

Sonochemical synthesis of lead hydroxy bromide needles

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A sonochemical approach to the preparation of elongated needles of Pb(OH)Br using a cationic surfactant, cetyltrimethylammonium bromide (CTAB) is reported. A shape transition of the particles is found to occur due to the presence of an organized medium consisting of a cylindrical, interconnected network of thread-like micelles. Transmission electron micrographs (TEM) show the presence of elongated Pb(OH)Br particles. The needles have been characterized by powder XRD, IR, TGA and DSC. The needles have also been found to decompose in the electron beam during TEM measurements, the decomposition product being one of the polymorphic forms of PbO·PbBr₂.

1 Introduction

There have been increasing contributions from chemists in the use of colloidal systems as templates to the synthesis of materials with enhanced or novel properties. These offer a unique way to tailor the shape and size of particles, using a rich array of liquid crystalline and amphiphilic self-assembled systems. Numerous methods have been used for the preparation of elongated particles. The use of colloidal assemblies as templates,¹ as well as the use of microemulsion media for the synthesis of the nanosized particles² using reverse micelles as microreactors,³ electron beam lithography,⁴ the sol-gel method⁵ and using a plasma polymer matrix⁶ are amongst the several reported techniques for the formation of elongated particles.

Recently, sonochemical processing has proved to be a useful technique for generating novel materials with unusual properties.⁷ The chemical effects of ultrasound arise from acoustic cavitation; the formation, growth and implosive collapse of a sonochemical bubble in a liquid which produces unusual chemical and physical environments.⁷ The extreme conditions thus attained have been exploited to prepare nanoscale metals,⁸ metal oxides,⁹ and nanocomposites.¹⁰

Studies on lead oxides and related compounds are of fundamental importance. Glasses based on lead oxyhalides are used in the conversion of infrared light into visible light. PbO–PbBr₂ based materials, the dehydroxylation products of Pb(OH)Br, are used in the preparation of low melting glasses useful as glass scintillators in the field of high energy physics.^{11,12} PbO·PbBr₂ based materials are found in automobile engine deposits and a study of these compounds is of fundamental significance in understanding the nature of these deposits.¹³

Increased focus on the preparation of materials through a surfactant-mediated process¹⁴ led us to devise a new method, wherein elongated particles of Pb(OH)Br can be prepared in the presence of a cationic surfactant, cetyltrimethylammonium bromide (CTAB), [CH₃(CH₂)₁₅N(CH₃)₃]Br. This surfactant in water shows the presence of elongated thread-like micelles.¹⁵ The presence of organized assemblies during the preparation of material has been shown to have an effect on the shape of the particles formed.¹⁴ It is also believed that the interparticle collisions which happen at very high speed during high intensity ultrasound radiation ultimately lead to agglomeration, changing the morphology of the particles.¹⁶

The objective of the present work is to use the sonochemical method for the preparation of elongated particles of Pb(OH)Br

with the surfactant CTAB, using an interconnected network of thread-like micelles as a template. The formation of an interconnected network of elongated thread-like micelles favors the uniaxial growth of the particles within the assembly, leading to the formation of elongated needles.

2 Experimental

To a 1% aqueous solution of CTAB, 1.2 g of lead acetate trihydrate, Pb(CH₃COO)₂·3H₂O was added in a round bottom sonication flask (capacity, 80 ml, 26 mm od). The slurry was purged with argon for 30 min and sonicated for 2 h by employing a direct immersion titanium horn (Sonics and Materials, 20 kHz, 100 W cm⁻²) under an argon atmosphere. The titanium horn was inserted to a depth of ≈ 1 cm in the solution. The temperature during the sonication experiment increased to 80 °C as measured by an iron–constantan thermocouple. A pH measurement before and after the sonication showed an increase in pH from 5.56 to 6.25. The resultant product was centrifuged, washed thoroughly with distilled water and ethanol and finally dried under vacuum. The yield of the Pb(OH)Br needles was found to be ca. 39%. If the sonication was carried out for shorter times (30 min and 1 h), the formation of needles of Pb(OH)Br was found to be incomplete. In the case of sonication for a longer time (4 h), there was neither noticeable improvement in the yield nor change in the morphology of the products. The presence of the surfactant should have an effect on the shape and morphology of the Pb(OH)Br particles. A sample of Pb(OH)Br was also synthesized according to a literature procedure due to Knowles.¹⁷ A solution containing 9.0 g of KBr dissolved in 200 ml of distilled water was slowly added, while stirring, to an aqueous solution containing 6.7 g of lead acetate in 150 ml of distilled water. The precipitate obtained was filtered, washed thoroughly with distilled water and dried under vacuum overnight.

