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Thermodynamics of formation of hybrid perovskite-type methylammonium lead halides

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ABSTRACT

Enthalpies of solution of hybrid perovskites $CH_3NH_3PbX_3$ (X = Cl, Br, I) in DMSO were measured using solution calorimetry. Standard enthalpies and Gibbs free energies of formation of $CH_3NH_3PbX_3$ (X = Cl, Br, I) hybrid perovskites from halides as well as from elements at 298 K were calculated on the basis of experimental data obtained and compared with the data available in literature. Excellent agreement was obtained between the standard Gibbs free energy of decomposition of $CH_3NH_3PbX_3$ into solid PbX_2, gaseous HX and methylamine calculated on the basis of our data and that evaluated on the basis of vapor pressure measurement results reported by other authors. Entropy contribution was shown to play a major role in the stability of hybrid organic–inorganic perovskites with respect to their decomposition on constituent halides.

1. Introduction

The problem of green power generation is one of the most important today. The solar power is one of the promising solutions of this problem. Hybrid perovskite-type methylammonium lead halides have received great attention in recent years due to high conversion efficiency obtained in solar cells based on such materials [1]. Since the time of the first demonstration [2] photovoltaic devices based on the hybrid perovskites $CH_3NH_3PbX_3$ (X = Cl, Br, I) have showed huge progress in increase of conversion efficiency reaching currently 20.1% [3]. However, despite very promising achievements fundamental chemistry and physics of hybrid organic-inorganic (HOIP) perovskites is far from being completely understood. In particular it is true for thermodynamic properties of HOIP perovskites $CH_3NH_3PbX_3$ (X = Cl, Br, I). The heat capacity, Cp, as well as standard entropy as a function of temperature in the range 13–365 K were reported for these materials by Onoda-Yamamuro et al. [4] as early as in 1990. At the same time, there is no reliable data on the standard enthalpy of formation of these materials up to now. Recently, there have been published two works [5,6] dealing with solution calorimetry [5] and equilibrium vapor pressure [6] measurements aiming to provide the necessary thermodynamic data. As a result, authors of the former reported the standard enthalpy of formation of HOIP perovskites from corresponding crystalline CH_3NH_3X and PbX_2 salts

$$CH_3NH_3X_{(s)} + PbX_{2(s)} \rightarrow CH_3NH_3PbX_{3(s)}, \Delta_f^{hal}H^\circ_{298} \quad (1)$$

whereas ones of the latter calculated standard enthalpy, Δ_rH°, and Gibbs free energy, Δ_rG°, of decomposition of $CH_3NH_3PbX_3$ (X = Cl, Br, I) perovskites with formation of gaseous CH_3NH_2, HX and solid PbX_2 as a function of temperature

$$CH_3NH_3PbX_{3(s)} \rightarrow PbX_{2(s)} + CH_3NH_{2(g)} + HX_{(g)}, \Delta_rH^\circ_{298}, \Delta_rG^\circ_{298} \quad (2)$$

as well as their standard enthalpy of formation, $\Delta_fH^\circ_{298}$, from elements at 298 K.

For the sake of comparison the results obtained by Nagabhushana et al. [5] and Brunetti et al. [6] are summarized in Table 1 along with $\Delta_fH^\circ_{298}$ and $\Delta_rG^\circ_{298}$ of $CH_3NH_3PbX_3$ (X = Cl, Br, I) perovskites at 298 K calculated by us on the basis of Nagabhushana et al. [5] data using available standard enthalpies and entropies of gaseous CH_3NH_2, HX and crystalline PbX_2 [4,7–12] shown in Table 8.

