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Preparation and characterization of $[H_3N(CH_2)_6NH_3]PbI_4$ and similar compounds with a layered perovskite structure

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The preparation, crystal structure and optical absorption spectra of $[H_3N(CH_2)_6NH_3]PbX_4$ (X = I, Br, Cl) and similar compounds based on Sn are described. The compounds $[H_3N(CH_2)_6NH_3]PbX_4$ consist of ordered perovskite sheets of the corresponding-corner sharing PbX_6 octahedra, which alternate with the $H_3N(CH_2)_6NH_3$ sheets. The excitonic peaks in the optical absorption spectra of these compounds occur at shorter wavelengths than those of the corresponding compounds with the formula $[C_6H_5CH_2CH_2NH_3]_2MX_4$.

Introduction

During the last ten years a number of compounds of the general formulae $[CH_3(CH_2)_nNH_3]_2MX_4$, $[C_6H_5(CH_2)_nNH_3]_2MX_4$, and $[H_3N(CH_2)_nNH_3]PbX_4$ (M = Pb, Sn, Ge, Cu, Mn, *etc.*; X = I, Br, Cl) have been prepared and studied.[1–20] Almost all of these compounds have a layered perovskite structure consisting of layers of MX_6 corner-sharing octahedra sandwiched between the organic alkylammonium spacers. The absorption spectra of these compounds exhibit excitonic peaks that are attributed to the MX network. The most important characteristic of these materials is the stability of the exciton. In the two-dimensional case the binding energy of the exciton is much larger than that of the bulk material.[11,17] Due to this enhanced binding energy of the excitons, narrow excitonic peaks are observed even at room temperature. The room temperature optical absorption spectra of $[CH_3(CH_2)_nNH_3]_2PbI_4$ ($n \geqslant 6$) and $[C_6H_5CH_2CH_2NH_3]_2PbI_4$ exhibit an excitonic peak at *ca.* 510 nm. In $[C_{10}H_{21}NH_3]_2PbI_4$, phase transitions take place upon lowering the temperature. These phase transitions are associated with the structures of the inorganic and organic parts of material. The crystal of this compound has at least four different phases.[3–5,11] The first phase (I), above 65 °C, is tetragonal in terms of the heavy atoms; the alkylammonium chains seem to be "melting" as judged from the large diffracted patterns. The second phase (II), at room temperature, is rhombohedral. In this phase the alkylammonium chains are fairly disordered. The third phase (III), from *ca.* 15 °C to *ca.* −30 °C, has the same structure with the alkylammoniums more ordered. The fourth phase (IV) is monoclinic ($\leqslant -40$ °C); the crystal was found to have twin structures and it is impossible to identify the atomic positions. The optical absorption spectrum of phase II exhibits an excitonic peak at *ca.* 510 nm, while that of phase IV is at *ca.* 480 nm.[3–6,11,12,17] The compound $[C_6H_5CH_2CH_2NH_3]_2PbI_4$ is crystallized in the monoclinic system[6,10] and is isostructural with the Sn analogue.[10] The authors of ref. 16 suggested similar structures for the bromide and chloride analogues. Because of the bulky phenyl ring in the organic layers, the adjacent layers do not overlap with each other as in $[C_{10}H_{21}NH_3]_2PbI_4$ and other *n*-alkylammonium tetraiodoplumbates. Probably for the same reason, this compound does not have any structural phase transition. There is disorder in both the phenylethyleneammonium chains and the bridging iodine atoms at room and lower temperatures.[6,10] The optical absorption spectrum exhibits an excitonic peak at *ca.* 510 nm even at low temperatures.[6,11,12,17]

In this paper the room temperature structural and optical properties of $[H_3N(CH_2)_6NH_3]PbI_4$ and similar compounds with Br and Cl instead of I and Sn instead of Pb are described. The main features in these new compounds are the order in the PbX_6 and SnX_6 networks as well as the blue shifted excitonic peak in comparison to those of previously reported compounds of Pb and Sn.

