

Effect of Heating/Cooling Rate on the Local Electronic Structure of Amorphous Calcium Carbonate

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Abstract

Here, the impact of heating/cooling rate was investigated on the formation of amorphous calcium carbonate (calcite) during sol-gel synthesis by probing local electronic structure. The amorphous calcium carbonate was synthesized by annealing precursor at 400°C at different heating/cooling rates i.e., 1.5 and 3°C /min. X-ray diffraction studies revealed amorphous nature at both heating/cooling rates. Fourier transformed infrared spectroscopic measurements characteristics bands in the spectra of both materials. Near edge X-ray absorption fine structure measurements at Ca *L*-edge, C *K*-edge and O *K*-edge were utilized to reveal the associated changes in the local electronic structure during synthesis. Local electronic structure investigation using near edge X-ray absorption fine structure measurements shows onset of moisture absorption on the surface particles when kept in the open environment.

Keywords- Amorphous calcium carbonate, Local electronic structure, Heating/cooling rate, NEXAFS, Stability.

1. Introduction

In recent years, there has been tremendous growth of research activities towards the synthesis of natural materials and understanding their growth behavior. One such material, which considerably attracts researchers, is amorphous calcium carbonate (ACC) (Page et al., 2022; Lázár et al., 2023). Though ACC exists in the form of microcrystal in the nature and is the most abundant material, but its formation in the form of amorphous nature has several issues. Thus, numerous strategies are being developed to synthesize ACC in the laboratory (Fadia et al., 2021; Niu et al., 2022) in order to overcome these issues. These studies envisage that synthesis of calcium carbonate is extremely sensitive to the method of treatment given during synthesis. Thus, our group has investigated the role of annealing temperature (Singh et al., 2016), precursor formation treatment on the structure/local electronic structure of amorphous and crystalline calcium carbonate by using near edge X-ray absorption fine structure measurements (NEXAFS) (Singh et al., 2017). The impact of heating/cooling rate has not been investigated so far.

Apart from synthesis, the stability of calcium carbonate has been an issue. Thus, the stability of these materials was investigated in different environments by numerous researchers (Sun et al., 2020; Wu et al., 2023). Our group has also extended X-ray absorption fine structure measurements (EXAFS) to probe local atomic structure using extended at various synthesis treatments and NEXAFS measurements to investigate the stability of synthesized calcium carbonate (Singh et al., 2020; Singh et al., 2021). The importance of these techniques, motivated our group to investigate the synthesis and stability of ACC critically. Since, a slight change in synthesis temperature can affect the phase of calcium carbonate, hence, effect of

heating/cooling rate was used as one parameter to synthesize these materials. Further, the local electronic structure of amorphous calcium carbonate for several ages from 0 to 60 weeks by keeping in the open environment.

2. Experimental Details

As like Figure 1, Materials are synthesized using a sol-gel approach by taking calcium nitrate as the starting material. Citric acid was used as the host. The details of the synthesis procedure are depicted in previous work from our group (Singh et al., 2016). The obtained precursor in the synthesis procedure was annealed at 400°C by utilizing two different heating and cooling rates viz 1.5°C/min and 3°C/min.

Amorphous Calcium Carbonate (ACC)

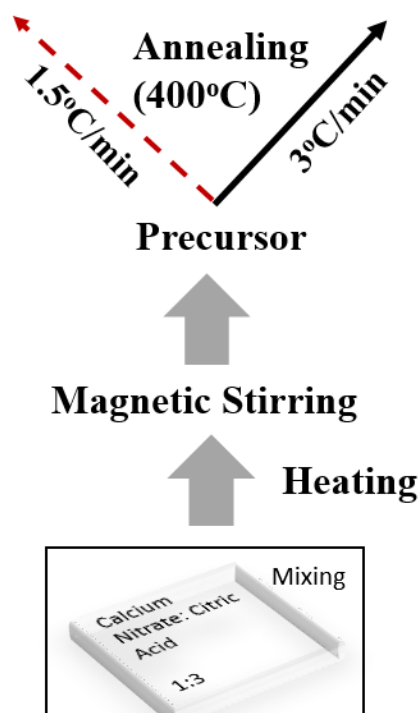


Figure 1. Synthesis route for amorphous calcium carbonate at different heating/cooling rates.

