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Solid state synthesis of calcium borohydroxyapatite

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ABSTRACT

Calcium borohydroxyapatite was synthesized by the solid-state reaction of colemanite ($Ca_2B_6O_{11}\cdot 5H_2O$) and diamonium hydrogenphosphate ($(NH_4)_2HPO_4$) at 1200 °C for 12 h. X-ray diffraction pattern showed only the formation of calcium borohydroxyapatite. The experimental analysis assigned the chemical formula as $Ca_{10}[(PO_4)_{5.80}(BO_3)_{0.20}](OH)_2$. It was indexed in the hexagonal system with the refined unit cell parameters of $a = 9.557(3)$ Å, $c = 6.926(8)$ Å and space group $P6_3/m$. The experimental results verified that if colemanite was used as a primary reactant for both calcium and boron source, the calcium borohydroxyapatite could be obtained.

1. Introduction

Apatite is the most common phosphate mineral, and the main source of the phosphorus required by plants. The bones and teeth of most animals, including humans, are of the same material as apatite [1]. Apatites are a chemically-important group of supplies in industrial applications such as bone replacement, ceramic membranes, environmental improvement and catalysis [2,3]. Additionally, in terms of their biomaterial properties, apatites have piezoelectric, bioelectric and luminescence feature [4–6]. Apatite mineral family has a common structural formula of $A_{10}(XO_4)_6Y_2$ (A:alkaline earth element, X = P, S, V, Si and $Y = Cl^-$, F^-, OH^-, CO_3^{2-}) [7,8].

The most common subgroup of the apatite group is phosphate apatite. It is not only a geological mineral but also a bioceramic material [9]. Indeed the apatite structure is very hospitable for the substitutions of many other ions for instance AsO_4^{3-}, VO_4^{3-}, CrO_4^{3-}, HPO_4^{2-}, CO_3^{2-}, SO_4^{2-} and SiO_4^{4-}. Lattice parameters, morphology, crystallinity, thermal stability and solubility of hydroxyapatite may change significantly upon such substitutions [8]. In this article only the boron substitution has been argued.

Borophosphate compounds including crystalline apatites were investigated intensively in order to improve the physical and chemical properties such as microhardness and water resistance to be used as bioceramic materials by several research groups [4,8–14]. The other groups had also specified a new single phase of oxyboroapatites, $Ca_x(PO_4)_yB_zO_t$ in the $CaO-P_2O_5-B_2O_3$ ternary system at 900 °C and 1200 °C [15,16].

Ito et al. were discovered single crystals with a non-stoichiometric formula of $Ca_{9.64}(P_{5.73}B_{0.27}O_{24})(BO_2)_{0.73}$ as a solid solution in the system $Ca_{10}(PO_4)_5BO_4-Ca_{9.5}(PO_4)_6BO_2$ by standard flux growth technique with the composition $35CaO-5P_2O_5-60B_2O_3$ (wt%) by heating at 1200 °C for 10 h and then cooled at a rate of 8.3 °C/h. The material was crystallized in hexagonal prismatic system with the cell parameters $a = 9.456$ (1), $c = 6.905$ (1) Å and space group $P\bar{3}$ [12]. On the other hand, Ternane et al. studied the boron addition in hydroxyapatites in detail and they found a new type calcium borohydroxyapatite with a nominal stoichiometry of $Ca_{10}\{(PO_4)_{6-x}(BO_3)_x\}\{(BO_3)_Y(BO_2)_Z(OH)_{2-3Y-Z}\}$ crystallized in hexagonal system with the unit cell parameters $a = 9.418$, $c = 6.884$ Å and space group $P6_3/m$. They prepared the compound from the initial reactants of $CaCO_3$, $(NH_4)_2HPO_4$ and H_3BO_3 with defined proportions. Firstly, they fired the pellet mixture at 400 °C for 12 h and then calcined the sample again at 700 °C for 24 h. Finally, the pellet was sintered at 1000 °C for 24 h. By the XRD pattern of the sample obtained at 700 °C, the borohydroxyapatite was observed together with the following phases of $CaCO_3$, $Ca_3(BO_3)_2$, CaO, and β-$Ca_3(PO_4)_2$. They synthesized the pure borohydroxyapatite at 1000 °C for 24 h and other phases disappeared. The XRD peaks of the borohydroxyapatite were indexed in the apatitic space group $P6_3/m$ agreeing with the 9-432 ICDD file. As a result, with boron joining, phosphate and hydroxyl groups were moderately substituted by borate groups such as BO_3^{3-} and BO_2^-, respectively, and AB-type borohydroxyapatite was obtained [6,8]. Finally, Hayakawa et al. synthesized boron containing

