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Short communication

Aqueous gelcasting of silica ceramics using DMAA ☆

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Abstract

A low-toxicity and water-soluble monomer N, N-dimethylacrylamide (DMAA) was used as gelling agent in gelcasting of silica ceramics. In order to prepare high solid loading and low viscosity gelcasting slurries, effects of various parameters such as zeta potential, pH value, dispersant dosage and solid loading on rheological behaviors of the suspensions were investigated. The results suggest that the best conditions are pH 7.7 and dispersant dosage 0.1 wt%. The maximum flexural strength of green bodies with only 2 wt% organics in the slurry could be up to 15.3 MPa. The sintering shrinkage, bulk density, coefficient of linear expansion and flexural strength of sintered ceramics are 5.2%, 1.95 g/cm^3, 0.58×10^{-6} k^{-1} (200 °C) and 67.4 MPa, respectively. The dielectric constant and loss (1 MHz) are 3.26 and 7.8×10^{-4}, respectively.

Keywords: Gelcasting; Silica ceramics; Low-toxicity; Slurry; Rheological behavior

1. Introduction

Silica ceramics possess prominent corrosion and thermal shock resistance (no breakage after thermal shock between 25 °C and 1100 °C for more than 30 times), low thermal expansion coefficient (0.54×10^{-6} °C^{-1}, 0–800 °C) and thermal conductivity (2.09 W/m · K), low dielectric constant (3.1–3.8), and good insulating property (resistance: $10^{15}\Omega$ at room temperature). These properties make fused silica ceramics an excellent candidate as structural and functional materials in many fields, such as glass, metal, aerospace and polysilicon industry [1–3].

Gelcasting is a rapidly developed near net shape colloidal forming process for fabricating high-strength and complex shape ceramic green bodies which can be machined with out the risk of breakage [4]. Acrylicamide (AM) was the most widely used gel monomer in gelcasting of ceramics including silica [5–7]. However, industry has been reluctant to use AM because of its neurotoxicity.

Many non-toxicity natural materials have been used in gelcasting systems like chitosan [8], agarose [9], starch [10], cellulose ethers [11], etc., but low strength of green bodies seems inevitable in these systems. Therefore, developing new gel systems which have similar or superior properties to the AM system, yet low-toxicity has become an area of intense interest in the field for years. Low-toxicity monomers, such as 2-hydroxyethyl methacrylate (HEMA) [12], DMAA [13], methacrylamide (MAM) [14], etc., have been successfully used in gelcasting of ceramics. But researches about gelcasting of silica ceramics using low-toxicity gel systems have been reported not many. HEMA was used as gel monomer in gelcasting of fused silica by Zhang and Cheng [15]. But the monomer concentration in their study reached 30 vol% and the four-point flexural strength of green bodied is about 4 MPa. DMAA is a water soluble low-toxicity monomer which has shown excellent properties similar to AM in gelcasting of SiC [13], AlN [16] and ZTA [17].

In this work, the low-toxicity and water-soluble monomer N, N-dimethylacrylamide (DMAA) was used as gelling agent in the aqueous gelcasting of silica ceramics. In order to obtain concentrated slurries with low viscosity and good liquidity, the effects of zeta potential, pH value, dispersant dosage and solid loading on rheological properties of the slurry were investigated. Properties of the green and sintered bodies were studied as well.

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2. Experimental

2.1. Raw materials

Commercial silica powders (99.9% purity) with an average particle size of 3.98 μm were used as raw materials. The phase and morphology of the powders are shown in Fig. 1. DMAA (Kowa Co. Ltd., Japan), N,N′-Methylenebisacrylamide (MBAM, Tianjing Chemical Reagent Research Institute, China), ammonium persulfate (APS, Lingfeng Chemical Reagent Co., Ltd., Shanghai, China) and acrylic acid-2-acrylamido-2-methypropane sulfonic acid copolymer (AA-AMPS, Taihe Water Treatment Co., Ltd., Shandong, China) were used as gel monomer, cross-linker, initiator and dispersant, respectively.

2.2. Experimental procedure

Firstly, premixed solution was prepared by adding 10 wt% DMAA and 1 wt% MBAM into the distilled water. Then, silica powders and AA-AMPS were added into the prepared premixed solution. After ball milling for 5 h, the slurry was obtained. Then, the slurry was casted into a stainless steel mold and solidified at 75 °C for 1 h after adding APS as initiator and being degassed in the vacuum chamber. To avoid cracking and deformations, green bodies were dried under a certain temperature and humidity condition. Finally, Sintering was carried out in an electric furnace in air, soaking in 1250 °C for 4 h.

