

Binary Systems Formed by Lead Bromide with (Li, Na, K, Rb, Cs and Tl)Br: a DTA and Diffractometric Study

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The phase diagrams of the systems $\text{PbBr}_2 + \text{MeBr}$ (Me = Li, Na, K, Rb, Cs, Tl) have been measured by visual and DTA methods.

The structures and the thermal characteristics of the intermediate compounds have been pointed out by X-ray diffractometric technique and by DTA-calorimetric measurements, respectively.

Moreover, the thermodynamic behaviour of these systems has been discussed.

During the last few years, the study of systems containing lead bromide has caught the attention of many authors. In particular, for the systems formed by $\text{PbBr}_2 + \text{MeBr}$ (Me = alkali metal or thallium), Russian authors¹ have investigated various combinations of different salts including binary, ternary and reciprocal systems.

The present work was undertaken to continue the study of the thermodynamic properties of systems formed by two salts with bi-monovalent cations and common anion². In order to eliminate gaps found in the work of previous authors, particularly in the study of the solid phases, we have analyzed the systems formed by PbBr_2 with (Li, Na, K, Rb, Cs and Tl)Br.

Diffractograms taken on intermediate compounds enabled us to characterize the lattice parameters. Moreover, measurements of transition and fusion effects were carried out for compounds with congruent melting points, in order to discuss the solid-liquid (SL) curves in the phase diagrams on the basis of structural models.

Experimental Section

DTA measurements: The SL curves were measured by DTA and direct visual techniques already described². For the determination of the heats of transition

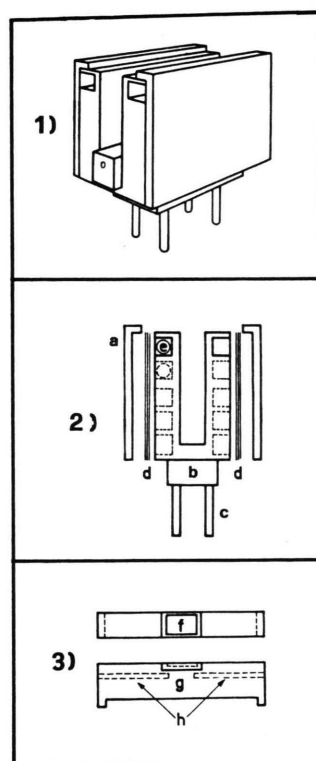


Fig. 1. Oven in stainless steel: 1) General view; 2) Open section; 3) Sample holder seen from the top and the side: a) steel plates, b) alumina support, c) steel bolts, d) mica sheets, e) quartz tubes with heating elements, f) gold container, g) steel support, h) lodgment for thermocouples.

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¹ S. D. GROMAKOV, Zhur. Fiz. Khim. 24, 641 [1950]. — I. I. ILYASOV, S. D. DIONISEV, and A. G. BERGMAN, Russ. J. Inorg. Chem. 5, 320, 546 [1960]. — A. G. BERGMAN and YU. I. ANDRYUSHCHENKO, Russ. J. Inorg. Chem. 8, 882 [1963]. — I. I. ILYASOV, S. D. DIONISEV, and A. G. BERGMAN, Zhur. neorg. Khim. 11, 1981 [1966]. — I. I. ILYASOV and S. D. DIONISEV, Zhur. neorg. Khim. 11, 1986 [1966].

² C. SINISTRI, R. RICCARDI, and A. MAGISTRIS, Ber. Bunsenges. Phys. Chem. 71, 376 [1967]. — R. RICCARDI, C. SINISTRI, A. MAGISTRIS, and G. CAMPARI VIGANÒ, Z. Naturforsch. 25 a, 781 [1970].

³ N. F. M. HENRY, H. LIPSON, and W. A. WOOSTER, The Interpretation of X-ray Diffraction Photographs, McMillan & Co. Ltd., London 1951.

⁴ P. M. DE WOLFF, Acta Cryst. 10, 590 [1957]; 11, 664 [1958].



and fusion, a Du Pont 900 Thermal Analyzer fitted with a Differential Scanning Calorimeter was used.

