CONTENT

Darko Landek, Lidija Ćurković, Ivana Gabelica, Irena Žmak, Zrinka Švagelj

Application of Simplex Lattice Mixture Design for Optimization of Rheological Properties of Alumina Suspensions for Slip Casting

[1] Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, Zagreb, Croatia

Abstract

In this work highly concentrated (70 wt. %) aqueous suspensions of alumina (Al_2O_3) were prepared for slip casting. The suspensions were stabilized with different combinations of three dispersants: (A) disodium salt monohydrate (Tiron), (B) Darvan C-N, 4,5-dihydroxy-1,3-benzenedisulfonic acid, and (C) citric acid monohydrate. The amounts of the dispersants were selected using the Simplex lattice mixture design to evaluate the effect of the dispersants content and their combination on the rheological properties of highly concentrated alumina suspensions. The regression analysis and the response surface plots showed a synergistic effect on decreasing the apparent suspension viscosity below 12 mPa·s, after the addition of small concentrations of the dispersants Tiron and the citric acid to the Darvan C-N. The antagonistic effect of the mixture of dispersants was obtained after adding small amounts of the Darvan C-N and citric acid to the Tiron, which increased the apparent viscosity up to 20 mPa·s.

Keywords: *alumina suspension, slip casting, viscosity, Simplex lattice mixture design.*

1. Introduction

Aluminium oxide or alumina (Al_2O_3) is an oxide technical ceramic material containing α-Al_2O_3 or corundum, the thermodynamically most stable form with the hexagonal unit cell (Figure 1). Also, alumina is available in various metastable polymorphs such as γ, δ, η, θ, κ, χ [1,2]. The oxygen anions (O^{2-}) define a nearly hexagonal close-packed (HCP) structure and the aluminium cations (Al^{3+}) occupy 2/3 of the octahedral sites in the HCP lattice. Each Al^{3+} centre is octahedral.

Among the ceramic materials, alumina is the most commonly used oxide ceramic due to its unique properties such as high elastic modulus, high wear resistance, high chemical corrosion resistance, high-temperature stability, retention of strength at high temperatures, but also brittleness and low fracture toughness [3]. Commonly, alumina is the first choice as a refractory material because of the low cost, simple handling and production, and the possibility to be shaped and sintered to full density without the use of protective atmosphere [4].

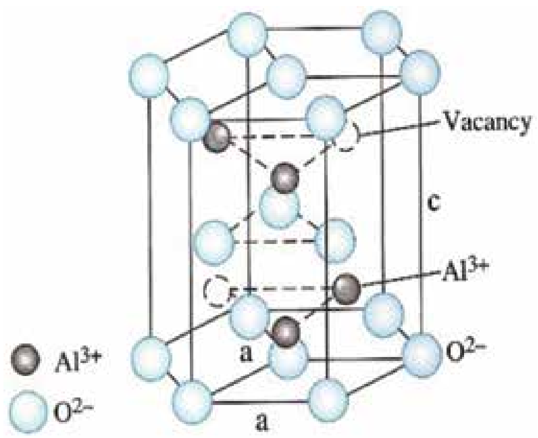

Fig. 1. Structure of α-Al_2O_3 [1].

Biocompatibility makes alumina a high-potential material in medical applications (dental, cardiologic, orthopaedic, bionic) [5,6]. High purity alumina (> 99.5 wt. %) may be used as a structural element and electric insulator in nuclear reactors, for corrosion and wear protection, in automobile and spacecraft industry, in environmental industries, in water vapor processing, as well as in oil and gas energy production [6,7].

The selection of raw materials and additives, the forming of the green bodies, and the sintering process (conventional and non-conventional) together influence the formation of the vitally important microstructure, and thereby the desired properties of the final ceramic product (Figure 2) [8-10].

The methods for forming ceramic parts can be divided into the following basic types:

- pressing (0 – 15 % moisture)
- plastic forming (15 – 25 % moisture)
- casting (> 25 % moisture).

One of the simple forming casting methods is slip casting. It can be used for the manufacture of prototypes, parts with complex geometries as well as for large items.