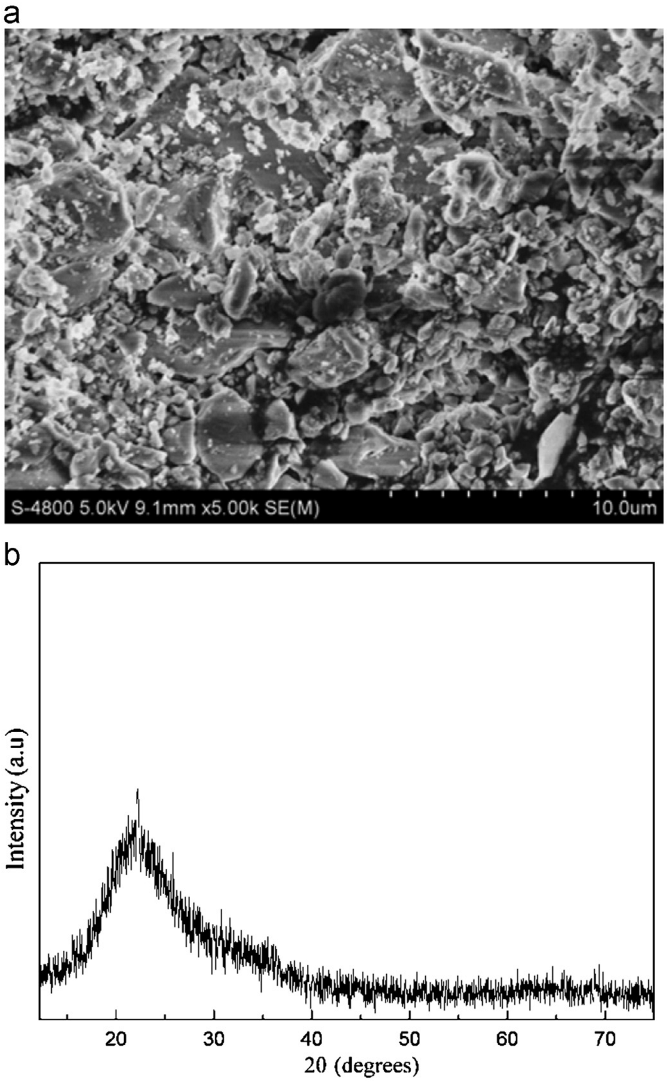

Fig. 1. Morphology (a) and phase (b) of silica powders.

2.3. Characterization

Zeta potential of silica powders in slurries was determined by the Zeta Potential Analyzer (Ver.3.54, Brookhaven Instruments Corporation, PALS). R/S Rheometer (R/S CC 25, Brookfield Corporation, USA) was used to characterize the rheological behaviors of slurries. The pore size distribution of green and sintered bodies was got by the mercury porosimeter (Quantachrome Company Poremaster). X-ray diffractometer (XRD, ARL, Cuk$_\alpha$, Switzerland) and scanning electron microscope (SEM, HITACHI S4800, Japan) were used to analyze the phase and observe the microstructure, respectively. Dielectric properties of the sintered samples were measured by an impedance analyzer (Agilent 4294A) with a test frequency of 1 MHz. Flexural strength was examined using an universal testing machine (CMT-6203, MTS System Corporation, China) by the three-point flexural method with a sample dimension of 3 mm × 4 mm × 40 mm. Archimedes method was employed to determine the bulk density and porosity of green and sintered bodies.

3. Results and discussion

3.1. Rheological behaviors of slurries

3.1.1. Zeta potential of silica slurry

As we know that stabilizing mechanisms of ceramic particles in solution mainly include electrostatic stabilization, steric stabilization, and electrical steric stabilization. According to DLVO theory, the greater the absolute value of zeta potential, the greater the electrostatic repulsion between particles and thus the more stable the slurry. The zeta potential of silica slurry without and with 0.1 wt% AA-AMPS dispersant as a function of pH value is shown in Fig. 2. It can be seen that the isoelectric point (IEP) of silica powders is about 2.2 and the absolute value of zeta potential increases with pH value on the right side of the isoelectric point. The maximum value of zeta potential is obtained at pH value about 10.5. In addition, it can be seen that the absolute value of zeta potential of the slurry with AA-AMPS is higher than that without AA-AMPS, which indicates that AA-AMPS has obvious dispersive action.

