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Synthesis and apatite-formation ability of akermanite

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Abstract

Pure akermanite ($Ca_2MgSi_2O_7$) powders were synthesized by sol–gel method. The akermanite powders were composed of polycrystalline particles with dimensions of 5–40 μm. The apatite-formation ability of the akermanite was examined by soaking it in a simulated body fluid (SBF), and the result showed that hydroxyapatite (HAp) was formed after soaking for 10 days. Our study indicated that akermanite possessed apatite-formation ability and might be used for preparation of new biomaterials.

Keywords: Akermanite; Simulated body fluid; Hydroxyapatite

1. Introduction

Previous studies have shown that some glasses and glass-ceramics containing Si, Ca and Mg were highly bioactive and could be used for biomedical applications [1–3]. Furthermore, diopside ($CaMgSi_2O_6$), a Si, Ca and Mg containing ceramic, has been reported to be bioactive and closely bonded to bone tissue when implanted in rabbits [4–7]. As an analogue with diopside in component, akermanite ($Ca_2MgSi_2O_7$) is also a Si-, Ca- and Mg-containing ceramic. Therefore, it is reasonable to assume that akermanite may be a bioactive material. Akermanite is a mineral, with a melting temperature of >1450 °C and a density of 2.944 g/cm^3, and so far has no important industrial applications. The naturally occurring akermanite was often not pure and associated with other minerals, and to our knowledge, there was no report about chemical synthesis of pure akermanite.

In this communication, we reported the chemical synthesis of the pure akermanite powders using sol–gel method, and evaluation of apatite-formation ability of the akermanite by soaking the powders in a simulated body fluid (SBF).

2. Experimental procedure

Akermanite powders were prepared by sol–gel process using tetraethyl orthosilicate ($(C_2H_5O)_4Si$, TEOS), magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$) and calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) as raw materials. Briefly, the TEOS was mixed with water and 2N HNO_3 (mol ratio: $TEOS/H_2O/HNO_3 = 1:8:0.16$) and hydrolyzed for 30 min under stirring. Then, the $Mg(NO_3)_2{\cdot}6H_2O$ and $Ca(NO_3)_2{\cdot}4H_2O$ were added into the mixture (mol ratio: $TEOS/Mg(NO_3)_2{\cdot}6H_2O/Ca(NO_3)_2{\cdot}4H_2O = 2:1:2$), and reactants were stirred for 5 h at room temperature. After the reaction, the solution was maintained at 60 °C for 1 day and dried at 120 °C for 2 days to obtain the dry gel. The dry gel was ground and sieved to 250-mesh, transferred into a corundum crucible and calcined at 1100, 1200 and 1300 °C for 3 h, respectively.

Calcined powders were analyzed by X-ray diffraction (XRD, Geigerflex, Rigaku, Japan) with a monochromated CuKá radiation, and the microstructure of calcined powders was observed by scanning electron microscopy (SEM; JSM-6700F, JEOL, Tokyo, Japan).

For the evaluation of apatite-formation ability, the obtained akermanite powders were soaked in SBF solution at pH 7.25 for 10 days at a solid/liquid ratio of 1.5 mg/ml. The SBF solution was prepared according to the procedure described by Kokubo [8]. After soaking for 10

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days, the samples were filtrated, rinsed with water, dried at 60 °C and characterized by XRD and SEM.

3. Results and discussion

Fig. 1 showed the XRD patterns of the akermanite powders prepared by sol–gel method and calcined at different temperatures. The XRD patterns of the powders calcined at temperatures between 1100 and 1300 °C all showed a strong akermanite peak at about 31° 2θ, which indicated that the main resultant was akermanite. However, at lower temperature (1100 and 1200 °C), the calcined powders contained impurities of merwinite ($Ca_3MgSi_2O_8$) and diopside ($CaMgSi_2O_6$), and the content of impurities of $Ca_3MgSi_2O_8$ and $CaMgSi_2O_6$ in the powders decreased with the increase of calcination temperature (Fig. 1a and b), When the temperature increased to 1300 °C, pure akermanite powders were obtained, and all impurities of $Ca_3MgSi_2O_8$ and $CaMgSi_2O_6$ completely transformed into akermanite (Fig. 1c). The result suggests that 1300 °C was the optimal calcination temperature for the synthesis of pure akermanite powders by sol–gel method. The akermanite grain size and surface morphologies were shown in Fig. 2a, which indicated that particles agglomerated and the size of particles was about 5–40 μm. The high magnification SEM micrograph showed that the particles were porous and the pores size was about 1–5 μm (Fig. 2b).