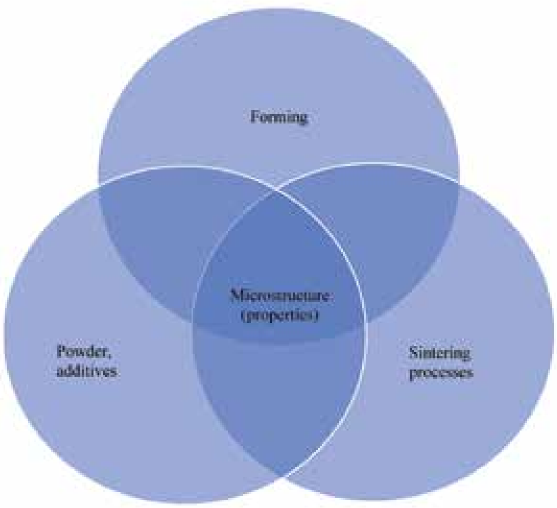

Fig. 2. Influences on microstructure and properties of ceramic parts.

The production of sintered products from slip cast alumina ceramics is carried out in three interdependent steps consisting of [11,12]:

(i) preparation of a stable suspension;
(ii) green body formation;
(iii) densification of the body during sintering.

To produce high-quality aluminium oxide ceramics by slip casting, an Al_2O_3 powder with particle sizes between 1nm and 1 mm is used, which is mixed with water, dispersants, and additives to form a stable highly concentrated suspension (a slip). The slip casting method uses gypsum moulds in which the suspensions dry by absorbing water (Figure 3). To produce a high-quality sintered ceramic product, it is necessary to ensure the stability of the ceramic suspension, which determines the homogeneity of the composition and the isotropic properties of the green body. The stability of the suspension is disturbed by the adhesion of the grains to aggregates that fall to the bottom in the form of sediment or the lifting of the grain by hydromechanical buoyancy and the formation of a surface film. Both phenomena result in the appearance of inhomogeneous areas in the suspension composition and later to the formation of porosity and poorer properties of the sintered product. The application of the dispersants reduces the apparent viscosity of the suspensions with very high solid content and increases the suspension stability, which allows good filling of the mould and obtaining uniform formation of the green body [5,6,13].

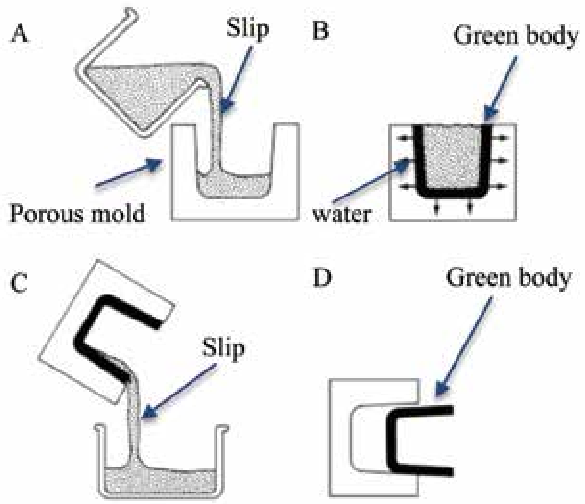

Fig 3. Schematic illustration of slip casting process: (A) filling a porous mould with slip, (B) removing water from suspension by capillary action through small pores in mould and formation of compact (green body) along mould walls, (C) draining excess slip, (D) green body drying and removing from mould [14].

The difference between the ceramic product obtained by slip casting a stable and an unstable suspension is best illustrated in Figure 4.

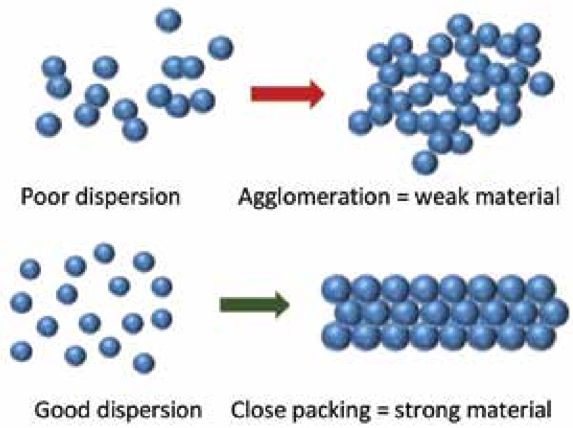

Fig. 4. Influence of particles dispersion on properties of sintered ceramic products [3].

The influence of the dispersant content and combination was investigated in several papers [15-17]. The usual industrial dispersants are ammonium polymethacrylate ("Darvan C-N") [18,19], 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt ("Tiron") [20], poly(maleic acid) (PMA) [21] etc. It was found that the minimal viscosity (7 mPa·s) of highly concentrated alumina (70 wt. % of Al_2O_3 powder) water suspension was obtained with the addition of 0.75 wt. % of Darvan C-N, or 0.1 wt. % of Tiron or 0.3 wt. % of citric acid [5,6].