3.1.2. Effect of pH value on rheological properties

According to Fig. 2, it is known that silica slurry should have good dispersity in high pH value owing to the high absolute zeta potential value. However, silica is an acidic

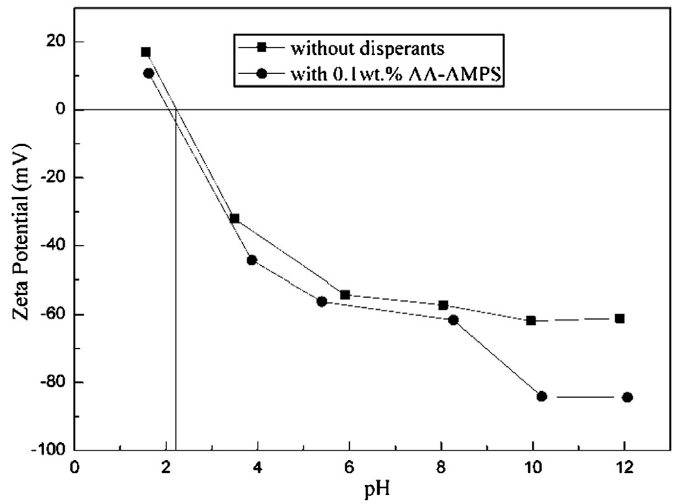

Fig. 2. Zeta potential of silica slurries.

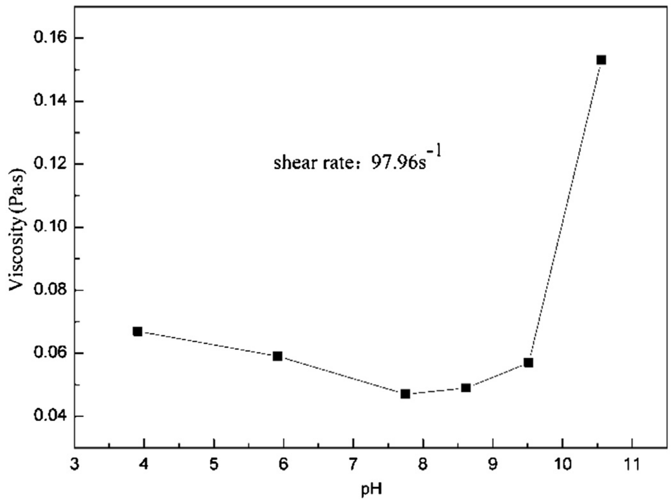

Fig. 3. Effect of premix solution pH value on viscosity of silica slurries.

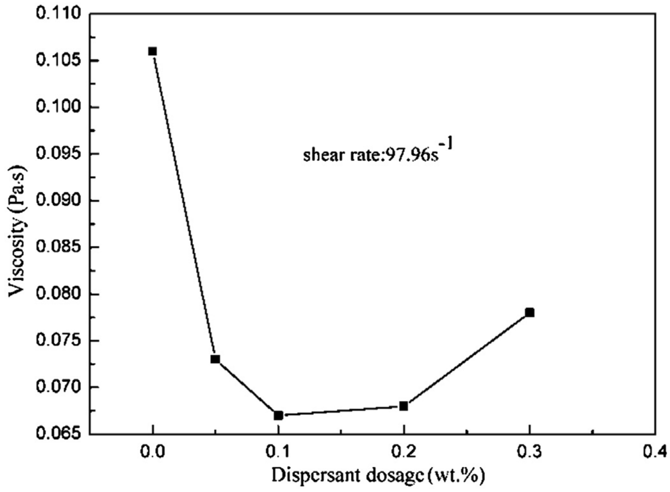

Fig. 4. Effect of dispersant dosage on viscosity of silica slurries.

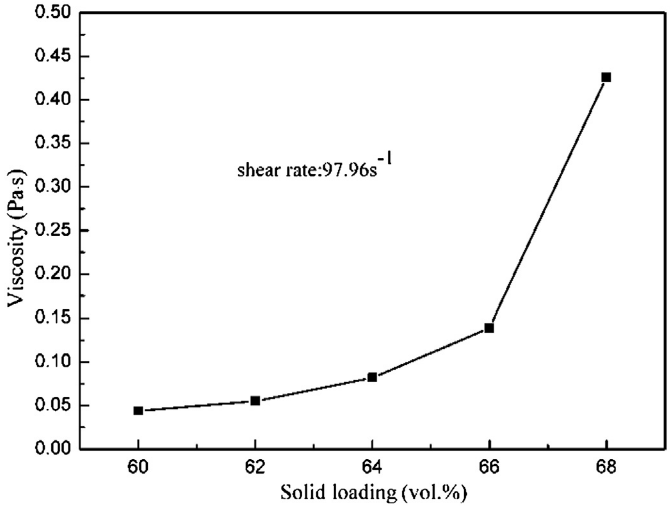

Fig. 5. Effect of solid loading on viscosity of silica slurries.

