The effect of heating on the morphology of crystalline neodymium hydroxycarbonate, NdCO$_3$OH

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ABSTRACT

The crystallization of hexagonal NdCO$_3$OH through hydrothermal synthesis carried out at slow (reaching the desired temperature within 100 min) and quick (50 min) rates of heating but at variable temperatures (165–220ºC) are reported here. The formation of NdCO$_3$OH occurs via the crystallization of an amorphous precursor. Both the precursor and the crystalline NdCO$_3$OH were characterized by X-ray diffraction, infrared spectroscopy and high-resolution electron microscopy. The mechanism of crystallization is very dependent on the experimental conditions (rate of heating and temperature treatment). With increasing temperature, the habit of NdCO$_3$OH crystals changes progressively to more complex spherulitic or dendritic morphologies. The development of these crystal morphologies is suggested here to be controlled by the level at which supersaturation was reached in the aqueous solution during the breakdown of the amorphous precursor. At the highest temperature (220ºC) and during rapid heating (50 min) the amorphous precursor breaks down rapidly and the fast supersaturation promotes spherulitic growth. At the lowest temperature (165ºC) and slow heating (100 min), however, the supersaturation levels are approached more slowly than required for spherulitic growth, and thus more regular, previously unseen, triangular pyramidal shapes form.

KEYWORDS: rare earths, neodymium, carbonate, crystallization, spherulitic growth, hydroxylbastnäsite.

Introduction

The formation of carbonate minerals plays a crucial role in controlling the global carbon cycle (Mackenzie and Andersson, 2013). Carbonate deposits have formed ubiquitously throughout the geological record and these are now often used for various industrial applications. Among the carbonate systems of interest, rare earth carbonates are of prime importance as they are the main source for the much sought after rare earth elements (REE) in the modern industrial world. Among REE carbonates, specifically hydroxycarbonates, REECO$_3$(OH), constitute the most important group of REE compounds that are highly valued for a plethora of industrial processes such as automotive, ceramics, oil, metallurgy, high-performance luminescent devices, magnets, etc. (Adachi and Imanaka, 1998; Castor and Hedrick, 2006). Two

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REECO$_3$(OH) polymorphs (orthorhombic and hexagonal) have been described, with the hexagonal polymorph of the neodymium hydroxy carbonate occurring in REE deposits as the mineral hydroxy bastna¨site (e.g. Bayan Obo deposit, China; Zhongxin et al., 1992). Nd-hydroxy bastna¨site [NdCO$_3$(OH)] is believed to form through hydrothermal reactions with sedimentary carbonate rocks, yet a mechanism for this process is still unknown (Miyawaki and Nakai, 1996). The interest in understanding the formation pathways of Nd-hydroxybastna¨site is also linked to its role in optical (e.g. lasers) and electronic (e.g. neodymium-iron-boron permanent magnets) applications (Chakhmouradian and Wall, 2012). Most previous studies addressed the NdCO$_3$(OH) structure (e.g. Christensen 1973; Michiba et al., 2011; Tahara et al. 2007) or its decomposition behaviour (Hinode et al., 1990) under hydrothermal conditions. Those studies, revealed that various synthesis conditions lead to hexagonal NdCO$_3$(OH) crystals with different morphologies (e.g. hexagonal prisms, dendrites or rodlike crystals; Michiba et al., 2011; Shang et al., 2009; Gai et al., 2014). Such morphologies play a key role in the physicochemical properties of many materials involved in technological advances in magnetic, electronic and optoelectronic devices (Gai et al., 2014; Li et al., 2013; Shang et al., 2009; Vallina et al., 2014). However, the factors that control the formation conditions or the possible morphologies of hexagonal NdCO$_3$(OH) are not well understood.

To address this, the present authors carried out hydrothermal crystallization experiments with the goal of producing hexagonal NdCO$_3$(OH) from a poorly ordered precursor. This was done at different rates of heating (slow and fast) and different temperatures (165–200°C) to evaluate the effects of these two parameters on the crystallinity and morphology of the hexagonal NdCO$_3$(OH) product. The morphologies of the resulting NdCO$_3$(OH) are proposed here to be a consequence of varying crystallization mechanisms that in turn are controlled by the degree of supersaturation after the breakdown of a poorly ordered Nd-carbonate precursor.

