

Crystalline lanthanum hydroxycarbonates with controlled phases and varied morphologies prepared on non-crystalline substrates

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Abstract

Lanthanum hydroxycarbonate crystals with controlled phases and varied morphologies were prepared on the surface of a non-crystalline substrate, glass. The phases and morphologies of the crystals were controlled conveniently by varying the reaction temperature and the quantity of starting materials. Orthorhombic crystals were obtained at 160 °C, distributed individually on the substrate and had a flaky rhombic shape. Hexagonal crystals were obtained at 180 °C. The crystals had a rhomboidal shape, were uniform and continuous enough to form a solid film on the substrate. The substrates were corroded under the hydrothermal conditions and offered a coarse surface for the crystal growth. The hexagonal lanthanum hydroxycarbonate was discovered to show significant second harmonic generation, which would be of interest for developing novel optical materials.

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1. Introduction

Rare earth hydroxycarbonates are common products when rare earth oxides are exposed to air. The hydroxycarbonates had been viewed as an undesirable component in lanthanum oxide catalysts as they could deactivate the catalysts. Therefore, much efforts have been made in trying to remove or avoid the hydroxycarbonate [1,2]. But as early as 1978, the solids were studied as a type of useful inorganic materials, for instance, cerous hydroxycarbonate was proposed as a potential hydrogen producing species in the closed thermochemical cycles for water-splitting [3]. Since then, rare earth hydroxycarbonates have been increasingly used for many purposes, such as matrixes for luminescence materials [4], and precursors for oxide phosphor materials [5–7]. Recently, we measured spectroscopic properties of cerous hydroxycarbonate and found that

the solid shows photoluminescence around 373 nm [8], which matches very well with the spectral sensitivity curve of general insects in near-ultraviolet region [9]. Accordingly, if the hydroxycarbonate is used as a black light material, its emission at 373 nm will be attractive to general insects and therefore is potentially interesting for insect control. Also, we found the crystals of different phases and morphologies could display varied photoluminescence intensity [8,10]. Therefore, preparing the rare earth compounds with controlled phases and morphologies, and providing candidates materials for extensive measurement of their various physical properties, will be of great importance for developing materials with optimal performance for specific applications.

Lanthanum hydroxycarbonate (LaOHCO₃) is a typical member of the rare earth hydroxycarbonates family. Previous study has demonstrated that bulk rare earth hydroxycarbonate generally remains stable up to 700 °C [11], therefore the solid has a good thermal stability. Over the past few years people have prepared particles of such rare earth compounds [12–14]. In the work

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reported here, we managed to prepare LaOHCO_3 on a substrate, aiming to obtain solid films with varied phases and morphologies. The samples were characterized by various techniques, and some preliminary but interesting properties were discovered.

2. Experimental section

Lanthanum chloride heptahydrate ($\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, A.R. 99%, Aldrich Chemicals Company Inc., USA) and thiourea (A.R. 99.0%, BDH Chemicals Ltd., England) were used as starting materials to LaOHCO_3 , and common $18 \times 18 \text{ mm}^2$ glass cover slips provided non-crystalline substrates for the crystal growth. The preparation was conducted under hydrothermal conditions in a Teflon-lined stainless steel autoclave with a total volume of 25 ml. The glass substrates were ultrasonically treated by dilute nitric acid and then by ammonia solution, and finally rinsed by deionized water before use. The substrate was set vertically into the autoclave first; the $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and an appropriate amount of thiourea were dissolved in deionized water, and the solution was then poured into the autoclave. More water was added to make the substrate submerged into the solution and total volume of solution in the reaction vessel was about 20 ml. Subsequently, the hydrothermal process was allowed to proceed at a given temperature for 6 h. After reaction, the autoclave was cooled down to ambient temperature, and the substrate deposited with solids was collected and rinsed by deionized water. A series of samples were prepared from the reactants of different amounts and varied temperatures, maintaining the same volume and following the same procedure.

The samples were characterized at room temperature. X-ray diffraction (XRD) was conducted on a Shimadzu XRD-6000 X-ray diffractometer. Scanning electron microscope (SEM) images and energy dispersive spectra (EDS) were taken on a Philips XL30 CP scanning microscope. Second harmonic generation effects of typical samples were examined by a Leica TCS MD multi-photon microscope. The microscope was equipped with a Coherent Mira titanium sapphire laser, which produced 150 fs pulses at 830 nm with an average powder of 300 mW; a 415/10-nm narrow bandpass filter was applied to exclude fluorescent signals.

