

NON-AMBIENT FTIR STUDY OF THERMALLY TREATED SEASHELLS

**Cristina Mosoarca, Radu Banica, Raul Bucur,
Mihai-Cosmin Pascariu, Alexandra Bucur, Zoltan Szabadai***

*Renewable Energy and Electrochemistry Department, National Institute of R&D for
Electrochemistry and Condensed Matter - INCEMC,
144 Aurel Păunescu-Podeanu, RO-300569, Timișoara, Romania
Corresponding author: szabadai@umft.ro

Introduction

A large quantity of waste seashells (millions of tons) is discarded annually after mollusc consumption, which becomes a problem for the environment worldwide as these shells are a habitat for microbes which could turn into a public health issue [1]. On the other hand, waste shell biomaterials need a small amount of energy for recycling and processing into useful products for various applications.

Calcium carbonate is essential in biomineralization, where it is the primary constituent of mollusc shells, crustacean cuticles, corals etc. In its pure form, it occurs naturally, under normal temperature and pressure conditions, in three anhydrous crystalline forms, namely calcite, aragonite and vaterite [2]. At high pressures, two further forms, namely calcite II and calcite III, are formed. The most stable form of calcium carbonate at atmospheric pressure and room temperature is calcite. The presence of both calcite and aragonite is very frequent in biologically produced calcium carbonate minerals. Though aragonite is metastable in aqueous solution, it can nucleate [3]. Aragonite is found in the nacre of the shells of bivalve molluscs, which provide a protection for these animals [4]. From the study of the marine bivalve species *Mercenaria mercenaria* and *Crassostrea gigas*, Weiner et al. [5] have shown that amorphous calcium carbonate is a precursor phase of aragonite.

The present study, which is part of our efforts to convert seashells into useful products like hydroxyapatite, investigates the temperature influence on the calcite and aragonite in a processed shell sample by using Fourier-transform infrared spectroscopy (FTIR).

Experimental

Seashells were thermally treated by using a Hygiena dry block incubator and closed glass tubes. First, the shell fragments used in these tests were mechanically processed to give a diameter between 1.0 and 1.6 mm. The $\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$ reagent was used, giving a pH of 9.1, and the tube samples were kept at a temperature of 90 °C for 16 h. The 0.468 mol L⁻¹ Na_2HPO_4 concentration, in relation to the amount of shells used, should have led to a degree of conversion for calcium carbonate of maximum 5%. However, the target compound hydroxyapatite was not confirmed by XRD or FTIR.

FTIR investigations of the obtained products were performed by using a Vertex 70 (Bruker) FTIR spectrometer. In order to characterize the pre-treated material, the temperature dependence of spectrum change in the middle infrared domain was studied in the 20–200 °C temperature range with 20 degrees increments. The triturated sample was incorporated in a 13 mm KBr pellet and subjected to a pressure of 9 kPa. For a better signal-to-noise ratio, 128 recordings were accumulated for each temperature.

Results and discussion

Although hydroxyapatite crystallization did not seem to occur, even at high temperatures, in our sample, and thus the compound was not confirmed in the tests we performed, some

interesting observations were made regarding the FTIR spectra at different temperatures. In the 400–4000 cm^{-1} spectral range, the characteristic bands of carbonate ion, mainly in calcite form, were identified (Fig. 1). The absorption band at 1466 cm^{-1} corresponds to the antisymmetric stretching vibration of two C-O bonds whereas the band at 1080 cm^{-1} can be attributed to symmetric stretching vibration of the same bonds. The absorption appearing at 861 cm^{-1} is generated by the out-of-plane vibration of the whole carbonate anion and the band at 712 cm^{-1} is due to the antisymmetric deformation of the angle between two C-O bonds.