Experimental

Starting materials and apparatus

The following starting materials were used without further purification. PbO (Ferak 01 881), SnI_2 (Alfa 71112), $SnBr_2$ (Johnson Mattley 7110), hydroiodic acid 57% (Merck 341), hydrobromic acid 47% (Merck 304), hydrochloric acid 25% (Merck 312) and 1,6-diaminohexane (Fluka puris 33000).

Crystal X-ray intensity data were collected on a Crystal Logic[21] Dual Goniometer diffractometer using graphite-monochromated Mo-Kα radiation. For $[H_3N(CH_2)_6NH_3]PbI_4$ **1** all H-atoms were introduced at calculated positions as riding on bonded atoms and refined isotropically. All non-H atoms refined anisotropically. For $[H_3N(CH_2)_6NH_3]PbBr_4$ **2** the crystals were of poor quality with weak intensities and large ω-widths, probably twins. The unit cell parameters indicate that compounds **1** and **2** are isostructural, thus we collected data only to $2\theta = 39°$ to establish the structure of **2**. Hydrogen atoms were not included in the refinement; all non-H atoms refined anisotropically. The structures were solved by Patterson methods using SHELXS-86[22] and refined by full-matrix least-squares technique on F^2 with SHELXL-93.[23]

The room temperature optical absorption spectra were recorded on a Perkin-Elmer model Lambda19 UV/VIS/NIR spectrometer.

Preparation of compounds

Compound **1** was prepared for the first time in the form of small crystals by reacting PbI_2 and $H_3N(CH_2)_6NH_3{\cdot}2HI$ in DMF, followed by crystallization after evaporation of DMF or precipitation with the addition of CH_3CN at low temperatures.[24] However, good crystals of the material were obtained as follows: a solution of $H_2N(CH_2)_6NH_2$ (0.18 g, 1.5 mmol) and PbO (0.11 g, 0.5 mmol) in 20 ml of aq. HI (57%) was refluxed for 0.5 h. The solution was left to cool to room temperature. The yellow precipitate was recrystallized from aq. HI (57%) to give yellow crystals in 48% yield (mp > 280 °C). Analysis for $[H_3N(CH_2)_6NH_3]PbI_4$: Calc. C 8.65, H 2.18, N 3.36, I 60.93; Found C 8.68, H 2.19, N 3.36, I 60.95%.

Compound **2** was prepared by refluxing a solution of $H_2N(CH_2)_6NH_2$ (0.18 g, 1.5 mmol) and PbO (0.11 g, 0.5 mmol) in 20 ml of aq. HBr (47%) for 0.5 h. The solution was left to cool to room temperature to give white crystals in 60% yield (mp > 280 °C). Analysis for $[H_3N(CH_2)_6NH_3]PbBr_4$: Calc. C 11.17, H 2.81, N 4.34, Br 49.55; Found C 10.95, H 2.93, N 4.06, Br 50.12%.

$[H_3N(CH_2)_6NH_3]PbCl_4$ **3** was prepared by refluxing a solution of $H_2N(CH_2)_6NH_2$ (0.18 g, 1.5 mmol) and PbO (0.11 g, 0.5 mmol) in 20 ml of aq. HCl (25%) for 0.5 h. The solution was left to cool to room temperature to give colourless plates in 63% yield (mp > 280 °C). Analysis for $[H_3N(CH_2)_6NH_3]PbCl_4$: Calc. C 15.42, H 3.88, N 6.00; Found C 15.66, H 3.65, N 5.48%.

$[H_3N(CH_2)_6NH_3]SnI_4$ was prepared by refluxing under nitrogen a solution of $H_2N(CH_2)_6NH_2$ (0.116 g, 1 mmol) and SnI_2 (0.186 g, 0.5 mmol) in 5 ml of aq. HI (57%) for 0.5 h. The solution was left to cool to room temperature to give red crystals. Analysis for $[H_3N(CH_2)_6NH_3]SnI_4$: Calc. C 9.68, H 2.44, N 3.76, I 68.18; Found C 10.02, H 2.59, N 3.54, I 69.01%.

