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INVESTIGATION OF PHASE DIAGRAMS BY DTA AND X-RAY METHODS

THE SYSTEMS AX/CoX_2 (A = Na–Cs, Tl; X = Cl, Br, I)

HANS-J. SEIFERT
Institute of Inorganic Chemistry, University Kassel, Kassel (G.F.R.)

ABSTRACT

A combination of differential thermal analysis and X-ray structure analysis is advantageously used to investigate the formation of double halides in complicated systems between alkali halides, AX, and divalent halides, MX_2. Among the systems of CoX_2 (X = Cl, Br, I) this is particularly valid for the systems $TlCl/CoCl_2$ and $TlBr/CoBr_2$.

INTRODUCTION

In order to investigate which double halides $A_nMX_{(n+2)}$ are formed in a particular system between an alkali halide, AX, and a divalent halide, MX_2, the phase diagram of the system may be elucidated by means of differential thermal analysis. However, it is important to check the results of DTA by taking X-ray powder patterns of the solidified melts. In difficult systems, it may be necessary to use crystal structure determinations in order to find the exact compositions of some of the compounds. Such combination of DTA and X-ray methods is a powerful investigative tool. This is to be demonstrated using, as an example, our investigations of the systems of alkali chlorides, bromides, and iodides with the corresponding cobalt(II) halides.

The results of DTA and X-ray structure investigations have been published elsewhere[1]. Detailed results of these investigations will be covered only insofar as required by the particular subject of this paper.

INSTRUMENTATION

DTA-equipment

The systems $ACl/CoCl_2$ and $ABr/CoBr_2$ were measured using open quartz crucibles. The DTA cell has been described previously[2].

Thallium halides are volatile at elevated temperatures, and CoI_2 decomposes upon melting. Therefore, systems involving these compounds were measured in

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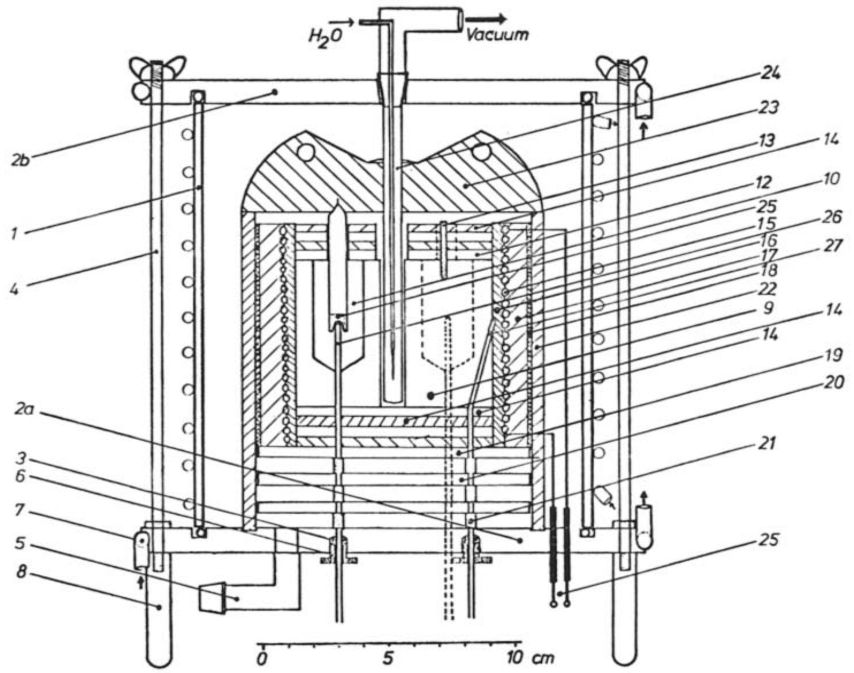

Fig. 1. DTA-cell. 1 = Jacket (brass); 2 = plates (brass); 3 = O-rings (Viton); 4 = six bolts; 5 = connection to vacuum; 6 = seals; 7 = cooling coil; 8 = three feet; 9 = metal block (made of Fe/Ni/Al; Kanthal Incop., A_1); 10 = bore for sample; 11 = sample in quartz ampoule; 12 = cover plates (Kanthal A_1); 13 = ceramic centering device; 14 = asbestos insulation; 15 = heating filament; 16 = ceramic tube for 15; 17 = embedding mixture ($MgO \cdot SiO_2 + Al_2O_3$); 18 = asbestos sheet; 19 = basis plate of measuring cell (stainless steel); 20 = radiation protective shield; 21 = ceramic tubes; 22 = axial ceramic support; 23 = upper ceramic cover; 24 = cooling element (quartz); 25 = electric leads; 26 = thermocouple for measuring sample temperature; 27 = thermocouple for controlling metal block temperature.

