Na_3EuCl_6 *, $NaEuCl_4$ *	[27]
$GdCl_3$-$NaCl$	0.306	Na_3GdCl_6 *, Na_2GdCl_5 *, $NaGdCl_4$	[28]
$TbCl_3$-$NaCl$	0.301	Na_3TbCl_6 *, Na_2TbCl_5 *, $NaTbCl_4$ *, $NaTb_2Cl_7$ *	[29]
$YbCl_3$-$NaCl$	0.280	Na_3YbCl_6, $NaYbCl4$ *	[21]
$LaCl_3$-KCl	0.256	K_2LaCl_5	[22]
$CeCl_3$-KCl	0.249	K_3CeCl_6, K_2CeCl_5, $K_2Ce_5Cl_{18}$ *	[23]
$PrCl_3$-KCl	0.244	K_3PrCl_6, K_2PrCl_5 *	[24]
$NdCl_3$-KCl	0.240	K_3NdCl_6, K_2NdCl_5 *, KNd_2Cl_7 *	[25]
$LaCl_3$-$RbCl$	0.237	Rb_3LaCl_6, Rb_2LaCl_5 *, $RbLa_2Cl_7$ *	[22]
$SmCl_3$-KCl	0.231	K_3SmCl_6, K_2SmCl_5 *, KSm_2Cl_7	[26]
$CeCl_3$-$RbCl$	0.231	Rb_3CeCl_6, Rb_2CeCl_5 *, $RbCe_2Cl_7$ *	[23]
$EuCl_3$-KCl	0.229	K_3EuCl_6, K_2EuCl_5 *, KEu_2Cl_7	[27]
$PrCl_3$-$RbCl$	0.227	Rb_3PrCl_6, Rb_2PrCl_5 *, $RbPr_2Cl_7$ *	[24]
$GdCl_3$-KCl	0.226	K_3GdCl_6, K_2GdCl_5 *, KGd_2Cl_7	[28]
$TbCl_3$-KCl	0.222	K_3TbCl_6, K_2TbCl_5 *, KTb_2Cl_7	[30]
$NdCl_3$-$RbCl$	0.222	Rb_3NdCl_6, Rb_2NdCl_5 *, $RbNd_2Cl_7$ *	[25]
$HoCl_3$-KCl	0.216	K_3HoCl_6, K_2HoCl_5 *, KHo_2Cl_7	[31]
$SmCl_3$-$RbCl$	0.216	Rb_3SmCl_6, Rb_2SmCl_5 *, $RbSm_2Cl_7$	[26]
$EuCl_3$-$RbCl$	0.212	Rb_3EuCl_6, Rb_2EuCl_5 *, $RbEu_2Cl_7$	[27]
$TmCl_3$-KCl	0.209	K_3TmCl_6, K_2TmCl_5 *, KTm_2Cl_7 *	[32]
$GdCl_3$-$RbCl$	0.209	Rb_3GdCl_6, Rb_2GdCl_5 *, $RbGd_2Cl_7$	[28]
$LaCl_3$-$CsCl$	0.208	Cs_3LaCl_6, Cs_2LaCl_5 *, $CsLa_2Cl_7$ *	[22]
$TbCl_3$-$RbCl$	0.206	Rb_3TbCl_6, $RbTb_2Cl_7$	[30]
$CeCl_3$-$CsCl$	0.202	Cs_3CeCl_6, Cs_2CeCl_5 *, $CsCe_2Cl_7$	[23]
$HoCl_3$-$RbCl$	0.200	Rb_3HoCl_6, Rb_2HoCl_5 *, $RbHo_2Cl_7$	[31]
$PrCl_3$-$CsCl$	0.198	Cs_3PrCl_6, Cs_2PrCl_5 *, $CsPr_2Cl_7$	[24]
$NdCl_3$-$CsCl$	0.195	Cs_3NdCl_6, Cs_2NdCl_5 *, $CsNd_2Cl_7$	[25]
$TmCl_3$-$RbCl$	0.194	Rb_3TmCl_6, Rb_2TmCl_5 *, $RbTm_2Cl_7$	[32]
$SmCl_3$-$CsCl$	0.189	Cs_3SmCl_6, Cs_2SmCl_5 *, $CsSm_2Cl_7$	[26]
$EuCl_3$-$CsCl$	0.186	Cs_3EuCl_6, Cs_2EuCl_5 *, $CsEu_2Cl_7$	[27]
$GdCl_3$-$CsCl$	0.183	Cs_3GdCl_6, Cs_2GdCl_5 *, $CsGd_2Cl_7$	[28]
$TbCl_3$-$CsCl$	0.181	Cs_3TbCl_6, Cs_2TbCl_5 *, $CsTb_2Cl_7$	[30]
$HoCl_3$-$CsCl$	0.175	Cs_3HoCl_6, Cs_2HoCl_5 *, $CsHo_2Cl_7$, $Cs_3Ho_2Cl_9$ *	[31]
$TmCl_3$-$CsCl$	0.170	Cs_3TmCl_6, Cs_2TmCl_5 *, $CsTm_2Cl_7$, $Cs_3Tm_2Cl_9$ *	[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 ($IP_{M+}/IP_{Ln3+} = 0.256$),