Materials after synthesis were characterized using Bruker D8 Advance X-ray diffractometer and Fourier Transform Infrared Spectrometer, Korea Institute of Science and Technology (KIST), Korea for the information phase. The local electronic structure of these materials was investigated using near edge X-ray absorption fine structure (NEXAFS) measurements at 10D KIST beamline, Pohang Accelerator Laboratory (PAL), Pohang South Korea. For these measurements, materials were mounted on copper plate with the help of Indium foil. NEXAFS spectra were recorded in energy ranges of 270-310 eV, 320-360 eV and 520-580 eV to get C *K*-edge, Ca *L*-edge and O *K*-edge spectra (Singh et al., 2016).

This copper plate containing both materials was kept in an open environment for the investigation of moisture related effects on these materials. These measurements were performed at O *K*-, C *K*- and Ca *L*-edge for different ages viz 4, 20 and 30 weeks (w).

3. Results and Discussion

Figure 2 shows the XRD patterns of synthesized materials. These patterns indicate the amorphous nature of calcium carbonate and reported by researchers working in the field. At higher heating/cooling rate, splitting in broad features (shown by arrow) is more visible compared to that of low heating/cooling rate. This effect may be ascribed to the initiation of crystallization at a high heating/cooling rate.

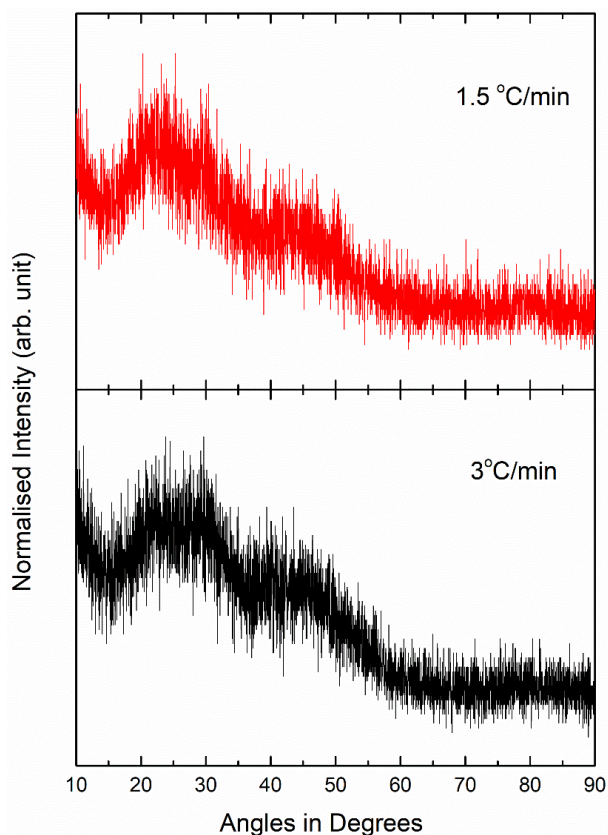


Figure 2. XRD patterns of synthesized materials showing amorphous nature of calcium carbonate at different heating and cooling rates.

Figure 3 shows the FTIR spectra of these materials synthesized at different heating and cooling rates. The broad band shown by the rectangular region and centered at 3383 cm^{-1} in the FTIR spectra of both materials is associated with O-H modes of water species or absorbed moisture from the environment (Seki et al., 2020). A major band having splitting centers at 1550 cm^{-1} and 1401 cm^{-1} is also observed in both spectra. This band is associated with C-O vibration of calcium carbonate. The presence of splitting in this band is characteristic of the amorphous nature of calcium carbonate. (Cai et al., 2010; Kiefer et al., 2018). A minor band can be clearly seen at 1079 cm^{-1} and is ascribed to the presence vaterite phase of calcium carbonate at both heating/cooling rate (Chakrabarty et al., 1999). Bands appearing in the region $1000\text{--}600\text{ cm}^{-1}$ are shown in Figure 4 for better visualization.

Bands at 864 cm^{-1} , 784 cm^{-1} and 636 cm^{-1} are well defined in the spectra of both materials. The presence of these bands is the characteristic of vaterite phase of calcium carbonate (Vagenas et al., 2003; Cai et al., 2010; Kiefer et al., 2018).