oxide, so alkalinity solution will promote its hydrolyzation that produces silicic acid hydrosol which has thickening function to the slurry. As shown in Fig. 3, the higher the pH value of the premix solution is, the thicker the slurry is. When pH value increases to about 10, the viscosity of the slurry rises sharply, which suggests that massive silica powders begin to dissolve. Moreover, no matter what the pH value of the premix is, the pH value of the slurry is about 4. The suitable pH value of the premix solution is about 7.7 (the pH value of distilled water), which corresponds to a pH value of slurry of about 4.5.

3.1.3. *Effect of dispersant dosage on rheological properties*

As mentioned above, the zeta potential of silica slurry with AA-AMPS is higher than that without AA-AMPS, which indicates that AA-AMPS has dispersive action to silica powders. As can be seen in Fig. 4, viscosity of the slurry decreases sharply when AA-AMPS is added. The optimum dosage of AA-AMPS is 0.1 wt% of silica powders. Both insufficient and excessive dosage of dispersant will lead to the increase of viscosity. When the dosage of AA-AMPs is insufficient, it is difficult for AA-AMPS to form saturation absorption on the surface of silica powders, which leads to weak electrical steric stabilization function. When the dosage of AA-AMPs is excessive, addition of AA-AMPS will increase the ion concentration in the suspension, which can condense the double layer electric field and then reduce the absolute value of zeta potential, resulting in the increase of viscosity.

3.1.4. *Effect of solid loading on rheological properties*

In order to improve density of green and sintered bodies, a high solid loading of slurries is essential. However, the high solid loading may increase the viscosity of slurry and simultaneously the difficulty in casting the slurry to mold. The reason is that when solid loading increases, the free water between particles will be reduced and the interaction of powders in the suspension will be enhanced.

Effect of solid loading on viscosity of silica slurries is shown in Fig. 5. It can be seen that viscosity increases with solid loading. Solid loading of silica slurries can be up to

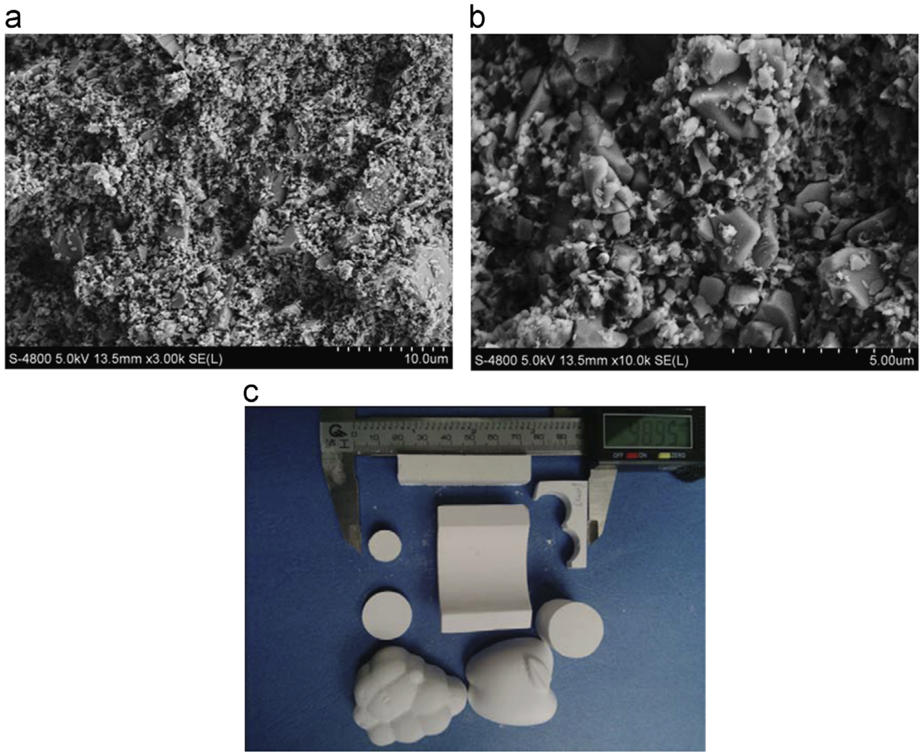

Fig. 6. SEM micrographs (a,b) of the fracture surface of silica green bodies and the photography (c) of complex shape green bodies. (a) x3000 and (b) x10000.

