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CALORIMETRIC INVESTIGATIONS OF THE MBr–NdBr$_3$ MELTS (*M*=Li, Na, K, Cs)

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Abstract

Present work is a part of thermodynamic research program on the MX–LnX$_3$ system (M=alkali metal, X=Cl, Br and Ln=lanthanide). Molar enthalpies of mixing in the LiBr–NdBr$_3$, NaBr–NdBr$_3$ and KBr–NdBr$_3$ liquid binary systems have been determined at temperature 1063 K by direct calorimetry in the whole range of composition. Investigated systems are generally characterized by negative enthalpies of mixing with minimum at X_{NdBr_3}≈0.3–0.4. These enthalpies decrease with decrease of ionic radii of alkali metals.

Molar enthalpies of solid–solid and solid–liquid phase transitions of K$_3$NdBr$_6$ and Cs$_3$NdBr$_6$ have been also determined by differential scanning calorimetry (DSC). K$_3$NdBr$_6$ is formed at 689 K from KBr and K$_2$NdBr$_5$ with enthalpy of 44.0 kJ·mol^{-1} whereas Cs$_3$NdBr$_6$ is stable at ambient temperature and undergoes phase transition in the solid state at 731 K with enthalpy of 8.8 kJ·mol^{-1}. Enthalpies of melting have been also determined.

Keywords: alkali metal bromides, DSC high-temperature calorimetry, mixing enthalpy, neodymium bromide, phase transition

Introduction

Presented in this work investigations are part of general research program concerning thermodynamic properties and electrical conductivity of MX–LnX$_3$ systems (where M=Li, Na, K, Rb, Cs; Ln=La, Ce, Pr, Nd; X=Cl, Br). Special attention has been paid to solid and liquid compounds M$_3$LnX$_6$. They exist only in systems with M=K, Rb, Cs [1–5]. Enthalpies of mixing in systems LiBr–NdBr$_3$, NaBr–NdBr$_3$ and KBr–NdBr$_3$ have been determined as well as enthalpies of mixing in systems RbBr–NdBr$_3$ and CsBr–NdBr$_3$ at X_{NdBr_3}=0.25. Molar enthalpies and entropies of phase transitions of K$_3$NdBr$_6$ and Cs$_3$NdBr$_6$ compounds were also determined by differential scanning calorimetry.

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Experimental

Chemicals

$NdBr_3$ had been prepared from Nd_2O_3 (99.9%) produced by Chemistry Department of Lublin University (Poland). The following procedure of preparation was adopted:

Nd_2O_3 had been dissolved in concentrated HBr and solution was filtered if necessary. Then NH_4Br was added to solution in the molar ratio $NdBr_3$:NH_4Br=1:4. Solution was gradually heated to vaporise most of the water – residue was a very wet mixture of crystals of the neodymium bromide hydrate. This mixture was placed into a quartz ampoule and gradually heated under reduced pressure to 570 K to remove the residual water. Then temperature was increased and ammonium bromide was sublimated (NH_4Br prevents formation of NdOBr during dehydration process). By heating to 1100 K synthesis was completed and ampoule with crude $NdBr_3$ was cooled and opened in a dry-box. $NdBr_3$ was purified by distillation under vacuum in a quartz at 1070 K (the idea of this distillation was presented in a figure in previous paper [1]). It has been found that even after single distillation quality of product was better than 99.9%. Because neodymium bromide is very sensitive to moisture, all handlings with the compound had been done under argon in a dry-box and products were stored in sealed glass ampoules.

MBr alkali bromides (M=Li, Na, K) were Merck Suprapur reagents (minimum 99.9%). They were dehydrated by heating and melting under atmosphere of gaseous HBr in quartz ampoules. Excess of HBr was removed from the melt with argon. Dry salts were crushed under argon in dry-box and stored in sealed glass ampoules.