X-ray measurements have been made by means of a Philips apparatus fitted with a high temperature camera (Materials Research Corporation mod. X-86 N-II) employing Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). For measurements at relatively high temperature, we found it necessary to replace the original heating element (which also acted as sample holder) with a small furnace built in our laboratory. Thus, better temperature homogeneity and regulation were obtained. Our furnace, which was made of stainless steel is schematically illustrated in Fig. 1: it can reach a maximum temperature of about 600°C , and the temperature is controlled by a CAT (Leeds & Northrup) within a precision of $\pm 1^\circ\text{C}$.

For the analysis of the diffractograms, the HESSELIPSON³ and DE WOLFF⁴ methods have been used. In some cases, the analysis of the crystals with a microscope using polarized light has also been very useful.

Materials: All the salts (BDH) were dried following the rules suggested in the literature.

Generally, the compounds for X-ray analysis have been prepared by mixing PbBr_2 and MeBr in the solid state; the mixture was then melted and held at the proper temperature as indicated by the phase diagram for a sufficient length of time.

When possible, the compounds were also prepared by crystallization from aqueous solutions: this enabled us to compare diffractograms of samples obtained by different methods.

Results and Discussion

1. Phase Diagrams and Structure of the Intermediate Compounds

Fig. 2 shows the phase diagrams of the systems studied, along with the temperatures and the compositions of the characteristic points. Sometimes it proved impossible to determine the composition of the incongruent intermediate compounds by the DTA technique because the formation reaction of the compound was not sufficiently fast. In these cases, a choice among the possible compositions was made possible by diffractometric measurements at different temperatures on samples having appropriate compositions.

Compound $2\text{PbBr}_2 \cdot \text{KBr}$. This compound has been studied by POWELL and TASKER⁵ who reported a tetragonal structure (isomorphous with $2\text{PbBr}_2 \cdot \text{RbBr}$ and $2\text{PbBr}_2 \cdot \text{NH}_4\text{Br}$).

The compound we obtained by slowly cooling the melt showed a diffractogram identical to that of the

compound obtained by crystallization from aqueous solution according to WELLS^{6,7}. Crystallization from aqueous solution yields crystals that can be studied by single crystal methods: therefore the elementary cell constants have been determined with a Buerger camera.

On the basis of our measurements, the compound $2\text{PbBr}_2 \cdot \text{KBr}$ at room temperature has orthorhombic symmetry, with constants:

$$a = 9.28_0; \quad b = 8.39_3; \quad c = 13.08_8 \text{ \AA}.$$

Extinction conditions: for $h0l$ $l = 2n + 1$; most probable space groups: $n. 26(\text{Pmc}2_1)$; $n. 28(\text{P}2\text{cm})$; $n. 51(\text{Pmcm})$; $Z = 4$; $d_{\text{obs}} = 5.53$; $d_{\text{calc}} = 5.60 \text{ g/cm}^3$.

The DTA curves recorded for this compound (see Fig. 2) show a transition at 242°C , with a small thermal effect ($\cong 0.1 \text{ kcal/mole}$).

The diffractograms at 320°C differ from those at room temperature only for a uniform shift toward smaller diffraction angles and for the intensities of some peaks. From these diffractograms a new cell cannot be suggested.

Compound $\text{PbBr}_2 \cdot 2\text{KBr}$. It is possible to assign indexes to the diffractogram of this compound on the basis of a orthorhombic cell with the following constants:

$$a = 12.9_7; \quad b = 20.7_2; \quad c = 14.2_0 \text{ \AA};$$

$Z = 16$; $d_{\text{obs}} = 4.26$; $d_{\text{calc}} = 4.24 \text{ g/cm}^3$. There is no extinction characteristic of a particular type of lattice, thus the cell seems to be primitive.

Compound $2\text{PbBr}_2 \cdot \text{RbBr}$. A tetragonal cell has been previously⁵ assigned to this salt: $a = 8.41$; $c = 14.5 \text{ \AA}$; $Z = 4$; space group: $n. 140 \text{ I}(4/\text{m cm})$.

Our results well confirm this structure with constants: $a = 8.42_5$; $c = 14.56_0 \text{ \AA}$; $Z = 4$; $d_{\text{obs}} = 5.83$; $d_{\text{calc}} = 5.82 \text{ g/cm}^3$.