vacuum-sealed quartz tubes (10 mm diameter, 30 mm length). Samples of approximately 1g were weighted in a dry box. The samples were melted by heating with a gas flame, homogenized by shaking, and solidified by rapid cooling. The solids thus obtained were sufficiently homogeneous to be used to measure heating curves or for annealing experiments. The DTA apparatus that was developed is shown in Fig. 1. The chromel/alumel thermocouples were standardized against substances which have transition points in the region[3] of 300–700°C. Quartz (t.p. = 517°C) was also used as reference substance. In general, cooling curves were taken (rate of cooling, 2°C min^{-1}; rate of heating, 1°C min^{-1}). Deviations of the measurements were estimated to be ±2°C and ±0.3 mol-%.

X-Ray equipment

Powder patterns at room temperature were taken using a goniometer equipped with a counter and a vacuum attachment (Philips, Eindhoven). High temperature patterns by varying temperatures were taken with a Simon Guinier camera, series 553 from Enraf-Nonius, Delft.

RESULTS OF DTA

For all systems in which double halides are formed the characteristic data are given. Diagrams are given for those systems that were measured by a combination of DTA and X-ray analysis.

Systems of CoI_2

The system NaI/CoI_2 is a simple eutectic one. All other systems of CoI_2 contain congruently melting 2:1 compounds A_2CoI_4. However, K_2CoI_4 represents a hybride between congruent and incongruent melting. Cs_2CoI_4 and Rb_2CoI_4 have transition points at higher temperatures. For Rb_2CoI_4, this was confirmed by high temperature patterns and structure determinations of both modifications.

CHARACTERISTIC DATA

All temperatures in °C; compositions in mol-% CoX_2;
m.p. = melting point; t.p. = transition point.

System CsI/CoI_2
CsI (m.p.) = 620°C
1. Eutectic point = 443°C; 27.4%
M.p. of Cs_2CoI_4 = 499°C; t.p. = 483°C
2. Eutectic point = 303°C; 56.5%

System KI/CoI_2
KI (m.p.) = 684°C
M.p. of K_2CoI_4 = 317°C
Eutectic point = 259°C; 45.0%

System RbI/CoI_2
RbI (m.p.) = 640°C
1. Eutectic point = 372°C; 29.9%
M.p. of Rb_2CoI_4 = 388°C; t.p. = 207°C
2. Eutectic point = 275°C; 46.2%

System TlI/CoI_2
TlI (m.p.) = 442°C; t.p. = 166°C
1. Eutectic point = 283°C; 27.5%
M.p. of Tl_2CoI_4 = 287°C
2. Eutectic point = 274°C

Systems of $CoBr_2$

The results of our investigations of the systems alkali bromide/$CoBr_2$ have been published recently[4]. The system $TlBr/CoBr_2$, which had not been investigated before, is shown in Fig. 2.

System $TlBr/CoBr_2$
TlBr (m.p.) = 460°C
Peritect. p. Tl_3CoBr_5 = 302°C; ~ 25.0%
1. Eutectic point = 300°C; ~ 25.1%
M.p. of Tl_2CoBr_4 = 318°C; t.p. = 178°C
2. Eutectic point = 293°C; 40.0%

It contains a congruently melting compound Tl_2CoBr_4 which exists in a high temperature and a low temperature modification. A second compound, Tl_3CoBr_5, melts incongruently. However, since peritectic and eutectic temperatures differ only about 2°C, it was impossible to resolve both points according to the composition by DTA methods. The probable form of the phase diagram is shown in the upper left part of Fig. 2. The existence of the compound Tl_3CoBr_5, which could not be