K_3NdBr_6 and Cs_3NdBr_6 compounds were prepared from MBr and $NdBr_3$ in the molar ratio 3:1. Mixtures of substrates were prepared in a dry-box and melted in sealed under vacuum quartz ampoules. Samples of compounds were ground in a dry-box under argon. Though only small masses of samples were used for DSC experiments (300–500 mg) more than 10 g of each compound was synthesized in order to avoid deviation from stoichiometry.

Measurements

All experiments of mixing were of simple liquid–liquid type. They were carried out under argon at atmospheric pressure. Calvet-type high temperature microcalorimeter, quartz mixing cells and details of the experimental method have been described elsewhere [6]. Generally, mixing of two molten salts were performed by break-off-ampoule technique.

Apparatus was calibrated with NIST α-alumina [7] by dropping weighed pieces of α-alumina directly into the melt. Integration of pick surfaces of thermograms was performed automatically by computer. Experimental uncertainty of calibration was about 3% and experimental uncertainty of mixing enthalpy was estimated as about 6% of measured value.

Differential scanning calorimeter (DSC 121 Setaram) was used for determination of temperature and enthalpy of phase transitions. Details of these experiments have been described elsewhere [5]. Experimental quartz cells (7 mm of diameter and 15 mm of length) were filled with the salt and sealed under reduced pressure of argon. DSC experiments were performed at heating and cooling rates of 1–5 deg·min^{-1}. Experimental error of enthalpy measurements was estimated as 2–4% and depended on the sample and area of thermal effect.

Results

Enthalpy of mixing

Calorimetric mixing experiments were carried out at 1063 K for all investigated systems. Experimental enthalpies of mixing, $\Delta_{mix}H_m$, plotted against composition of the melt are presented in Fig. 1. During evaluation of results all data coming from experiments with poor homogeneity of the melt or serious evaporation were disregarded; furthermore, in order to improve the overall accuracy

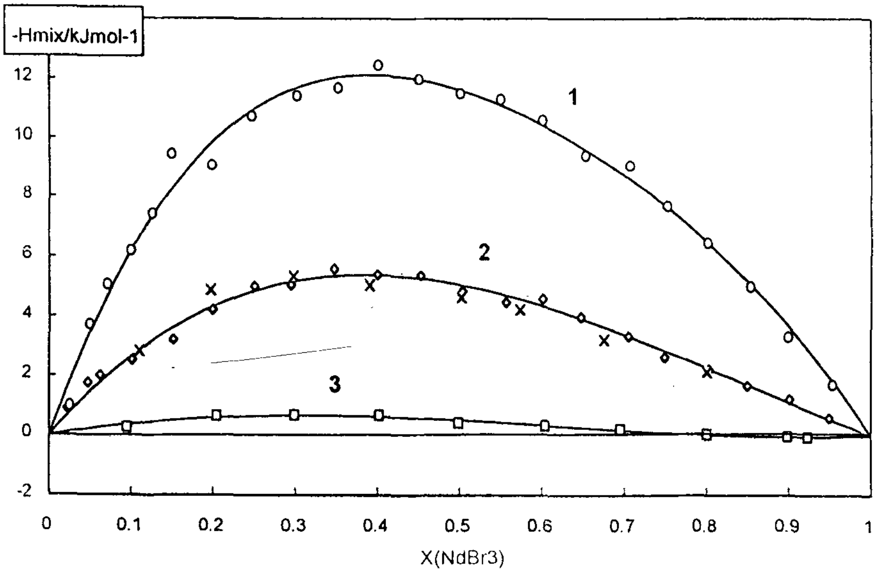

Fig. 1 Experimental enthalpies of mixing $\Delta_{mix}H_m$, for LiBr–NdBr$_3$ (3), NaBr–NdBr$_3$ (2) and KBr–NdBr$_3$ (1) at 1063 K. 'x'-denotes literature data for NaBr–NdBr$_3$ system [13]

some experimental points were taken as the average of several independent runs.