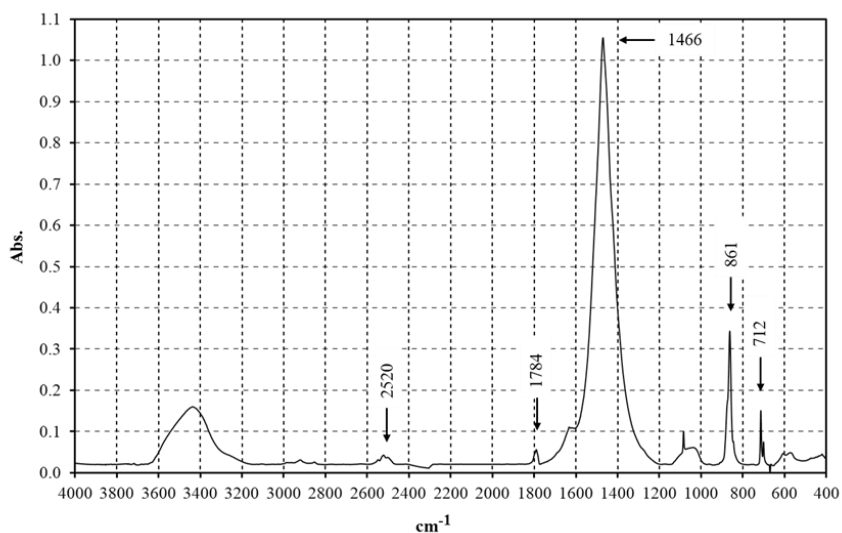


Figure 1. Middle infrared spectrum of shell sample at 20 °C

The intensity variations of some selected absorption bands exhibit particular regularities vs. temperature in selected wavenumber ranges. The absorption in the 3200 – 3600 cm^{-1} domain is characteristic to the hydroxyl group (Fig. 2). Regarding the dependence of the absorption intensity on the temperature, two temperature zones can be distinguished. Below 40 °C the intensity decreases drastically, but above this temperature there is a significantly moderate decrease, indicating a distinct event. Up to 40 °C, the residual moisture is removed from the sample, but above this value there is a process of elimination of the more strongly bounded crystallization water (Fig. 3). The heating effect upon the absorbance at 712 cm^{-1} , associated with in-plane asymmetric vibration (Fig. 4), exhibits a change of slope at 40 °C as well (Fig. 5).