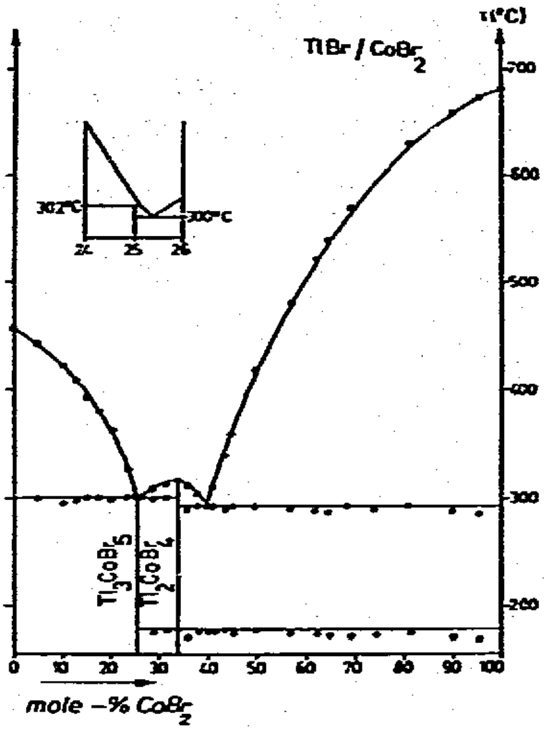

Fig. 2. System $TlBr/CoBr_2$.

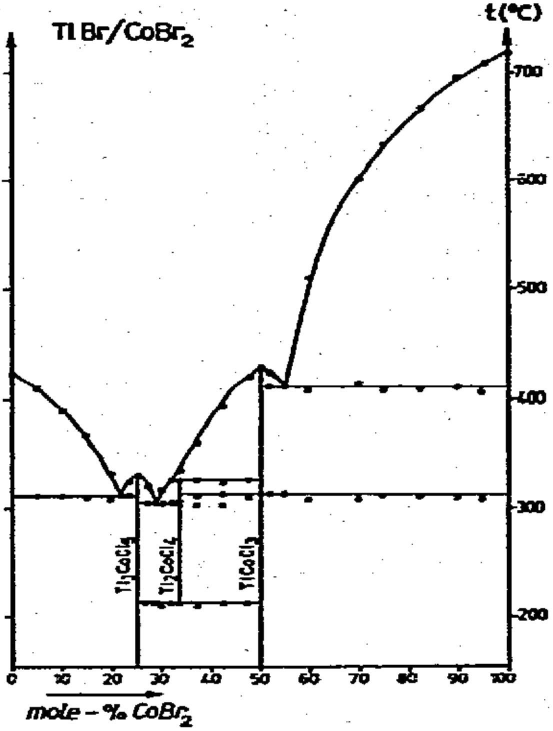

Fig. 3. System $TlCl/CoCl_2$.

found by DTA, was confirmed by X-ray methods. A powder pattern of a solidified sample with the composition 25 mol-% $CoBr_2$ could be easily indexed analogous to the known structure of Cs_3CoCl_5.

Systems of $CoCl_2$

Compared to the previous investigations by Seifert[5] the following differences have been found:

(1) The system $CsCl/CoCl_2$ does not contain the componnds $Cs_3Co_2Cl_7$ and $Cs_5Co_2Cl_9$; the transition point of $CoCl_2$ could not be confirmed.

(2) In the system $RbCl/CoCl_2$ no transition was observed for Rb_2CoCl_4.

(3) System $KCl/CoCl_2$: In addition to the transition point at 345°C, $KCoCl_3$ undergoes a second transition at 125°C which was found from heating curves.

In the system $TlCl/CoCl_2$, the compounds $TlCoCl_3$ and Tl_2CoCl_4 had been found by Belyaev[6]. Our investigations showed two congruently melting compounds, $TlCoCl_3$ and Tl_3CoCl_5 (Fig. 3) $TlCoCl_3$ undergoes a transition at 312°C which was confirmed by high temperature X-ray patterns and structure determinations of both modifications. An additional compound, Tl_2CoCl_4, melts incongruently and exists only above 212°C. This was confirmed by high temperature Guinier patterns of samples that had been annealed at 200°C (Fig. 4): The reflections up to 210°C are a superposition of these of Tl_3CoCl_5 and $TlCoCl_3$; the reflections observed above 210°C suggest an orthorhombic structure (β-K_2SO_4-type) for Tl_2CoCl_4.

