Preparation of siloxane-containing vaterite doped with magnesium

Shinya YAMADA, Yoshio OTA,† Jin NAKAMURA,** Yoshio SAKKA** and Toshihiro KASUGA*†

Department of Frontier Materials, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan
*Yabashi Industries Co., Ltd., 226 Akasaka-cho, Ogaki, Gifu 503–2213, Japan
**Advanced Key Technologies Division, Materials Processing Unit, National Institute for Materials Science, 1–2–1 Seneng, Tsukuba, Ibaraki 305–0047, Japan

Siloxane-containing vaterite doped with magnesium (MgSiV) was prepared by a carbonation process for application in bone regeneration. Ca(OH)2, aminopropyltriethoxysilane (APTES) and Mg(OH)2 were mixed with a solvent consisting of methanol and distilled water under CO2 gas. After the mixture was aged, the translucent precursor gel was dried, resulting in the formation of MgSiV particles containing 2.0 wt% magnesium and 2.8 wt% silicon. The MgSiV consists of distorted spherical particles with diameters of approximately 1.3 μm and a thickness of approximately 0.6 μm while the siloxane-containing vaterite without magnesium (SiV) was spherical with a diameter of approximately 1.5 μm. X-ray diffraction (XRD) analysis suggests the incorporation of magnesium into the vaterite structure. Fourier transform infrared spectroscopy (FTIR) indicated the presence of amorphous calcium carbonate (ACC) while the magnesium and the siloxane formed Si–O–Mg bonds. After heating the MgSiV at 500°C, the magnesium removed from the vaterite structure formed Si–O–Mg bonds with the siloxane. The MgSiV released Ca2+ and Mg2+ ions into a Tris buffer solution. The amount of Ca2+ ion dissolved in the Tris buffer solution increased within the initial 12 h and subsequently decreased with time because of the formation of precipitates.

Key-words : Calcium carbonate, Vaterite, Ion release, Magnesium, Siloxane

1. Introduction

In the field of biomaterials for bone regeneration, various types of bioactive ceramics and glasses have been proposed3–4 since the first direct bone to bioactive glass bonding was observed by Hench et al.5 This group thus introduced the first third-generation biomedical materials.6 These materials are designed to induce specific cellular responses with activating genes that stimulate the regeneration of living tissue. Maeno et al. suggested that the Ca2+ ion released from composite materials forms a type II collagen gel with hydroxyapatite (HA) and it has a stimulatory effect on the activation of osteoblasts.7 Ca2+ ion concentrations of 2–4 mM are suitable for the proliferation and survival of osteoblasts whereas concentrations of 6–8 mM favor osteoblast differentiation and matrix mineralization. Ca2+ ion concentrations higher than 10 mM are cytotoxic. On the other hand, Xynos et al. reported stimulatory effects for the enhancement of bone formation by soluble silica species and calcium ions that were released from Bioglass® 45S5 containing 45% SiO2 w/w.8 The number of human osteoblasts (HOBs) cultured in the ionic products of Bioglass® 45S5 upon dissolution in Dulbecco’s modified eagle medium (DMEM) increased by 155.1 ± 6.5% compared with normal DMEM after 4 days in culture. Alkaline phosphatase (ALP)-specific activity, which is known to be associated with osteoblast differentiation, of HOBs on the Bioglass® 45S5 disk was higher than that on the bioinert (plastic) substrate on day 6.9 Trace amounts of silicon (or silicate) and calcium ions are considered to be beneficial for the promotion of bone formation.

We have reported siloxane-containing vaterite, SiV, as a carrier for the release of these ions and demonstrated bioactivity toward polymer-based composites.10–13 Vaterite is the most thermodynamically unstable polymorph among the calcium carbonates and it releases Ca2+ and carbonate ions upon dissolution in body fluid. For the preparation of SiV, aminopropyltriethoxysilane (APTES) was added as a silicate source during a conventional carbonation process for the preparation of vaterite. The coexistence of amorphous calcium carbonate (ACC) in the SiV particles was confirmed by Fourier transform infrared spectroscopy (FTIR). The APTES molecules were believed to be condensed in the vicinity of the vaterite crystals and the ACC.13) The resulting SiV particles have diameters of approximately 1.4 μm that consist of primary particles of 5–20 nm.