Some experiments were also performed to determine accurately enthalpy of formation at $X_{NdBr_3}=0.25$ for all MBr–NdBr$_3$ system (M=Li, Na, K, Rb, Cs), i.e. enthalpy of reaction:

$$3\ \mathrm{MBr(l)} + \mathrm{NdBr_3(l)} = \text{‘}\mathrm{M_3NdBr_6}\text{’}\mathrm{(l)} \qquad (1)$$

Notation ‘M_3NdBr_6’(l) was adopted since there is no such compound in systems LiBr–NdBr$_3$ and NaBr–NdBr$_3$.

Experimental values of formation enthalpies of ‘M_3NdBr_6’(l) are presented in Table 1. The same table includes also formation enthalpies of analogue ‘M_3NdCl_6’(l) compounds (mixtures of alkali metal chlorides and NdCl$_3$ [1]) as well as ionic radii of alkali cations [8].

Table 1 Molar enthalpy of formation $\Delta_f H_m$ (M_3LnX_6, l,T) / kJ·mol^{-1} of liquid mixtures according to reaction: 3 MX(l) + NdX$_3$(l) = ‘M_3NdX_6’(l), where M = Li, Na, K, Rb, Cs and X = Cl, Br

MCl	$\Delta_f H_m$ (M_3LnCl_6, l, 1122 K) kJ·mol^{-1}	MBr	$\Delta_f H_m$ (M_3LnBr_6, l, 1063 K) kJ·mol^{-1}	r_{M^+} [8]
LiCl	$-6.9_{(1065\ K)}$	LiBr	–2.6	74
NaCl	–24.8	NaBr	–19.4	102
KCl	$-55.2_{(1065\ K)}$	KBr	–43.9	138
RbCl	–68.8	RbBr	–65.7	149
CsCl	–80.8	CsBr	–73.02	170

r_{Cl^-} = 181 pm [8], r_{Br^-} = 196 pm [8], $r_{Nd^{3+}}$ = 99.5 pm [8]

Entropies of phase transitions

Reproducibility of phase transition enthalpies calculated from DSC heating and cooling curves was very good and difference between particular runs not exceeded 2%. Supercooling effects were observed in several experiments, especially for K$_3$NdBr$_6$. The results are given in Table 2. Due to supercooling only temperatures taken from heating curves are given in the Table 2. Some literature data are also presented.

Discussion

During these investigations enthalpies of mixing in the systems LiBr–NdBr$_3$, NaBr–NdBr$_3$ and KBr–NdBr$_3$ were investigated in the whole range of composition. Systems are generally characterized by negative enthalpies of mixing.

Table 2 Molar enthalpies and entropies of formation or solid-solid phase transition and fusion of K_3NdBr_6 and Cs_3NdBr_6 compounds

Compound	T_f / K	$\Delta_f H_m$ / kJ·mol^{-1}	$\Delta_f S_m$ / J·mol^{-1}K^{-1}	T_{trs} / K	$\Delta_{trs} H_m$ / kJ·mol^{-1}	$\Delta_{trs} S_m$ / J·mol^{-1}K^{-1}	T_{fus} / K	$\Delta_{fus} H_m$ / kJ·mol^{-1}	$\Delta_{fus} S_m$ / J·mol^{-1}K^{-1}	Ref.
K_3NdBr_6	684	44.0	64.3				918	41.4	45.1	
				683			933			[9]
Cs_3NdBr_6				731	8.8	12.0	1055	61.5	58.3	
				723			1043			[10]

These enthalpies decrease with decrease of ionic radius of alkali metal – Fig. 1. LiBr–NdBr$_3$ system is an interesting exception – enthalpy of mixing is positive in a narrow range of composition: from $X_{\mathrm{NdBr_3}}=0.8$ to $X_{\mathrm{NdBr_3}}=1.0$. From $X_{\mathrm{NdBr_3}}=0.0$ to $X_{\mathrm{NdBr_3}}=0.8$ enthalpy of mixing is, as usual, negative. Generally, the minimum of mixing enthalpy is shifted to compositions with higher concentration of alkali metal bromide for all investigated systems and usually is located between $X_{\mathrm{NdBr_3}}=0.3$ and 0.4. This is typical also for neodymium chloride systems which we investigated previously [1], observations of Papatheodorou and Kleppa [11] as well as Papatheodorou and Østvold [12] for cerium and lanthanum chlorides with alkali metal chlorides. There are given only enthalpies of mixing for NaBr–NdBr$_3$ system in the literature [13]. They are very close to our results – Fig. 1.