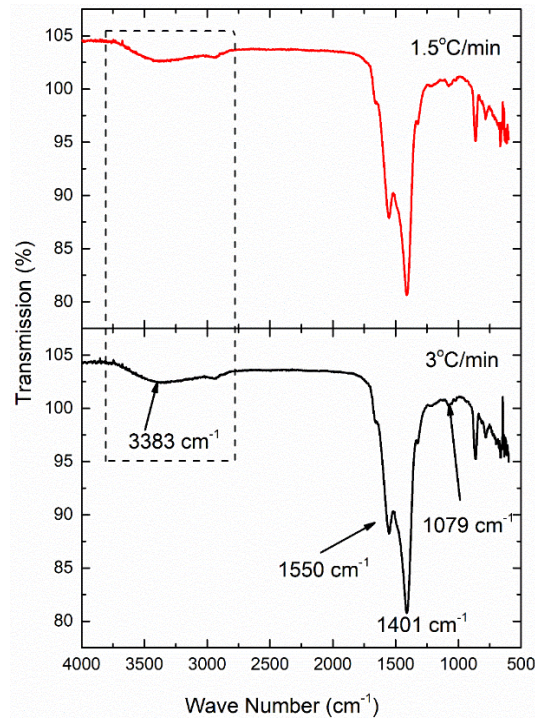


Figure 3. FTIR Spectra of amorphous calcium carbonate at different heating and cooling rates.

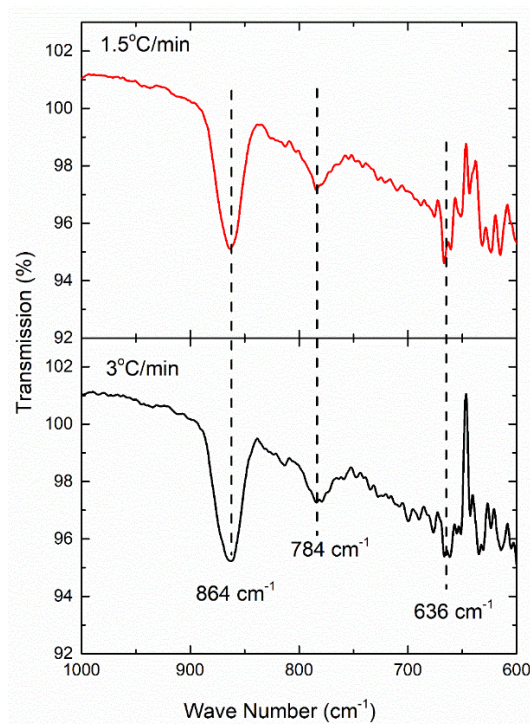


Figure 4. FTIR Spectra of amorphous calcium carbonate at different heating and cooling rates in wave number range 1000-600 cm^{-1} .

Figure 5 shows O *K*-edge Spectra of amorphous calcium carbonate materials at 4w, 20w and 30w. These spectra exhibit one structure in pre-edge region and two structures (shown by dotted lines) in post regions for a duration of 4w and 20w. Presence of such structures analogues to the formation of calcium carbonate in amorphous form. When these materials are kept in open environment for more longer duration (30w), the nature of O *K*-edge spectra modifies. Pre-edge region exhibits two structures- One centered at 534 eV (A_1) and second centered at 531.8 eV shown by arrow. Presence of second structure in the pre-edge region may be due to presence of oxygen adsorbed from the environment on the surface (Singh et al., 2018; Vogt et al., 2021) in the form of hydroxyls (Nagasaka et al., 2003; Kim et al., 2011). Post-edge region of these spectra also exhibits major changes and three distinct structures A_2 , A_3 and A_4 are clearly visible. These structures are analogues to that of crystalline calcium carbonate. Thus, the presence of short ranged crystalline order is expected after 30w of formation.

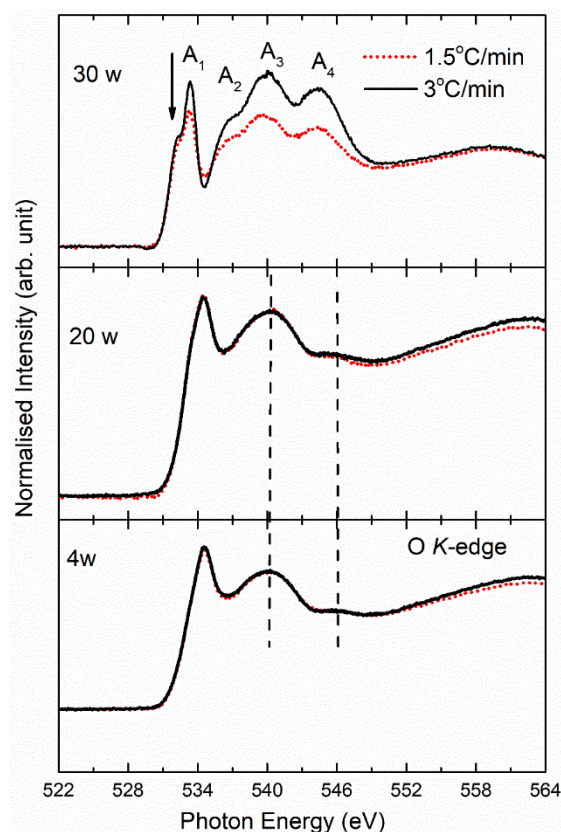


Figure 5. O *K*-edge Spectra of amorphous calcium carbonate at different heating and cooling rates measured for different durations.

