MINERALOGICAL AND SPECTROSCOPIC STUDY OF NESQUEHONITE SYNTHESIZED BY REACTION OF GASEOUS CO₂ WITH MG CHLORIDE SOLUTION

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Abstract

Nesquehonite, a hydrous carbonate with promising uses such as building raw material and treatment of wastewaters, was synthesized under low pressure conditions by reaction of gaseous CO₂ with Mg chloride solution and it was studied by means of X-Ray Diffraction, optical and scanning/transmission electron microscopy, and FT-IR and Raman spectroscopic methods. Synthesized nesquehonite forms elongated fibers, exhibiting transparent to translucent diaphaneity and vitreous luster. It is characterized by high crystallinity. IR and Raman spectroscopy indicated the presence of OH⁻ and HCO₃⁻ in the crystal structure of nesquehonite. The nesquehonite synthesis described herein constitutes a potential permanent storage of CO₂ emissions.

Keywords: nesquehonite, hydrous magnesium carbonate, low-pressure mineralization, CO₂ storage.
1. Introduction

Nesquehonite is a magnesium carbonate mineral with proposed chemical formula either MgCO$_3$$\cdot$3H$_2$O (Kloprogge et al., 2003; Dong et al., 2009; Stephan and McGillavry, 1972) or Mg(OH)(HCO$_3$)$\cdot$2H$_2$O (Hales et al., 2008; Hales et al., 2008; Frost and Palmer, 2011), named after a location in Pennsylvania, USA, where found for first time. It is crystallized in the monoclinic crystal structure in space group P21/n, Z = 4 and it has unit cell parameters of a = 7.70Å, b = 5.37Å, c = 12.12 Å and β= 90°, 45ˊas described by Stephan and MacGillavry (1972) and by Giester et al. (2000). Its structure consists of infinite flat ribbons of corner-sharing MgO$_6$ octahedra (Fig. 1a) along the b axis of the crystal, which is the fiber axis, linked by hydrogen bonds and contains only one crystallographically inequivalent carbon (Fig.1b). Within the chains, CO$_3$ groups link three MgO$_6$ octahedra by one edge and two common corners. The Mg atoms are in a distorted coordination, and each atom is coordinated by two H$_2$O ligands; one free H$_2$O molecule is located between the chains as shown in Figure 2 (Wang et al., 2008; Ferrini et al., 2009; Ballirano et al., 2009; Giester et al., 2000; Moore et al., 2015; Stephan and McGillavry, 1972). In Greece, natural nesquehonite has been reported in Lavrion (Giester et al., 2000).

Figure 1 – Crystal structure of nesquehonite in projections parallel to a [100] and b [010] (Giester et al., 2000).

Nesquehonite exhibits promising uses as a raw material of magnesium cement (Ferrini et al., 2009) as well as in wastewater treatment (Shan et al., 2013). Besides, recent studies showed that nesquehonite can be the product of CO$_2$ mineralization under low pressure conditions (Ferrini et al., 2009; De Vito et al., 2012). Given that nowadays, the reduction of CO$_2$ emissions has become a first priority for all industrial activities, CO$_2$ mineralization, i.e. CO$_2$ carbonation, constitutes one of the main carbon capture and sequestration (CSS) methods (Verduyn, 2011). Whereas, first studies dealt with the laboratorial reaction of CO$_2$ with the Mg-rich minerals of ultramafic rocks under high pressure conditions to form pure magnesite (Lackner et al., 1995) followed by studies on the in-situ storage of high pressure CO$_2$ gas in ophiolite complexes (Kelemen and Matter, 2008; Kelemen et al., 2011), an increasing interest on CO$_2$ mineralization under low pressure conditions is coming up (Ferrini et al., 2009; De Vito et al., 2012). Apart from the synthesis procedure, of great interest is the detailed characterization of the synthesized nesquehonite.
In this work, nesquehonite was synthesized under low pressure conditions by reaction of gaseous CO$_2$ with Mg chloride solution and its characterization was carried out by means of X-Ray Diffraction, optical and scanning/transmission electron microscopy, and FT-IR and Raman spectroscopic methods.