One may define interaction parameter λ:

$$\lambda=\Delta_{\mathrm{mix}}H_{\mathrm{m}}/X_{\mathrm{MBr}}\cdot X_{\mathrm{NdBr_3}}$$

This parameter represents energetic asymmetry for investigated melts. Coefficients of polynomials which describe dependence of λ on composition are given in Table 3 and curves of these dependences are given in Fig. 2. For LiBr–NdBr$_3$ system values of λ are almost equal to zero (in the range $X_{\mathrm{NdBr_3}}=$ 0.8–1.0 they are positive) and general course of this dependence seems rather unique. For NaBr–NdBr$_3$ and KBr–NdBr$_3$ systems dependence of interaction parameter λ on composition is close to linear in the range of $X_{\mathrm{NdBr_3}}$ from 0.2 to 1.0. In the range of $X_{\mathrm{NdBr_3}}$ from 0.0 to 0.2 this linearlity disappears but the minimum is not so visible as it was observed for KCl–NdCl$_3$ system [1].

Table 3 Least-square coefficients of λ dependence on composition for liquid MBr–NdBr$_3$ mixtures: $\lambda=A+B\cdot X_{\mathrm{NdBr_3}}+CX^2_{\mathrm{NdBr_3}}+DX^3_{\mathrm{NdBr_3}}$; λ in kJ·mol^{-1}

	A	*B*	*C*	*D*
Li	–2.700	–8.850	27.10	–14.67
Na	–40.32	86.29	–123.0	67.84
K	–66.64	2.954	116.5	–95.34

Detailed discussion of possible complexes which may be formed in chloride melts has been presented in previous paper [1]. Very recent report of Fukushima *et al.* [14] on the structure of LaBr$_3$ and Raman spectroscopy data combined with molecular dynamics simulation of Matsuoka *et al.* [15] (ionic melts of GdCl$_3$ with some alkali metal chlorides) give a support to conclusion that complexes of octahedral type exist in these ionic melts. Therefore, assumption that $\mathrm{NdBr_6^{3-}}$ anion is always present in investigated melts seems quite justified. Stability of complex forms in the melt should be related to solid compounds which are formed in investigated systems – especially to congruently melting compounds. There are no data for the system LiBr–NdBr$_3$ but this system should be simple eutectic one as NaBr–NdBr$_3$ [10]. In the system KBr–NdBr$_3$ K$_3$NdBr$_6$ and KNd$_2$Br$_7$ are the compounds which melt congruently in contradiction to K$_2$NdBr$_5$ with peritectical decomposition [9]. It suggests that complex anions such as NdBr$_6^{3-}$ and Nd$_2$Br$_7^-$ should dominate in melts of neodymium(III) bromide with alkali metal bromides – especially in systems with heavier alkali metal cation. Moreover, comparison of formation enthalpies of 'M$_3$NdBr$_6$'(l) and 'M$_3$NdCl$_6$'(l) compounds – Table 1 – reveals that bromide complexes are less stable in the sense of energy of formation.

There are no literature data on enthalpies of formation, transition in the solid state and fusion of M$_3$NdBr$_6$ compounds. It has been reported only that K$_3$NdBr$_6$ undergoes solid –solid phase transition at 683 K and melts at 933 K [9]. However, it seems that effect at 684 K (683 K according to reference [9]) is not phase transition but formation of the compound. This conclusion comes from comparison with data for K$_3$NdCl$_6$ analogue [3] and from high value of energy of the effect. Of course, this suggestion should be verified by X-ray or EMF measurements. Molar enthalpies and entropies of formation or solid–solid phase transition and fusion of K$_3$NdBr$_6$ and Cs$_3$NdBr$_6$ compounds are given in Table 2.