Product characterization

Powder X-ray diffraction patterns were recorded by employing a Bruker D8 Advance diffractometer and a Rigaku X-ray diffractometer (Model-2028, CuKα). The transmission electron micrographs (TEM) were obtained by employing a JEOL-JEM 100SX microscope. Samples for TEM were prepared by placing a drop of the sample suspension in ethanol on a copper grid (400 mesh, electron microscopy sciences) coated with carbon film and were allowed to dry in air. High resolution TEM

(HREM) measurements were made using a Philips CM-120 electron microscope operating at 120 kV. FT-IR spectra were recorded on a Nicolet (Impact 410) infrared spectrophotometer using the KBr disc method in the range 4000–400 cm^{-1} . The thermogravimetric analysis was carried out using a Mettler Toledo TGA/SDTA851 in the temperature range 30–900 °C at the rate of 10 °C per minute, in an argon atmosphere in the temperature range 30–550 °C. The differential scanning calorimetry (DSC) profile of the sonication product was recorded on a Mettler DSC-30 instrument with a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. Elemental composition was determined by energy-dispersive X-ray spectroscopy (EDX) using a JEOL-JSM 840 scanning electron microscopy instrument. Elemental analysis of C, H, and N was carried out on an Eager 200 CE Instruments EA 1110 Elemental Analyzer.

3 Results and discussion

From the EDX results in combination with the thermal gravimetric measurements, the stoichiometry of the product was found to be $\text{Pb}(\text{OH})\text{Br}$. Also, elemental analysis of the product for carbon, hydrogen and nitrogen indicated the absence of these elements.

Fig. 1a shows the transmission electron micrograph of the elongated particles of $\text{Pb}(\text{OH})\text{Br}$. The presence of the surfactant during the preparation stage dictates the shape of the ultrasonically formed particles. The sizes of the elongated particles were approximately 900 nm in length and 150 nm in width. Some needles are bigger than these dimensions. No coating of needles with the surfactant could be noticed in the transmission electron micrographs. A TEM picture of the $\text{Pb}(\text{OH})\text{Br}$ sample synthesised according to the literature¹⁷ procedure showed no needle-like structure. The particles are irregular in shape and are also shown in Fig. 1b. If the concentration of the surfactant, CTAB, was below the critical micellar concentration (= 1 mmol), we were not able to get needles of $\text{Pb}(\text{OH})\text{Br}$. Particles of irregular shape similar to those shown in Fig. 1b were obtained. The needles were found to decompose in the electron beam during the TEM measurements. Annealing in the electron beam during the HRTEM experiments produced a compound with a lattice spacing, $d=0.33$ nm and this particular d spacing is the most intense one reported for $\text{PbO}\cdot\text{PbBr}_2$ (R-form). Hence this compound has been assigned as $\text{PbO}\cdot\text{PbBr}_2$ (R-form) as supported by powder XRD results to be discussed below.

Fig. 2 displays the powder XRD pattern of the elongated particles. The peak positions observed are consistent with those reported for $\text{Pb}(\text{OH})\text{Br}$ (JCPDS file no. 30-697). Table 1 lists the observed and reported d values along with the hkl values for $\text{Pb}(\text{OH})\text{Br}$ needles. This XRD pattern matches well with that of