**Experimental**

Neodymium carbonates were synthesized by adding a 50 mm solution of NdCl$_3$·H$_2$O (Alfa Aesar, 99% purity) to a 50 mm Na$_2$CO$_3$ solution (Fisher Scientific, 99.9% purity) at room temperature (RT, 21°C). Immediately after mixing, a pink gel-like precipitate formed. Aliquots of this material were treated using four different hydrothermal treatment approaches. The hydrothermal crystallization reactions were carried out in Teflon-lined stainless steel (40 ml; Parr®) reactors in ovens at temperatures between 25 and 220°C and at saturated water-vapour pressures and all were reacted for 1 week. Two aliquots of the pink gel-like precursor (referred to hereafter as batches A and B) were aged in their native solution at 165 and 220°C. This was achieved by half filling a reactor at RT with pink gel, inserting into a preheated oven at the desired temperature and shaking the reactor manually every 20 min. Tests have shown that the desired temperature inside the reactors was reached within ~100 min (at 165°C) and ~50 min (at 220°C). The other two aliquots (batches C and D) were aged in their native solution at 220°C but using a different heating protocol, where the temperature was ramped to 220°C at a constant rate of 10°C/min. Batch D was ramped from 25 to 220°C, while batch C was inserted into an oven that was already preheated to 100°C and subsequently ramped to 220°C. Although the temperature ramps reached the desired temperature within 20 min, the temperature of the suspension inside the reactors in these two batches was reached more slowly. A schematic summary of all four experiments is shown in Fig. 1.

To characterize the initial pink gel and the final reaction products (after quenching to room temperature) sample slurries were vacuum filtered through 0.2 μm polycarbonate membranes, washed with water and isopropanol following Rodriguez-Blanco et al. (2008) and dried at RT. The resulting solids were characterized by powder X-ray diffraction (XRD; Bruker D8 diffractometer; CuK$_a$1; 10–75°2θ; 0.005°/step and 0.1 s/step), Fourier transform infrared (FTIR) spectroscopy (A2 Technologies MicroLab spectrometer; spectra collected between 650 and 4000 cm$^{-1}$; 4 cm$^{-1}$ resolution and by co-adding 1024 scans). Furthermore, all solids were imaged and analysed using a field emission gun scanning electron microscope (FEG-SEM, LEO 1530 Gemini, operated at 3 kV and with an in-lens detector and a FEG-transmission electron microscope, FEG-TEM; FEI CM200; operated at 197 kV).

The saturation index (SI) with respect to the crystalline solids was calculated using the computer code PHREEQC (Parkhurst, 1995, using the LLNL database) and is defined as the
The ratio between the ionic activity product (IAP) of the dissolved ions and the solubility product of the solid phase ($K_{sp}$):

$$SI = \log \frac{IAP}{K_{sp}}$$

Taking equation 1 into account, the saturation index (SI) is positive when the solution is supersaturated with respect to the solid phase, and negative when it is undersaturated.

**Results and discussion**

The FEG-TEM images of the initial pink gel-like phase revealed roughly spherical nanoparticles with diameters of between 10 and 20 nm (Fig. 2a) and with few to no lattice fringes visible. Powder XRD patterns of the gel contained only three broad humps centred at ~20, 30 and 45º2θ indicating that the gel was poorly crystalline (Fig. 2b). The FTIR spectra (Fig. 2c) confirmed the carbonate (bands between 1450 and 680 cm⁻¹), highly hydrated (broad band at ~3000 cm⁻¹), and poorly ordered nature of the Nd-carbonate gel (lack of peak at 725 cm⁻¹; for a similar pattern for a Dy-carbonate gel see Vallina et al., 2013).

Upon hydrothermal treatment, this amorphous phase transformed to a crystalline material the XRD pattern of which matched in all cases that of hexagonal neodymium hydroxycarbonate, NdCO₃OH ($a = 12.3579(11)$ Å and $c = 9.9025(9)$ Å; Fig. 2d). The FEG-SEM images of the final products revealed different morphologies, however, depending on the heating and temperature. The solids at the end of the reaction in batch A (165°C, normal heating, no controlled temperature ramp) exhibited regular, triangular pyramidal shapes with large individual crystals ~8 μm in diameter (Fig. 3a,b), while under the same heating regime but at 220°C in batch B (normal heating, no controlled temperature ramp), cauliflower-like aggregates (up to 25 μm in diameter) were observed. These cauliflower-like aggregates had very complex micro-textures and were made up of small crystal subunits that were <500 nm in size (Fig. 3c,d). When the initial amorphous precursor gel was heated from 100 to 220°C through a 10°C/min temperature ramp (batch C), the resulting morphologies were different again. Spine-shaped aggregates between 10 and 25 μm in size consisting of subunits 1–5 μm long were formed (Fig. 3e,f). Finally, when the suspension was heated from RT to 220°C with a 10°C/min ramp (batch D) the end product consisted of long fishbone-shaped morphologies (up to 25 μm long) but again consisting of subunits with crystals of <1 μm (Fig. 3g,h).