$[H_3N(CH_2)_6NH_3]SnBr_4$ was prepared by refluxing under nitrogen a solution of $H_2N(CH_2)_6NH_2$ (0.116 g, 1 mmol) and $SnBr_2$ (0.139 g, 0.5 mmol) in 5 ml of aq. HBr (47%) for 0.5 h. The solution was left to cool to room temperature to give the product as yellow-orange plates and a by-product consisting of yellow rods of $[H_3N(CH_2)_6NH_3]_2SnBr_6$. Analysis for $[H_3N(CH_2)_6NH_3]SnBr_4$: Calc. C 12.95, H 3.26, N 5.03; Found C 13.22, H 3.63, N 4.87%.

Results and discussion

Morphology of materials

The compounds studied herein were prepared in a pure crystalline form. Only the crystals of $[H_3N(CH_2)_6NH_3]PbI_4$ and $[H_3N(CH_2)_6NH_3]PbBr_4$ were large enough for a complete X-ray structure determination.

Crystal structure

The packing diagram of **1**, Fig. 1, shows that the structure consists of alternating perovskite sheets and layers of the alkylammonium dication. The $H_3N(CH_2)_6NH_3$ dication is in the extended form and links adjacent inorganic layers *via* hydrogen bonds between the two NH_3 moieties and iodine ions. The perovskite sheet consists of distorted PbI_6 octahedra each sharing a corner with four adjacent octahedra through the bridging iodine I2. The Pb–I bond lengths (Table 1) vary from 3.183(2) to 3.225(1) Å and the bond angles around Pb, which occupies a center of symmetry, vary between 88.25(3)° and 92.25(2)° while the *trans* angles are of course 180°. The bridging angle Pb–I2–Pb is 148.47(2)° which is an indication of the rotation and tilt between adjacent octahedra. Simple cubic perovskites typically have unit cell axis $a_p \approx 6.2$, 5.8, 5.6 Å for I, Br, Cl respectively. The perovskite layer in the present compounds, which is the *bc* plane, has axes *b* and *c*, Table 2, which are close to $\sqrt{2}a_p$. This has been observed for many organic–inorganic layered perovskite structures.[18]

The distances between Pb and I is *ca.* 3.2 Å which compares more favourably with the sum of the ionic radii (1.19 + 2.20 = 3.39 Å) than with the sum of the covalent radii (2.87 Å). This shows that the chemical bonding in the inorganic layer is mainly ionic.

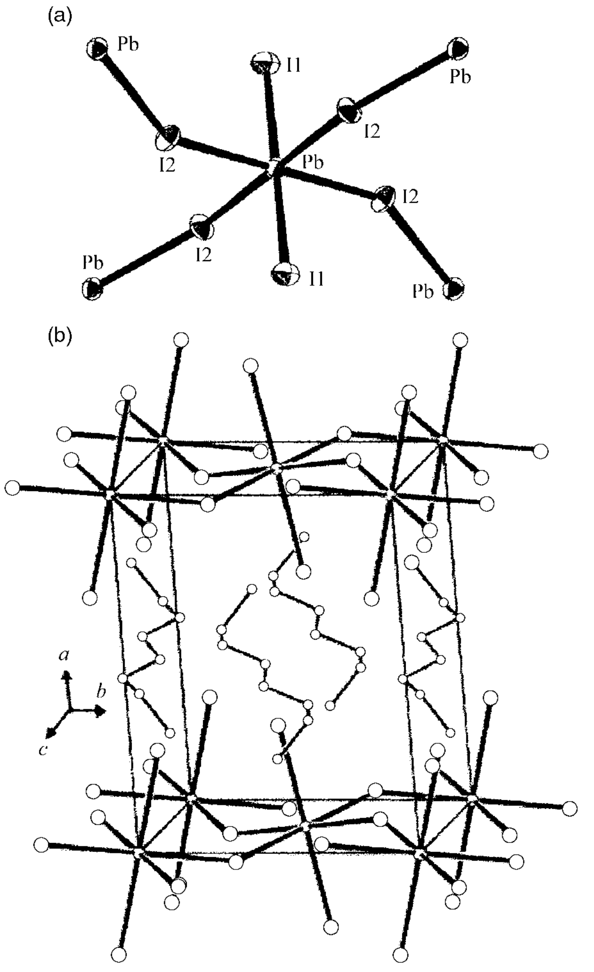

Fig. 1 (a) A drawing of a PbI_6 unit showing the atoms and the 50% probability ellipsoids. (b) A drawing of the unit cell of compound **1** viewed approximately along the *c* axis, with the unit cell outlined.