In this research, the influence of the combination of three dispersants Tiron (4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt monohydrate), Darvan C-N (an ammonium polymethacrylate water solution), and citric acid monohydrate on the viscosity of highly concentrated alumina suspensions for slip casting was investigated and statistically optimized.

2. Materials and methods

2.1. Preparation of alumina suspensions

Aqueous alumina suspensions with a solid loading of 70 wt. % were prepared from high purity Al_2O_3 powder (chemical composition of Al_2O_3 powder, according to the manufacturer's data, is given in Table 1) with an average particle size between 300 nm and 400 nm (Alcan Chemicals, Stamford, CT, USA), deionized water and three dispersants denoted as A, B, C:

- Dispersant "A" is 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt monohydrate (Sigma-Aldrich Chemie GmbH, Germany) commercially named Tiron.

- Dispersant "B" is an ammonium polymethacrylate water solution (Vanderbilt Chemicals, LLC, CT, USA), commercially named Darvan C-N.

- Dispersant "C" is citric acid monohydrate, >99.7 % purity (VWR Chemicals, BDH Prolabo, Belgium).

Table 1. Chemical composition of Al_2O_3 powder.

Component, wt. %					
MgO	**Fe_2O_3**	**SiO_2**	**Na_2O**	**CaO**	**Al_2O_3**
0.066	0.015	0.02	0.05	0.013	balance

All suspensions were prepared by adding deionized water, dried ceramic powder, and dispersant into the grinding jar of a planetary ball mill. The grinding jar and ten balls used for the homogenization are made of alumina ceramics to prevent the contamination of suspensions. Each of the prepared suspensions was homogenized for 90 min at a rate of 300 rpm in the planetary ball mill (PM 100, Retsch, Germany). To remove air bubbles and to achieve homogeneity of the prepared suspensions, each suspension was treated in an ultrasonic bath.

2.2. Rheological measurements

Rheological measurements were conducted using the rotational viscometer DV-III Ultra (Brookfield Engineering Laboratories, Inc., MA, USA) in a small sample chamber with the SC4-18 spindle. Pre-shearing lasted for 2 min at a shear rate of 100 s^{-1}. The shear rate was gradually increased from 0.1 to 180 s^{-1}, and then reduced back to 0.1 s^{-1}. The shear rate increase/decrease interval was divided into 50 equal time frames of 3 seconds each. Rheological measurements were conducted just before each shear rate change. The temperature was kept constant at 25 °C ± 1 °C using the thermostatic bath Lauda EcoRE 415 (Lauda-Brinkmann, LP, USA). Flow curves were recorded for each dispersant type and each dispersant concentration.

2.3. Simplex lattice mixture design

The simplex lattice mixture design was used to evaluate the effect of different amounts of dispersants: Tiron (x_A), Darvan C-N (x_B), and citric acid (x_C) on the apparent viscosity of highly concentrated alumina suspensions. The concentrations of each dispersant in the 70 wt. % alumina suspensions were expressed as fractions of the mixture as shown in Figure 5.

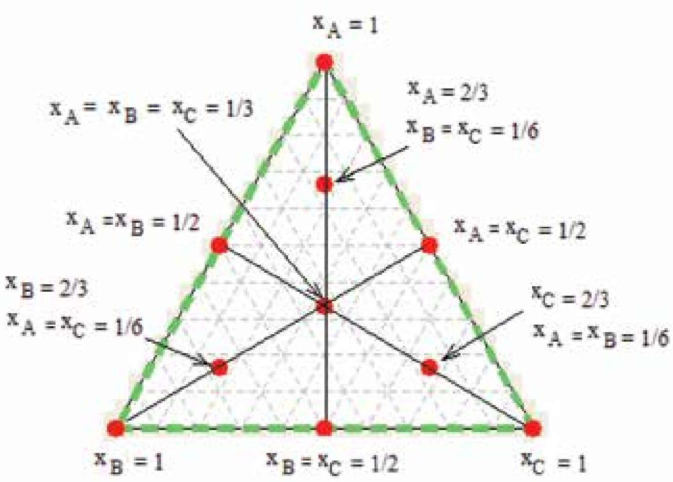

Fig. 5. Simplex lattice mixture test design for the addition of dispersants used in the preparation of 70 wt. % alumina suspensions.

The mixtures of dispersants were prepared as shown in Table 2. Three tested combinations were obtained with three single dispersants (label 1 to 3), three test combinations with two dispersants (label 5, 7, and 9), and four test combinations with three dispersant mixtures (label 4, 6, 8, and 10).