3. Results and discussion

A LaOHCO_3 crystal could have two polymorphs, the orthorhombic one and the hexagonal one. Using 2 mmol of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and 8 mmol of thiourea as reactants, the two polymorphs of this solid were controlled by simply varying the reaction temperatures. Fig. 1 shows XRD

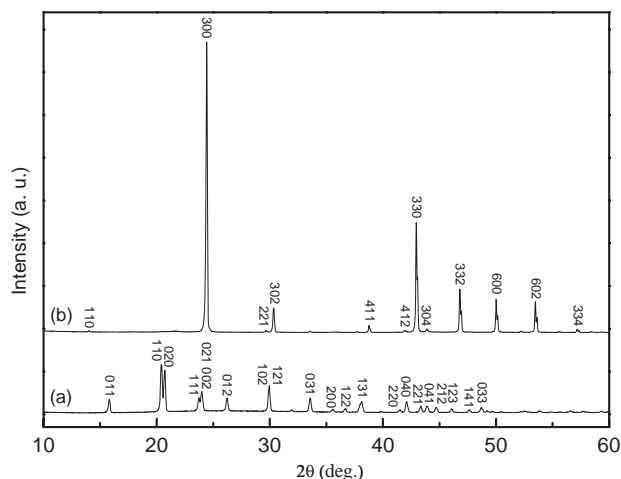


Fig. 1. XRD patterns of LaOHCO_3 crystals grown on non-crystalline surfaces using 2 mmol of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and 8 mmol of thiourea at different temperatures: (a) orthorhombic phase, 160 °C, and (b) hexagonal phase, 180 °C.

patterns of the samples of different phases, the sharp diffraction peaks demonstrate that both samples are well crystallized on the non-crystalline substrate of the substrates. The sample prepared at 160 °C is indexed as orthorhombic LaOHCO_3 (JCPDS Database #49-981: $a=5.033$, $b=8.598$, $c=7.401 \text{ \AA}$), while the sample prepared at 180 °C is indexed as hexagonal LaOHCO_3 (JCPDS Database JCPDS #26-815: $a=12.61$, $c=10.02 \text{ \AA}$). No impurity peaks are observed in the diffraction, so the solids of the two single phases are in good purity. Using the reactants of a different relative amount, for instance, 2 mmol of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and 6 mmol of thiourea, the solid produced at 160 °C is also orthorhombic LaOHCO_3 , while that produced at 180 °C is predominated by hexagonal LaOHCO_3 . The results demonstrate that a moderate lower temperature (160 °C) is favorable for the crystal growth of orthorhombic LaOHCO_3 , whereas a higher temperature (180 °C) is favorable for the crystal growth of hexagonal LaOHCO_3 on the substrate. This trend is same as that in the preparation of CeOHCO_3 , in that case the solids of orthorhombic and hexagonal phases were obtained at a lower temperature and a higher temperature, respectively [8,15].

The relative amount of the reactants was found to affect the results. Keep the quantity of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ to be 2 mmol, when temperature is 160 °C, the sample produced using different amounts of the reactants show varied crystallinity. Compared with the diffraction hump around 25° of the glass substrate in Fig. 2(a), there is a small peak at 20.7° in the XRD pattern of the sample prepared using 4 mmol of thiourea, shown in Fig. 2(b), the peak belongs to the 020 diffraction of the orthorhombic LaOHCO_3 phase, which suggests the phase is poorly crystallized and the particle size is small.

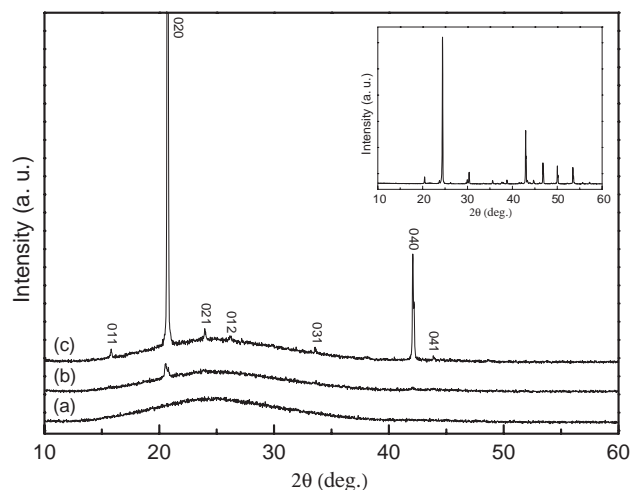


Fig. 2. XRD patterns of (a) a glass substrate, (b) orthorhombic LaOHCO_3 on glass prepared at 160°C using 2 mmol of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and 4 mmol of thiourea, and (c) orthorhombic LaOHCO_3 on glass prepared at 160°C using 2 mmol of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and 6 mmol of thiourea. The inset shows the orthorhombic and hexagonal mixed phases prepared at 180°C using 2 mmol of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and 6 mmol of thiourea.