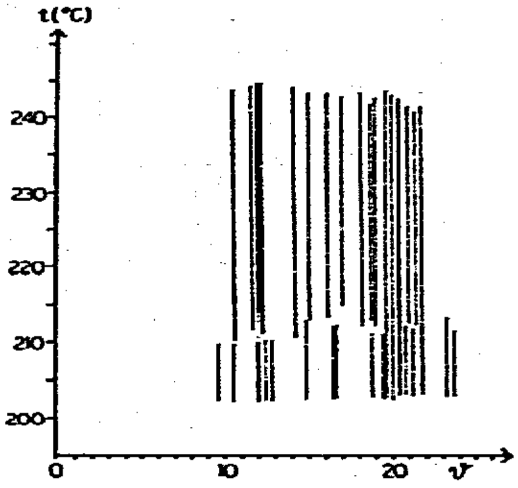

Fig. 4. Tl_2CoCl_4—Guinier high temperature powder pattern (reflexes copied by hand).

TABLE 1

LATTICE PARAMETERS [Å] OF DOUBLE HALIDES OF Co^{2+}

$CsNiCl_3$-type (hexagonal)	*a*	*c*	*Cs_3CoCl_5-type (tetragonal)*	*a*	*c*
$CsCoCl_3$*	7.202	6.032	Cs_3CoCl_5	9.219	14.554
$RbCoCl_3$*	6.999	5.996	Rb_3CoCl_5	8.799	14.239
$KCoCl_3$*	6.870	6.091	Tl_3CoCl_5	8.431	14.497
$TlCoCl_3$	6.907	5.981	Rb_3CoBr_5*	9.239	14.875
$CsCoBr_3$*	7.517	6.323	Tl_3CoBr_5*	8.747	15.232
$RbCoBr_3$*	7.331	6.262	Cs_3CoBr_5*	9.643	15.127

β-K_2SO_4-type (orthorhombic)

	a	*b*	*c*		*a*	*b*	*c*
Cs_2CoCl_4	9.737	7.392	12.972	Rb_3CoBr_4*	9.718	7.651	13.371
Rb_2CoCl_4	9.272	7.283	12.723	H-K_2CoBr_4*	9.61	7.77	13.43
K_2CoCl_4*	8.933	7.240	12.421	H-Tl_2CoBr_4*	9.424	7.520	13.145
Tl_2CoCl_4*	9.131	7.182	12.635	Cs_2CoJ_4*	10.833	8.297	14.414
Cs_2CoBr_4*	10.181	7.723	13.492				

Sr_2GeS_4-type (monoclinic)

	a	*b*	*c*	*β*[°]
T-K_2CoBr_4*	9.184	7.542	7.276	108.8
T-Tl_2CoBr_4*	9.522	7.376	6.910	110.2
T-Rb_2CoJ_4*	10.384	8.144	7.657	109.8
K_2CoJ_4*	9.677	8.090	7.702	108.4
Tl_2CoJ_4*	9.762	7.972	7.519	108.9

STRUCTURE DETERMINATIONS

Structural data for the double halides of Co^{2+} are compiled in Table 1. Our own results are indicated by an asterisk. Literature references for the remaining compounds are given in ref. 1.

The 1:1 compounds, $ACoX_3$, crystallize with the $CsNiCl_3$-structure: the Co^{2+} ion is octahedrally surrounded by six Cl^--ions. These octahedra are connected to infinite columns by sharing opposite faces along the c-axis of the hexagonal cell. The columns are held together by the alkali ions.

In the 2:1 compounds isolated CoX_4^{2-}-tetrahedra exist. In the β-K_2SO_4 type the alkali ions have the coordination numbers 9 and 10, in the Sr_2GeS_4 type the C.N. is only (6 + 2). The Sr_2GeS_4 type is formed, if the holes in the network of the halide ions in the β-K_2SO_4 type have become too large for the alkali ions. This happens in the case of double iodides with Rb^+, Tl^+ and K^+, in the case of double bromides with K^+ and Tl^+. The high temperature modifications crystallize with the K_2SO_4-structure because of the thermal movement.

It seems that H–Rb_2CoI_4 has the spinell structure.

The 3:1 compounds should also be formulated as $A_3[CoX_4]X$ with tetrahedra.

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