As seen in Table 1 the results obtained by Nagabhushana et al. [5] and Brunetti et al. [6] are not consistent with each other. For example, in the case of $CH_3NH_3PbI_3$ a difference between $\Delta_fH^\circ_{298}$ values reaches almost 10%! Moreover, as pointed out by Nagabhushana et al. [6] highly positive value of $\Delta_f^{hal}H^\circ_{298}$ obtained for iodide $CH_3NH_3PbI_3$ makes it unstable with respect to its binary halide components. However, this conclusion is inconsistent with the observation that simple equimolar mixture of two salts: methylammonium halide and corresponding lead halide spontaneously reacts already at room temperature [13]. Evidence of that is change

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Table 1
Comparison of available thermodynamic data for hybrid organic-inorganic perovskites.

Substance	$\Delta_f^{hal}H°_{298}$/kJ·mol^{-1}	$\Delta_fH°_{298}$/kJ·mol^{-1}			$\Delta_fG°_{298}$/kJ·mol^{-1}		
	[5]	[6]	Calculated*	Δ/(kJ·mol^{-1})	[6]	Calculated*	Δ/(kJ·mol^{-1})
$CH_3NH_3PbCl_3$	−9.03 ± 0.68	−660.5 ± 7.8	−666.73 ± 1.86	-6.23	110.9 ± 6.0	117.23 ± 1.97	6.33
$CH_3NH_3PbBr_3$	6.69 ± 1.41	−539.6 ± 8.7	−529.61 ± 2.87	9.99	128.5 ± 7.1	117.64 ± 2.94	-10.86
$CH_3NH_3PbI_3$	34.50 ± 1.01	−375.7 ± 9.7	−341.59 ± 1.09	34.11	128.9 ± 8.3	95.43 ± 1.27	-33.47

* Using data [5] and those summarized in Table 8.

of coloring since $CH_3NH_3PbX_3$ with x = Br and I have different color as compared to starting salts.

Thus there is obvious lack of reliable data on the enthalpies of formation of HOIP perovskites $CH_3NH_3PbX_3$ (X = Cl, Br, I). As a consequence, it is impossible to estimate the stability of these materials under different ambient conditions. Therefore, the main goal of the current work was to provide such data by means of solution calorimetry measurements using carefully prepared samples.

2. Experimental

CH_3NH_3X and PbX_2 (X = Cl, Br, I) were prepared using methylamine, CH_3NH_2 (Panreac, 38.5% water solution), lead (II) acetate three hydrate, $Pb(CH_3COO)_2 * 3H_2O$ (purity 99.8%) and concentrated (37–57 wt%) water solution of HX (X = Cl, Br, I) of high purity (99.9%) as starting materials. Both aforementioned compounds were used further for HOIP perovskites synthesis and calorimetric measurements.

For CH_3NH_3X (X = Cl, Br, I) synthesis methylamine was slowly added drop wise to concentrated solution of HX cooled to 0 °C up to its full neutralization. The resulting solution was slowly evaporated up to formation of a solid residue. The as prepared CH_3NH_3X powder was recrystallized from ethanol solution and then vacuum dried at 100 °C for 12 h.

PbX_2 (X = Cl, Br, I) was precipitated from the concentrated (1.6 M) solution of $Pb(CH_3COO)_2 * 3H_2O$ by addition of a slight excess of the concentrated HX solution. The precipitate was filtered, washed with cold water and then vacuum dried at 100 °C for 12 h.

Several synthesis techniques were tested to obtain single phase powders of $CH_3NH_3PbX_3$ (X = Cl, Br, I) perovskites. As a result, a technique enabled obtaining the powder of the highest possible quality was selected for each particular HOIP composition. These techniques are described in detail below.

$CH_3NH_3PbX_3$ with X = Cl and I were prepared by evaporation of dimethylformamide (DMF) from the solution containing the equimolar amounts (0.1–0.2 M) of starting CH_3NH_3X and PbX_2 salts. The as prepared powder of $CH_3NH_3PbCl_3$ was washed with small amount of hot DMF and vacuum dried at 100 °C for 12 h. The as prepared powder of $CH_3NH_3PbI_3$ was vacuum dried immediately after synthesis.