In comparison, the sample produced using 6 mmol of thiourea shows the 020 diffraction peak of much higher intensity, as shown in Fig. 2(c), which is indicative of an improved crystallinity. The presence of the diffraction hump of the glass substrate, however, reveals the crystals are sparse and/or very thin on the glass, since they are not able to mask the diffraction of the substrate. When the temperature is 180°C , the solid prepared using 6 mmol of thiourea at the same temperature is different from that produced from 8 mmol of thiourea. It is composed of two phases rather than a single hexagonal phase, as demonstrated by the inset in Fig. 2, although the hexagonal phase predominated in the solid. From these results, it can be seen that, changing the amount of reactant, like that changing the reaction temperature, can also be a measure to control the phases of the LaOHCO_3 solids on the glass substrates.

In a closed reaction system, a higher pressure tends to make a crystal grown adopt a more compact stacking [16]. In this work, the higher temperature applied to the aqueous solution resulted in a higher pressure, and an increased amount of thiourea would also result in a higher pressure due to more gases produced by thermal decomposition of the thiourea [17]. As a consequence, a higher temperature leads to hexagonal LaOHCO_3 crystals, while a lower temperature and/or less thiourea lead to orthorhombic LaOHCO_3 crystals in the closed hydrothermal system. The influence factors, however, are not just the reaction temperature and the relative amount of the starting materials. Double the quantity of the two reactants, use 4 mmol of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and 16 mmol of thiourea for an experiment, the sample

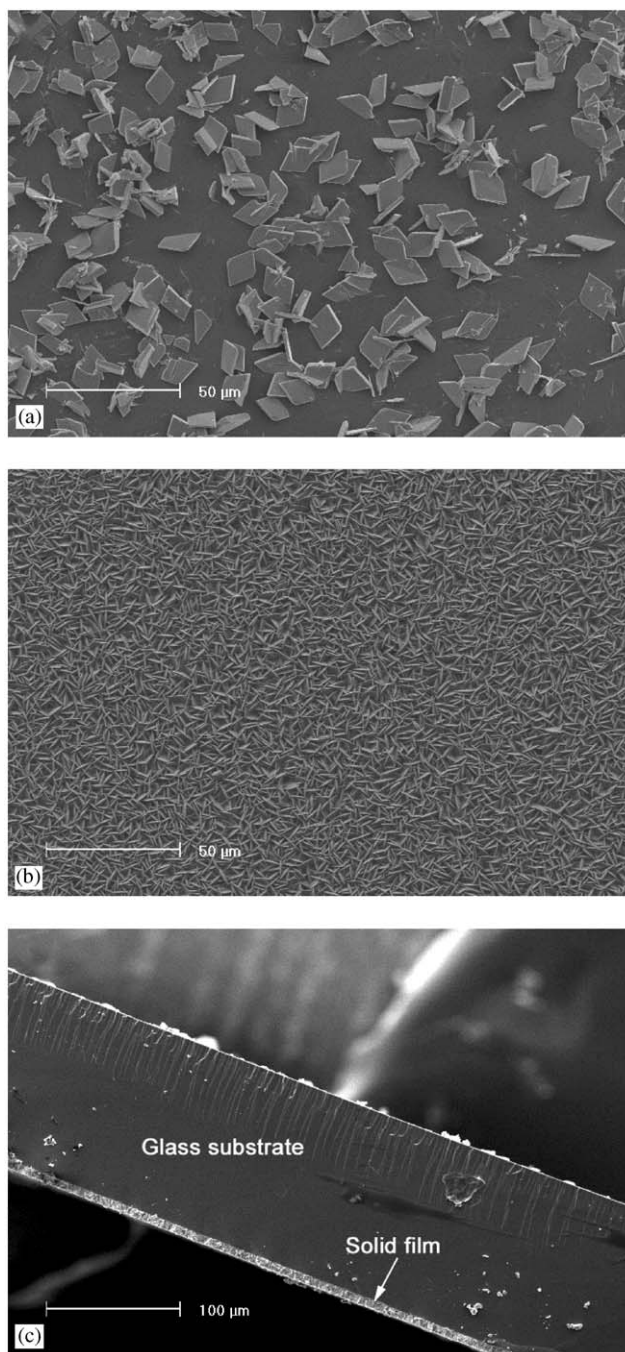


Fig. 3. SEM images of (a) orthorhombic LaOHCO_3 crystals on glass, (b) hexagonal LaOHCO_3 crystals on glass, and (c) the cross section of the hexagonal LaOHCO_3 film on glass.

