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Synthesis of morphologically controlled lanthanum carbonate particles using ultrasound irradiation

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Lanthanum carbonate particles, which can be used as precursors to lanthanum oxide, have been synthesised from lanthanum nitrate and urea in the presence and absence of ultrasound irradiation. The use of ultrasound irradiation was found to have a remarkable effect on the morphology of the lanthanum carbonate particles formed. Needle-shaped particles were found to be formed in the presence of ultrasound irradiation, whereas spherical carbonate particles were produced in the absence of ultrasound irradiation. Characterization by powder X-ray diffraction, transmission electron microscopy, scanning electron microscopy, thermogravimetric analysis, differential scanning calorimetry, FT-IR spectroscopy, as well as elemental analysis was carried out on the materials synthesised. The effect of heating on the chemistry and the morphology of the carbonate particles was also investigated. The carbonate particles were found to be completely converted into lanthanum oxide at *ca.* 725 °C. In the case of the needle-shaped lanthanum carbonate particles, the shape was found to be deformed to a small extent on heating, whereas a larger degree of deformation was observed for the spherical lanthanum carbonate particles.

1 Introduction

Ultrasound radiation has been routinely used in the field of materials science. Its chemical effects have recently come under investigation for the acceleration of chemical reactions and for the synthesis of new materials,[1] as well as for generating novel materials with unusual properties.[2] The chemical effects of ultrasound radiation arise from acoustic cavitation: the formation, growth and collapse of bubbles in a liquid irradiated with ultrasound. The extremely high temperatures (≈ 5000 K), pressures (>20 MPa) and cooling rates ($>10^{10}$ K s^{-1}) attained during acoustic cavitation lead to many unique properties in the irradiated solution and these extreme conditions have been exploited to prepare nanoscale metals, metal oxides, and nanocomposites.[3,4] It is also believed that the interparticle collisions, which happen at a very high speed during high intensity ultrasound irradiation, ultimately lead to fusion and agglomeration of the particles.[5]

Chemists are increasingly concerned with the synthesis of advanced materials with enhanced or novel properties. The use of the inorganic–organic interface to achieve shape-controlled synthesis of inorganic materials is an emerging soft chemical route.[6] Specific molecular interactions at the inorganic–organic interface seem to control nucleation and growth, often stabilizing new modifications and morphologies.[7]

Lanthanide compounds, especially oxides, are of interest with regard to their electric, catalytic and ceramic properties.[8,9] Lanthanum carbonates are precursors to the synthesis of lanthanum oxide particles. Rare earth carbonates are also useful starting materials for the preparation of water-soluble rare earth complexes.[10] Lanthanum(III) carbonates are conventionally produced by the hydrolysis of the corresponding trichloroacetate[11] and by the hydrothermal reaction of a lanthanum(III) salt and carbon dioxide.[12] However, their particle shapes are reported to be irregular. The factors that influence the crystallization of rare earth carbonates have been reported by Nagashima *et al.*[13] Recently, uniform carbonate hydroxide particles of lanthanum(III) and yttrium(III), as well as mixed lanthanides, were produced using urea at elevated temperatures under specific conditions.[14] Panchula and Akinc[15] have reported the synthesis of lanthanum carbonate particles with spherical and square planar morphologies. The synthesis of uniform spherical particles of lanthanum(III) carbonate hydroxide has been reported by Hamada *et al.*[16] from the corresponding ethane-1,2-diamine complex solution.

Homogeneous precipitation employing urea has been increasingly used to synthesise novel phases and fine particulate materials.[17] Urea is a very weak Brønsted base and its hydrolysis rate may easily be controlled by means of temperature.[18] Synthesis of lanthanide oxide precursor particles through urea decomposition has received considerable attention over the past few years.[15,16] This paper describes the synthetic conditions under which dispersed needle-shaped and spherical particles of carbonates may be formed from lanthanum, the lightest of the lanthanide elements. The objective of the present work is to utilize ultrasound radiation in the process of homogeneous precipitation and to study the effect of ultrasound irradiation on the morphology of the carbonates formed. The conversion of these carbonates into lanthanum oxide by thermal decomposition is also described.