Recently, Mg2+ ion has been reported to stimulate adhesion to materials, and the differentiation and calcification of osteoblastic cells. Zeiqa et al. demonstrated that the expression of integrins, which act as adhesion proteins, increased on Mg2+-modified alumina compared with Mg2+-free alumina.14) Saboori et al. reported that the high ALP activity of osteoblastic cells cultured on bioactive SiO2–CaO–P2O5–MgO glass originates from the stimulatory effects of Mg2+ ion on early bone cell differentiation.15) On the other hand, effects of Mg2+ ion on angiogenic function have also been reported. Maier et al. showed that Mg2+ ion stimulates the endothelial proliferation of human umbilical vein endothelial cells (HUVEC) and enhances the motogenic response to angiogenic factors.16) These stimulatory effects on cellular activities play an important role in bone regeneration.

Against this background, magnesium- and siloxane-containing vaterite might be beneficial for the preparation of new biomaterials. The precipitation of calcium carbonates is significantly

©2014 The Ceramic Society of Japan. All rights reserved.

DOI http://dx.doi.org/10.2109/jcersj2.122.1010

[Received August 8, 2014; Accepted October 1, 2014]
influenced by the presence of Mg$^{2+}$ ion during their crystallization. It is well known that the precipitation of calcite is preferentially induced and Mg is adsorbed and incorporated into the calcite lattice at low Mg/Ca ratios, while the precipitation of aragonite is induced at high Mg/Ca ratios.\(^{17-19}\) For magnesium-containing calcium carbonates (CaCO$_3$–MgCO$_3$ solid solutions), magnesium calcite (magnesite-rich calcite) has been widely investigated in biogenic and geochemical studies.\(^{20-22}\) The calcium carbonate particles from a mixture of CaCl$_2$ and Na$_2$CO$_3$ solutions with Mg$^{2+}$ ion concentrations of 5 or 10 $\times$ 10$^{-3}$ mol/L have been identified to be calcite and vaterite, respectively, and magnesium was considered to be preferentially included in the calcite.\(^{23}\) No magnesium has been shown to be incorporated into the vaterite phase to date. The incorporation of magnesium into ACC has also been reported.\(^{24-26}\)

In this work, we focused on the preparation of a new type of vaterite-based particle with high solubilities of calcium, magnesium, and silicate ions by a carbonation process.

2. Experimental procedures

2.1 Preparation and characterization of MgSiV particles

We have previously reported the preparation of siloxane-containing vaterite (SiV) particles by a carbonation process in methanol.\(^{27,28}\) Magnesium- and siloxane-containing vaterite (MgSiV) particles were prepared by a conventional method. As a Mg$^{2+}$ ion source, 11.7 g of magnesium hydroxide (Wako Pure Chemicals Inc., Osaka, Japan) was added to a solvent consisting of 2.0 L methanol (Wako Pure Chemicals Inc.) and 200 mL distilled water while stirring at 21°C. Carbon dioxide gas was added to the slurry at a feed rate of 2.0 L/min for 20 min. Subsequently, 133.4 g calcium hydroxide (Kishida Chemical Co., Ltd., Osaka, Japan) and 60 mL 3-aminopropyltriethoxysilane (APTES, Dow Corning Co., Midland, USA) were mixed into the slurry under carbon dioxide gas flow. The molar ratio of Mg/Ca was set to 1/9. Carbon dioxide gas was added over 40 min, resulting in the formation of a precursor gel. The resulting gel was aged at room temperature for 12 h and then dried at 110°C for 24 h to remove the residual solvent. The obtained agglomerated powder was ground to form MgSiV particles. SiV particles containing no magnesium were also prepared as a control by the carbonation process. Vaterite transforms into calcite upon heating at 460–490°C.\(^{29}\) For an evaluation of the thermodynamic stability of MgSiV, the particles were heated at 500°C for 6 h. The resulting particles are denoted MgSiV-500 hereafter.

2.2 Evaluation of the dissolution behavior of MgSiV

A Tris buffer solution with a concentration of 0.05 M was prepared for the MgSiV soaking test. We dissolved 6.118 g tris(hydroxymethyl)aminomethane (Kishida Chemical Co., Ltd.) in 900 mL distilled water at 37°C. The pH of the solution was adjusted to 7.40 using 1 M hydrochloric acid. The resulting solution was made up to 1000 mL with distilled water. The concentration of the Tris buffer solution was thus 0.05 M. The dissolution of the MgSiV particles was evaluated by soaking 500 mg of the particles in 50 mL Tris buffer solution. The samples were statically incubated at 37°C for 7 days. After soaking the SiV particles, MgSiV and Ca$^{2+}$ ion concentrations in the supernatants were measured using ICP-AES. The precipitates were filtered and subsequently dried at 80°C. After the soaking test, the crystalline phases of the obtained precipitates were examined by XRD.