prepared at 180°C was composed of two phases, rather than a single hexagonal phase. This suggests that the absolute concentration of the reactants influences the polymorph of the crystals as well, presumably by means of kinetics of the crystal growth on the substrate under the hydrothermal conditions.

It should be pointed out that one of the reactants, the thiourea, is vital to successful preparation of LaOHCO_3 on glass. A similar reagent, urea, seems to be a better

reactant for the production of LaOHCO_3 on the glass as it does not bring sulfur species that possibly contaminate the product or lead to bulk sulfate impurities. However, using the urea as an alternative reactant in our experiments failed to prepare the compound on the glass substrate. We think, maybe just owing to sulfur species contained in the thiourea, that make the LaOHCO_3 crystals grow on the non-crystalline glass. The intermediates derived from thiourea during the hydrothermal process could facilitate the crystal growth on the substrate by a yet unknown mechanism. When using thiourea as the reactant, it is possible to produce a sulfate solid in the final product, but this normally happens when the hydrothermal temperature is above 200°C [17]. By manipulating the appropriate hydrothermal temperature, one can make the LaOHCO_3 on the glass while avoiding sulfate solid impurities, as has been demonstrated by our examples, whose XRD patterns are presented in Figs. 1 and 2.

The LaOHCO_3 has a good adhesion to the substrate. Even when rubbed forcibly by hand, the solid is not removed from the substrate. The crystals on the substrate were examined by electron microscopy. Fig. 3 displays SEM images of typical samples. It shows the crystals of different phases on the substrates have varied morphologies. The orthorhombic LaOHCO_3 crystals are generally flaky, and a regular flaky crystal is rhombic and has an edge length of about $8\ \mu\text{m}$; but as revealed by Fig. 3(a), the rhombic crystals distribute randomly and separately on the substrate. In contrast, the hexagonal LaOHCO_3 crystals on the substrate are rhomboidal, and the average length of the rhomboidal crystals is $6\ \mu\text{m}$. The crystals distribute continuously on the substrate and obviously construct a uniform solid film, which is confirmed by Fig. 3(b). The interface between the film and the substrate was observed as well. Fig. 3(c) shows the cross-section of the hexagonal LaOHCO_3 film, it further demonstrates the film is pretty compact and uniform on the glass, and the thickness of the film is about $8\ \mu\text{m}$.

Despite the big contrast between the orthorhombic LaOHCO_3 crystals and the substrate, one cannot decide whether there is a very thin crystal layer under the large

rhombic crystals without relevant elemental analysis. To clarify this, electron microanalysis was conducted to detect the composition of the larger crystals and the background on which they are grown. Fig. 4 shows a SEM image of an orthorhombic sample with a bigger magnification, and EDS of a flaky rhombic crystal and of the substrate background are accompanied to the image. On the rhombic crystal, besides the Pt, a conductive coating material introduced for SEM characterization purpose, there are mainly La, C and O elements, which arguably demonstrate the crystal is a LaOHCO_3 crystal. Also, there are no obvious peaks of impurities, which are in agreement with the XRD results. On the background, besides the Pt, there are mainly Si, O, Na, K, Al and Ti elements, but no evident La. Given the reactants used in the experiments, the elements are totally ascribed to the glass substrate.

The glass, used to be smooth on the surface, however, apparently becomes coarse after deposited with the LaOHCO_3 crystals. This is especially evident when less thiourea used for the preparation, in those cases, the surface becomes so coarse that some lines and islands protrude on the substrate. Such a change suggests the substrate is not inert in the hydrothermal system, the common glass used here may be corroded to get a coarse surface, similarly, the pyrex glass also undergoes a change on the surface under hydrothermal conditions [18,19]. This way, some unbonded sites could be exposed on the surface of the glass so as to share electrons with other groups in the solution, and could be favorable for the crystal growth on the non-crystalline substrate. Referring to the crystalline hexagonal LaOHCO_3 film discussed above, one can think such a coarse surface might have facilitated the crystal growth of LaOHCO_3 to form a compact film on the substrate.