68 vol%. Viscosity of the 68 vol% slurry is only 0.4 Pa · s at the 97.96 s-1 shear rate, which makes the slurry still suitable for casting.

3.2. Properties of green bodies

It can be seen from the SEM micrographs of green bodies (Fig. 6) that silica powders are surrounded by three-dimensional network of colloids. Meanwhile, the structure of green body is uniform and no cracks are observed. Also it can be seen that green bodies with complex shape can be easily fabricated by gelcasing. The pore size distribution of green bodies is shown in Fig. 7. It can be seen that the pore size shows a smooth single peak distribution both before and after binder burnout, except a small shoulder in the range of small pore range for green bodies which may be caused by not perfect homogeneity of the silica particle size as shown in Fig. 1(a). Single peak distribution of pore size indicates that green bodies have a homogeneous structure.

As shown in Fig. 8, when solid loading varies from 60 vol% to 68 vol%, all green bodies show a flexural strength of about 14.5 MPa. When solid loading is lower, organics content is higher in green bodies but silica particles have a looser packing, which makes green bodies does not have the maximum flexural strength. When solid loading is higher, though organics content deceases but the space between powders also decreases, which makes flexural strength of green bodies does not reduce too much. The maximum flexural strength of 15.3 MPa is obtained at the solid loading of 64 vol%, with only 2 wt% organics in the gelcasting slurry.

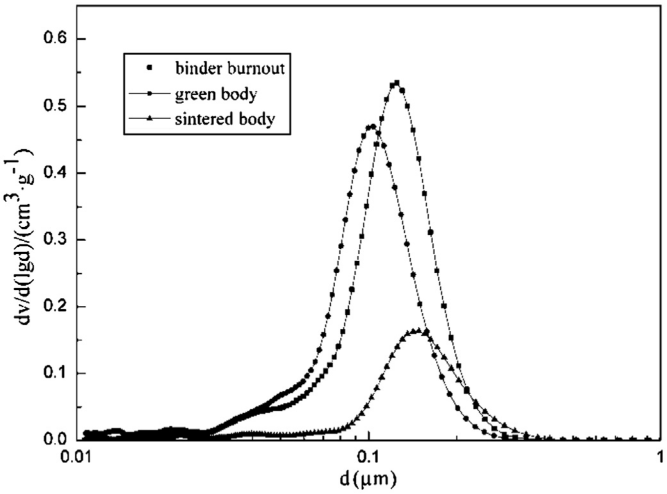

Fig. 7. Pore size distribution of green and sintered bodies.

3.3. Properties of sintered ceramics

The SEM photographs of the fracture surface and XRD pattern of the sintered ceramics are shown in Fig. 9. It can be seen that silica ceramics have a neat fracture surface, relatively high density and homogeneous pore distribution. According to the pore size distribution of sintered ceramics in Fig. 7, it also can be known that pore size distribution of ceramics is smooth single peak distribution, which suggests that ceramics have a homogeneous microstructure. From XRD result (Fig. 9), it can also be seen that no obvious crystallization has taken place and the main phase of silica ceramics is amorphous, which is essential for the expected excellent properties of silica ceramics. The detailed properties of the sintered ceramics are listed in Table 1. In the Low-toxicity HEMA gelcasting system reported by Zhang and Cheng [15], bulk density and flexural strength of silica ceramics reached 1.84 g/cm^3 and 28 MPa, respectively. In the AM gelcasting system reported by Hu et al. [5], bulk density and flexural strength of silica ceramics (nanometer silica was used as sintering aids) reached 2.05 g/cm^3 and 40 MPa, respectively. Apparently, properties of silica ceramics prepared by gelcasting using DMAA in the present work is superior to that using HEMA. Silica ceramics obtained in this study have a higher flexural strength than that prepared by gelcasting using AM, although bulk density of silica ceramics obtained in this study is lower.