- the first congruently melting compound that occurs at $IP_{M+}/IP_{Ln3+} = 0.256$ is K_2LnX_5 (X = Cl, Br, I),

- the congruently melting M_2LnX_5 compounds exist within a very narrow ionic potential ratio range ($0.256 \geq IP_{M+}/IP_{Ln3+} \geq 0.249$),

- at smaller ionic potential ratio ($IP_{M+}/IP_{Ln3+} < 0.249$), the M_2LnX_5 compounds melt incongruently,

- the congruently melting compounds M_3LnX_6 form at smaller IP_{M+}/IP_{Ln3+} 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 $IP_{M+}/IP_{Ln3+} \leq 0.244$.

Table 2. Ionic potential ratio and type of phase diagram in the systems LnBr3-MBr

System	IP_{M+} / IP_{Ln3+}	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_7SmBr_{10}*	[37]
$GdBr_3$-NaBr	0.306	Na_3GdBr_6*	[37]
$HoBr_3$-NaBr	0.292	Na_3HoBr_6*	[38]
$TmBr_3$-NaBr	0.284	Na_3TmBr_6*	[39]
$LaBr_3$-KBr	0.256	K_2LaBr_5	[40]
$CeBr_3$-KBr	0.249	K_3CeBr_6, K_2CeBr_5*	[41]
$PrBr_3$-KBr	0.244	K_3PrBr_6, K_2PrBr_5*, KPr_2Br_7*	[7]
$NdBr_3$-KBr	0.240	K_3NdBr_6, K_2NdBr_5*, KNd_2Br_7	[7]
$LaBr_3$-RbBr	0.237	Rb_3LaBr_6, Rb_2LaBr_5*	[40]
$SmBr_3$-KBr	0.231	K_3SmBr_6, K_2SmBr_5*, KSm_2Br_7	[7]
$CeBr_3$-RbBr	0.231	Rb_3CeBr_6, Rb_2CeBr_5*, $RbCe_2Br_7$*	[42]
$PrBr_3$-RbBr	0.227	Rb_3PrBr_6, Rb_2PrBr_5*, $RbPr_2Br_7$*	[7]
$GdBr_3$-KBr	0.226	K_3GdBr_6, K_2GdBr_5*, KGd_2Br_7	[7]
$TbBr_3$-KBr	0.222	K_3TbBr_6, K_2TbBr_5*, KTb_2Br_7*	[43]
$NdBr_3$-RbBr	0.222	Rb_3NdBr_6, Rb_2NdBr_5*, $RbNd_2Br_7$	[7]
$DyBr_3$-KBr	0.219	K_3DyBr_6, K_2DyBr_5*	[7]