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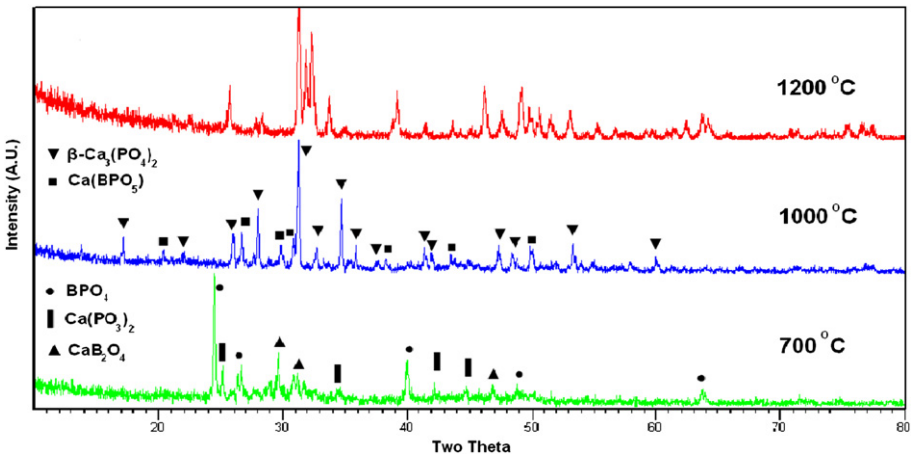

Fig. 1. XRD patterns of the products synthesized at 700, 1000 and 1200 °C.

hydroxyapatite (BHAp) by the wet chemical processing way and also examined the effect of boron introduction on the microstructure. They were observed that the boron substitution process realized at 900 °C between HAp and $B(OH)_3$ resulting the formation of boron substituted HAp go along with the phase of β-TCP. Eventually, at above 1200 °C, β-TCP was transformed into the α-TCP [13].

The aim of this work is devoted to the synthesis and structural characterization of the calcium borohydroxyapatite when colemanite is directly used as a primary reactant for both calcium and boron source.

2. Experimental procedure

2.1. Synthesis

The reactants were prepared by the conventional solid-state reactions using the initial reactants of $Ca_2B_6O_{11}\cdot 5H_2O$ (colemanite, purity 99.5%) and $(NH_4)_2HPO_4$ (Merck, analytical grade) with defined mole proportion (Ca/P molar ratio 1.67). Then the mixture was transferred into an alumina porcelain crucible, weighed and put into a high temperature furnace (Carbolite Furnaces HTC 1600) for heating. Firstly the mixture was calcined at 400 °C for 12 h and after intermediate groundings the sample was heated at 700, 1000 and 1200 °C for 12 h, respectively. At the end of the treatments, the sample was allowed to cool down to room temperature in the furnace. In order to get clear of unreacted boron residual, the product was dissolved in hot water, thereby the excess boron was moved away from the sample. Hot water extraction method was especially used to remove residual boron, because of high solubility of B_2O_3 [17].

2.2. Characterization

The phases were identified from their X-ray powder diffraction (XRD) pattern using Panalytical X'Pert Pro Diffractometer and