Fig. 3a and b shows the XRD patterns of the akermanite before and after soaking in the SBF solution for 10 days. A crystalline peak of hydroxyapatite (HAp) at 31.7° 2θ corresponding to the 211 reflection was evident in the XRD pattern after 10 days of soaking, and the characteristic peaks of akermanite disappeared, which suggested that akermanite induced the HAp formation when soaked in SBF. Fig. 4 showed the SEM micrographs of akermanite

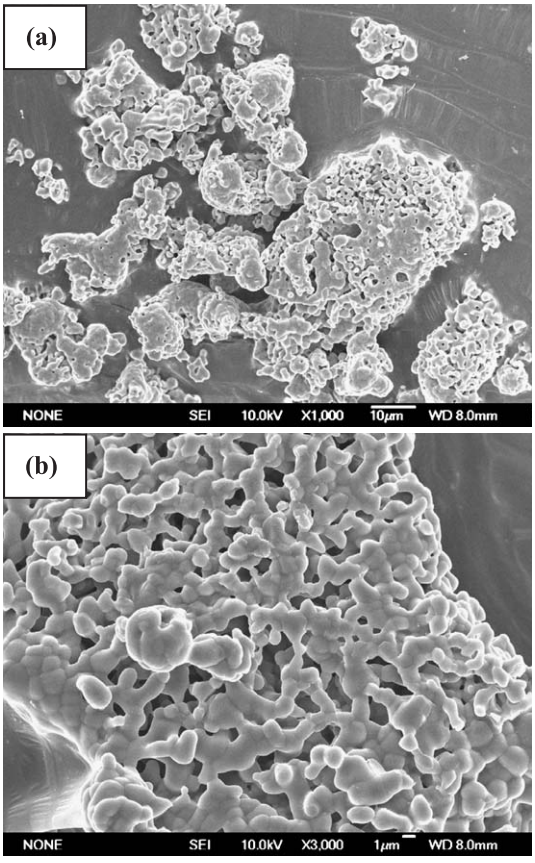

Fig. 2. SEM photographs of microstructures of the calcined powders of akermanite at 1300 °C. (a) Low magnification; (b) high magnification.

powders before and after soaking in SBF solution for 10 days. It was obvious that the surface of the akermanite powders before soaking was smooth (Fig. 4a), and the surface after soaking became coarse and the micropores were disappeared due to the deposition of HAp crystals (Fig. 4b). The higher magnification SEM micrograph

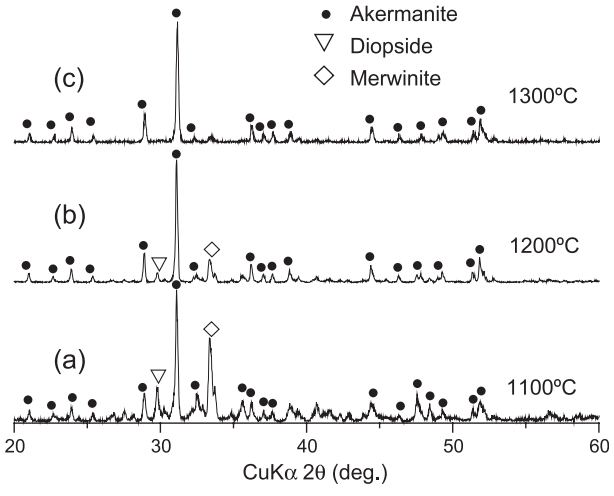

Fig. 1. XRD patterns of the synthesized powders at different temperature.