Cs$_3$NdBr$_6$ compound is stable at ambient temperature and undergoes solid–solid phase transition at 731 K with enthalpy of 7.4 kJ·mol^{-1} (Table 2).

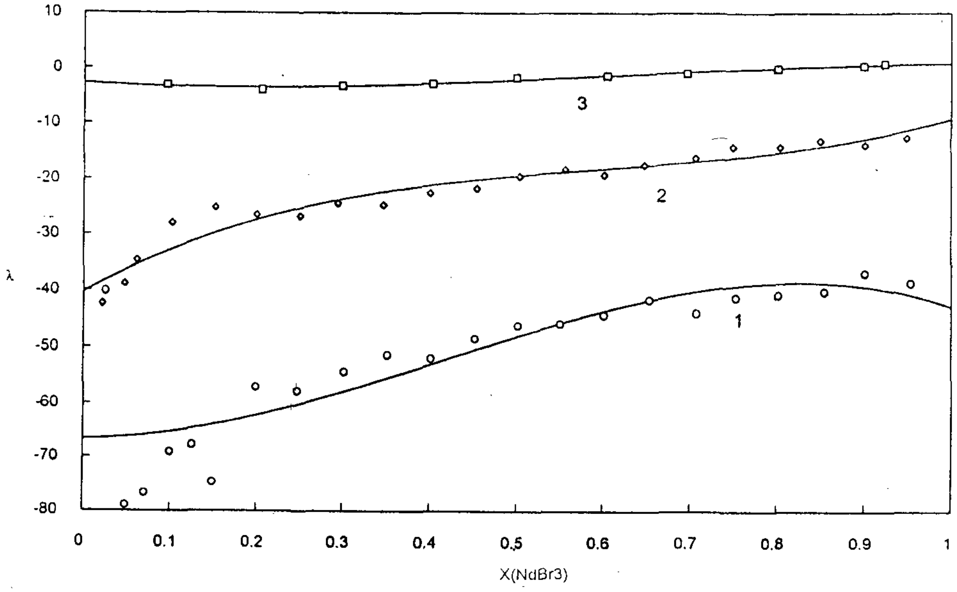

Fig. 2 Dependences of interaction parameter λ on composition of the melt for LiBr–NdBr$_3$ (3), NaBr–NdBr$_3$ (2) and KBr–NdBr$_3$ (1); λ in kJ·mol^{-1}

Temperature of this transition is in a good agreement with literature data [10]. Temperature of melting of Cs_3NdBr_6 is 10 K higher than value given in literature [10] (1055 and 1043 K, respectively).

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Zusammenfassung — Vorliegende Arbeit ist ein Teil eines thermodynamischen Forschungsprogrammes an MX–LnX_3-Systemen (*M*=Alkalimetall, *X*=Cl,Br und *Ln*=Lanthanid). Mittels direkter Kalorimetrie wurden die molaren Mischungsenthalpien in den flüssigen binären Systemen LiBr–$NdBr_3$, NaBr–$NdBr_3$ und KBr–$NdBr_3$ bei 1063 K im gesamten Konzentrationsbereich bestimmt. Die untersuchten Systeme sind generell durch negative Mischungsenthalpien mit einem Minimum bei X_{NdBr_3} ≈0.3–0.4 gekennzeichnet. Diese Enthalpien sinken mit abnehmendem Alkalimetallradius.

Mittels DSC wurden weiterhin die molaren Enthalpien für Feststoff-Feststoff- und für Feststoff-Flüssigkeits-Umwandlungen von K_3NdBr_6 und Cs_3NdBr_6 ermittelt. K_3NdBr_6 wird bei 689 K aus KBr und K_2NdBr_5 mit einer Enthalpie von 44.0 kJ/mol gebildet, während Cs_3NdBr_6 bei Raumtemperatur stabil ist und im Festzustand bei 731 K einer Phasenumwandlung mit einer Enthalpie von 8.8 kJ/mol unterliegt. Die Schmelzenthalpien wurden ebenfalls ermittelt.