2 Experimental

Preparation

The synthesis of the lanthanum carbonate particles has been carried out with the aid of ultrasound radiation. Typically, 5 g of urea (Aldrich) were added to an aqueous solution of 1.5 g of $La(NO_3)_3 \cdot 6H_2O$ (Fluka) in a sonication flask (total capacity 80 ml, 26 mm od). The solution was purged with argon for 30 min and irradiated with high intensity ultrasound radiation at room temperature (25 °C) for 2 h by employing a direct immersion titanium horn (Sonics and Materials, 20 kHz, 100 W cm^{-2}). The titanium horn was inserted into the solution to a depth of ~ 1 cm. The temperature during the sonication experiment increased to *ca.* 80 °C as measured by an iron–constantan thermocouple. After the precipitation process was complete, the precipitates were separated from the solution by centrifugation. The recovered precipitates were washed several times with doubly distilled water and dried under vacuum at

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room temperature. A sample of the lanthanum carbonate particles was also synthesised under the same conditions at 80 °C, but without ultrasound irradiation.

Elemental analysis of the carbon and hydrogen content of the particles synthesised by sonochemical means showed 6% carbon and 0.3% hydrogen, whereas the thermally synthesised carbonate particles contained 7% carbon and 0.7% hydrogen.

Product characterization

The powder X-ray diffraction patterns were recorded by employing a Rigaku X-ray diffractometer (Model-2028, Cu-Kα, $\lambda = 1.5418$ Å) and a Bruker D8 Advance X-ray diffractometer. The morphologies of the products were determined by transmission electron microscopy (TEM) (JEOL-JEM 100SX microscope). The powder morphology was also examined by a scanning electron microscope (SEM) (JEOL-JSM-840). Samples for TEM were prepared by placing a drop of the sample suspension on a copper grid coated with carbon film (400 mesh, Electron Microscopy Sciences) and allowing them to dry in air. FT-IR spectra were recorded on a Nicolet (Impact 410) infrared spectrophotometer with KBr pellets over the range 400–4000 cm^{-1}. The thermogravimetric analysis was performed in a nitrogen atmosphere using a Mettler Toledo TGA/SDTA851 instrument attached to a mass spectrometer (Balzers Instruments), over the temperature range of 30–900 °C (heating rate = 10 °C min^{-1}). DSC patterns of the samples were recorded using a Mettler TC15 instrument over the temperature range of 30–550 °C under a nitrogen atmosphere. Elemental analysis for carbon and hydrogen was carried out using an Eager 200 CHN analyser.

3 Results

From the elemental analysis, in combination with the results obtained from thermal gravimetric measurements, the stoichiometry of the lanthanum carbonate particles synthesised by sonochemical means was found to be $La_2O(CO_3)_2 \cdot 1.4H_2O$. On the other hand, the stoichiometry of the lanthanum carbonate synthesised without the use of ultrasound irradiation was found to be $La_2(CO_3)_3 \cdot 1.7H_2O$.

The phase identification of both the carbonate particles was performed by powder X-ray diffraction. The sample synthesised with the aid of ultrasound irradiation showed a crystalline X-ray pattern (Fig. 1), which matches that reported[9] for $La_2O(CO_3)_2 \cdot nH_2O$ ($n = 1$–2) (JCPDS file No. 28-0512). The carbonate sample synthesised without the aid of ultrasound radiation showed an amorphous X-ray diffraction pattern.

In Fig. 2(a) and (b), we show the results of transmission electron microscopic investigations of the synthesised lanthanum carbonate particles. There is a clear morphological difference in particle shape between the two carbonate samples synthesised with and without the aid of ultrasound irradiation. The sample synthesised *with the aid of ultrasound radiation* was found to have a needle-shaped morphology [Fig. 2(a)] (length *ca.* 1500 nm, width *ca.* 200 nm), whereas the sample prepared *without sonication* consisted of spherical particles of size *ca.* 250 nm [Fig. 2(b)]. Fig. 3 shows the SEM pictures of the lanthanum carbonate particles. Both the needle-like morphology for the sonochemically prepared carbonate particles and the spherical morphology for the thermally synthesised