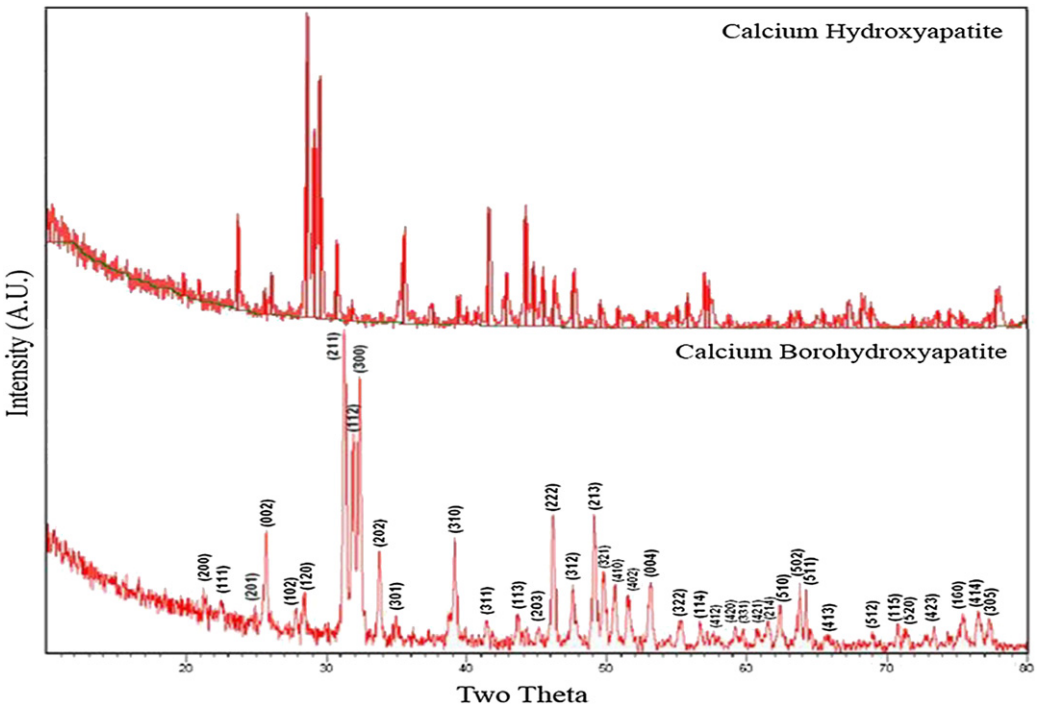

Fig. 2. XRD pattern of calcium hydroxyapatite and calcium borohydroxyapatite synthesized at 1200 °C.

Table 1
XRD data of Calcium borohydroxyapatite.

hkl	I/I_o	d_{obs}, Å	d_{cal}, Å
200	4.44	4.1447	4.1251
111	6.43	3.9407	3.918
201	5.83	3.5652	3.5392
002	35.62	3.4655	3.4448
102	8.43	3.1990	3.1778
120	14.30	3.1406	3.1183
211	100	2.8509	2.8409
112	73.38	2.8033	2.7913
300	92.42	2.7631	2.7501
202	31.85	2.6563	2.6441
301	5.81	2.5641	2.5541
310	37.86	2.2966	2.2882
311	7.16	2.1748	2.1716
113	10.43	2.0728	2.0687
203	5.34	2.0082	2.0065
222	43.17	1.9613	1.9590
312	19.84	1.9080	1.9060
213	41.04	1.8505	1.8492
321	23.11	1.8287	1.8251
410	21.49	1.8025	1.8003
402	16.78	1.7714	1.7696
004	22.08	1.7215	1.7224
322	9.83	1.6592	1.6588
114	8.71	1.6197	1.6198
412	3.18	1.5997	1.5956
420	7.65	1.5591	1.5591
331	4.00	1.5478	1.5472
421	6.75	1.5209	1.5207
214	8.01	1.5054	1.5077
510	14.3	1.4875	1.4818
502	22.14	1.4591	1.4602
511	21.17	1.4489	1.4487
413	3.43	1.4183	1.4169
512	4.35	1.3618	1.3612
115	8.85	1.3296	1.3236
520	5.17	1.3191	1.3211
423	7.74	1.2882	1.2899
160	9.79	1.2579	1.2581
414	10.57	1.2416	1.2446
305	9.64	1.2328	1.2319

CuK_α radiation (λ = 1.54056 Å, 40 mA, 50 kV). Infrared spectra were recorded between 4000 and 400 cm^{-1} using a Perkin Elmer FTIR spectrum BX2 and KBr pellets were prepared by mixing the sample to KBr (1 mg/300 mg in the order). The elemental boron analysis was determined by using the azomethine H spectrometric method which is one of the qualified procedures with high sensitivity. The method has been described in detail in the referred research articles [18,19]. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were used to determine crystal composition and observe surface morphology of the material.

Table 2
FTIR bands and wavenumbers (cm^{-1}) for experimental product of the Calcium borohydroxyapatite.

FTIR bands	Wavenumbers (cm^{-1})
ν_s (OH)	3534
ν_3 (BO_3)	1220
ν_3 (PO_4)	1165, 1111
ν_1 (PO_4)	984
ν_L (OH)	638
ν_2 (BO_3)	751
ν_4 (PO_4)	560

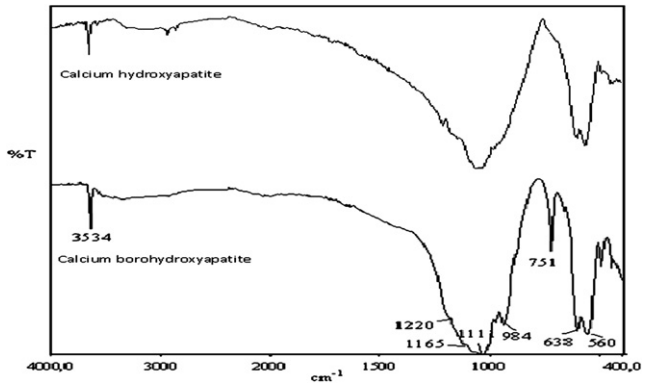

Fig. 3. FTIR Spectrum of calcium hydroxyapatite and calcium borohydroxyapatite.