The distinct morphologies of the crystals are undoubtedly ascribed to the nature of crystal growth. In addition, the effect of the substrate to the crystal morphology was investigated by a contrast experiment conducted at 180°C : using $4\ \text{mmol}$ of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and $16\ \text{mmol}$ of thiourea without introducing a substrate to produce LaOHCO_3 particles and comparing their

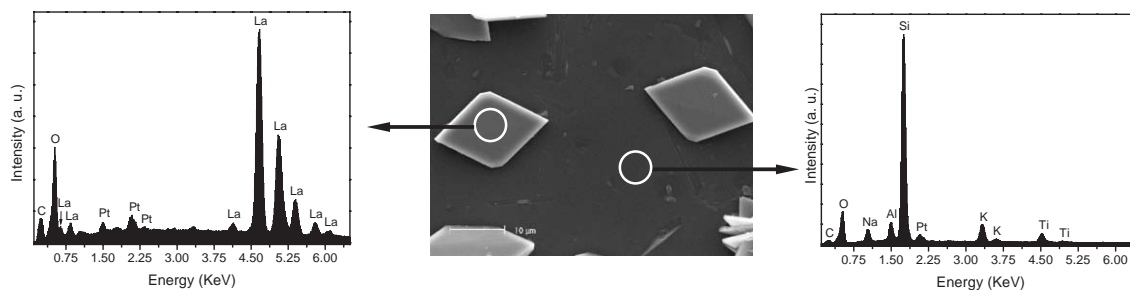


Fig. 4. SEM image of an orthorhombic LaOHCO_3 sample with a bigger magnification (middle), and EDS of a flaky crystal (left) and of the substrate on which the crystals are grown (right).

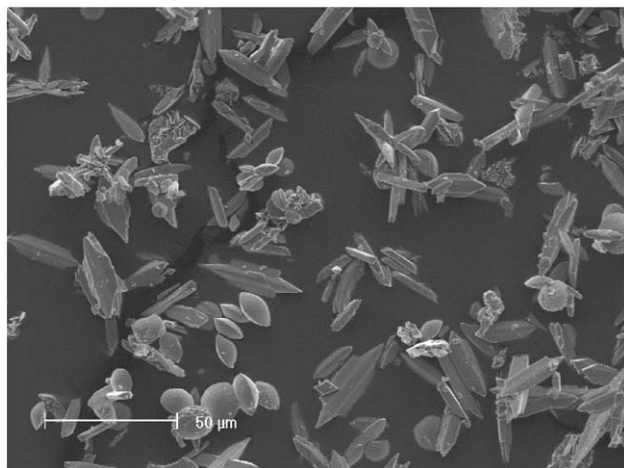


Fig. 5. SEM image of LaOHCO₃ powders of two phases hydrothermally prepared using 4 mmol LaCl₃ · 7H₂O and 16 mmol thiourea at 180 °C.

morphologies to those of the crystals on the substrates. Fig. 5 shows SEM image of the particles obtained. The LaOHCO₃ particles are composed of prismatic crystals and discoid crystals, supposedly corresponding to above-discussed flaky crystals and the rhomboidal crystals, respectively. The difference in the crystal morphologies demonstrates that the substrate can influence the morphology of the crystal grown on it.

The LaOHCO₃ samples were measured for second harmonic generation effects. Some typical second harmonic images are shown in Fig. 6. The orthorhombic polymorph prepared using less thiourea gives very weak second harmonic signals, as indicated by Fig. 6(a), because the very sparse and limited crystals on the substrate make very limited contribution to the second harmonic generation. For the well-developed orthorhombic crystals, brighter light spots are exhibited on the dark background of the substrate; and the light spots show an analogous shape to the rhombic crystals, as shown in Fig. 6(b), which are unambiguously owing to the orthorhombic LaOHCO₃ crystals. In contrast to the orthorhombic crystals on the substrate, the hexagonal polymorph gives much stronger second harmonic generation, and the shape of bright spots is also analogous to that of the rhomboidal crystals, as demonstrated by Fig. 6(c). Compared with the noncentrosymmetric hexagonal polymorph, the orthorhombic polymorph shows much weaker second harmonic generation, caused by its specific symmetry. The orthorhombic polymorph so prepared are centrosymmetric and normally not able to cause second harmonic generation; however, as every surface is noncentrosymmetric [20], so the surface could yield some second harmonic signals, this is consistent with that the orthorhombic crystals display weak signals only.