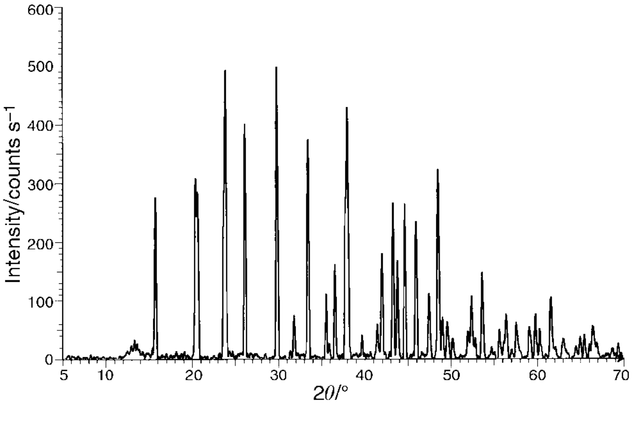

Fig. 1 Powder XRD pattern of the lanthanum carbonate samples synthesised in the presence of ultrasound irradiation.

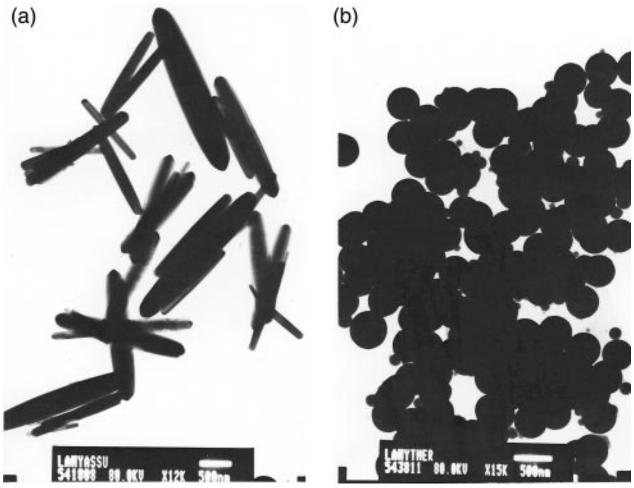

Fig. 2 TEM pictures of the lanthanum carbonate samples synthesised (a) in the presence and (b) in the absence of ultrasound irradiation.

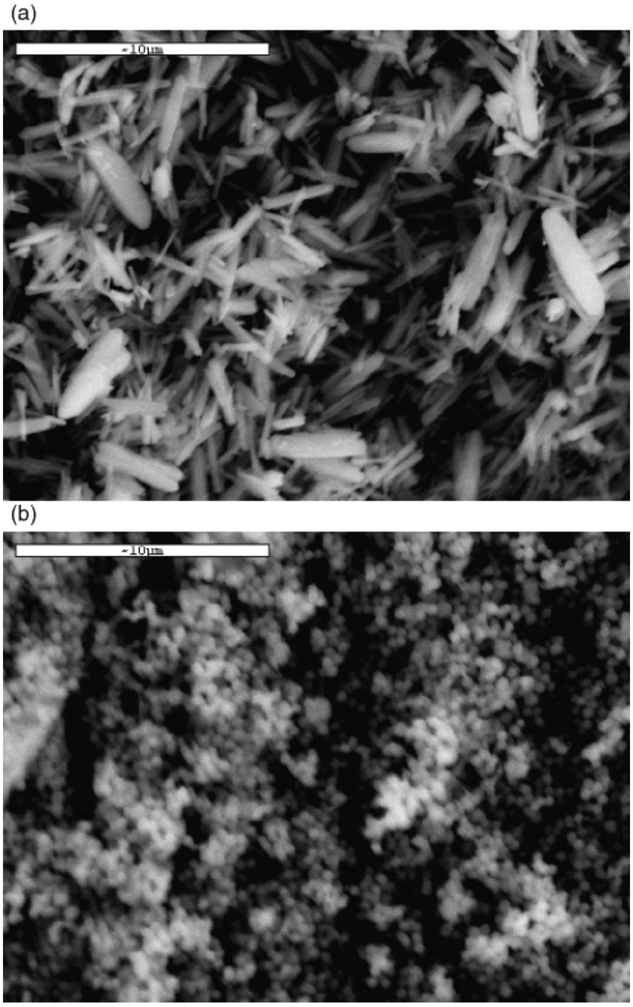

Fig. 3 SEM pictures of the carbonate samples synthesised (a) in the presence and (b) in the absence of ultrasound irradiation.

carbonate particles can be clearly seen. Sonication of the solution during the homogeneous precipitation process helps in the formation of needle-shaped particles.