3. Results and discussion

The XRD pattern of the products obtained at 700, 1000 and 1200 °C was given in Fig. 1. The phases of BPO_4 (ICDD 74-1169), CaB_2O_4 (ICDD 76-0747) and $Ca(PO_3)_2$ (ICDD 09-0363) were observed at 700 °C. At 1000 °C, $Ca(BPO_5)$ (ICDD 89-7584) and β-$Ca_3(PO_4)_2$ (ICDD 70-2065) phases were identified by the XRD pattern. When the reaction temperature is increased to 1200 °C, only the calcium borohydroxyapatite was observed. All the XRD peaks were indexed in the hexagonal system with the refined unit cell parameters of a = 9.557(3) Å, c = 6.926(8) Å and space group $P6_3/m$ (Fig. 2 and Table 1). When the cell parameters of the calcium hydroxyapatite, $Ca_5(PO_4)_3(OH)$ (a = 9.418 Å and c = 6.884 Å (ICDD 09-432)) were matched against our product, it was seen that the unit cell parameters extended slightly. This enlargement could be explained by the boron substitution. In Fig. 2, the XRD pattern of pure calcium hydroxyapatite was added for comparison (hexagonal, a = 9.407 and c = 6.871 Å, $P6_3/m$). Experimentally boron quantity was calculated as 0.195 mol by using the azomethine H spectrometric method [18,19]. Expected reaction could be given as follows:

$$5Ca_2B_6O_{11}\cdot 5H_2O + (6NH_4)_2HPO_4 \rightarrow Ca_{10}\left[(PO_4)_{5.80}(BO_3)_{0.20}\right] \times (OH)_2 + 14.9B_2O_3 + 0.2PO_4^{3-} + 12NH_3 + 32.7H_2O + 0.6H^+$$

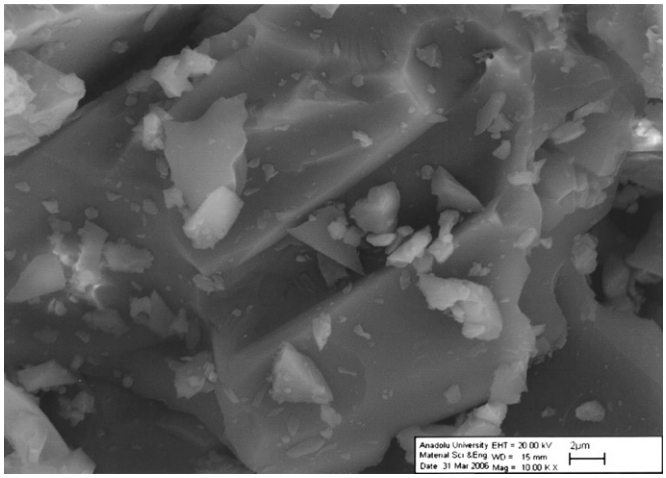

Fig. 4. SEM micrograph of calcium borohydroxyapatite.