For compound **3** the unit cell dimensions ($a = 12.35$, $b = 7.71$, $c = 7.84$ Å, $\beta = 104.76°$) and space group ($P2_1/c$) indicate that it is isostructural to **1** and **2** but the structure was not solved because of twinning.

CCDC reference number 1145/194. See http://www.rsc.org/suppdata/jm/a9/a906161d/ for crystallographic files in .cif format.

Optical properties

Fig. 2 shows the optical absorption spectra of thin deposits of compounds **1**–**3** on quartz plates at room temperature. The low energy excitonic peaks occur at 482 (2.57),[24] 390 (3.18) and 332 nm (3.73 eV), respectively. Assuming that the energy gap (E_g) occurs at the dip, which is close to the excitonic band, we can estimate the values of the excitonic binding energy (E_b) of the materials. Thus, we found $E_g = 2.726$ eV, $E_b = 153.3$ meV

Table 1 Selected bond lengths (Å) and angles (deg) for compounds **1** and **2**

Pb–I1	3.183(2)	I1–Pb–I2	90.27(2)
Pb–I2	3.225(1)	I1–Pb–I2#1	92.25(2)
Pb–I2#2	3.217(1)	I2–Pb–I2#1	88.25(3)
Pb–Br1	2.987(4)	Pb#2–I2–Pb	148.47(2)
Pb–Br2	3.004(3)	Br1–Pb–Br2	90.96(7)
Pb–Br2#2	3.005(3)	Br1–Pb–Br2#1	92.92(7)
		Br2–Pb–Br2#1	89.58(8)
		Pb#2–Br2–Pb	149.31(8)

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $y+1/2$, $-z-1/2$, #2 x, $-y-1/2$, $z-1/2$.

Table 2 Summary of crystal, intensity collection and refinement data

Empirical formula	$[H_3N(CH_2)_6NH_3]PbI_4$	$[H_3N(CH_2)_6NH_3]PbBr_4$
Formula weight	833.02	645.06
Temperature/K	298	298
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	11.856(5)	12.02(1)
b/Å	8.486(4)	8.045(4)
c/Å	9.043(4)	8.342(4)
β/degrees	106.89(1)	105.66(3)
V/Å^3	870.6(7)	777(2)
Z	2	2
μ/mm^{-1}	16.757	21.122
Refl. coll/unique/used	1605/1526/1526	702/651/651
R_{int}	0.0402	0.0402
R indices	$R1 = 0.0284$, $wR2 = 0.0758$[a]	$R1 = 0.0333$, $wR2 = 0.0828$[b]

[a]For 1472 reflections with $I > 2\sigma(I)$. [b]For 556 reflections with $I > 2\sigma(I)$.

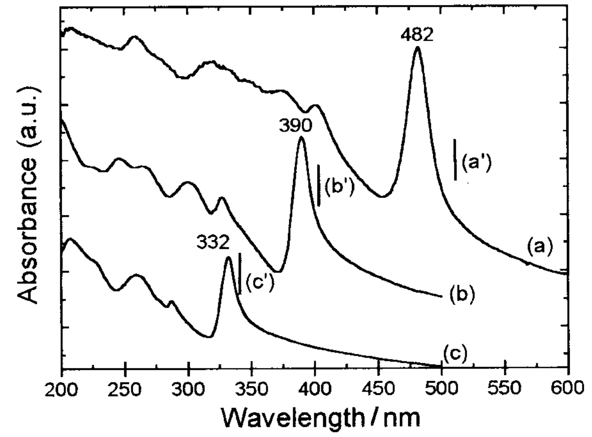

Fig. 2 Room temperature optical absorption spectra of $[H_3N(CH_2)_6NH_3]PbI_4$ (a), $[H_3N(CH_2)_6NH_3]PbBr_4$ (b) and $[H_3N(CH_2)_6NH_3]PbCl_4$ (c). Vertical bars indicate the optical absorption (excitonic) peak positions of $[C_6H_5CH_2CH_2NH_3]_2PbI_4$ (a′), $[C_6H_5CH_2CH_2NH_3]_2PbBr_4$ (b′) and $[C_6H_5CH_2CH_2NH_3]_2PbCl_4$ (c′).

