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Orthorhombic low-temperature modifications of compounds Cs_3LnCl_6 (Ln = Nd–Yb)-preparation and thermodynamic stability

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Abstract

The compounds Cs_3LnCl_6 (Ln=Nd-Yb) can be obtained from aqueous solutions with an orthorhombic structure /S.G. Pbcm/, whereas from solutions in anhydrous acetic acid a modification with the monoclinic Cs_3BiCl_6 structure /S.G. C 2/c/ is formed. By solution calorimetry, the orthorhombic phase could be proved to be the low temperature modification. Molar volumes determined from X-ray powder patterns increase from Pbcm to C 2/c. The transition from the orthorhombic into the monoclinic phase is irreversible for kinetical reasons. © 1997 Elsevier Science B.V.

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1. Introduction

In 1993 we published results of investigations on the relationship between crystal structures and thermodynamic properties of compounds A_3LnCl_6 with A = Rb, Cs and Ln = La to Gd [1]. All these compounds have high temperature modifications above 400°C with the cubic elpasolite structure / S.G.: $Fm\bar{3}m$/. At ambient temperature their structure is that of Cs_3BiCl_6 /S.G.: C 2/c / [2]. For Cs_3LaCl_6 the atomic positions could be determined from powder patterns with the Rietveld method. Later we found the same structural relations for Cs_3TbCl_6 [3] and Cs_3DyCl_6 [4].

Mattfeld and Meyer [5] completed these findings for Cs_3ErCl_6, Cs_3YCl_6 and the Rb-compounds with Ln = Tb–Lu. For Rb_3YCl_6 they could perform a complete single crystal structure determination.

Reuter and Frenzen [6] prepared hydrated compounds $Cs_3LnCl_6 \cdot 3H_2O$ with Ln = La–Nd from hydrochloric acid; they can be dehydrated at 100°C. With neodyme the anhydrous compound could be obtained directly from hot solutions as single crystals. Thus, for Cs_3NdCl_6 a complete structure determination was performed. It crystallizes in the orthorhombic space group Pbcm.

In this work these investigations are expanded to the other lanthanoides (Pm and Lu excepted), because it was not known whether the new elpasolite variant is either a metastable dehydration product or a thermodynamically stable low temperature modification, which cannot be prepared from the melt for kinetical reasons. The thermodynamic relations between the phases were investigated by solution calorimetry.

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2. Experimental

2.1. Materials

The compounds $LnCl_3.6H_2O$ were prepared by dissolving the oxides (99.99%, Fa. Johnson-Matthey, Karlsruhe,Germany) in hydrochloric acid, evaporating the solutions and drying the chloride hydrates at 60°C. Cesium acetate (reinst, Merck, Darmstadt,Germany) was dried at 200°C in vacuum. Acetic acid (99–100%, Fa. Merck) was treated for 24 h with P_4O_{10}, then refluxed for 4 h and distilled. Acetyl chloride and thionyl chloride (Fa. Merck, zur Synthese) were purified by distillation.

2.2. X-ray analysis

Powder patterns from ambient temperature to 130°C were taken with a Phillips PW 1050/25 goniometer equipped with a proportional counter and a vacuum attachment. During exposure (Cu-K_α radiation) the samples were under He atmosphere. The digital data were collected and analyzed with PROFIL [7]. The calculations were performed with the program LAZY PULVERIX [8]. The graphic was drawn by SCHAKAL 92 [9]. Cell parameters were determined from powder patterns (internal standard: α-Al_2O_3, a=475.9 pm; b=1299.0 pm) with the least squares method of Warczewski and de Wolff [10].

2.3. Thermochemical methods

The thermal behavior of the compounds was investigated by means of the differential scanning calorimeter DSC 7 (Perkin Elmer) (heating rates: 10 to 1 K min^{-1}, purge gas flow: N_2 10 ml min^{-1}) in the temperature range from 40 to 500°C. The heats of solution were measured using an isoperibolic under water calorimeter firstly described in 1978 [11].