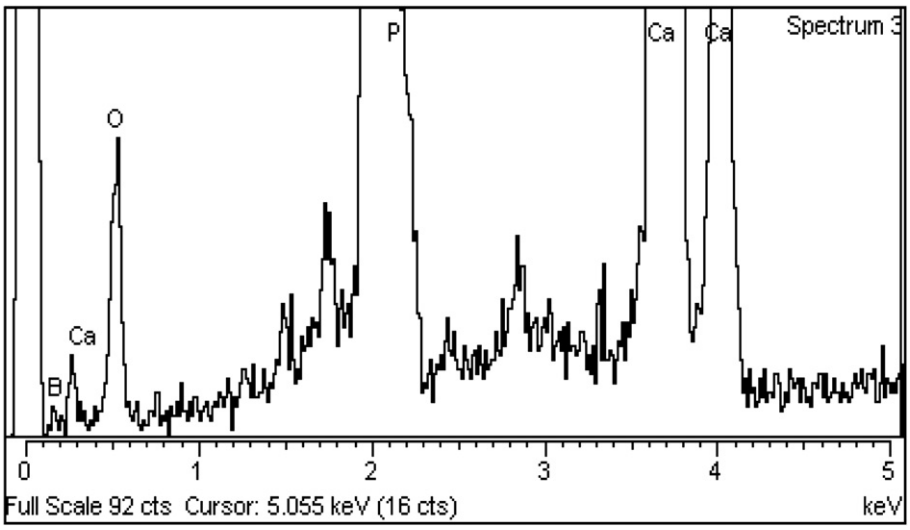

Fig. 5. EDX analysis of calcium borohydroxyapatite.

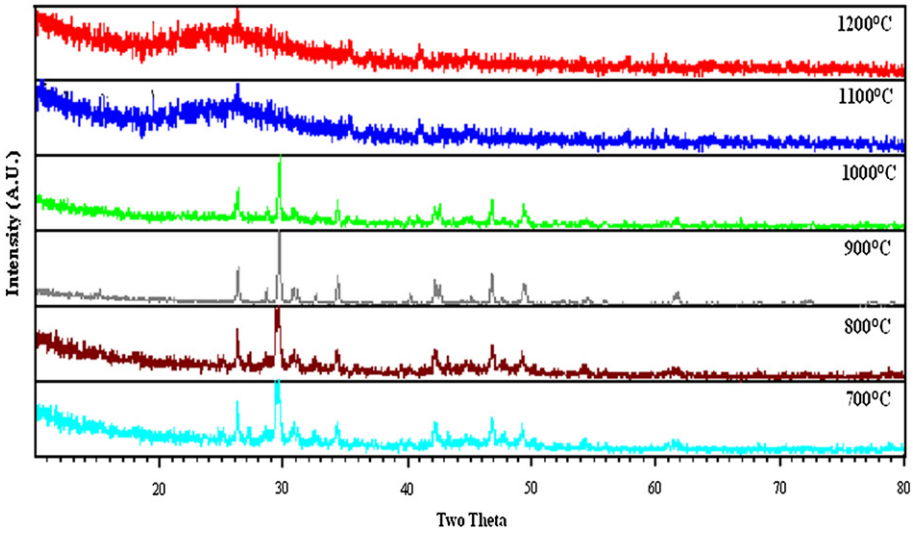

Fig. 6. XRD patterns of colemanite at 700, 800, 900, 1000, 1100 and 1200 °C.

The FTIR spectrum of the sample was shown in Fig. 3. The IR peaks corresponded to the functional groups of PO_4^{3-}, BO_3^{3-} and OH^- (Table 2). The wave numbers 3534 and 638 cm^{-1} belonged to OH^- group. The peaks at 1165, 1111, 984 and 560 cm^{-1} were assigned to the PO_4^{3-} ions. The band at 1220 and 751 cm^{-1} was attributed to the symmetric bending υ_3 and υ_2 modes of the BO_3^{3-} group, respectively [20]. Even though Ternane et al. [8] observed the BO_2 substitution in the IR analyses, we did not investigate any similar event. Since the BO_3 replaced partially with the PO_4 groups, the assigned chemical formula could be formulated as $Ca_{10}[(PO_4)_{5.80}(BO_3)_{0.20}](OH)_2$ [21–23]. For comparison, the FTIR spectrum of pure calcium hydroxyapatite was also added. The peak of BO_3 group was not observed in this spectrum.

Scanning electron microscopy and energy dispersive X-ray analysis were given in Figs. 4 and 5. SEM micrograph and EDX analyses were used to determine surface morphology and crystal composition for the sample. Average sizes of crystalline particles were calculated as 30 μm respectively. The evidence of the atoms (B, Ca, P and O) in the crystal structure of $Ca_{10}[(PO_4)_{5.80}(BO_3)_{0.20}](OH)_2$ was confirmed by EDX analysis.

Fig. 6 shows the XRD results of colemanite heated at 700, 800, 900, 1000, 1100 and 1200 °C, separately. Colemanite decomposes into $Ca(BO_2)_2$ (ICDD 73-0079) at the range of 700–1000 °C. At the higher temperatures, 1100 and 1200 °C, colemanite transforms into glassy form.