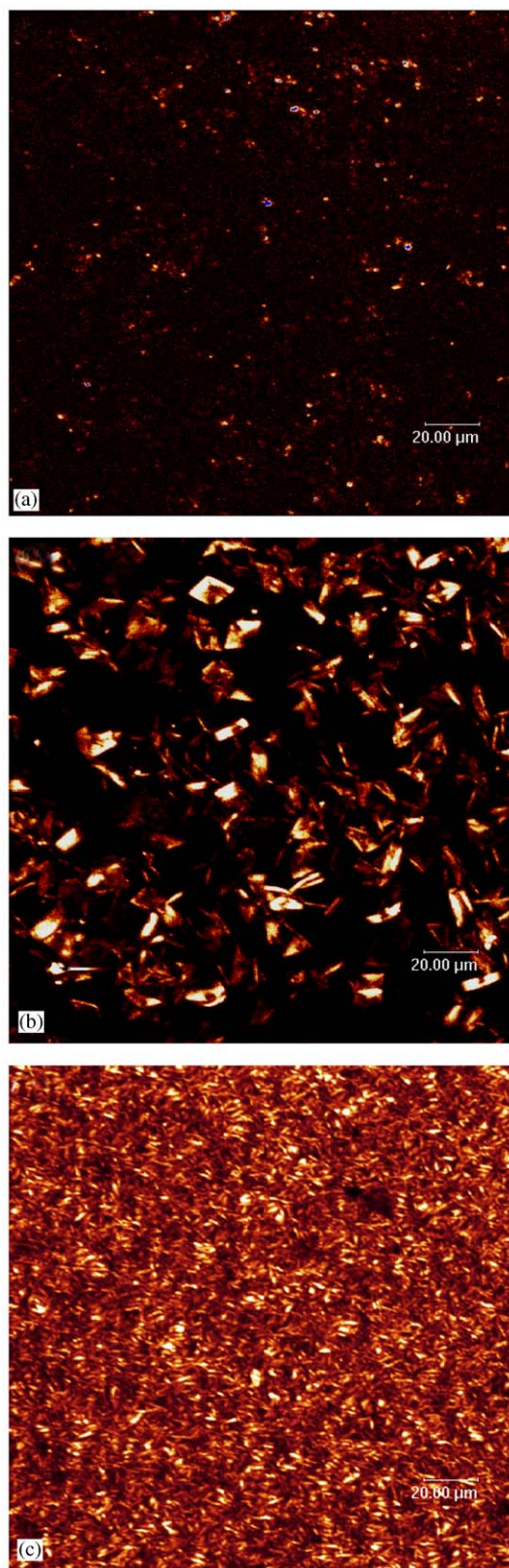


Fig. 6. Second harmonic images of (a) orthorhombic LaOHCO₃ crystals on glass prepared at 160 °C using 2 mmol of LaCl₃ · 7H₂O and 6 mmol of thiourea, (b) orthorhombic LaOHCO₃ crystals on glass prepared at 160 °C using 2 mmol of LaCl₃ · 7H₂O and 8 mmol of thiourea, and (c) hexagonal LaOHCO₃ crystals on glass prepared at 180 °C using 2 mmol of LaCl₃ · 7H₂O and 8 mmol of thiourea.

4. Conclusion

Crystallized LaOHCO_3 have been produced on the common non-crystalline substrates by a simple hydrothermal process. The crystals are of different phases and varied morphologies, dependent on the reaction temperature and the quantity of the starting materials applied for the preparation. The orthorhombic phase was obtained at a moderately lower temperature, whereas the hexagonal phase was prepared at a higher temperature. The orthorhombic crystals are flaky, and if well developed, adopt a rhombic shape; but the crystals grown on the non-crystalline substrate sparsely. The hexagonal crystals are rhomboidal, grown on the substrate continuously and uniformly, forming a compact solid film. The substrates were corroded and offered coarse surfaces for the crystal growth. The produced hexagonal LaOHCO_3 film was discovered to show significant second harmonic generation. The hydrothermal method that is effective to control over the phases and morphologies of LaOHCO_3 crystals on substrates will offer a strategy to realize the phase and morphology control of the rare earth hydroxycarbonate materials, which will be important for developing rare earth materials with novel applications.

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