In the case of $CH_3NH_3PbBr_3$ the method described above did not enabled obtaining pure HOIP phase. Another technique was used for this reason. We found that diethyl ether (DEE) can be considered as antisolvent for $CH_3NH_3PbBr_3$ perovskite. Therefore, its synthesis was carried out at room temperature in the closed vessel containing two glass beakers. One of these beakers contained 0.2 M DMF solution of starting CH_3NH_3Br and $PbBr_2$ salts whereas the other one contained pure DEE. DEE possesses significant vapor pressure even at room temperature. Therefore, it slowly diffused into the first beaker with DMF solution and caused its saturation with respect to $CH_3NH_3PbBr_3$ perovskite. As a result, $CH_3NH_3PbBr_3$ crystals grew on the walls and bottom of the beaker. In this way in a matter of weeks it was possible to obtain single crystals of $CH_3NH_3PbBr_3$ perovskite of high purity. These crystals were washed with small amount of DEE after synthesis, grinded into powder and then vacuum dried at 100 °C for 12 h.

It is worth mentioning that powder of $CH_3NH_3PbI_3$ obtained by DMF solution process always contained small amount of PbI_2 as a secondary phase (up to 1.5 wt%). In order to solve this challenge another preparation technique, namely solid state reaction between predried CH_3NH_3I and PbI_2 salts in a vacuum sealed glass ampoule at 200 °C for 48 h, was applied. The ampoule after synthesis was slowly (for 6 h) cooled to room temperature and then opened. This synthesis procedure allowed obtaining powder of $CH_3NH_3PbI_3$ perovskite of high purity, which, as will be discussed later, surprisingly has cubic crystal structure at room temperature instead of expected tetragonal one [5] whereas the same perovskite obtained using solution technique described above had tetragonal structure.

The phase composition of all starting materials and the powder samples prepared as described above was studied at room temperature by means of X-ray diffraction (XRD) with XRD 7000 diffractometer (Shimadzu, Japan) using Cu Ka radiation λ = 1.54184 Å.

The element analysis of hybrid organic-inorganic perovskites was carried out using CHN analyzer PE 2400 (Perkin Elmer, USA). The uncertainty of the composition analysis was within ±0.3 wt%.

Dimethyl sulfoxide (DMSO, purity 99.66%) dried with zeolites (NaA, pore size 4 Å) was used as a calorimetric solvent due to its ability to quickly and completely dissolve all compounds studied in this work.

Enthalpies of solution of hybrid perovskites $CH_3NH_3PbX_3$(X = Cl, Br, I), lead (II) halides PbX_2 (X = Cl, Br, I) and methylammonium halides CH_3NH_3X (X = Cl, Br, I) in DMSO at 298 K were determined using Calvet-type solution microcalorimeter DAK-1-1 (EZAN, Russia) with sensitivity 10^{-6} J/s calibrated using Joule heating. Temperature of the microcalorimeter was measured by means of thermistor. All measurements were carried out at temperature 298 ± 0.15 K. The volume of the calorimetric vessel used in this study was 5 ml. Weighed samples (15–40 mg) were sealed into thin walled glass ampoules. The ampoule was thermostated in the working cell of the apparatus at 298 K and then broken using a special tool. During each experiment the change in the cell's thermal electromotive force was registered before it returned to zero, and the amount of heat evolved (consumed) during the experiment (which was in proportion to the area under the thermal effect curve) was calculated. The accuracy of the experimental results was checked by dissolution of KCl as a standard substance. The difference between the measured and recommended [14] value of enthalpy of KCl dissolution was found to be within 2%.

The source of all compounds, purification methods used, and final purity of the substances are summarized in the Table 2.

3. Results and discussion

3.1. Samples characterization

The XRD-patterns of the HOIP perovskites prepared as described above are shown in Figs. 1–3. The calculated lattice parameters are summarized in Table 3. As seen they are quite consistent with those reported previously [6].