4. Conclusion

In this study, the calcium borohydroxyapatite was synthesized in crystalline powder form via solid-state reaction by using the initial reactants of colemanite ($Ca_2B_6O_{11}\cdot 5H_2O$) and diamonium hydrogenphosphate ($(NH_4)_2HPO_4$). Firstly the mixture was calcinated at 400 °C for 12 h and after intermediate groundings the sample was heated at 700, 1000 and 1200 °C for 12 h, respectively. At 700 °C, the phases of BPO_4 (ICDD 74-1169), CaB_2O_4 (ICDD 76-747) and $Ca(PO_3)_2$ (ICDD 9-363) were observed together. At 1000 °C, $Ca(BPO_5)$ (ICDD 89-7584) and β-$Ca_3(PO_4)_2$ (ICDD 70-2065) phases were seen in the XRD pattern. But at 1200 °C, only the calcium borohydroxyapatite was obtained in a pure form. Analytical analyses assigned the non-stoichiometric formula of the sample as

$Ca_{10}[(PO_4)_{5.80}(BO_3)_{0.20}](OH)_2$. It was crystallized in the hexagonal system with the refined unit cell parameters of $a = 9.596(6)$ Å and $c = 6.973(7)$ Å.

References

[1] L. Yan, Y. Li, Z.X. Deng, J. Zhuang, X. Sun, Inor. Mater. 3 (2001) 633–637.
[2] T.J. White, D. Zhili, Acta Crys. B. 59 (2003) 1–16.
[3] R. Ternane, M.Th. Cohen-Adad, G. Panczer, C. Goutaudier, C. Dujardin, G. Boulon, N. Kbir-Ariguib, M. Trabelsi-Ayedi, Solid State Sci. 4 (2002) 53–59.
[4] A. Baykal, G. Gurbuz, M. Kızılyallı, R. Kniep, Key Eng. Mater. 264–268 (2004) 2017–2022.
[5] J.F. Ducel, J.J. Videau, Mater. Lett. 18 (1993) 69–72.
[6] J.F. Ducel, J.J. Videau, K.S. Suh, J. Senegas, Phys. Status Solidi A 144 (1994) 23–30.
[7] H. Yuan, K. Kurashina, J.D. Bruijn, Y. Li, K. Groot, X. Zhang, Biomaterials 20 (1999) 1799–1806.
[8] R. Ternane, M.Th. Cohen-Adad, G. Panczer, C. Goutaudier, N. Kbir-Ariguib, M. Trabelsi-Ayedi, P. Florian, D. Massiot, J. Alloys Comp. 333 (2002) 62–71.
[9] C.P., Rodrigo, Master thesis, Univ. of Navada, Las Vegas, 2005.
[10] T. Kitsugi, T. Yamamuro, T. Nakamura, S. Yoshii, T. Kokubo, Biomaterials 13 (1992) 393–399.
[11] R. Ternane, M.Th. Cohen-Adad, G. Boulon, P. Florian, D. Massiot, M. Trabelsi-Ayedi, N. Kbir-Ariguib, Solid State Ionics 160 (2003) 183–195.
[12] A. Ito, H. Aoki, M. Akao, N. Miura, R. Otsuka, S. Tsutsumi, J. Ceram. Soc. Jpn. 96 (1988) 305–309.
[13] S. Hayakawa, A. Sakai, K. Tsuru, A. Osaka, E. Fujii, K. Kawabata, C. Jäger, Key Engin. Mater. 361–363 (2008) 191–194.
[14] S. Barheine, S. Hayakawa, A. Osaka, C. Jaeger, Chem. Mater. 21 (2009) 3102–3109.
[15] P. Ramamoorthy, T.J. Rockett, J. Am. Ceram. Soc. 57 (1974) 501–503.
[16] H. Bauer, Bull. Soc. Chim. (1968) 1703.
[17] R.N. Sah, P.H. Brown, Plants and Soil 193 (1997) 15–33.
[18] R. Capelle, Anal. Chim. Acta 24 (1961) 555–572.
[19] L. Zaijun, Y. Yuling, P. Jiaomai, T. Jan, The Analyst 126 (2001) 1160–1163.
[20] G. Gözel, A. Baykal, M. Kizilyalli, R. Kniep, J. Europ. Ceram. Soc. (1998) 2241–2246.
[21] N. Leroy, E. Bres, Europ. Cells Mater. 2 (2001) 36–48.
[22] G. Penel, G. Leroy, C. Rey, B. Sombret, J.P. Huvenne, E. Bres, J. Mater. Sci. Mater. Med. 8 (1997) 271–276.
[23] B. Perdikatsis, Mater. Sci. Forum 79/82 (1991) 809–814.