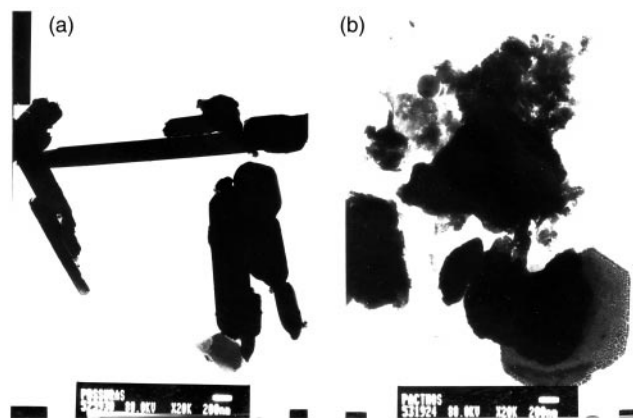


Fig. 1 (a) Transmission electron micrograph of $\text{Pb}(\text{OH})\text{Br}$ needles; (b) TEM of $\text{Pb}(\text{OH})\text{Br}$ synthesised according to a literature procedure.

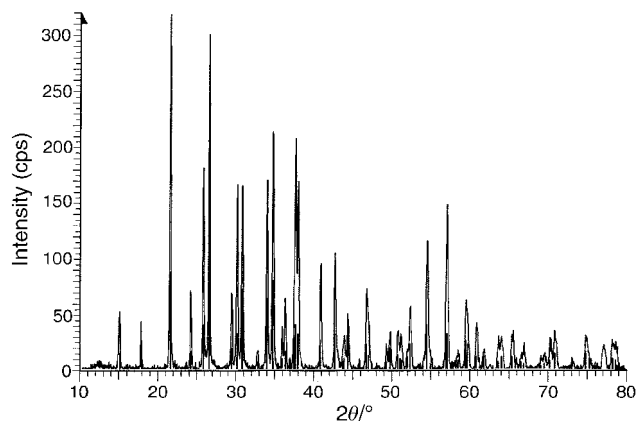


Fig. 2 Powder X-ray diffractogram of $\text{Pb}(\text{OH})\text{Br}$ needles. The position of peaks from the JCPDS file (30-697) are marked as vertical solid lines.

Table 1 Observed and reported d spacings for $\text{Pb}(\text{OH})\text{Br}$ needles

d_{obs}	d^{r}	hkl
5.984	5.930	110
5.045	4.998	020
4.160	4.139	120
3.713	3.693	011
3.480	3.462	210
3.379	3.363	111
3.054	3.042	130
2.982	2.970	220
2.917	2.908	121
2.747	2.737	201
2.649	2.641	211
2.593	2.584	031
2.511	2.504	040
2.481	2.475	230
2.443	2.403	221
2.398	2.391	310
2.375	2.371	140
2.215	2.210	320
2.122	2.118	231
2.068	2.064	311
2.047	2.043	002
1.986	1.982	330
1.944	1.943	321
1.895	1.890	022
1.850	1.848	241
1.834	1.831	122
1.800	1.797	051
1.786	1.786	202
1.764	1.759	250
1.750	1.747	151
1.698	1.695	132
1.685	1.682	401
1.616	1.615	430
1.578	1.575	232
1.554	1.553	350
1.522	1.521	260
1.501	1.499	322
1.462	1.461	510
1.455	1.451	351
1.426	1.425	261
1.404	1.403	152
1.398	1.396	441
1.382	1.381	360
1.366	1.369	402
1.359	1.357	450
1.352	1.349	071
1.339	1.338	521
1.329	1.327	171
1.294	1.292	123
1.284	1.282	531
1.268	1.266	213
1.236	1.242	133
1.221	1.219	262
1.216	1.214	541

^aFrom JCPDS file (30-697).

the conventionally synthesised material according to the literature.^{17,18}

The IR spectrum of the sample in the 4000–400 cm⁻¹ region did not show any band that could be assigned to the vibrations of the surfactant (CTAB). The spectrum showed a sharp band at 3509 cm⁻¹ which can be assigned to the OH stretching mode, ν_{OH} and another band at 595 cm⁻¹ which has been attributed to the OH bending mode, δ_{OH} . The spectral features were very much similar to those reported in ref. 19 for Pb(OH)Br. From the IR spectroscopy and TEM results it can be concluded that there is no coating of the surfactant on the needles.

