Journal of Thermal Analysis and Calorimetry, Vol. 71 (2003) 667–673

PHASE TRANSITIONS IN TERNARY CAESIUM LEAD BROMIDE

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(Received January 25, 2002; in revised form May 31, 2002)

Abstract

Phase transitions in ternary caesium lead bromide ($CsPbBr_3$) were studied by means of DSC, TMA and high temperature X-ray diffraction. The samples were prepared from the solution by water evaporation and from the melt. On the DSC curves as well as on the temperature dependence of the lattice constants of $CsPbBr_3$ only two effects were found belonging to the earlier published phase transitions at 88 and 130°C and no further effects. Linear thermal expansion coefficient α of individual $CsPbBr_3$ modifications were calculated from both TMA and high temperature X-ray diffraction. The structural parameters of the room temperature orthorhombic phase were refined and the results are presented. $CsPbBr_3$ prepared from the solution contained about 10% of $CsPb_2Br_5$ and so the DSC curve of pure $CsPb_2Br_5$ was also measured and an effect at a temperature of 68.5°C was found.

Keywords: DSC, high temperature X-ray diffraction, phase transitions, ternary caesium lead bromide ($CsPbBr_3$), thermal expansion coefficient, TMA

Introduction

Ternary caesium lead bromide $CsPbBr_3$ (CPB) is a compound in which several successive phase transitions occur between room and melting temperatures. Møller [1] was the first, who studied these phase transitions in CPB by means of X-ray diffraction method. He specified that CPB is monoclinic at room temperature and with rising temperature its symmetry is transformed to a tetragonal one. Above 130°C CPB is cubic with the perovskite structure. Cola *et al*. [2] only found the phase transition at 123°C with a very small thermal effect (less than 0.7 J g^{-1}). By detailed study Hirotsu *et al*. [3, 4] defined the phase transitions of the second and first orders occurring at 88 and 130°C, respectively. They determined that the low temperature modification is orthorhombic (Pbnm, No. 62). The modification existing between 88 and

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1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

130°C is tetragonal (P4/mbm, No. 127) and the high temperature modification is cubic (Pm3m, No. 221). When measuring ionic conductivity Narayan *et al*. [5] observed the only phase transition at 90°C and no effect at 130°C. Petrov *et al*. [6] confirmed the existence of the phase transitions at 87 and 132°C. In addition they found a segnetoelectric transition at 147°C.

In our study of polymorphism in $PbCl_2$ and $PbBr_2$ by means of TMA [7] crystal samples of CPB grown from the melt and consisting of the frozen high temperature cubic modification [8] were used as a comparative compounds. Besides early published effects at 88 and 130°C a very weak effect at a temperature of 124°C was found. As this effect could be a sign of a phase transition, we decided to study the polymorphism of CPB in detail.

This paper deals with the study of phase transition in $CsPbBr_3$ by means of DSC, TMA and high temperature X-ray diffraction. Its aim is to find whether the effect at 124°C is really a phase transition.

Experimental

In this study the crystalline samples of CPB high temperature modification, mixture of CPB low temperature modification with 10% of $CsPb_2Br_5$ and pure $CsPb_2Br_5$ were used. The crystal of high temperature modification (CPB-m) was made from the melt by the Bridgman method. Starting material was obtained by the direct synthesis of CsBr and $PbBr_2$ stoichiometric mixture at a temperature above 700°C under a protective atmosphere of bromine and hydrogenbromide [8].

When preparing low temperature modification (CPB-l), first 2.15 g CsBr and 4.7 g $PbBr_2$ were dissolved in 400 ml water at 80°C. After cooling down to room temperature white scales, identified as $CsPb_2Br_5$, about 2×2 mm in size crystallised. After their removal by filtration the solution was put in an air thermostat heated to 35°C. Within one month fine yellow-orange crystals of $CsPbBr_3$ grew.

Linear thermal expansion of the CPB-m sample was measured on a DuPont TA Instruments 990 TMA 943 in dried nitrogen from room temperature up to 230°C, heating rate was 10 K min^{-1}.

DSC was carried out on a TA Instruments DSC 2920 in the temperature range from 20 to 150°C at a heating rate of 5 K min^{-1}. The charges were approximately 30 mg in mass.

The phase composition and lattice parameters were determined from X-ray diffraction (XRD) measurement on a Bruker D8 powder diffractometer using CuK_α radiation over the angular range 14–70°2θ. The diffractometer was equipped with an MRI high-temperature chamber for the measurement of the temperature dependence of lattice parameters up to 160°C. The temperature was risen in steps of 5 K, which were shortened to 1–2 K near the expected transitions. The diffraction patterns were refined by the program FULLPROF [9] using the structural data from [10].

Chemical composition of the CPB-l and $CsPb_2Br_5$ samples was determined by chemical analysis.

Results and discussion

The CPB crystal consisting of the frozen high temperature cubic modification was grown from the melt by the Bridgman method [8]. For our TMA measurement non-oriented samples of 3×3×6 mm in size were cut from this crystal.