Compound $\text{PbBr}_2 \cdot \text{RbBr}$. The DTA curves measured on this compound (see Fig. 2) show peaks at the constant temperature of 267°C : the estimated thermal effect is $1.7 \pm 0.1 \text{ kcal/mole}$.

X-ray measurements have been carried out at room temperature, at 310°C and 370°C . At room temperature it was not possible to obtain a compound of formula $\text{PbBr}_2 \cdot \text{RbBr}$, not even with quenching: the sample at room temperature constantly showed peaks of the $2\text{PbBr}_2 \cdot \text{RbBr}$ com-

⁵ H. M. POWELL and H. S. TASKER, J. Chem. Soc. 1937, 119.

⁶ H. L. WELLS, Amer. J. Sci. 45, 121 [1893].

⁷ H. L. WELLS, Z. Anorg. Chem. 4, 128 [1893].

pound, along with other peaks that remained unidentified.

It is thus probable that DTA peaks at 267 °C are due to a disproportionation reaction



instead of a polymorphic transition.

Diffraction patterns obtained at 310 °C show that $\text{PbBr}_2 \cdot \text{RbBr}$ has a pseudo-cubic structure type perovskite (probably with a monoclinic symmetry). It is possible to assign indexes to the dif-

fractograms, with sufficient precision, on the basis of a cell with dimensions: $a = 11.53$; $b = 11.47$; $c = 11.59 \text{ \AA}$, $\gamma = 91^\circ 7'$.

Diffraction patterns at 370 °C are very similar to those observed at 310 °C. Thus the $\text{PbBr}_2 \cdot \text{RbBr}$ compound does not assume the perfect perovskite structure.

Compound $\text{PbBr}_2 \cdot 4 \text{ RbBr}$. Diffraction patterns for this compound give a tetragonal cell with constants: $a = 18.90_0$; $c = 19.32_0 \text{ \AA}$; $Z = 16$; $d_{\text{obs}} = 3.99$; $d_{\text{calc}} = 3.99 \text{ g/cm}^3$. There is no extinction charac-