2. Materials and Methods

1.1 Analytical methods

X-Ray Diffraction patterns were obtained with a Bruker D8 Focus diffractometer in a 0-0 configuration employing CuKα radiation (λ = 1.5406 Å) with a fixed divergence slit size of 0.5° and a rotating sample stage. The samples were scanned between 4 and 70° 2θ. The step size and time per step were set to 0.017° 2θ and 80 s, respectively. Stereoscopic study was carried out under a Leica MZ8 binocular stereoscope. Scanning Electron Microscopy (SEM) was performed using a JEOL 6380LV-SEM equipped with an Oxford EDX-WDS. Transmission Electron Microscopy was performed with a JEOL 2100 HR-TEM at 200kV. A Fourier-transform infrared FT-IR spectrophotometer, Perkin Elmer Spectrum GX, and a Renishaw’s inVia-micro-RAMAN (532 nm excitation laser wavelength) were employed to obtain additional information on nesquehonite composition and structure.

1.2 Synthesis of Nesquehonite

Nesquehonite was synthesized at laboratory conditions by using a gas cylinder of CO$_2$ and chemical reagents MgCl$_2$·6H$_2$O and NaHCO$_3$. 80 g MgCl$_2$·6H$_2$O were dissolved into 500 ml of dionized water. CO$_2$ gas was then introduced into the solution at pressure of 0.1 kbar under continuous magnetic stirring at 1100 rpm. A solution of 60 g NaHCO$_3$ was added by using peristaltic pump. CO$_2$ gas was continually added into the solution for an hour under stirring. After that, the solution was left to precipitate for 24 hours. During the experiment solution temperature was kept stable at 25°C. The chemical reaction that took place was

$$\text{MgCl}_2\cdot6\text{H}_2\text{O} + 2\text{NaHCO}_3 + 3\text{CO}_2 \rightarrow \text{MgCO}_3\cdot3\text{H}_2\text{O} + 2\text{NaCl} + 4\text{H}_2\text{CO}_3$$

Figure 2 - XRD pattern of the nesquehonite synthesized herein.
The precipitated nesquehonite was then separated from the solution by using a vacuum pump and suitable paper filters and washed out with dionized water to dissolve any salts that might have been remained. Moisture was removed from the sample by putting it into an oven at 50°C for 24 hours.

3. Results and Discussion

As can been seen in the representative XRD diagram (Fig. 2) the produced precipitate is pure nesquehonite, with characteristic peaks at d= 6.52, 3.86, 3.04, 2.62, 2.51 and 1.92 Å, which corresponds to [-101], [200], [-211], [021], [-301] and [400] Miller indices (Stephan and McGillavry, 1972).

Nesquehonite formed as a white precipitate. Study under the binocular stereoscope, showed that it exhibits transparent to translucent diaphaneity and vitreous luster and it forms elongated fibers (Fig. 3).

Figure 3 – Stereoscopic view of the nesquehonite synthesized herein.

Scanning Electron Microscopy (SEM) showed that nesquehonite fibers were developed around a centerpiece creating a structure called rosettes (Fig. 4). EDS point analyses (Fig. 5) showed the presence of only one chemical phase; any salts might have been removed during the sample preparation.

Transmission Electron Microscopy (TEM) study showed that nesquehonite is highly crystalline (Fig. 6). The Selected Area Diffraction (SAED) pattern (Fig. 7) confirms the high crystallinity of the nesquehonite crystals and the absence of any amorphous phase (Egerton, 2005).

Fourier-Transform Infrared (FTIR) and Raman analyses were performed in the samples, to obtain additional information on their chemistry and structure. IR spectra (Fig. 8) showed the symmetric stretching (ν1) and the bending (ν2) modes of CO$_3^{2-}$ at 1097.94 cm$^{-1}$ and at 853.61 cm$^{-1}$, respectively. The three bands at 1520, 1466.06, 1420.06 cm$^{-1}$ are ascribed to the split ν3 antisymmetric stretching mode (Kloprogge et al., 2003; Coleyshaw et al., 2003; Morgan et al., 2015). The stretching of the O-H and the H$_2$O molecule gives rise to broad bands in the region between 2500-4000 cm$^{-1}$ (Ferrini et al., 2008; Kloprogge et al., 2003). The bands at 3326.33, 3455.14, 3564.25 cm$^{-1}$ can be ascribed to OH-stretching modes of water in the crystal structure of the nesquehonite (Hopkinson et al., 2012; Hopkinson et al., 2008). At 1653.43 cm$^{-1}$ a H-O-H bending band is observed, which is associated with structural H$_2$O (Lanas and Alvarez, 2004; Hopkinson et al., 2008; Hopkinson et al., 2012) and absorbed H$_2$O (Kloprogge et al., 2003).
Figure 4 – Secondary electron (SE) images of nesquehonite showing prismatic crystals in the form of rosettes.