The thermal decomposition behaviour of the synthesised carbonate particles depends upon their chemistry and morphology. The needle-shaped carbonate particles showed two steps in the TGA pattern [Fig. 4(a)]: i) at *ca.* 478 °C (weight loss = 16.2%) and ii) at *ca.* 743 °C (weight loss = 9.3%) with an overall weight loss of 25.5%. The spherical lanthanum carbonate particles showed three steps [Fig. 4(b)]: i) at *ca.* 135 °C (weight loss = 6.2%), ii) at *ca.* 484 °C (weight loss = 18.5%) and iii) at *ca.* 743 °C (weight loss = 8.4%) with an overall weight loss of 33.1%. Both the samples showed peaks at *m*/*z* 44 in the mass spectrum at *ca.* 480 and *ca.* 740 °C, which can be ascribed to the evolution of CO_2 during the thermal decomposition.

The major differences between the thermal behaviour of the needle-shaped and the spherical carbonate particles are a) the needle-shaped particles showed a plateau in the temperature range of 30–300 °C that was absent in the case of spherical particles, b) the needle-shaped particles showed an overall weight loss of 25.5%, whereas the spherical ones showed an overall weight loss of 33.1% and c) the weight loss step at *ca.* 135 °C in the case of spherical carbonate particles was absent in the case of the needle-shaped particles. The observed weight loss agreed well with what was expected from the formulae obtained from elemental analysis (carbon, hydrogen) for the needle-shaped carbonate particles (expected weight loss = 25.8%, observed weight loss = 25.5%) as well as for the spherical carbonate particles (expected weight loss = 33.3%, observed weight loss = 33.1%). The expected weight losses were calculated on the basis of the observation that the end product of TGA is La_2O_3 for both the needle-shaped as well as the spherical lanthanum carbonate particles.

The DSC measurements on the needle-shaped carbonate particles [Fig. 5(a)] showed a major irreversible exothermic peak at *ca.* 491 °C in addition to a smaller exotherm at *ca.* 300 °C. On cooling, an exothermic reversible peak at *ca.* 456 °C was observed. The features in the DSC spectrum of the spherical carbonate particles [Fig. 5(b)] were similar to those observed for the needle-shaped particles. In addition, an endotherm at *ca.* 162 °C with a shoulder on the low temperature side of the curve was observed. Powder XRD measurements (Fig. 6) on the thermal decomposition products of the carbonate samples showed that both the samples decompose at 550 °C to give $La_2O_2CO_3$. On further heating at 725 °C, both the carbonate particles form La_2O_3.

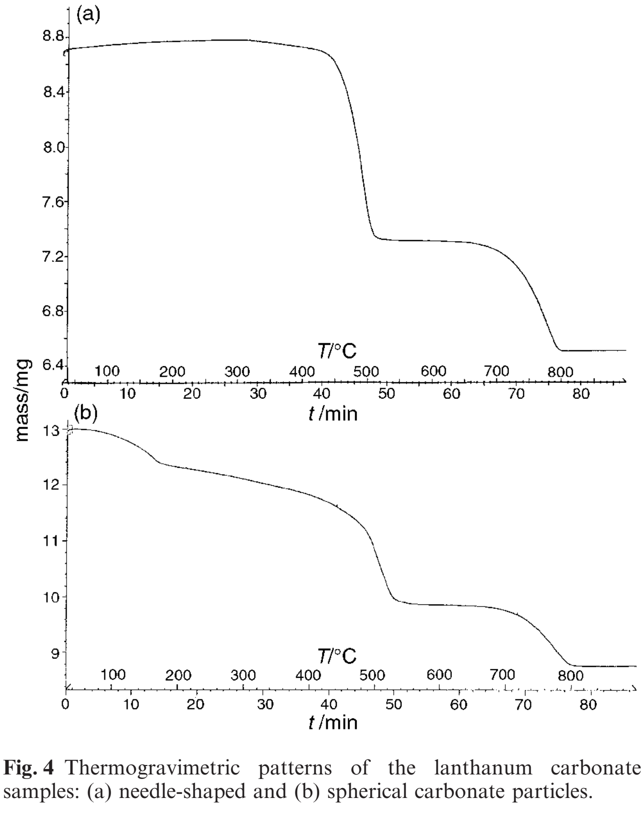

Fig. 4 Thermogravimetric patterns of the lanthanum carbonate samples: (a) needle-shaped and (b) spherical carbonate particles.