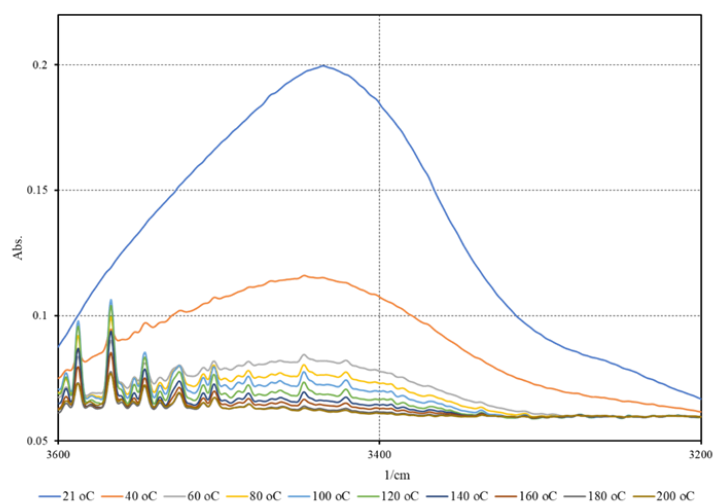


Figure 2. Absorbance of the OH stretching vibration range vs. temperature

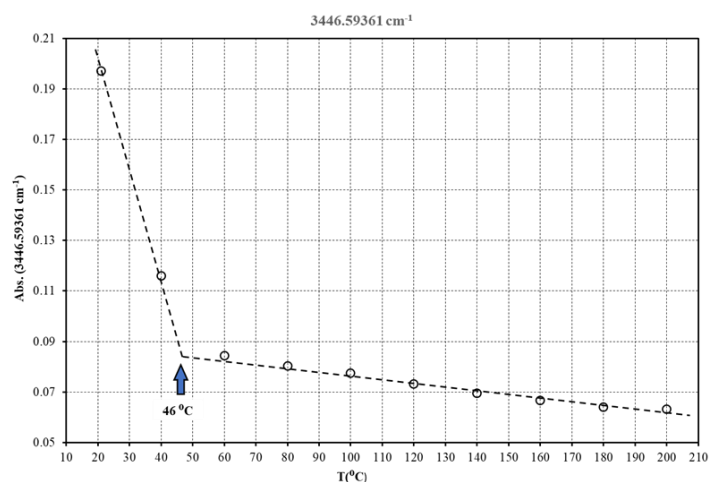


Figure 3. Absorption intensity vs. temperature at 3446.59 cm⁻¹

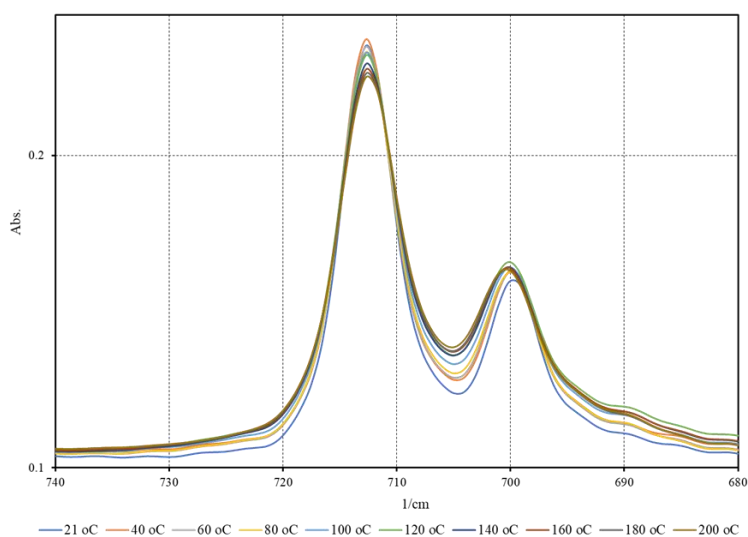


Figure 4. Absorbance in the range 680 - 740 cm⁻¹ vs. temperature

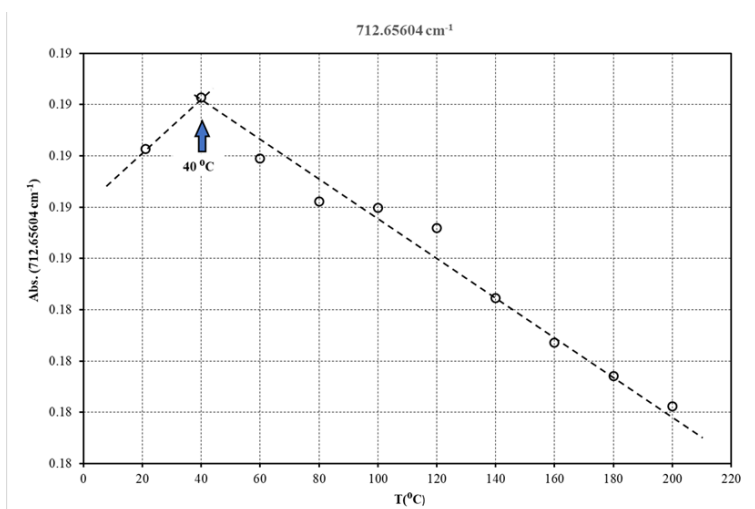


Figure 5. Absorption intensity vs. temperature at 712.65 cm⁻¹

Further remarkable slope breakings, regarding the absorbance vs. temperature, are found for the absorption bands placed at 1458.10 cm^{-1} (Fig. 6) and 1506.32 cm^{-1} (Fig. 7), but in these cases the slope break appears at $100\text{ }^{\circ}\text{C}$.