The reaction vessel is made of silver. The substances are in thin-walled glass ampoules which are cracked under water at the beginning of the measurement. The solution heat generates a temperature change ΔT against the surroundings. A thermostat with a temperature constance of $2\cdot 10^{-4}$°C is used. ΔT is measured with a thermopile and corrected for the inevitable heat-loss according to the Dickinson-compensation. This corrected temperature change ΔT^* is calibrated by Joule's heat Q_E, giving a temperature change ΔT_E. The heat of solution Q_L is finally calculated from the relation

$$\frac{Q_L}{\Delta T^*} = \frac{Q_E}{\Delta T_E}.$$

The volume of the vessel is 1.3 l. Thus, samples of 3–4 g yielded virtually ideal solutions (dissolution ratio 1 : 15 000 mol). At least two samples of each substance were measured. For the solution enthalpy of KCl we found.17.67±0.08 $kJmol^{-1}$, compared with 17.54±0.05 $kJmol^{-1}$ from literature [12].

3. Results

3.1. Preparation of ternary lanthanoide chlorides from acetic acid (HAc)

Solutions of lanthanoide chloride hydrates in HAc were dehydrated by boiling with acetyl chloride. After adding dried cesium acetate the ternary chlorides were precipitated with gaseous HCl. The composition of the precipitated compounds does not depend on the molar ratios A^+/Ln^{3+}; it is only determined by the thermal stability of the compounds. Beginning with praseodyme the 3 : 1 compounds Cs_3LnCl_6 are stable at ambient temperature and therefore are precipitated, because they are less soluble than the as well stable compounds Cs_2LnCl_5. As found from e.m.f.-measurements Cs_3LaCl_6 and Cs_3CeCl_6 [1] are stable only at elevated temperatures; in this case the 2 : 1 compounds are precipitated from the solutions.

A .typical procedure is given for Cs_3GdCl_6: 0.005 mol (1.86 g) $GdCl_3\cdot 6H_2O$ were heated together with 20 ml acetic acid in a three-necked flask fitted with a reflux condensor and hot-plate magnetic stirrer until all particles were dissolved. Then 8 ml acetyl chloride were added. This solution was heated to approximately 80°C. 0.015 mol cesium acetate (2.88 g) were dissolved in acetic acid and added to the first solution. Cs_3GdCl_6 was precipitated by saturating the solution with gaseous HCl. The precipitate was filtered, washed twice with acetic acid and absolute ether.

The precipitated Cs compounds possess the Cs_3BiCl_6-structure, only with neodyme at room temperature the orthorhombic modification is formed,

Table 1
Lattice parameters for Cs_3LnCl_6 (Ln = Nd to Yb) obtained from powder patterns, their molar volumes and ΔV_m (V_m mon.- V_m orth.)