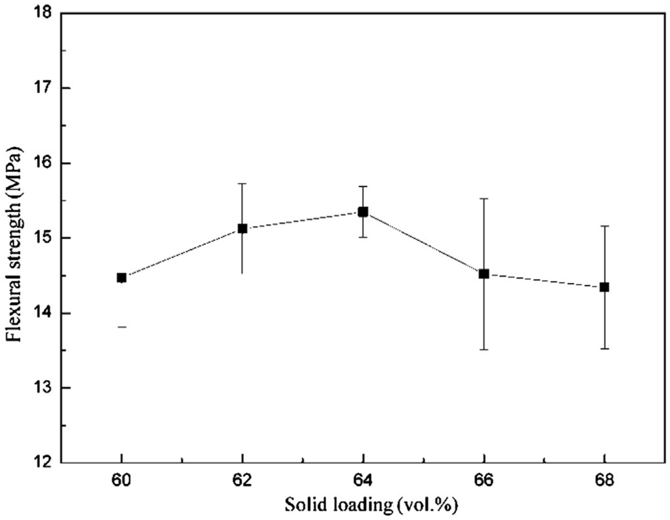

Fig. 8. Effect of solid loading on flexural strength of green bodies.

4. Conclusions

Silica ceramics with excellent properties are successfully prepared by the aqueous gelcasting using a low-toxicity monomer DMAA as gelling agent. The best conditions are pH value of 7.7 and dispersant dosage 0.1 wt%, which helps to prepare the concentrated slurry with low viscosity and good liquidity. Silica green bodies have a homogeneous structure and the maximum flexural strength of green bodies can be up to 15.3 MPa when the solid loading is 64 vol% while organics content is only 2 wt% in the gelcasting slurry.

The sintering shrinkage, bulk density, coefficient of linear expansion and flexural strength are 5.2%, 1.95 g/cm^3, 0.58×10^{-6} k^{-1} (200 °C) and 67.4 MPa, respectively. The dielectric constant and loss (1 MHz) are 3.26 and 7.8×10^{-4}, respectively.

Table 1
Properties of sintered silica ceramics.

Property	Value
Sintering linear shrinkage (%)	5.2
Bulk density (g/cm^3)	1.95
Flexural strength (MPa)	67.4
Coefficient of linear expansion at 200 °C (k^{-1})	0.58×10^{-6}
Dielectric constant (1 MHz)	3.26
Dielectric loss (1 MHz)	7.8×10^{-4}

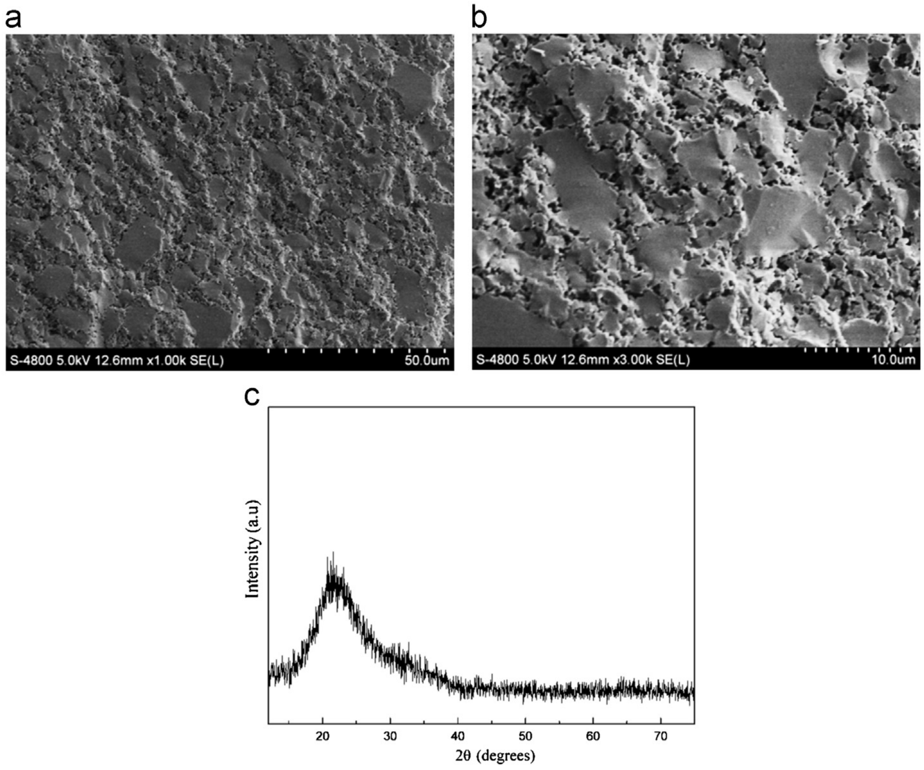

Fig. 9. SEM micrographs (a,b) and XRD pattern (c) of sintered ceramics. (a) x1000 and (b) x3000.

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