CPB prepared from water solution was yellow-orange fine crystalline powder (the size of crystals was less than 0.5 mm) formed by low temperature orthorhombic modification. According to the XRD it contained about 10% of $CsPb_2Br_5$.

The temperature dependencies of relative linear thermal expansion $\Delta l/l$ and its derivation – linear coefficient of thermal expansion α – of the sample CPB-m are shown in Fig. 1. At a temperature of 91°C there is an apparent change of the slope of the temperature dependence of $\Delta l/l$, which represents a phase transition of the second order. During this transition the low temperature orthorhombic modification increased its symmetry to the tetragonal one. The jump on the curve occurring at 132°C confirms a phase transition of the first order when the tetragonal symmetry is transferred to the cubic one. At a temperature of 124°C a small change in the slope appeared which could indicate another phase transition. All the above mentioned effects are evident on the temperature dependence of coefficient α_l, shown in Fig. 1.

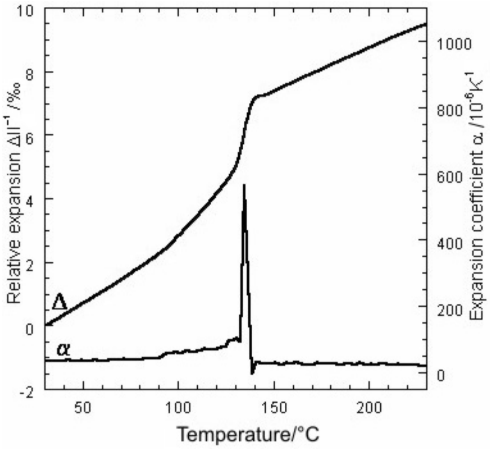

Fig. 1 The temperature dependencies of the linear thermal expansion $\Delta l/l$ and the linear coefficient of thermal expansion α of the sample CPB-m

The DSC curves of the samples CPB-m and CPB-l are shown in Fig. 2. On the CPB-m curve there are only two pronounced effects at 91 and 132°C which correspond to the earlier published transitions. The energy of phase transition occurring at 132°C is equal to 0.3043 J g^{-1}.

On the CPB-l curve one can observe also features at 91 and 132°C, and in addition another effect appears at a temperature of 72°C. However, this does not originate in CPB but in the doping impurity $CsPb_2Br_5$ as an impurity phase. On the measured curve of pure $CsPb_2Br_5$, shown in Fig. 2, this effect appears at a temperature of 68.5°C.

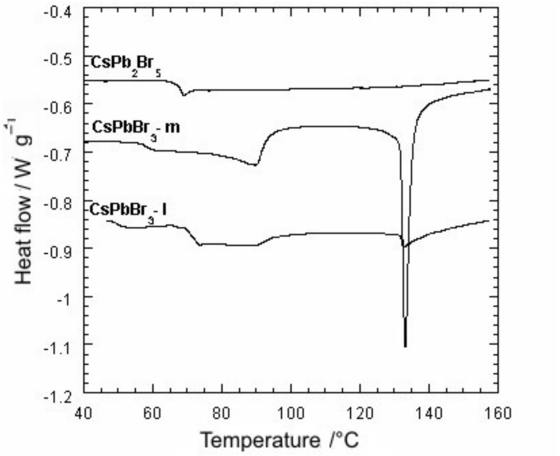

Fig. 2 The DSC curves of the CPB-m, CPB-l and $CsPb_2Br_5$

Figure 3 shows the temperature dependence of the individual lattice parameters of CPB. The lattice parameters were recalculated with respect to the ideal perovskite cell (a_p) described by Pm3m space group with one formula unit per cell (Z=1). The cell with P4/mbm space group is doubled ($\sqrt{2}a_p\times\sqrt{2}a_p\times a_p$) and the cell with Pbnm space group is quadrupled ($\sqrt{2}a_p\times\sqrt{2}a_p\times 2a_p$).

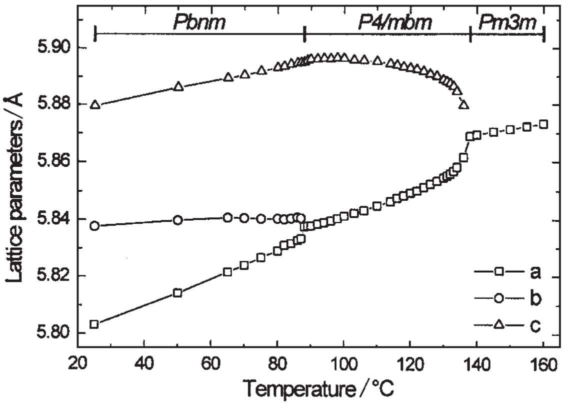

Fig. 3 Temperature dependence of the lattice parameters of CPB-l

While raising the temperature, the lattice parameters *a* and *c* expand whereas the parameter *b* remains almost constant. At *T*=88°C the parameters *a* and *b* become indistinguishable and the symmetry changes to the tetragonal one. In the tetragonal phase the parameter *c* stops expanding and remains constant up to 100°C and then slowly decreases until about 130°C, while the parameter *a* increases. Above 130°C the tetragonal distortion starts to decrease rapidly and at a temperature of 138°C the transition to the cubic symmetry is finished. In the thermal analysis the temperature of the transition onset is taken as the temperature transition and the same rule will be used for high temperature XRD. The temperature of the transition to cubic symmetry is then 130°C.