	S.G.	a/pm	b/pm	c/pm	$\beta/^\circ$	V_m/cm^3mol^{-1}	$\Delta V_m/cm^3mol^{-1}$
Cs_3NdCl_6	Pbcm	824.7(3)	1324.2(3)	2668.6(8)		219.3	
	C2/c	2719.3(7)	824.8(2)	1327.9(2)	99.96(2)	220.8	1.5
Cs_3SmCl_6	Pbcm	822.4(3)	1317.5(3)	2660.9(5)		217.0	
	C2/c	2705.4(7)	820.2(2)	1321.9(4)	99.94(2)	217.5	0.5
Cs_3EuCl_6	Pbcm	820.4(3)	1315.3(3)	2658.0(8)		215.9	
	C2/c	2706.5(8)	819.2(2)	1320.3(4)	99.93(2)	217.1	1.2
Cs_3GdCl_6	Pbcm	818.5(2)	1314.2(3)	2655.7(5)		215.0	
	C2/c	2702.2(7)	818.9(2)	1318.1(3)	100.01(2)	216.2	1.2
Cs_3TbCl_6	Pbcm	816.0(3)	1311.4(3)	2652.2(7)		213.6	
	C2/c	2699.0(8)	818.0(3)	1317.1(4)	99.97(2)	215.8	2.2
Cs_3DyCl_6	Pbcm	815.5(3)	1308.2(4)	2648.1(8)		212.7	
	C2/c	2694.6(8)	815.4(3)	1313.7(4)	100.15(2)	213.9	1.2
Cs_3HoCl_6	Pbcm	815.8(3)	1306.6(5)	2645.7(7)		212.3	
	C2/c	2692.7(8)	813.1(2)	1313.9(5)	100.23(3)	213.1	0.8
Cs_3ErCl_6	Pbcm	814.6(3)	1307.4(6)	2644.2(7)		211.9	
	C2/c	2690.7(8)	813.2(2)	1307.7(4)	99.96(2)	212.2	0.3
Cs_3TmCl_6	Pbcm	811.5(2)	1304.3(3)	2636.6(7)		210.1	
	C2/c	2685.1(8)	811.5(2)	1308.9(6)	100.14(3)	211.3	1.2
Cs_3YbCl_6	Pbcm	808.9(3)	1307.7(3)	2636.6(7)		209.9	
	C2/c	2683.8(9)	817.4(4)	1303.5(4)	100.22(3)	211.8	1.9

from hot solution the Cs_3BiCl_6 modification is also obtained.

3.2. *Double chlorides from aqueous solutions*

In this case the composition depends on the ratio A^+/Ln^{3+} and often on temperature. In molar ratios $A^+ : Ln^{3+}$ 3 : 1 and 4 : 1, with Ln= La–Nd hydrates are precipitated with HCl or by evaporating below 60°C. In all other cases Cs_3LnCl_6 (Ln= Nd–Yb) in the orthorhombic modification is obtained. As recently found [13] Cs_4LnCl_7 with Ln= Ho–Yb is formed when the molar ratio is 4 : 1.

In the molar ratio, 2 : 1, compounds of the composition $Cs_2LnCl_5{\cdot}6H_2O$ exist below 50°C with Ln= Nd–Ho, beginning with erbium monohydrates $Cs_2LnCl_5{\cdot}H_2O$ (erythrosiderite type- S.G. Pnma [14]) crystallize above 90°C.

3.3. *Crystal structure determinations*

X-ray powder patterns of all new phases crystallizing in the S.G. Pbcm were indexed in analogy to the structure of Cs_3NdCl_6, which was known from our previous single crystal work [6]. The unit cell parameters and the molar volumes were calculated from patterns with Al_2O_3 as inner standard. The results are compiled in Table 1, together with values for the C 2/c - modifications. The lattice parameters were either derived from our older paper [1] or calculated in this work. In some cases (Tb [3], Dy [4] and Er [5]) older findings had to be slightly corrected. In both modifications slightly distorted octahedra exist, which are mutually orientated in different ways.

3.4. *Thermodynamic properties of the compounds*

For the determination of the solution enthalpies of both modifications 3–4 g of Cs_3LnCl_6 for each measurement were used. From two results with deviations in general less than 1.0 KJ mol^{-1} the mean values were formed. For Cs_3LnCl_6 in S.G. C2/c with Ln=Nd to Tb values from older papers were used. The formation enthalpies $\Delta_f H^0$ for the reactions

$$3CsCl + LnCl_3 \rightarrow Cs_3LnCl_6$$

can be calculated with the equation

$$\Delta_f H^0(Cs_3LnCl_6) = \{\Delta_{sol} H^0(LnCl_3). + 3\Delta_{sol} H^0(CsCl)\} - \Delta_{sol} H^0(Cs_3LnCl_6).$$

The transformation enthalpies Pbcm → C2/c are:

Table 2
Solution enthalpies in kJ mol^{-1} for Cs_3LnCl_6 in S.G. Pbcm and C2/c

Compound	$\Delta_{sol}.H^0$ (Pbcm)		Δ_{sol} H^0 (C2/c)		Difference
	Meas. values	Mean values	Meas. values	Mean values	
Cs_3NdCl_6	−50.12 −50.37	−50.3(2)	x	−56.3^a	6.0
Cs_3SmCl_6	−50.80 −50.17	−50.5(3)	x	−54.1^a	3.6
Cs_3EuCl_6	−52.59 −53.16	−52.9(3)	x	−57.3^a	4.4
Cs_3GdCl_6	−54.21 −55.65	−54.9(7)	x	−59.3^a	4.4
Cs_3TbCl_6	−56.14 −55.98	−56.1(1)	x	−61.0^a	4.9
Cs_3DyCl_6	−56.10 −57.17	−57.6(5)	−60.40 −60.46	−60.4(1)	2.8
Cs_3HoCl_6	−60.38 −59.92	−60.1(3)	−62.98 −63.16	−63.1(1)	3.0
Cs_3ErCl_6	−60.91 −61.13	−61.0(2)	−63.09 −64.08	−63.6(5)	2.6
Cs_3TmCl_6	−62.22 −63.15	−62.7(5)	−63.75 −63.90	−63.8(1)	1.1
Cs_3YbCl_6	−63.28 −63.87	−63.6(3)	−64.55 −64.71	−64.6(1)	1.0

( ) = range of error for values, measured for this paper
^{a} = values from own older papers

$$\begin{aligned}\Delta_{tr}H^0 &= \Delta_f H^0(2/c) - \Delta_f H^0(\mathrm{Pbcm})\\ &= -\Delta_{sol}H^0(\mathrm{C2/c}) + \Delta_{sol}H^0(\mathrm{Pbcm})\end{aligned}$$

The latter values are compiled together with the measured solution enthalpies and their mean values in Table 2. Obviously all solution enthalpies of the Pbcm- modifications are less exothermic than those of the C2/c modifications; the difference between both decrease with decreasing size of lanthanoide ions. For Cs_3YbCl_6 the difference is 1.0 KJmol^{-1} and therefore at the border of significance. Nevertheless, for all hypothetical transitions Pbcm → C2/c the transition enthalpy is endothermic.

With this knowledge we tried to measure this phase transition directly by DSC with heating rates down to 1 K min^{-1}. However, no transition of the orthorhombic into the monoclinic modification occured; but at about 400°C the transition into the cubic high temperature modification was observed. After cooling to ambient temperature, the X-ray pattern of the monoclinic modification as now metastable phase was found.

Due to these findings annealing experiments with both modifications were performed for about 6 weeks in the range from 200 to 350°C. It was not possible to transfer the monoclinic modification to that with the Pbcm structure. Otherwise at 250°C a partial transition from Pbcm to C2/c occurs; at 300°C it is completed in about 10 h.

4. Discussion

Both modifications can be described as derivates of the elpasolite-structure A_2BMX_6: AX_3 layers with octahedral holes, partially filled with B and M are stacked with the motif of cubic close-packing along the space-diagonal of the cubic unit cell. In the compounds A_3MCl_6 A- and B-ions are identical. In the Cs_3NdCl_6- type the stacking axis is the orthorhombic c-axis, in Cs_3BiCl_6 it is standing perpendicular to the rectangular bc-plane, the monoclinic a-axis forms an angle of about 10° with this axis. To characterize the different mutal