for compound **1**, $E_g = 3.346$ eV, $E_b = 166.4$ meV for compound **2** and $E_g = 3.940$ eV, $E_b = 205.4$ meV for compound **3**. As can be seen, the excitonic peak positions and the band-gaps are shifted to lower energies in the order I < Br < Cl, while the excitonic binding energy is increased in the same order.

The corresponding peaks for $[C_6H_5CH_2CH_2NH_3]_2PbX_4$ compounds[16] occur at *ca.* 510, 404, and 341 nm for X = I, Br, Cl respectively (see refs. 12,15,17).

The excitonic peak of $[H_3N(CH_2)_6NH_3]PbI_4$ is located at the same position as that of $[C_{10}H_{21}NH_3]_2PbI_4$ phase IV (*e.g.* at *ca.* 480 nm).[3–6,11,12,17] Both of these structures are ordered. In contrast, the excitonic peak of $[C_{10}H_{21}NH_3]_2PbI_4$ phase II and that of $[C_6H_5CH_2CH_2NH_3]_2PbI_4$, which both have a disordered structure, are located at *ca.* 510 nm. Similar results were obtained for the excitonic bands of compounds **2** and **3** in comparison to those of $[C_6H_5CH_2CH_2NH_3]_2PbBr_4$ and $[C_6H_5CH_2CH_2NH_3]_2PbCl_4$, respectively.

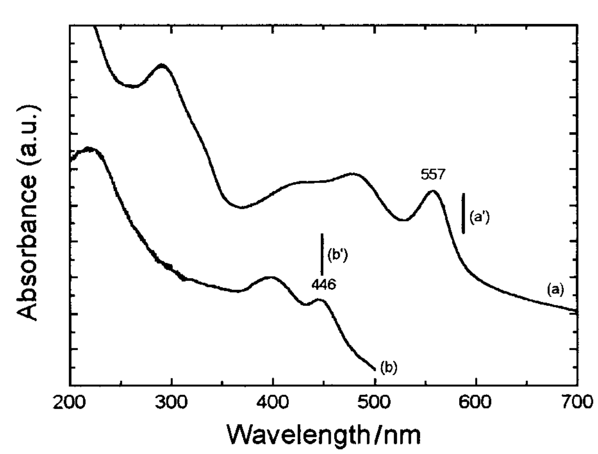

Fig. 3 Room temperature optical absorption spectra of $[H_3N(CH_2)_6NH_3]SnI_4$ (a) and $[H_3N(CH_2)_6NH_3]SnBr_4$ (b). Vertical bars indicate the optical absorption (excitonic) peak positions of $[C_6H_5CH_2CH_2NH_3]_2SnI_4$ (a′) and $[C_6H_5CH_2CH_2NH_3]_2SnBr_4$ (b′).

Also, similar results were obtained for the SnI based compounds. The optical absorption spectrum of a thin deposit of $[H_3N(CH_2)_6NH_3]SnI_4$ on quartz plates, exhibits an excitonic peak at 557 nm, while that of $[C_6H_5CH_2CH_2NH_3]SnI_4$ occurs at *ca.* 590 nm[7,10,12] (Fig. 3). However, the excitonic peaks of SnBr based compounds occur at the same position (*i.e.* at 446 nm), independently of the nature of the organic component. From the absorption spectra we suggest that the $[H_3N(CH_2)_6NH_3]SnI_4$ and $[H_3N(CH_2)_6NH_3]SnBr_4$ compounds have a 2-dimensional ordered structure.

Details on the optical and reflectance properties of these new compounds at low temperatures will be discussed elsewhere.

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