$SmBr_3$-RbBr	0.216	Rb_3SmBr_6, Rb_2SmBr_5*, $RbSm_2Br_7$	[7]
$ErBr_3$-KBr	0.212	K_3ErBr_6, K_2ErBr_5*	[7]
$GdBr_3$-RbBr	0.209	Rb_3GdBr_6, Rb_2GdBr_5*, $RbGd_2Br_7$	[7]
$LaBr_3$-CsBr	0.208	Cs_3LaBr_6, Cs_2LaBr_5*, $CsLa_2Br_7$*	[40]
$YbBr_3$-KBr	0.207	K_3YbBr_6, K_2YbBr_5*	[7]
$TbBr_3$-RbBr	0.206	Rb_3TbBr_6, $RbTb_2Br_7$*	[43]
$DyBr_3$-RbBr	0.203	Rb_3DyBr_6, Rb_2DyBr_5*, $RbDy_2Br_7$*	[7]
$CeBr_3$-CsBr	0.202	Cs_3CeBr_6, Cs_2CeBr_5*, $CsCe_2Br_7$	[44]
$PrBr_3$-CsBr	0.198	Cs_3PrBr_6, $CsPr_2Br_7$	[37]
$ErBr_3$-RbBr	0.197	Rb_3ErBr_6, Rb_2ErBr_5*	[7]
$NdBr_3$-CsBr	0.195	Cs_3NdBr_6, $CsNd_2Br_7$	[37]
$YbBr_3$-RbBr	0.192	Rb_3YbBr_6, Rb_2YbBr_5*	[7]
$SmBr_3$-CsBr	0.189	Cs_3SmBr_6, Cs_2SmBr_5*, $CsSm_2Br_7$	[7]
$GdBr_3$-CsBr	0.183	Cs_3GdBr_6, Cs_2GdBr_5*, $CsGd_2Br_7$	[7]
$TbBr_3$-CsBr	0.181	Cs_3TbBr_6, $CsTb_2Br_7$*	[43]
$DyBr_3$-CsBr	0.178	Cs_3DyBr_6, $CsDy_2Cl_7$*, $Cs_3Dy_2Br_9$*	[45]
$HoBr_3$-CsBr	0.175	Cs_3HoBr_6, $CsHo_2Br_7$*	[38]
$ErBr_3$-CsBr	0.173	Cs_3ErBr_6, Cs_2ErCl_5*	[7]
$YbBr_3$-CsBr	0.168	Cs_3YbBr_6, Cs_2YbBr_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 $IP_{M+}/IP_{Ln3+} \leq 0.256$,
- MLn_2X_7 compounds, present in chloride and bromide systems at $IP_{M+}/IP_{Ln3+} \leq 0.244$, practically do not occur in iodide systems (with the exception of $RbNd_2I_7$),
- $M_3Ln_2X_9$ compounds that exist in chloride ($IP_{M+}/IP_{Ln3+} \leq 0.175$) and iodide ($IP_{M+}/IP_{Ln3+} \leq 0.198$, systems practically do not occur in bromide systems (excepted for $Cs_3Dy_2Br_9$).