3. Results and discussion

3.1 Morphologies of the MgSiV particles

Figure 1 shows SEM images of the SiV and MgSiV particles before and after heating at 500°C. In our previous work, the SiV particles were found to be secondary particles and they had spherical morphology with a mean diameter of approximately 1.4 μm, as shown in Fig. 1(a). They consist of primary particles of 5–20 nm in size.\(^{13}\) The MgSiV particles were of flat-spherical morphology [Fig. 1(b)]. The MgSiV particles had a mean diam-

---

**Fig. 1.** SEM images of (a) SiV, (b) MgSiV and (c) MgSiV-500 particles.
Fig. 2. XRD patterns of SiV, MgSiV and MgSiV-500.

3.2 Characterization of the MgSiV particles

By ICP-AES analysis, the MgSiV particles were estimated to contain 2.0 wt% magnesium and 2.8 wt% silicon. Figure 2 shows XRD patterns for the SiV, MgSiV and MgSiV-500 particles. The predominant crystalline phase of MgSiV was identified as vaterite. Peaks corresponding to calcite (Cu Kα, 2θ = 29.4°) and calcium magnesium carbonate (2θ = 29.7°) were also detected. The peaks that correspond to the c-axis-dependent plane of vaterite such as the (112) and (114) planes shifted to a higher angle while no ab plane (110) shift was observed. The lattice spacing for the vaterite (004) plane that was estimated from the XRD patterns is 0.426 nm for SiV and 0.421 nm for MgSiV. It is thus possible that Mg was incorporated into the vaterite crystalline structure. Some of the Ca-sites in vaterite may be substituted by Mg. To clarify the local structure changes on Mg2+ ion, some analyses are now in progress.

Vaterite is a calcium carbonate polymorph and has been reported to be transformed to calcite at 460–490°C. The XRD pattern of MgSiV-500 indicated that the predominant crystalline phase was vaterite. In contrast, a phase transition to calcite occurred for SiV (not indicated in Fig. 2) after heating at 500°C. The peaks shifted toward a higher angle and disappeared (see dotted line in Fig. 2) and the peak that corresponds to calcium magnesium carbonate became slightly weaker after heating. Mg, which is incorporated in the vaterite and calcium magnesium carbonate, was thus removed from these structures.

Figure 3 shows the FTIR spectra of SiV, MgSiV and MgSiV-500. Figure 3(a) shows the absorption band assigned to the asymmetric stretching (ν1) of carbonate ions. Split peaks were observed at 1485 and 1475 cm⁻¹ for both SiV and MgSiV. These split peaks are characteristic of amorphous calcium carbonate (ACC), which implies the presence of ACC. In the MgSiV-500 spectrum, no split peaks were observed. The ACC in MgSiV transforms to vaterite and/or calcite crystals upon heat-treatment. In Fig. 3(b), absorption bands corresponding to a siloxane-containing layer derived from APTES is present at 1200, 1138 and 1029 cm⁻¹ in the SiV and MgSiV spectra. The bands at 1089, 876 and 747 cm⁻¹ originate from symmetric stretching (νs), out-of-plane bending (νb) and in-plane bending (νi) of carbonate ions, respectively. Moreover, a narrow absorption band because of Si–O–Mg bonding was observed at 460 cm⁻¹. The Mg2+ ion in MgSiV might interact with a silanol group in the siloxane-containing layer. In the spectrum of MgSiV-500 in the region of 900–1200 cm⁻¹, the bands corresponding to the siloxane-containing layer change. The bands that originate from Si–CH₂ (1200 cm⁻¹) and Si–O–Si bonding (1138 and 1029 cm⁻¹) disappear, whereas the bands that originate from Si–O– (1120 and 975 cm⁻¹), Si–OH (930 cm⁻¹) and in-plane bending (νi) of carbonate ions (710 cm⁻¹) appear. The band at 713 cm⁻¹ that corresponds to the νi of carbonate ions has been reported to be typical for a calcite phase. The absorption band that originates from Si–O–Mg bonding is observed more clearly in the MgSiV-500 spectrum than in the MgSiV spectrum. The Mg2+ ion that was removed from the vaterite structure and/or ACC form partial Si–O–Mg bonds after heating. The thermal removal of the organic components derived from APTES and the subsequent formation of inorganic networks is assumed. The thermal stability of vaterite in MgSiV (Fig. 2) may be related to the formation of these inorganic networks.