Figure 5 – Nesquehonite SE image (left) and the respective EDS spectrum (right), showing the presence of a magnesium carbonate mineral phase.
Figure 6 – TEM image showing the highly crystalline structure of the nesquehonite sample.

Figure 7 – SAED pattern of nesquehonite crystal indicating a highly crystalline structure. Each ring is created by Hall Effect and is assigned to d-spacing values which correspond to a certain set of hkl, compared with the diffraction data from literature (Egerton, 2005; American Mineralogy Crystal Structure Database; Stephan and McGillavry, 1972).

The two peaks observed at 699.97 cm\(^{-1}\) and 607.12 cm\(^{-1}\) are assigned to the \(v_4\) in-plane bending mode of the HCO\(_3\)\(^-\) (Hales et al., 2008; Frost and Palmer, 2011).

Raman spectra showed a very strong vibration at 1100 cm\(^{-1}\) (Fig. 9) that is ascribed to the \(v_l\) symmetric stretching vibration of the CO\(_2\)\(^-\) (Hales et al., 2008). The peak at 1515 cm\(^{-1}\) (Fig. 9) corresponds to \(v_l\) antisymmetric stretching vibration of CO\(_2\)\(^-\) and appears less intense. The two bands at 3123 cm\(^{-1}\) (Fig. 9) and 3444 cm\(^{-1}\) (Fig. 10) are assigned to the stretching vibration of H\(_2\)O molecules. The peak at 3556 cm\(^{-1}\) (Fig. 10) corresponds to the vibration tendency of O-H hydroxyl. The vibration at 1423 cm\(^{-1}\) (Fig. 9) is ascribed to the antisymmetric stretching of the HCO\(_3\)\(^-\) (Hales et al., 2008; Frost and Palmer, 2011).
Figure 8 – FTIR spectrum of the nesquehonite synthesized herein.

Figure 9 – Raman spectrum of the nesquehonite synthesized herein, from 50-3200 cm\(^{-1}\) wavelengths.

Figure 10 – Raman spectrum of the nesquehonite synthesized herein, from 3200-4000 cm\(^{-1}\) wavelengths.
Nesquehonite has a chemical composition of MgCO$_3$·3H$_2$O (Kloprogge et al., 2003; Dong et al., 2009; Stephan and McGilavry, 1972), but has been described also as Mg(OH)(HCO$_3$)·2H$_2$O (Hales et al., 2008; Hales et al., 2008; Frost and Palmer, 2011). Our IR and Raman results showed the presence of OH$^-$ and HCO$_3^-$ in the crystal structure of nesquehonite.

4. Conclusion

Nesquehonite, a hydrous carbonate, was synthesized under low pressure conditions by reaction of gaseous CO$_2$ with Mg chloride solution. Detailed study by means of X-Ray Diffraction, optical and scanning/transmission electron microscopy, and FT-IR and Raman spectroscopic methods showed that the synthesized nesquehonite

- forms elongated fibers developed as rosettes around of centerpieces with transparent to translucent diaphaneity and vitreous luster
- exhibits high crystallinity
- is characterized by the presence of OH$^-$ and HCO$_3^-$ in its crystal structure.

Nesquehonite is a thermodynamically and chemically stable solid product. The nesquehonite synthesis described herein is simple, fast and environmentally friendly and it constitutes a potential long-term CO$_2$ storage method. It might be applied in larger/industrial scale with the aim to capture and permanent store CO$_2$ emissions.

5. References

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