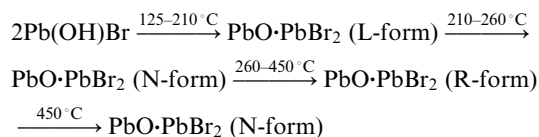
Fig. 3 displays the thermogravimetric spectrum of the elongated needles of Pb(OH)Br from 30 to 900 °C. The TGA spectrum exhibits a step around 210 °C with a weight loss of 2.52% followed by a continuous weight loss starting from 520 °C. The first weight loss around 210 °C is attributed to the loss of water by dehydroxylation to give PbO·PbBr₂.



The continuous weight loss after about 520 °C has been attributed to sublimation of PbBr₂ resulting from dissociation of PbO·PbBr₂ and continues until the end temperature of the TG run, 900 °C as reported in ref. 19 for Pb(OH)Br.

A DSC study (Fig. 4) in the temperature range 30–550 °C shows two endothermic peaks; one at 207 °C and another peak at 496 °C. On cooling, two exothermic peaks are observed; a smaller but detectable one at 322 °C and another larger peak at 455 °C. On re-heating the sample two endothermic peaks are observed; one at 325 °C and another one at 498 °C.

Before discussing the DSC results, a brief description of the thermal behaviour of lead hydroxy bromide is given.^{13,18,19} A study involving the dehydration and subsequent heat treatment of lead hydroxy bromide showed that PbO·PbBr₂, the dehydration product, may exist in more than one crystalline form denoted as L, N and R. Each of the polymorphic forms react with water to produce the hydrate. The thermal relationships among these polymorphic forms are indicated below.



In a study on the determination of the phase diagram of the PbO–PbBr₂ system both by thermal analysis and X-ray diffraction, it has been found that the N-form is the high temperature form and the R-form is the low temperature form. The structures of these various forms have not been reported but the *d* spacings from powder X-ray diffraction data have been listed in ref. 18.

The features observed in the DSC spectrum of Pb(OH)Br can now be explained as follows. The endothermic peak at ca. 207 °C can be attributed to the dehydration of Pb(OH)Br to give PbO·PbBr₂. This is observed in the TGA pattern as a

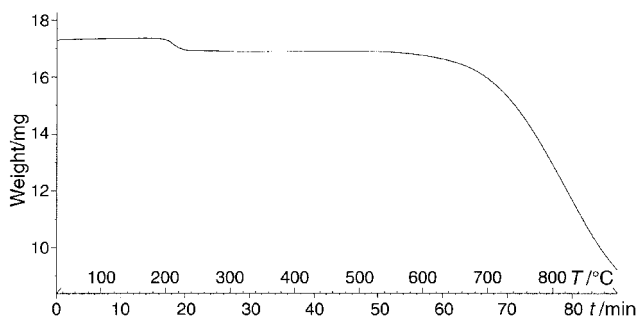


Fig. 3 TGA curve of the Pb(OH)Br needles.

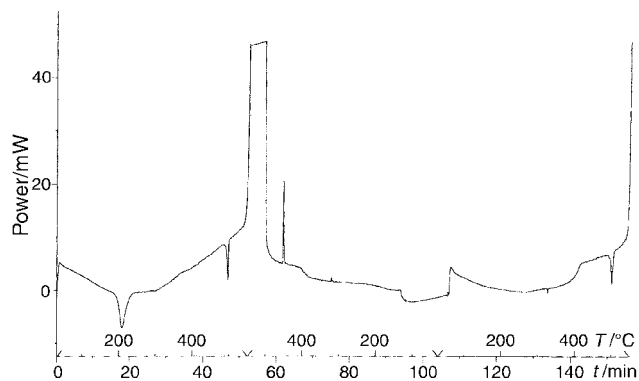


Fig. 4 DSC profile of Pb(OH)Br needles.