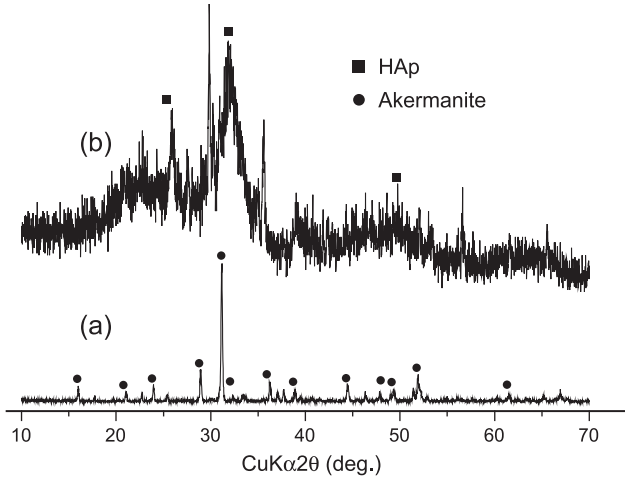

Fig. 3. XRD patterns of the akermanite before and after soaking in SBF for 10 days. (a) Before soaking; (b) after soaking.

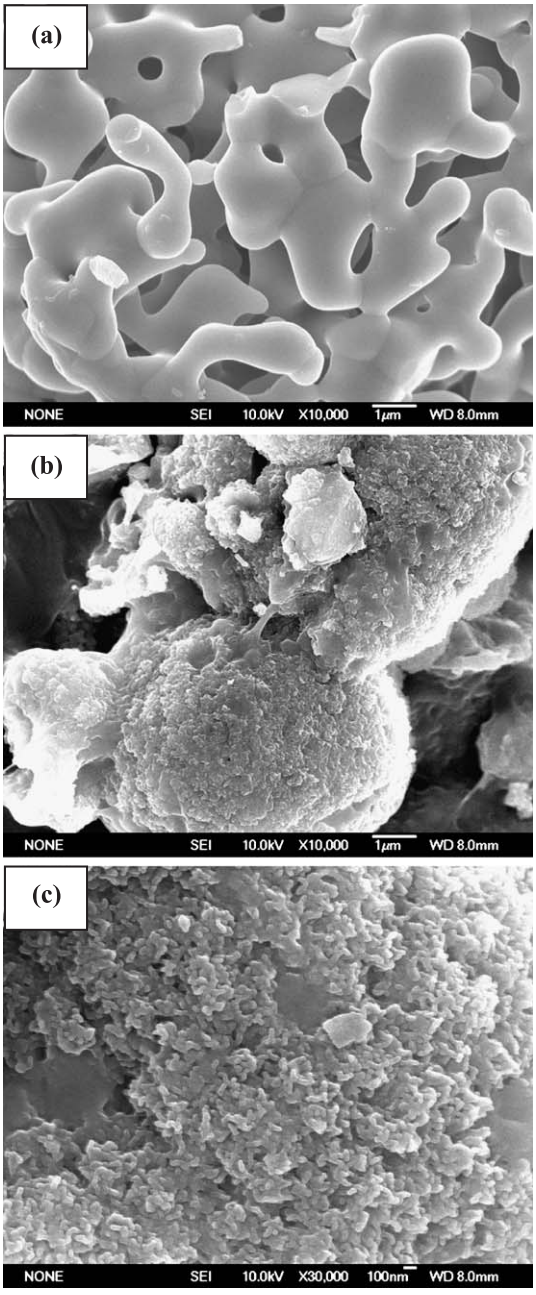

Fig. 4. SEM photographs of microstructures of the akermanite before and after soaking in SBF for 10 days. (a) Before soaking; (b and c) after soaking.

showed that numerous uniform and lathlike HAp crystallites were aggregated on the surface of akermanite powders and the size of the crystallites was about 100 nm in length (Fig. 4c). Previous study has shown that diopside was a bioactive material and could bond closely to bone tissue when implanted in animals [4–7]. Although the crystal structure between diopside and akermanite is clearly different, the composition of both materials is similar, and the only compositional difference is that akermanite has one more Ca and O in its chemical formula as compared with diopside. Our results showed that akermanite possessed apatite-formation ability, which suggested that compositional similarity was a more important factor to determine ability of the apatite deposition on ceramics than the structural factors, but further work needs to be done to confirm this assumption.

4. Conclusions

In summary, pure akermanite powders were synthesized by sol–gel method and calcination at 1300 °C, and the size of akermanite powders was about 5–40 μm. The in vitro study showed that powders could induce hydroxylapatite formation on their surface after 10 days of soaking in SBF. Our study suggests that akermanite possessed apatite-formation ability and might be a potential candidate as tissue repair biomaterials.

Acknowledgements

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