3.3 Ion-release behavior from MgSiV particles

Figure 4(a) shows the Mg²⁺ ion concentrations obtained in the Tris buffer solutions upon the dissolution of MgSiV and MgSiV-500 particles. After soaking the MgSiV particles for 12 h, the amount of dissolved Mg²⁺ ion was determined to be approximately 60% of the total. After 1 day of soaking, this ion was released constantly and after 2 days the total amount of dissolved...
Mg\(^{2+}\) ion reached 164 mg/L. On the other hand, after soaking MgSiV-500 for 12h, the amount of dissolved Mg\(^{2+}\) ion was \(~25\%\) of the total. After 1 day, almost no Mg\(^{2+}\) ion release was observed.

Figure 4(b) shows the Si\(^{4+}\) ion concentrations in the Tris buffer solution containing dissolved SiV, MgSiV and MgSiV-500 particles. The amount of Si\(^{4+}\) ion dissolved from SiV and MgSiV drastically increased within 1 day of soaking. For SiV\(^{13}\), a fast Si–O–Si hydrolysis of the aminopropyl-functionalized siloxane and the dissolution of uncondensed APTES molecules, which facilitate an increase in the Si\(^{4+}\) ion concentration, are believed to occur. The dissolution of Si\(^{4+}\) ion from MgSiV within 1 day is assumed to be due to the same dissolution behavior. Almost all the Si\(^{4+}\) ion in the SiV and MgSiV particles dissolve within 7 days. In contrast to SiV and MgSiV, MgSiV-500 dissolved approximately 83 mg/L of the Si\(^{4+}\) ion in 12 h, and after this period no release was observed. The Mg\(^{2+}\) and Si\(^{4+}\) ions in the Si–O–Mg bonds that formed by heating at 500°C are believed to be almost insoluble in Tris buffer solution.

Figure 4(c) shows the Ca\(^{2+}\) ion concentrations in the Tris buffer solution upon their release from the SiV, MgSiV and MgSiV-500 particles. The SiV and MgSiV particles exhibit almost the same Ca\(^{2+}\) ion release behavior over the entire soaking period. Approximately 240 mg/L SiV and 210 mg/L MgSiV dissolved within 12h and this decreased to 40 and 80 mg/L after 7 days, respectively. The rapid increase in Ca\(^{2+}\) ion that was observed within 12h is believed to originate from the dissolution of ACC. The decrease in Ca\(^{2+}\) ion concentration in the solution comes from the formation of precipitates, which were observed at the bottom of the soaking containers. The MgSiV-500 particles exhibited different Ca\(^{2+}\) ion dissolution behavior compared with SiV and MgSiV. Approximately 330 mg/L Ca\(^{2+}\) ion dissolved within 12h and after this period the Ca\(^{2+}\) ion concentration stabilized over 7 days. The higher Ca\(^{2+}\) ion dissolution during the initial stage comes from the instability of vaterite. Magnesium seems to be removed from the vaterite phase in MgSiV-500 upon heat-treatment. No decrease in Ca\(^{2+}\) ion because of precipitation was observed. The formation of calcite is believed to be inhibited by the dissolution of Mg\(^{2+}\) ion from MgSiV-500. After 7 days of soaking, a smaller amount of precipitate was observed at the bottom of the container than that derived from SiV or MgSiV.

Figure 5 shows the XRD patterns of SiV, MgSiV and MgSiV-500 before and after soaking in Tris buffer solution for 12h and 7 days. For the SiV particles, a phase transformation from vaterite to calcite occurred within 12h [Fig. 5(a)]. After 7 days, no phase transformation was observed since calcite is thermodynamically stable. The morphology of the residual particles after 7 days of soaking changed to irregular shapes, not spherical ones. In contrast, the crystalline phase of MgSiV predominantly transformed to the aragonite phase after 12h [Fig. 5(b)]. It is known that in the presence of a large amount of Mg\(^{2+}\) ion in an aqueous solution, the aragonite phase precipitates easily.\(^{17-20,21,24,39}\) It has been reported that no Mg\(^{2+}\) ion is incorporated in the lattice of aragonite as a solid solution since magnesium has a tightly bound hydration shell.\(^{30,41}\) Another possible origin is the difference in coordination number.\(^{42}\) Mg\(^{2+}\) ion is characterized by six-fold coordination while Ca\(^{2+}\) ion is considered to be nine-fold in aragonite. Although the crystalline phase in SiV completely transformed to calcite within 12h [Fig. 5(a)], the vaterite phase was still observed in MgSiV. The peaks that shifted in MgSiV are shown in Fig. 2, and they reverted to the original SiV positions. The magnesium that was incorporated into the vaterite crystalline structure dissolved from MgSiV within 12h. After 7 days of soaking, the peaks corresponding to vaterite disappeared and the predominant crystalline phase was aragonite. No original MgSiV particles were observed, whereas the needle-like crystals, which imply aragonite, were observed as shown in Fig. 5(b). The calcite phase was also observed and the peak intensity that corresponds to calcium magnesium carbonate became stronger with soaking time. The magnesium dissolved from MgSiV might form calcium magnesium carbonate.