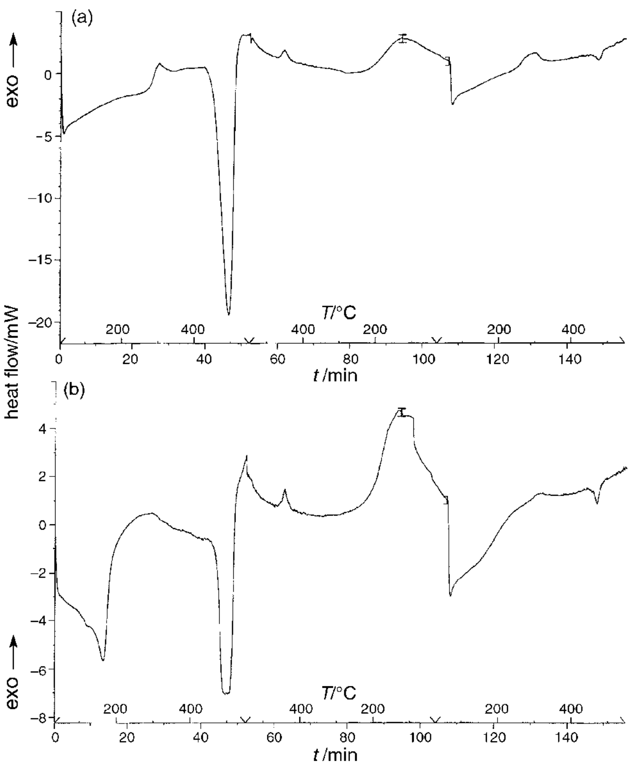

Fig. 5 DSC patterns of the lanthanum carbonate samples synthesised: (a) needle-shaped and (b) spherical carbonate particles.

The effect of heating on the particle morphology was investigated by TEM for both the carbonate samples. The results are shown in Fig. 7. It can be seen for the needle-shaped particles heated at 550 °C under vacuum that the needles are still intact [Fig. 7(a)]. However, at 725 °C, the needles are deformed to a smaller extent [Fig. 7(b)]. The spherical carbonate particles, on the other hand, are deformed to a larger extent even at 550 °C [Fig. 7(c)] and are completely deformed at 725 °C [Fig. 7(d)].

4 Discussion

On the basis of the thermal behaviour, the following decomposition patterns are proposed for the needle-shaped and spherical lanthanum carbonate particles.

Needle-shaped particles:

$$La_2O(CO_3)_2{\cdot}1.4H_2O \xrightarrow{ca.\ 550\ ^\circ C} La_2O_2CO_3 \xrightarrow{ca.\ 725\ ^\circ C} La_2O_3$$

Spherical particles:

$$La_2(CO_3)_3{\cdot}1.7H_2O \xrightarrow{ca.\ 135\ ^\circ C} La_2(CO_3)_3 \xrightarrow{ca.\ 550\ ^\circ C}$$
$$La_2O_2CO_3 \xrightarrow{ca.\ 725\ ^\circ C} La_2O_3$$

The dehydration of the crystallization water and the formation of $La_2O_2CO_3$ appear concurrently in the TGA pattern in the case of the needle-shaped particles, whereas the spherical carbonate particles show a separate dehydration step. Also, the individual experimental weight losses in the TGA pattern, corresponding to formation of the dehydrated