The X-ray diffraction patterns were indexed according to space groups proposed by Hirotsu *et al.* [3] for respective temperature ranges. The initial atomic positions for the structure with Pbnm symmetry were taken from isostructural $CsDyI_3$ [11] and for the P4/mbm symmetry from isostructural $CsSnI_3$ [12]. The space group Pm3m has no refinable atomic positions.

Table 1 Refined structural parameters of the CPB phase at 25°C in space group Pbnm

	x	*y*	*z*	B/Å^2	Wyckoff position
Cs	0.990(1)	0.971(1)	0.25	5.7(2)	4c
Pb	0.5	0	0	1.5(1)	4b
Br1	0.046(2)	0.505(2)	0.25	4.8(4)	4c
Br2	0.793(1)	0.205(1)	0.025(1)	3.8(2)	8d
	a=8.207(1) Å, b=8.255(1) Å, c=11.759(1) Å, Z=4, R_f=12.6%				

The structural parameters of the room temperature orthorhombic phase are summarised in Table 1. The Pb atom is at the centre of octahedra formed by 6 Br atoms in distances from 2.96 to 2.98 Å. The coordination of Cs atom is formed by 12 Br atoms in distances between 3.65 and 4.88 Å. The tilting of octahedra decreases the bond angles Pb–Br–Pb to 165°for Br1 and to 157° for Br2. The lattice parameters were recalculated with respect to the ideal perovskite are as follows: a'=5.803 Å, b'=5.838 Å and c'=5.880 Å. They are in good agreement with those determined by Møller [1] for the monoclinic cell a=b=5.827 Å and c=5.891 Å (γ=89.65°).

Table 2 The linear average coefficients of thermal expansion α of individual CPB modifications

Symmetry	Temperature range/°C	$\alpha/10^{-6}$ K^{-1}	
		from TMA	from XRD
Pbnm	30–85	38	45
P4/mbm	93–124	65	38
Pm3m	140–230	28	33

Between temperatures 91 and 132°C no change appears on either the DSC curves or the temperature dependence of the lattice constant. It means that there is no new phase transition in CPB in this temperature range.

Using temperature dependencies of $\Delta l/l$ and the lattice parameters, the linear average coefficients of thermal expansion α for the individual CPB modifications were calculated. They are summarised in Table 2 together with the temperature range of their existence. They are comparable with the average value of $\alpha=40\cdot10^{-6}$ K^{-1} calculated from the data measured by Møller [1]. The differences follow from the fact that Møller [1] did not consider a jump change in the volume at the transition to the cubic symmetry at 130°C. The coefficients of the linear thermal expansion α linearly dependent on temperature according to the equation $\alpha=\alpha_0 t+k$ (α_0 is a linear coefficient of thermal expansion at 0°C, t temperature in degrees of Celsius and k constant), were also calculated. The equation parameters α_0 and k obtained by fitting the experimental data are summarised in Table 3 together with the correlation coefficient R.

Table 3 Parameters of temperature dependence of coefficients α of individual CPB modifications

	Temperature range/°C	$\alpha_0/10^{-6}$ K^{-1}	k	R
$CsPbBr_3$	30–85	30.709	0.1206	0.82564
$CsPbBr_3$	93–124	0.6398	0.60148	0.91872
$CsPbBr_3$	140–230	37.795	–0.060495	0.57264

Conclusions

This complex study of phase transitions in $CsPbBr_3$ was initiated by the suspicion that another phase transition can occur in this compound. By TMA of cubic CPB an effect was registered on the temperature dependence of $\Delta l/l$ at 124°C [7], which could be a phase transition. That is why the samples of low temperature orthorhombic modification of CPB were prepared by crystallisation from water solution at 35°C and the test of phase transition was performed by means of DSC and high temperature X-ray diffraction in both low and high temperature modifications. Only two effects were found at 91 and 132°C and at 88 and 138°C on the DSC curves and on the temperature dependence of the lattice parameters of CPB, respectively. They correspond to the already published phase transitions at 88 and 130°C [3, 4]. It means that there is no new phase transition in CPB at 124°C. This weak effect on the TMA curve of high temperature cubic CPB was probably caused by the changes during the transition at 130°C which have already started at a temperature of 125°C. DSC of the pure $CsPb_2Br_5$ compound was also measured and an effect at 68.5°C was found.

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This work was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (Grant No. A 2010926). The access to the ICSD was enabled by the Grant No. 203/02/0436 of the Grant Agency of the Czech Republic.

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