weight loss step around 210 °C. The product is the N-form of PbO·PbBr₂ as evidenced by powder XRD measurements on a sample heated at 250 °C in argon shown in Fig. 5a. The endothermic peak at 496 °C has been ascribed to the peritectic transformation temperature. When the sample temperature increases to more than 520 °C, the compound starts to decompose. This is corroborated by the powder XRD measurement of the sample heated at 520 °C for 2 h in an argon atmosphere which showed that the decomposition product is lead (JCPDS file No. 4-686, Fig. 5b). During the cooling run, the exothermic peak observed at 455 °C has been attributed to the N (high temperature form) ↔ R (low temperature form) transformation of PbO·PbBr₂. The other exothermic peak at around 325 °C during cooling is attributed to the recrystallization of lead. On heating for a second time, we again observe the melting point of lead at 325 °C and the peritectic transformation temperature at 498 °C as endothermic peaks. The observation of the peritectic transformation temperature at 498 °C even during the second heating cycle is due to the fact that the decomposition of PbO·PbBr₂ is still incomplete during the DSC run. If we restrict the DSC measurements from 30 to 500 °C, no peak attributable to the melting/crystallization of lead (the decomposition product) around 325 °C could be observed.

We now consider the mechanism by which the needles of crystalline Pb(OH)Br are formed. The effect of ultrasound radiation on chemical reactions is due to the very high temperatures and pressures which develop during the sonochemical cavity collapse by a process called acoustic cavitation. There are two regions of sonochemical activity, as postulated by Suslick *et al.*:²⁰ the inside of the collapsing bubble and the interface between the bubble and the liquid which extends to about 200 nm from the bubble surface. If the reaction takes place inside the collapsing bubble ($T > 5000$ K) as is the case for

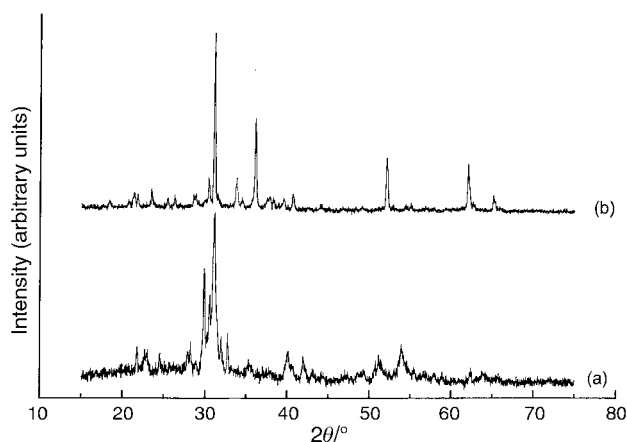


Fig. 5 XRD patterns of Pb(OH)Br needles heated (a) at 250 °C in argon for 2 h and (b) at 520 °C in argon for 2 h.

transition metal carbonyls, the product obtained is amorphous as a result of the high cooling rates ($>10^{10} \text{ K s}^{-1}$) obtained during the collapse. On the other hand, if the reaction takes place at the interface whose temperature has been measured to be 1900 K,²⁰ one expects to get nanocrystalline products. If the solute is ionic and so has a low vapour pressure, then during sonication the amount of the ionic species will be very low inside the bubble and little product is expected to occur inside the bubbles. We propose that the formation of Pb(OH)Br occurs at the interface between the bubble and the liquid.

The presence of the surfactant during the preparation stage of Pb(OH)Br affects the shape of the particles formed. The role of the surfactant is to provide an organized medium consisting of a cylindrical, interconnected network of thread-like micelles. These micelles favour the uniaxial growth of the particles within the assembly leading to the formation of elongated needles. The surfactant which acts as a template during the preparation stage of lead hydroxy bromide gets washed away during the centrifuging and washing process. This synthetic method thus produces needles of lead hydroxy bromide which are free of surfactant.

4 Conclusions

A sonochemical approach to the preparation of needles of lead hydroxy bromide, Pb(OH)Br, with the cationic surfactant, CTAB has been described. Using interconnected cylinders as a template, elongated particles are produced. The role of the surfactant is to stabilize the unidirectional growth in the sense that the surfactant inhibits the side interconnection of the particles. The needles have been characterized by a variety of techniques. The compound was found to thermally decompose around 520 °C, the decomposition product being metallic lead. Exposure of Pb(OH)Br to the electron beam during HRTEM measurements also leads to decomposition but the product was found to be one of the polymorphic forms of PbO·PbBr₂, the R-form.

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