After soaking MgSiV-500 for 12h, a phase transformation from vaterite to aragonite and calcite was observed. The peak intensity of the calcite in MgSiV-500 after soaking was stronger compared with that of MgSiV. This might be due to the small amount of Mg\(^{2+}\) ion that dissolved from MgSiV-500. After 7 days of soaking, the amount of aragonite phase decreased and the crystalline phase was predominantly calcite. However, the peaks corresponding to vaterite phase were confirmed, and flat-spherical particles, which imply MgSiV-500 particles, were observed in SEM image [in Fig. 5(c)]. Upon increasing the soaking time from 12h to 7 days, a dissolution-reprecipitation from aragonite to calcite seems to have occurred. It has been reported...
that a lower Mg/Ca ratio (less than 1/1) induces calcite precipitation while a higher Mg/Ca ratio induces aragonite precipitation at 37°C.17) The Mg/Ca ratio in the supernatant derived from MgSiV was approximately 2/1 and that of MgSiV-500 was approximately 1/7 after 7 days. The difference in Mg/Ca ratios could be related to the formation of crystals. Although vaterite is thermodynamically metastable, peaks that correspond to vaterite were still observed in MgSiV-500 after 7 days. Vaterite may be partially enclosed by a layer that contains Si–O–Mg.

4. Conclusion

Siloxane-containing vaterite doped with magnesium (MgSiV) was prepared for application in bone regeneration. The resulting MgSiV particles had distorted spherical shapes with diameters of 1.3 μm and contained 2.0 wt% magnesium and 2.8 wt% silicon. The incorporation of magnesium into vaterite was suggested by XRD analysis. FTIR spectroscopic analysis of MgSiV indicated the existence of amorphous calcium carbonate (ACC) and an interaction with magnesium (Si–O–Mg bonding). The incorporated magnesium may be removed from the vaterite structure after heating at 500°C and ACC then transforms partially to vaterite and/or calcite crystals. Mg2+ and Si4+ ions dissolve from MgSiV with soaking time and then aragonite predominately precipitates. In contrast, the amounts of Ca2+ and Si4+ ions that dissolve from MgSiV-500 are less than those from MgSiV.

MgSiV releases Ca2+, Mg2+, and silicate ions and it is an excellent inorganic particle candidate for bone regeneration. Investigations into biodegradable polymer-based composites containing MgSiV particles are now in progress.

Acknowledgments

This work was supported in part by the Institute of Ceramics Research and Education (ICRE), Nagoya Institute of Technology.