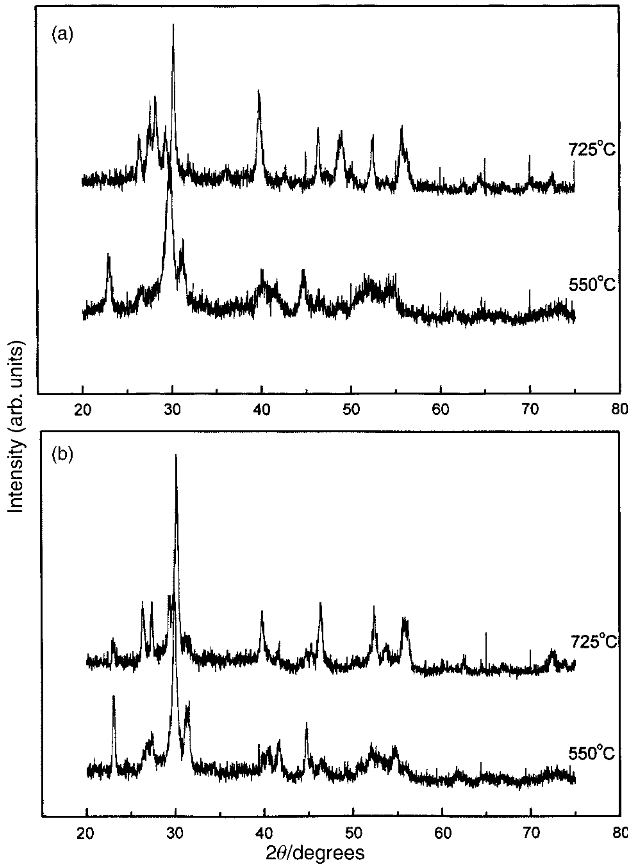

Fig. 6 Powder XRD patterns of the thermal decomposition products of (a) needle-shaped and (b) spherical lanthanum carbonate particles.

carbonate, the dioxycarbonate, and the oxide, agree well with the calculated weight losses. The exothermic peak in the DSC pattern around *ca.* 300 °C for the needle-shaped carbonate particles has been attributed to the formation of the anhydrous monooxo carbonate as reported in ref. 13 The exothermic peaks observed during cooling around *ca.* 450 °C for both the needle-shaped and the spherical carbonate particles have been ascribed to the transformation of $La_2O_2CO_3$ from one polymorphic form, Type II (hexagonal form), to another, Type I (tetragonal form).[19]

Studies on the thermal behaviour of both the needle-shaped and the spherical carbonate particles showed features similar to those observed for other lanthanum carbonates such as $La_2(CO_3)_3{\cdot}8H_2O$,[13] $La_2(CO_3)_3{\cdot}1.4H_2O$[15] $La_2(CO_3)_2(OH)_2{\cdot}H_2O$,[16] $La_2(CO_3)_3$,[20] *etc.* The above mentioned carbonates decompose to La_2O_3 through the intermediate, $La_2O_2CO_3$, as in the present study. Also, the decomposition temperatures corresponding to individual steps are approximately similar. The broad exothermic peak at *ca.* 300 °C observed in the DSC pattern of the needle-shaped carbonate particles has also been observed in the DTA pattern reported for $La_2O(CO_3)_2{\cdot}1.4H_2O$.[13] This peak has been ascribed to the formation of anhydrous monooxo carbonate.

The IR spectra of the synthesised carbonates (Fig. 8) showed a broad band at *ca.* 3400 cm^{-1}, which can be attributed to the stretching mode of hydroxy groups of bound water molecules. Also, a band at *ca.* 1400 cm^{-1} was observed, which is assigned to the bending vibrational mode of bound water molecules. The IR spectrum provided evidence for the presence of carbonate ions in both the samples. The absorption band at *ca.* 1481 cm^{-1} had been attributed to the ν_3 mode of the CO_3^{2-} ion. The other bands at *ca.* 1071, 850 and 725 cm^{-1} had been assigned to the ν_1, ν_2 and ν_4 modes of the carbonate ion, respectively.[21] The infrared spectra of needle-shaped as well as spherical carbonate samples showed multiple splitting of all the modes of the carbonate ion. The splitting was found to be more prominent in the case of the needle-shaped particles. This must be caused by various carbonate ions situated at crystallographically non-equivalent sites. Also, the IR spectrum of the spherical particles showed differences in the intensities of the bands due to the carbonate ions when compared to those of the needle-shaped carbonate particles. The above interpretation of the IR spectral results is based on the assumption that the synthesised carbonates are essentially pure materials. However, minor

Fig. 7 TEM pictures of the heat-treated lanthanum carbonate samples: needle-shaped carbonate particles heated at (a) 550 °C and (b) 725 °C; spherical carbonate particles heated at (c) 550 °C and (d) 725 °C.