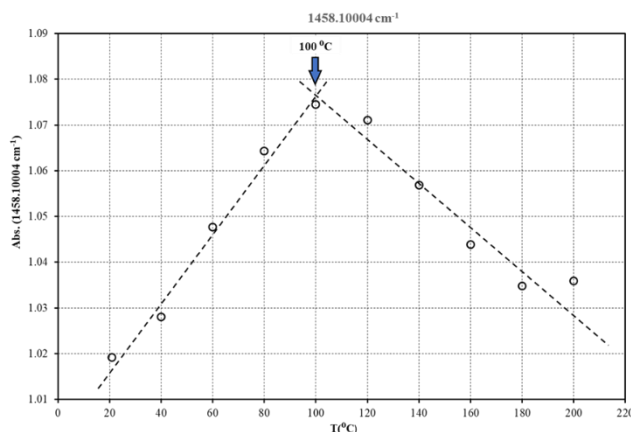


Figure 6. Absorption intensity vs. temperature at 1458.10 cm^{-1}

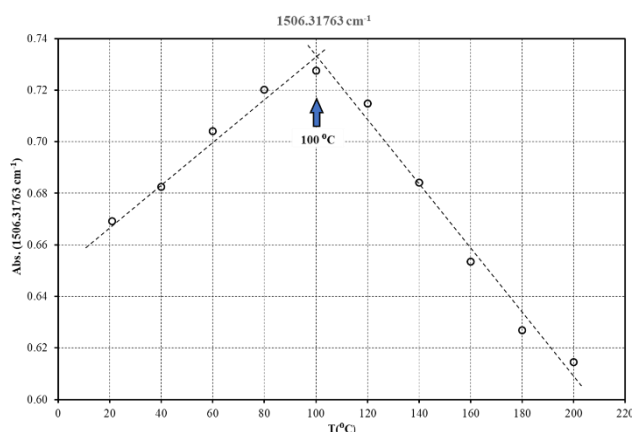


Figure 7. Absorption intensity vs. temperature at 1506.32 cm^{-1}

Outlining an isosbestic point around wavenumber 1073 cm^{-1} seems to support this interpretation. Figs. 8 and 9 illustrate the bathochromic shift of the position of maximum absorption vs. temperature.

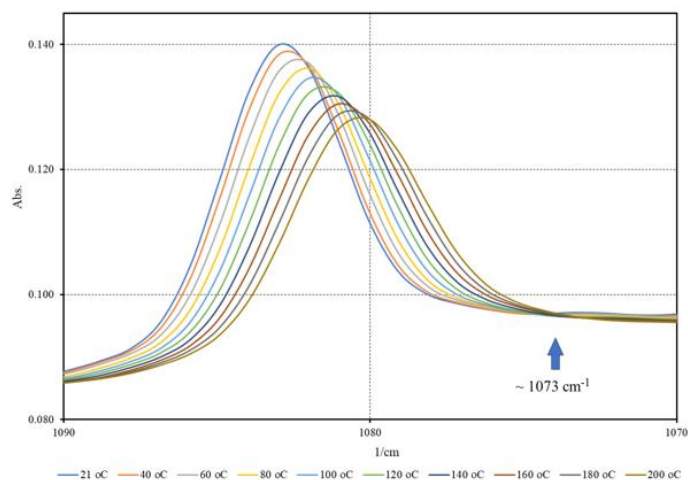


Figure 8. Bathochromic displacement of the absorption band in the range $1070 - 1090\text{ cm}^{-1}$ as the temperature rises

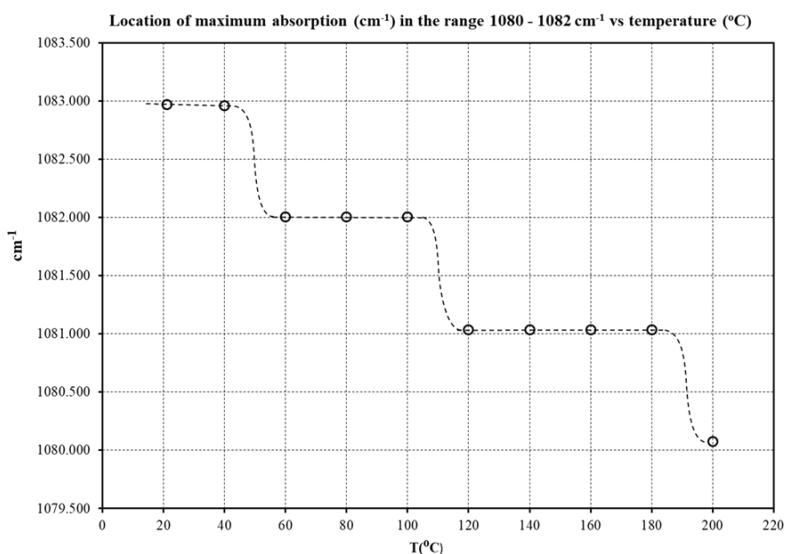


Figure 9. Position of the maximum absorption in the spectral range 1080 – 1082 cm^{-1}

Conclusion

The behavior of the bands between 1070 – 1090 cm^{-1} (Fig. 8) is more special in the sense that, as the temperature rises, their location changes progressively (Fig. 9), indicating the presence of at least two distinct phases in the sample that gradually transform into each other.

It is important to notify the two values of temperature (slightly over 50 °C and over 100 °C) at which the sudden variations of the wavenumber values occur, somewhat consistent with the results in the Figs. 3, 5, 6 and 7.

Although hydroxyapatite was not confirmed in these experiments, it can be stated that the studied material presents at least two distinct phases in the considered temperature domain.

Acknowledgements

This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS - UEFISCDI, project number PN-III-P1-1.1-TE-2019-2116, within PNCDI III.

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