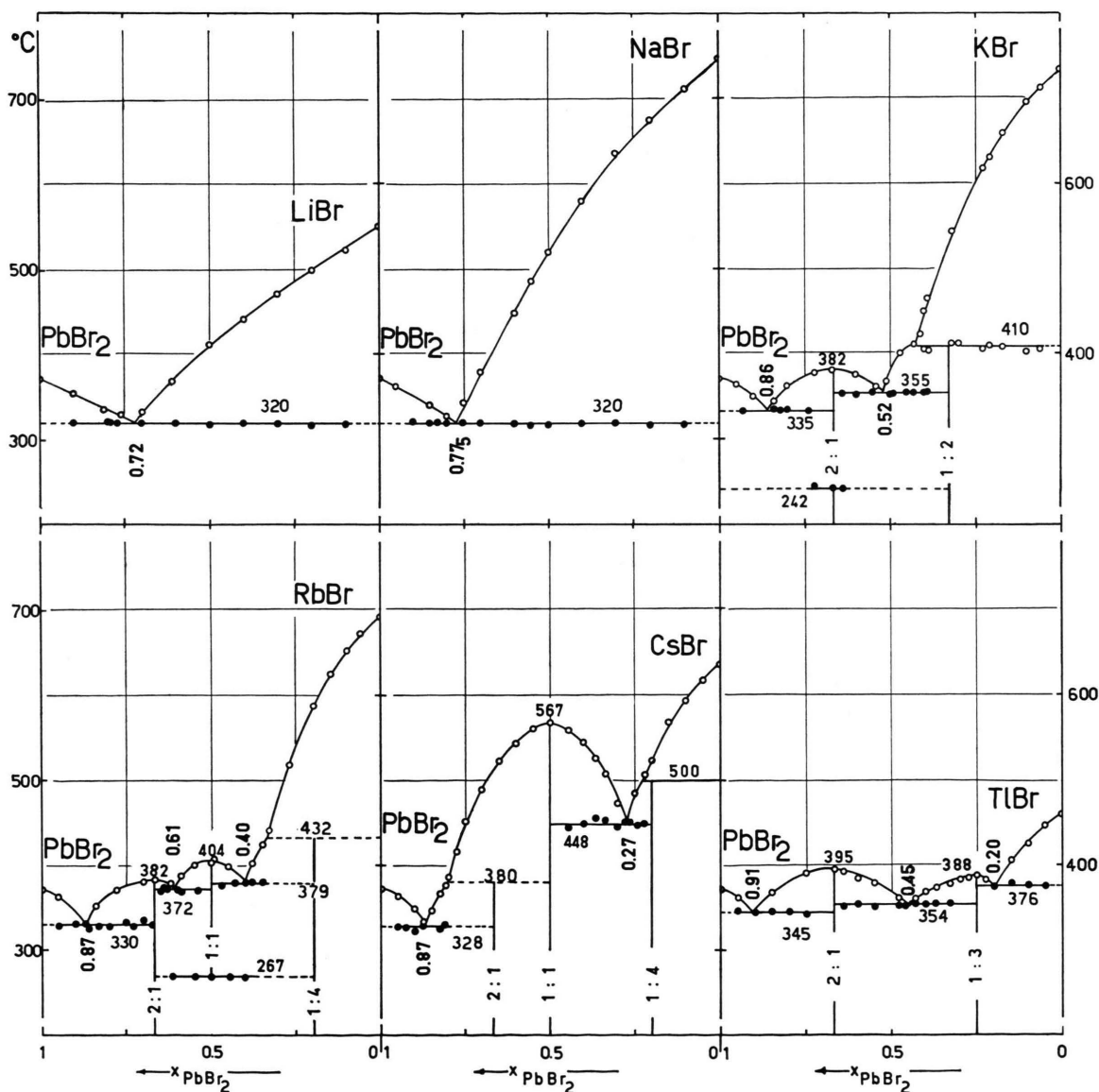


Fig. 2. Phase diagrams. The compound $\text{PbBr}_2 \cdot \text{CsBr}$ shows also a transition at 123 °C.

teristic of a particular type of lattice, thus the cell seems to be primitive.

Compound $2\text{PbBr}_2 \cdot \text{CsBr}$. Diffractograms for this compound give a tetragonal cell with constants: $a = 8.48_3$; $c = 15.25_0$ Å; $Z = 4$.

This cell is isotopic with that of $2\text{PbBr}_2 \cdot \text{RbBr}$, but in this case the characteristic extinctions of the body-centered lattice are not observed.

Compound $\text{PbBr}_2 \cdot \text{CsBr}$. This compound was first prepared by WELLS⁶ who observed two different crystalline forms: the first one consists of orange prism, the second one of thin white needles.

According to MØLLER⁸ the orange form undergoes phase transitions at 120° , 125° and 135°C . At room temperature he observed a monoclinic structure ($a = b = 5.827$; $c = 5.891$ Å; $\gamma = 89^\circ 65'$), while at temperatures above 135°C the structure is cubic, type perovskite.

By DTA measurements we found no evidence for the three different crystalline forms observed by Møller. Our DTA curves show only one transition at 123°C with a very small thermal effect (< 0.1 kcal/mole).

Our diffractometric measurements at room temperature confirm Møller's elementary cell, for the orange compound, provided that the dimension are doubled. This is in agreement with Møller's observation that some diffraction peaks could be interpreted only assuming double parameters. Therefore the constant are: $a = b = 11.69_5$; $c = 11.782$ Å; $\gamma = 89^\circ 39'$; $Z = 8$; $d_{\text{obs}} = 4.74$; $d_{\text{calc}} = 4.82$ g/cm³.

At temperatures above 135°C we observed a cubic structure in agreement with Møller's findings.

Compound $\text{PbBr}_2 \cdot 4\text{CsBr}$. This compound was studied by WELLS⁶ and by MØLLER⁹. This latter found an hexagonal structure ($a = 13.73_2$; $c = 17.32_4$ Å. Space group: $R\bar{3}c$ [most probable], or $R3c$).

Our measurements are an perfect agreement with Møller's ones.

Compound $2\text{PbBr}_2 \cdot \text{TlBr}$. The diffraction pattern of this compound is very similar to that of $2\text{PbBr}_2 \cdot \text{KBr}$ and gives a orthorhombic cell with constants: $a = 19.6_1$; $b = 17.4_9$; $c = 12.4_0$ Å; $Z = 16$; $d_{\text{obs}} = 6.34$; $d_{\text{calc}} = 6.40$ g/cm³.