Table 3. Ionic potential ratio and type of phase diagram in the systems LnI_3-MI

System	IP_{M+} / IP_{Ln3+}	System type	Reference
LaI_3-LiI	0.478	Eutectic	[46]
NdI_3-LiI	0.465	Eutectic	[46]
LaI_3-NaI	0.346	Eutectic	[47]
PrI_3-NaI	0.330	Eutectic	[47]
NdI_3-NaI	0.325	Na_7NdI_{10} (*	[47]
SmI_3-NaI	0.315	Na_3SmI_6 (*	[47]
GdI_3-NaI	0.306	Na_3GdI_6*	[47]
LaI_3-KI	0.256	K_2LaI_5	[47]
PrI_3-KI	0.244	K_3PrI_6, K_2PrI_5 *	[47]
NdI_3-KI	0.240	K_3NdI_6, K_2NdI_5 *	[47]
LaI_3-RbI	0.237	Rb_3LaI_6, Rb_2LaI_5*	[43]
SmI_3-KI	0.231	K_3SmI_6	[47]
GdI_3-KI	0.226	K_3GdI_6	[47]
NdI_3-RbI	0.222	Rb_3NdI_6, Rb_2NdI_5*, $RbNd_2I_7$*	[43]
DyI_3-KI	0.219	K_3DyI_6	[47]
ErI_3-KI	0.212	K_3ErI_6	[47]
LaI_3-CsI	0.208	Cs_3LaI_6, $CsLa_9I_{28}$*	[47]
PrI_3-CsI	0.198	Cs_3PrI_6, $Cs_3Pr_2I_9$*, $CsPr_9I_{28}$*	[47]
NdI_3-CsI	0.195	Cs_3NdI_6, $Cs_3Nd_2I_9$*, $CsNd_4I_{13}$*	[47]
SmI_3-CsI	0.189	Cs_3SmI_6, $Cs_3Sm_2I_9$*	[47]
GdI_3-CsI	0.183	Cs_3GdI_6, $Cs_3Gd_2I_9$	[47]
TbI_3-CsI	0.181	Cs_3TbI_6, $Cs_3Tb_2I_9$	[48]
DyI_3-CsI	0.178	Cs_3DyI_6, $Cs_3Dy_2I_9$	[49]
HoI_3-CsI	0.175	Cs_3HoI_6, $Cs_3Ho_2I_9$	[50-51]
ErI_3-CsI	0.173	Cs_3ErI_6, $Cs_3Er_2I_9$	[47]
TmI_3-CsI	0.170	Cs_3TmI_6, $Cs_3Tm_2I_9$	[48]

*incongruent melting

This classification was tested on the $CeBr_3$-MBr binary systems (M=Li, Na, K, Rb, Cs), still unknown at the time it was established. Further experimental investigations validated that $CeBr_3$-LiBr and $CeBr_3$-NaBr are simple eutectic systems [34] (IP_{M+}/IP_{Ce3+}=0.465 and 0.366, respectively), while two congruently melting compounds, namely K_3CeBr_6 and K_2CeBr_5 exist in the $CeBr_3$-KBr system [41] as expected from the corresponding ionic potential ratio ($IP_{K+}/IP_{Ce3+} = 0.249$). The $CeBr_3$-RbBr [42] and $CeBr_3$-CsBr [44] systems ($IP_{Rb+}/IP_{Ce3+} = 0.231$ and $IP_{Cs+}/IP_{Ce3+} = 0.202$, respectively) follow the predicted pattern. The former system is characterized by the existence of three compounds, namely Rb_3CeBr_6, Rb_2CeBr_5 and $RbCe_2Br_7$. Rb_3CeBr_6 melts congruently whereas Rb_2CeBr_5 and $RbCe_2Br_7$ melt incongruently. The $CeBr_3$-CsBr system includes three compounds: the congruently melting Cs_3CeBr_6 and $CsCe_2Br_7$ together with Cs_2CeBr_5, which decomposes in the solid state.