References

1) M. Winter, P. Griss, K. de Groot, H. Tagai, G. Heimke and H. J. a v Dijk, Biomaterials, 2, 159–160 (1981).
2) M. Jarcho, Clin. Orthop. Relat. Res., 157, 259–278 (1981).
3) R. Z. LeGeros, Clin. Orthop. Relat. Res., 395, 81–98 (2002).
4) L. L. Hench, J. Mater. Sci.: Mater. Med., 17, 967–978 (2006).
5) L. L. Hench, R. J. Splinter, W. C. Allen and T. K. Greenlee, J. Biomed. Mater. Res., Part A, 5, 117–141 (1971).
6) L. L. Hench and J. M. Polak, Science, 295, 1014–1017 (2002).
7) S. Maeno, Y. Niki, H. Matsumoto, H. Morioka, T. Yatabe, A. Funayama, Y. Toyama, T. Taguchi and J. Tanaka, Biomaterials, 26, 4847–4855 (2005).
8) I. D. Xynos, A. J. Edgar, L. D. K. Buttery, L. L. Hench and J. M. Polak, Biochem. Biophys. Res. Commun., 276, 461–465 (2000).
9) I. D. Xynos, M. V. J. Hukkanen, J. J. Batten, L. D. Buttery, L. L. Hench and J. M. Polak, Calcif. Tissue Int., 67, 321–329 (2000).
10) H. Maeda, T. Kasuga and L. L. Hench, Biomaterials, 27, 1216–1222 (2006).
11) S. Tokuda, A. Obata and T. Kasuga, Acta Biomater., 5, 1163–1168 (2009).
12) A. Obata, S. Tokuda and T. Kasuga, Acta Biomater., 5, 57–62 (2009).
13) J. Nakamura, G. Poologasundarampillai, J. R. Jone and T. Kasuga, J. Mater. Chem. B, 1, 4446–4454 (2013).
14) H. Zreiqat, C. R. Howlett, A. Zannettino, P. Evans, G. Schulze-Tanzil, C. Knabe and M. Shakhbaci, J. Biomed. Mater. Res., Part A, 62, 175–184 (2002).
15) A. Saboori, M. Rabiee, F. Mozarthadeh, M. Sheikhi, M. Tahriri and M. Karimi, Mater. Sci. Eng. C, 29, 335–340 (2009).
16) J. A. Maier, D. Bernardini, Y. Rayssiguier and A. Mazur, Biochim. Biophys. Acta, 1689, 6–12 (2004).
17) J. W. Morse, Q. Wang and M. Y. Tsio, Geology, 25, 85–87 (1997).
18) J. L. Bischoff, J. Geophys. Res., 73, 3315–3322 (1968).
19) Y. Kitano, Bull. Chem. Soc. Jpn., 35, 1973–1980 (1962).
20) M. E. Böttcher, P. L. Geltken and D. F. Steele, Solid State Ionics, 101–103, 1379–1385 (1997).
21) Y. Kitano, A. Tokuyama and T. Arakawa, Geochem. J., 13, 181–185 (1979).
22) A.ucci, Geochem. Cosmochim. Acta, 50, 2255–2265 (1986).
23) M. Kitamura, J. Colloid Interface Sci., 236, 318–327 (2001).
24) K. Sawada, T. Ogino and T. Suzuki, J. Cryst. Growth, 106, 393–399 (1990).
25) H. Nebel and M. Epstein, Z. Anorg. Allg. Chem., 634, 1439–1443 (2008).
26) Y. Politi, D. R. Batchelor, P. Zaslansky, B. F. Chmelka, J. C.
Weaver, I. Sagi, S. Weiner and L. Addadi, Chem. Mater., 22, 161–166 (2010).
27) T. Wakita, A. Obata and T. Kasuga, Mater. Trans., 50, 1737–1741 (2009).
28) A. Obata, T. Hotta, T. Wakita, Y. Ota and T. Kasuga, Acta Biomater., 6, 1248–1257 (2010).
29) M. S. Rao, Bull. Chem. Soc. Jpn., 46, 1414–1417 (1973).
30) D. L. Bish, J. Appl. Cryst., 21, 86–91 (1988).
31) J. Wang and U. Becker, Am. Mineral., 94, 380–386 (2009).
32) X. Xu, J. T. Han, D. H. Kim and K. Cho, J. Phys. Chem. B, 110, 2764–2770 (2006).
33) F. A. Andersen and L. Brecevic, Acta Chem. Scand., 45, 1018–1024 (1991).
34) J. Kim, P. Seidler, L. S. Wan and C. Fill, J. Colloid Interface Sci., 329, 114–119 (2009).
35) R. P. Alonso, F. Rubio, J. Rubio and J. L. Oteo, J. Mater. Sci., 42, 595–603 (2007).
36) N. V. Vagenas, A. Gatsouli and C. G. Kontoyannis, Talanta, 59, 831–836 (2003).
37) J. Madejová, J. Bujdak, M. Janek and P. Komadel, Spectrochim. Acta [A], 54, 1397–1406 (1998).
38) J. Madejová, Vib. Spectrosc., 31, 1–10 (2003).
39) Z. Zhang, Y. Xie, X. Xu, H. Pan and R. Tang, J. Cryst. Growth, 343, 62–67 (2002).
40) G. Falini, S. Fermani, G. Tosi and E. Dinelli, Cryst. Growth Des., 9, 2065–2072 (2009).
41) G. Falini, M. Gazzanob and A. Ripamonti, Chem. Commun. (Camb.), 1037–1038 (1996).
42) A. A. Finch and N. Allison, Mineral. Mag., 71, 539–552 (2007).