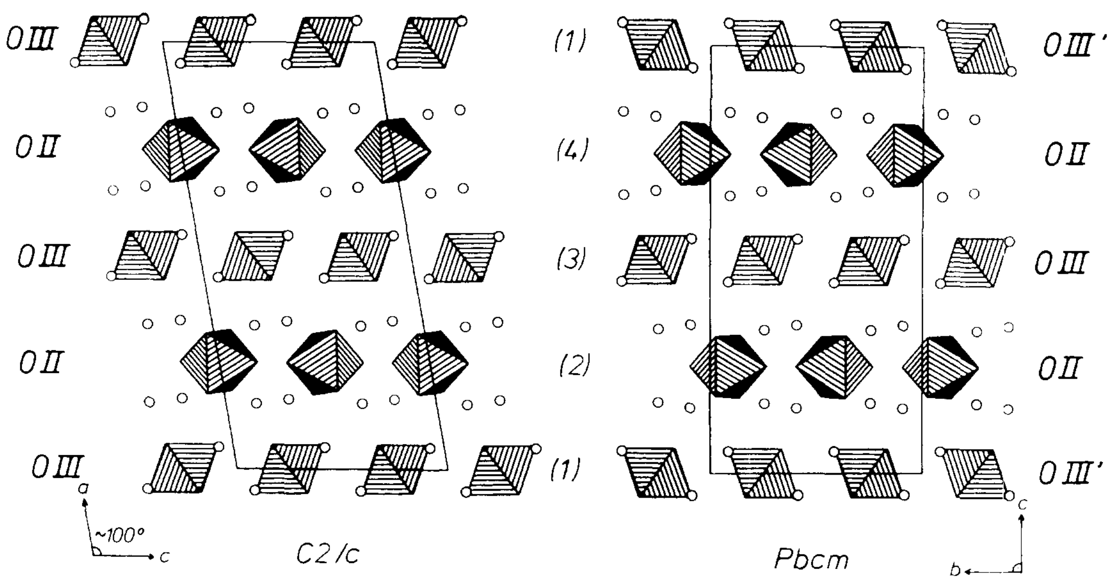

Fig. 1. Projections of layer sequences to the bc-planes.

orientations of the octahedra in the two modifications. A description given by Benachenhou et al. [2] is used: MX_6 octahedra are considered as entities either orientated in the packing direction with their threefold (O III) or with their twofold symmetry axis (O II). As Fig. 1 shows each layer consists of only one type of octahedra; layers of O III and O II alternate. It should be pointed out, that in the cubic elpasolite structure /S.G. Fm3m / only O III layers exist.

Neglecting the monoclinic inclination of the a-axis in C 2/c, for both modifications the layers (2), (3) and (4) are identical. However, in Pbcm the octahedra in (1) are rotated 180°/ 6=30° around the stacking axis; they are denoted as O III. (An easier description, used by Mattfeld and Meyer [5] cannot describe this differences, as discussed by Frenzen and Reuter [6])

The thermodynamic measurements have revealed, that the Pbcm-modification is the more stable one at ambient temperature. The transformation to the Cs_3BiCl_6 structure is an endothermic process, which is strongly kinetical hindered. It occurs only after a long time of annealing. Using the heating rate of DTA-about 1 $Kmin^{-1}$ after a certain degree of overheating a direct transition to the stable high temperature modification, crystallizing in the space group Fm3m, takes place at about 400°C.

Our actual knowledge about compounds A_3MCl_6 (A=Cs,Rb,K) is as follows:

1. All compounds are forming cubic high temperature modifications with the elpasolite structure.
2. All Cs and Rb compounds of the lanthanoides crystallize with the Cs_3BiCl_6, the potassium compounds with the K_3MoCl_6 structure.
3. For compounds Cs_3LnCl_6 from Nd to Yb (Lu?) at temperatures below 90°C the orthorhombic modification in Pbcm is stable.
4. Compounds Cs_3MCl_6 with M=Mo [15]; Fe and V crystallize with the Cs_3CrCl_6 structure (Pnnm) [16], while Cs_3TiCl_6 belongs to the Cs_3BiCl_6 type. The Rb and K compounds of these transition elements have the K_3MoCl_6 structure.

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