Other tests were performed more recently on the $PrBr_3$-based bromide systems that also follow this trend. The binary systems with LiBr and NaBr are of simple eutectic-type [35] ($IP_{M+}/IP_{Pr3+} = 0.456$ and 0.330, respectively) (Figs.1-2). In the system with KBr [52], the congruently melting compound, K_3PrBr_6 and two incongruently melting compounds (K_2PrBr_5 and KPr_2Br_7) were found ($IP_{K+}/IP_{Pr3+} = 0.244$) (Fig.3). The system with rubidium bromide ($IP_{Rb+}/IP_{Pr3+} = 0.227$) [53] was also characterized by two congruently (Rb_3PrBr_6 and $RbPr_2Br_7$) and one incongruently melting (Rb_2PrBr_5) compounds (Fig.4).
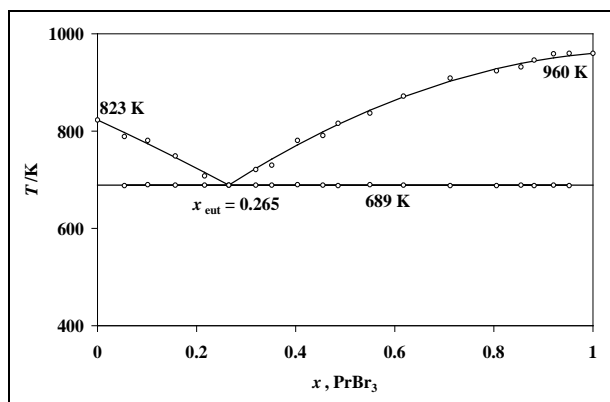
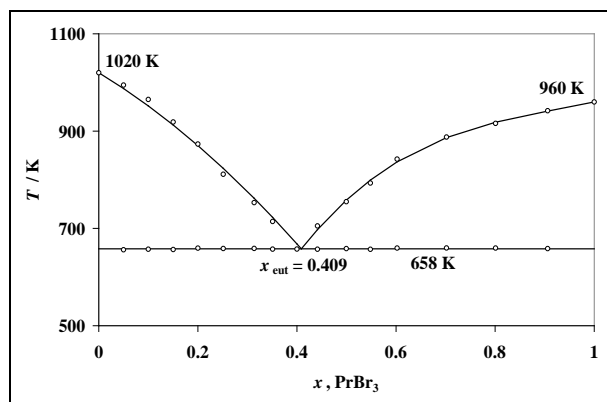Figure 1. Phase diagram of the PrBr$_3$–LiBr binary system.

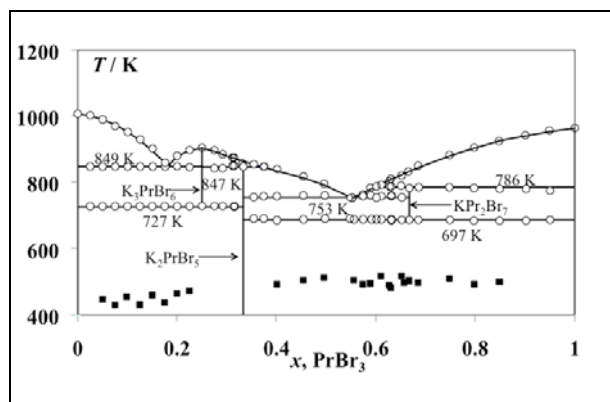Figure 2. Phase diagram of the PrBr$_3$–NaBr binary system

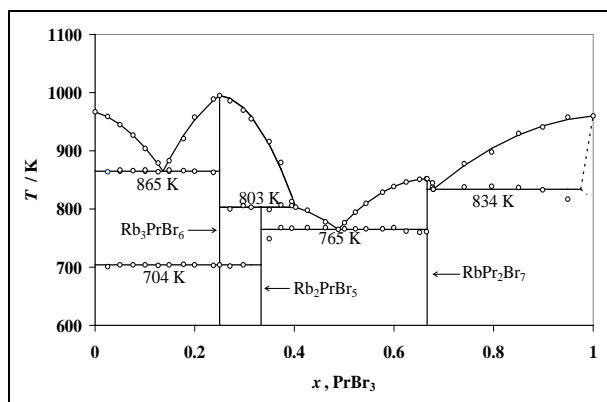Figure 3. Phase diagram of the PrBr$_3$–KBr binary system

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 LnX_2-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 LnX_2-MX (X= Cl, Br)