Compound $\text{PbBr}_2 \cdot 3\text{TlBr}$. The diffraction pattern gives a orthorhombic cell with constants: $a = 15.8_1$; $b = 15.5_9$; $c = 19.4_4$ Å; $Z = 16$; $d_{\text{obs}} = 6.79$; $d_{\text{calc}} = 6.81$ g/cm³.

2. Thermal Effects and Thermodynamic Behaviour

For a discussion of the thermodynamic behaviour of these systems it is necessary to know the heats ΔH_f and temperature T_f of fusion of all the congruent compounds, as well as those of the pure salts.

The heats of fusion of alkali bromide and of thallium bromide are available in the literature^{10, 11}.

For PbBr_2 on the contrary, there are conflicting figures: GOODWIN and KALMUS¹², who used a calorimetric method, found $\Delta H_f = 3.60$ kcal/mole and $T_f = 761^\circ\text{K}$; BLANC and PETIT¹³ by cryoscopic method gave $\Delta H_f = 5.00$ kcal/mole and $T_f = 643^\circ\text{K}$. The values determined in the present work are $\Delta H_f = 4.41 \pm 0.07$ kcal/mole and $T_f = 644^\circ\text{K}$.

The heats of fusion of all the congruent compounds were also measured. The corresponding values (ΔH_{exp}) are reported in Table 1 along with the additively calculated values (ΔH_{calc}) and with $\Delta(\Delta H) \equiv (\Delta H_{\text{exp}}) - (\Delta H_{\text{calc}})$. The latest quantities, as it has been shown in previous work², enable us to predict the exothermic heats of mixing.

It is possible to analyze the thermodynamic behaviour of these systems by assuming, for the melt, the total dissociation of the salt and the Temkin model. In particular, if there is no solubility in the solid phase, it is useful to consider the branches of the liquidus curves rich in alkali bromide. These, in fact, extend in large temperature and composition

Table 1. Heats of fusion (in kcal/mole) for PbBr_2 and the congruent compounds $\text{PbBr}_2 \cdot n\text{MeBr}$.

Compound	T_f ($^\circ\text{K}$)	ΔH_{exp}	ΔH_{calc}	$\Delta(\Delta H)$
PbBr_2	644	4.4	—	—
$2\text{PbBr}_2 \cdot \text{KBr}$	655	11.2	14.7	−3.5
$2\text{PbBr}_2 \cdot \text{RbBr}$	655	13.5	14.2	−0.7
$\text{PbBr}_2 \cdot \text{RbBr}$	677	5.3	9.8	−4.5
$\text{PbBr}_2 \cdot \text{CsBr}$	840	8.5	10.1	−1.6
$2\text{PbBr}_2 \cdot \text{TlBr}$	668	12.6	12.6	0.0
$\text{PbBr}_2 \cdot 3\text{TlBr}$	661	14.3	15.8	−1.5

⁸ C. KN. MØLLER, Kgl. Dan. Videnskab Selskab, Mat. Fis. Medd. **32**, 1 [1959].

⁹ C. KN. MØLLER, Kgl. Dan. Videnskab Selskab, Mat. Fis. Medd. **32**, 1 [1960].

¹⁰ A. S. DWORKIN and M. A. BREDIG, J. Phys. Chem. **64**, 269 [1960].

¹¹ D. CUBICCIOTTI and H. EDING, J. Chem. Eng. Data **10**, 343 [1965].

¹² H. M. GOODWIN and T. H. KALMUS, Phys. Rev. **28**, 1 [1909].

¹³ M. BLANC and G. PETIT, C. R. Acad. Sci. Paris **248**, 1305 [1959].

ranges, whilst the liquidus curves rich in PbBr_2 are always very short.

Fig. 3 shows the quantity $\Delta T \equiv (T_{\text{exp}} - T_{\text{id}})$ as a function of the composition for the liquidus curves rich in alkali bromide. The T_{id} value has been calculated according to equations previously given^{2, 14}.