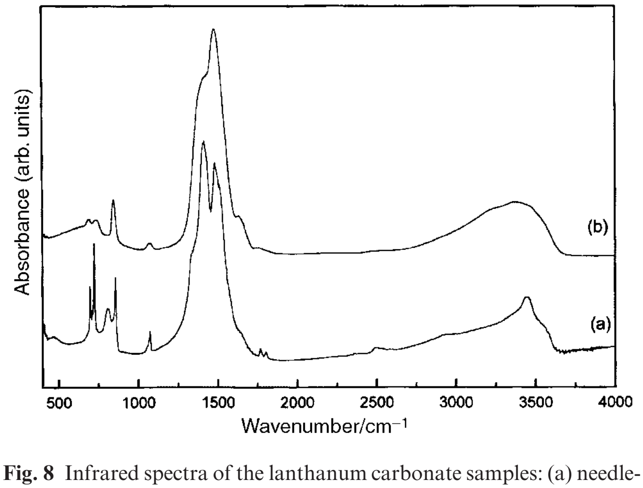

Fig. 8 Infrared spectra of the lanthanum carbonate samples: (a) needle-shaped and (b) spherical carbonate particles.

impurities such as $La_2CO_3 \cdot 8H_2O$, $La_2O(CO_3)_2 \cdot H_2O$, $La_2(CO_3)_2(OH)_2 \cdot H_2O$, *etc.*, which were not detected in the powder XRD measurements, may contribute to some of the observed spectral features.

The role of urea in the homogeneous precipitation of lanthanum carbonate particles is that urea decomposes by hydrolysis homogeneously in the solution upon heating, producing CO_2 gas, OH^- and NH_4^+ ions in the solution. This increases the pH of the medium, depending on the temperature, in a controlled manner.[18] This increase of pH is suitable for the formation of lanthanum carbonate particles. Measurement of the pH before and after the sonication experiment revealed that the pH of the solution increased from 5.2 to 6. The utilization of ultrasound radiation during this homogeneous precipitation process can accelerate the process and can also be beneficial for controlling particle size and shape.

We now consider the mechanism by which the needles of lanthanum carbonate particles are formed. The effects of ultrasound radiation on chemical reactions are due to the very high temperatures and pressures that develop during the sonochemical cavity collapse by acoustic cavitation. There are two regions of sonochemical activity, as postulated by Suslick *et al.*:[22,23] 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, as is the case for transition metal carbonyls in organic solvents, the temperature inside the cavitation bubble can be from 5100 to 2300 K depending on the vapour pressure of the solvent.[22] If water is used as the solvent, the maximum bubble core temperature that can be attained is close to 4000 K.[24] The product obtained in this case will be amorphous as a result of the high cooling rates ($>10^{10}$ K s^{-1}) reached during collapse. On the other hand, if the reaction takes place at the interface, where the temperature has been measured to be 1900 K,[22] one expects to get nanocrystalline products. If the solute is ionic, and hence 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. Since in the present study the solute is ionic, and we get nanocrystalline lanthanum carbonate particles, we propose that the formation of needles of the carbonate particles occurs at the interface between the bubble and the liquid.

The growth of spherical carbonate particles during the thermal synthesis can be explained by an aggregation mechanism in which aggregation of nuclei occurs to form spherical particles.[25] This suggests an amorphous growth process and the product is indeed amorphous as shown by the powder X-ray diffraction studies.

5 Conclusions

The use of ultrasound irradiation in the synthesis of lanthanum carbonate particles by homogeneous precipitation has a remarkable effect on the morphology of the particles produced. Needle-shaped lanthanum carbonate particles were found to be formed in the presence of ultrasound irradiation, whereas in the absence of ultrasound irradiation, the particles were found to have spherical morphology. The utilization of ultrasound irradiation is one of the ways in which to synthesise particles with controlled morphologies and this method may be potentially useful to other systems also employed to produce materials with novel morphologies.

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