$IP_{M+}/IP_{Ln+2(Sr+2)}$	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	$LiSr_2Br_5$	[59-67]
0.939	$EuCl_2$-LiCl	Eutectic	[54]	$EuBr_2$-LiBr	$LiEu_2Br_5$	[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_2SrCl_4,KSr_2Cl_5	[59-63]	$SrBr_2$-KBr	K_2SrBr_4, $KSrBr_3$, KSr_2Br_5	[65]
0.504	$EuCl_2$-KCl	K_2EuCl_4, KEu_2Cl_5	[64]	$EuBr_2$-KBr	K_2EuBr_4,$KEuBr_3$, KEu_2Br_5	[69]
0.464	$YbCl_2$-KCl	---	----	$YbBr_2$-KBr	---	----
0.473	$SmCl_2$-RbCl	---	----	$SmBr_2$-RbBr	---	----
0.470	$SrCl_2$-RbCl	$RbSrCl_3$, $RbSr_2l_5$	[65]	$SrBr_2$-RbBr	Rb_2SrBr_4,$RbSrBr_3$, $RbSr_2Br_5$	[70]
0.466	$EuCl_2$-RbCl	$RbEuCl_3$, $RbEu_2Cl_5$	[64]	$EuBr_2$-RbBr	Rb_2EuBr_4,$RbEuBr_3$, $RbEu_2Br_5$	[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 $LiLn_2X_5$. In the 0.627<IP_{M+}/IP_{Ln2+}< 0.691 range, only eutectic mixtures are present (NaX-LnX$_2$). 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 ($SmCl_2$-NaCl or $SmBr_2$-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 LnX_2'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 stoichometric compounds. The analogous CsCl and CsBr systems are simpler than we expected, only one congruently melting compound ($CsLnX_3$) was found. This is not the case for SmI_2-CsI and YbI_2-CsI systems, where several congruently and incongruently stoichiometric compounds were reported [53-54].

All literature information together with our recent experimental data on the $EuBr_2$-MBr binary mixtures [55-57] is presented in Table 4 for comparison with the SrX_2-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 $SrBr_2/EuBr_2$ being isostructural.

Table 4 evidences identical features in all those EuX_2-MX and SrX_2-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 (Ln(II)= Eu, Yb ; X= Br, I) _as also $LiSr_2Br_5$ in the $SrBr_2$-LiBr system.

The reason might be related to the fact that all these systems correspond to a high and identical ionic potential ratio ($IP_{Li+}/IP_{Eu2+(Sr2+)} \approx 1$). 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 LnI_2-MI

$IP_{M+}/$ $IP_{Ln+2(Sr+2)}$	System	System type	Ref.
0.953	SmI_2-LiI	---	----
0.946	SrI_2-LiI	---	----
0.939	EuI_2-LiI	---	----
0.865	YbI_2-LiI	Li_3YbI_5,$LiYb_2I_5$	[54]
0.691	SmI_2-NaI	Eutectic	[79]
0.686	SrI_2-NaI	---	----
0.681	EuI_2-NaI	Eutectic	[54]
0.627	YbI_2-NaI	$NaYb_2I_5$*	[74]
0.511	SmI_2-KI	KSm_2I_5, K_2SmI_4*	[54], [79]
0.507	SrI_2-KI	---	----
0.504	EuI_2-KI	KEu_2I_5, K_4EuI_6	[54]
0.464	YbI_2-KI	$KYbI_3$	[74], [78]
0.473	SmI_2-RbI	Rb_2SmI_4,$RbSm_2I_5$ Rb_4SmI_6	[54,71]
0.470	SrI_2-RbI	---	----
0.466	EuI_2-RbI	$RbEu_2I_5$,$RbEuI_3$, Rb_3EuI_5*,Rb_4EuI_6*	[77-79]
0.430	YbI_2-RbI	$RbYbI_3$, Rb_4YbI_6* Rb_4YbI_6	[71], [80]
0.415	SmI_2-CsI	Cs_2SmI_4*, $CsSmI_3$, Cs_3SmI_5*, $CsSm_2I_5$*, Cs_4SmI_6	[79-82]
0.412	SrI_2-CsI	---	----
0.408	EuI_2-CsI	$CsEuI_3$, Cs_4EuI_6	[54,77, 80-82]
0.376	YbI_2-CsI	$CsYbI_3$, Cs_2YbI_4*, Cs_6YbI_8, Cs_4YbI_6	[80-83]

*incongruent melting

3. Conclusion

The whole information available on the LnX_3-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 LnX_3-MX binary phase diagrams depends on the cationic potentials ratio. The trend to compound formation increases if IP_{M+}/IP_{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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