As it can be observed, only the system $\text{LiBr} + \text{PbBr}_2$ shows positive deviations with respect to ideality ($\Delta T > 0$), whereas all the other systems show negative deviations ($\Delta T < 0$) which increase as the radius of the alkali ion increases. As previously discussed, positive deviations from ideality can be interpreted on the basis of activity coefficients ($f_{\text{LiBr}} > 1$), whereas negative deviations can be interpreted on the basis of either activity coefficients ($f_{\text{MeBr}} < 1$) or formation of complexes.

Negative deviations from ideality are also in agreement with the prediction of a negative enthalpy of mixing for these systems.

Figure 4 shows the ideal behaviour of the liquidus curves for the congruent compounds, along with the experimental values.

Negative deviations are always observed: these deviations can sometimes be very noticeable (see for instance $\text{PbBr}_2 + \text{CsBr}$).

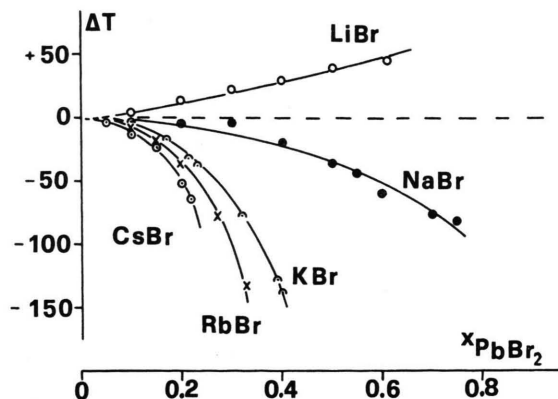


Fig. 3. Deviations from ideal behaviour for the curves rich in alkali bromide ($\Delta T \equiv T_{\text{exp}} - T_{\text{id}}$).

¹⁴ C. SINISTRI and P. FRANZOSINI, *Ric. Sci.* **33** (II A), 419 [1963].

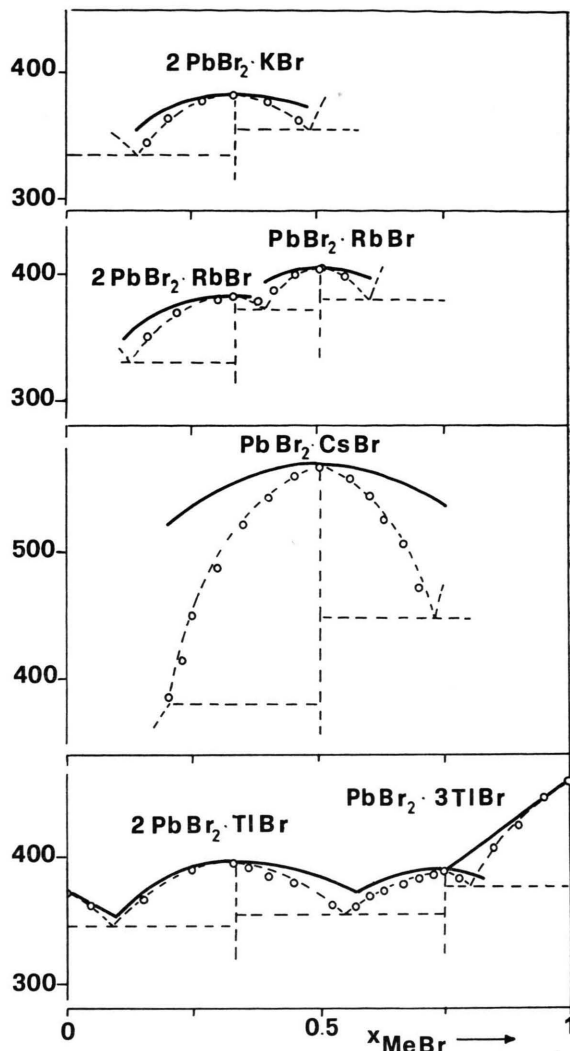


Fig. 4. Behaviour of the ideal curves regarding the congruent compounds (continuous lines) in comparison with the experimental data (small circles).

This figure also shows for the complete system $\text{PbBr}_2 + \text{TlBr}$, the comparison between the experimental data and the ideal behaviour. As it can be observed, deviations for this system are always negative and very small.