The data above show clearly that in the 220°C experiments, even small differences in heating procedures led to significantly different morphologies for the resulting hexagonal NdCO₃(OH) crystals. In addition, the present study is the first to report triangular pyramids and spine shapes for the highly crystalline hexagonal NdCO₃OH. In contrast the fishbone and cauliflower morphologies (although somewhat different in terms of dimensions) are similar to those reported by Shang et al. (2009) who synthesized fishbone or cauliflower NdCO₃OH much more quickly using an hydrothermal synthesis at 220°C over a period of 6 h. Such shape differences are important, as idiomorphic, well developed crystals of hexagonal NdCO₃OH are of interest for use in modern optical technologies (Li et al., 2013).

Our experiments show that NdCO₃OH develops the more regular morphologies at...
lower temperatures and the slowest rate of heating (165°C, 100 min; batch A). At the highest temperature (220°C) and with a higher rate of heating (85°C/50 min; batches B–D) the resulting NdCO₃OH morphologies were dendritic and similar to those of Shang et al. (2009) or similar to spherulitic crystal aggregates reported for other carbonate systems (e.g. calcium carbonates — Sand et al., 2012; Bots et al., 2012 and references therein; calcium phosphate — Teshima et al., 2009; and lanthanum carbonates — Sadhu et al., 2014). Spherulites, as observed in our experiments (Fig 3c,d and e,f), are most often interpreted as a result of continuous nucleation of new particles with random orientations (Shtukenburg et al., 2012). Such processes also require high levels of supersaturation throughout the whole crystallization reaction (e.g. Beck and Andreassen, 2010; Bots et al., 2012). In our experiments, supersaturation levels at 220°C could not be calculated because no solubility data for crystalline NdCO₃OH or the amorphous precursor exists in the literature. However, solubility data for the crystalline neodymium lanthanite (Nd₂CO₃·8H₂O) is only available at 25°C (Essington and Mattigod, 1985) and no solubility data for hexagonal Nd-hydroxylbastnäsite are available. The solubility data for Nd₂CO₃·8H₂O are used here as a proxy for hexagonal Nd-hydroxylbastnäsite. This analogy is justifiable because of the processes observed here compared with those in other carbonate systems (e.g. CaCO₃) where equivalent reactions prevail (Rodriguez-Blanco et al., 2011; Bots et al., 2012). The saturation index, SI (equation 1), for neodymium lanthanite (Nd₂CO₃·8H₂O) at 25°C is SIₙd-lanth = 11.01. As with many other carbonates (Plummer and Busenberg, 1982) it is expected that the solubility of Nd₂CO₃·8H₂O will decrease with temperature and thus by analogy with other systems, leads us to assume that the SI of the present crystalline NdCO₃OH will also increase with temperature and thus, at 220°C, the likely SIₙd-hyrbast will be >11.01. Such high SI

Fig. 2. (a) TEM image of the initial precursor showing spherical nanoparticles with diameters of between 10 and 20 nm; (b) XRD pattern of the gel-like precursor showing its amorphous character; (c) FTIR profile of the precursor showing bands corresponding to water and carbonate vibrations; and (d) pattern-matching refinement of the XRD pattern of the final end product indexed as hexagonal NdCO₃(OH).
values are typical for systems where spherulitic growth prevails (Shtukenberg et al., 2012). Such growth often leads to cauliflower-like or dendritic shapes during the breakdown and crystallization of the amorphous precursor (e.g. Sand et al., 2012; Bots et al., 2012; Saharay, 2013) and such breakdown reactions are often also highly temperature-dependent (e.g. for Dy-carbonate; Vallina et al., 2013). Current data on the crystallization of hexagonal NdCO$_3$OH also imply that as well as the reaction temperature, a second important parameter is the rate of heating. Higher heating

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<th>Batch A</th>
<th>Preheated oven at 165°C</th>
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<th>Batch D</th>
<th>Ramp from 21 to 222°C</th>
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Fig. 3. FEG-SEM images of NdCO$_3$(OH) produced via the four different hydrothermal treatments. The habits are changing as a function of the experimental conditions. (a,b) Triangular pyramid shapes obtained from batch A; (c,d) cauliflower-type morphologies obtained from batch B; (e,f) spine-shaped aggregates developed with batch C; (g,h) fishbone (dendritic) morphologies obtained with a heating ramp from 21 to 220°C (Batch D).
Conclusions

A reproducible hydrothermal synthesis method to control the morphologies of hexagonal NdCO$_3$OH has been demonstrated. The development of crystals of variable size and of simple or complex morphologies of NdCO$_3$OH (i.e. small crystals of variable size and of simple or complex shapes) is not suitable for inducing a quick breakdown of the amorphous precursor and in this experiment the supersaturation with respect to hexagonal NdCO$_3$OH was approached more slowly and thus the growth of the NdCO$_3$OH crystals was slower, leading to larger, more isometric crystals.

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