In Figure 6, Ca *L*-edge spectra of synthesized amorphous calcium carbonate at different heating and cooling rates are shown. Spectral features B_1 , B_2 , B_3 and B_4 can be clearly seen for various durations in the spectra of both materials. These spectra do not exhibit changes with duration or another influence as there is no change in the coordination around Ca^{2+} ions (Shiraishi et al., 2020).

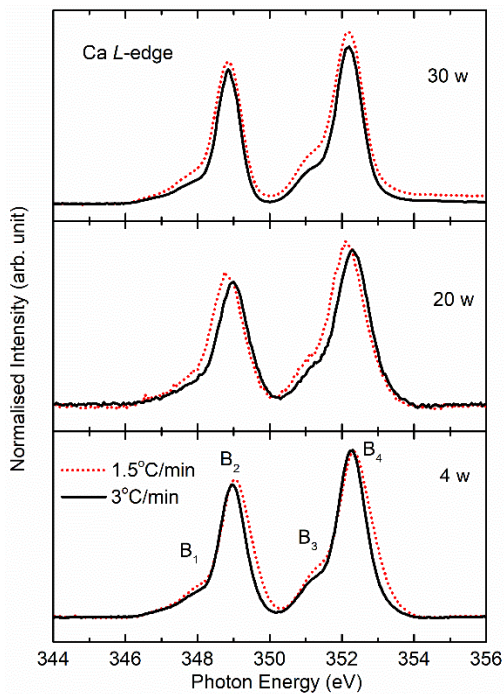


Figure 6. Ca *L*-edge Spectra of amorphous calcium carbonate at different heating and cooling rates measured for different durations.

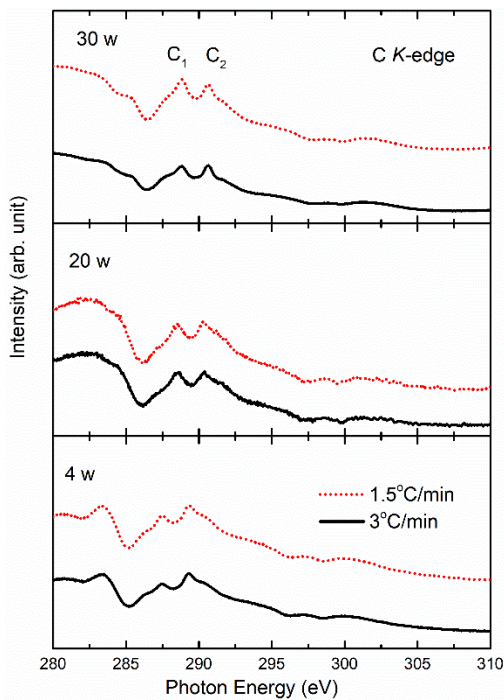


Figure 7. C *K*-edge Spectra of amorphous calcium carbonate at different heating and cooling rates measured for different durations.

Figure 7 shows the C *K*-edge spectra of amorphous calcium carbonate at different heating and cooling rate. These spectra show almost the same nature for all durations. The presence of spectral features C₁ and C₂ can be clearly seen in these spectra. This envisages that carbon ions after achieving a stable state do not alter in the system. Similar kinds of C *K*-edge spectra of calcium carbonate are also reported in the work by Singh et al. (2020) and Singh et al. (2021).

4. Conclusion

In the present work, amorphous calcium carbonate with calcite phase was synthesized successfully as observed from both the XRD and FTIR spectroscopic studies. It is observed that the amorphous phase exists at both heating/cooling rates. The Ca *L*-edge spectra do not exhibit significant changes if both materials are placed in the open environment for long durations. The O *K*-edge spectra of amorphous calcium carbonate are influenced with aging. Furthermore, these spectra are sensitive to both the heating/cooling treatments to the precursor.

Conflict of Interest

The authors confirm that there is no conflict of interest to declare for this publication.

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