Table 2. Amounts of dispersants (Tiron, Darvan C-N and citric acid) in 70 wt. % alumina suspensions.

Label of suspension	Dispersant, wt. %		
	A: Tiron	B: Darvan C-N	C: citric acid
1	0.50	0	0
2	0	1	0
3	0	0	0.30
4	0.16	0.66	0.23
5	0.30	0	0.20
6	0.36	0.66	0.13
7	0.3	0.80	0
8	0.16	0.86	0.13
9	0	0.80	0.20
10	0.23	0.73	0.16

The experimental results of the apparent viscosity measurements were analysed using the MiniTab software, with a combination of response surface and regression analysis.

3. Results and discussion

3.1. Viscosity measurements

Viscosity measurements are often used to estimate suspension stability. The stability of highly concentrated alumina suspensions (70 wt. % Al_2O_3) was estimated by rheological measurements at a shear rate of 50 s^{-1}. This shear rate is usually achieved during gravity slip casting. The measured values of the apparent viscosity and pH values for the prepared suspensions are presented in Table 3. The lowest viscosities were obtained in suspensions 7 (0.3 wt. % Tiron, 0.8 wt. % Darvan C-N), 8 (0.16 wt. % Tiron, 0.86 wt. % Darvan C-N, 0.13 wt. % citric acid), and 9 (0.8 wt. % Darvan C-N, 0.2 wt. % citric acid). These results showed the synergistic effect of a combination of dispersants A + B, and A + B + C. The suspensions 1 and 5 showed the highest values of apparent viscosity and the antagonistic effect of the combination of dispersants A + C.

Table 3. Apparent viscosity and pH value of 70 wt. % Al_2O_3 suspensions with variation of added dispersants (shear rate 50 s^{-1}).

Label of test sample	pH	η, mPa·s
1	6.74	23.93
2	8.70	13.62
3	6.06	15.08
4	5.63	13.77
5	6.23	22.24
6	6.20	14.85
7	7.75	12.16
8	6.57	12.62
9	6.20	13.01
10	6.15	13.62

3.2. Statistical analysis

The contour plot of the response surface for measured apparent viscosity dependent on the dispersant content is shown in Figure 6. From the contour view of the measured apparent viscosity, the area of lower viscosity values is observed in the lower left-hand corner of the view. These favourable lower viscosity values are achieved by a combination of dispersants B (Darvan C-N) and C (citric acid), possibly with a small addition of dispersant A ($x_A < 1/3$).

The regression analysis of the response surface of apparent viscosity dependent on the type and content of dispersants was conducted using the MiniTab software. The influence of interactions among the dispersants Tiron (factor A), Darvan C-N (factor B), and citric acid (factor C) on the apparent viscosity is shown in Table 4.

Using the regression analysis and the results in Table 4 the following regression equation for the prediction of viscosity (η, mPa·s) of 70 wt. % alumina suspensions dependent on wt. % of added dispersants is estimated:

$$\eta = 23.42 \cdot x_A + 14.28 \cdot x_B + 15 \cdot x_C - 30.61 \cdot x_A \cdot x_B + +5.32 \cdot x_A \cdot x_C - 8.66 \cdot x_B \cdot x_C \quad (1)$$

The coefficient of determination of the model in equation (1) is R^2 = 0.9082. The calculated regression model indicates a significant synergistic effect of the dispersants A and B on the reduction of suspension viscosity. This significance of an action is indicated by the *p*-value of their regression coefficient, which is 0.021 and satisfies the condition of statistical significance of the action of the observed effect in the experiment ($p < 0.05$), Table 4.

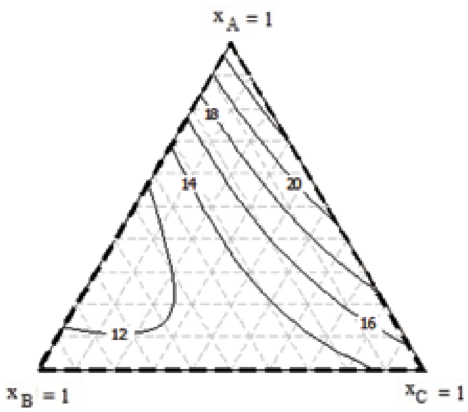

Fig. 6. Mixture contour plot of apparent viscosity (mPa·s) of the 70 wt. % alumina suspensions.

The estimated equation applies to the following concentrations of additives: Tiron from 0 to 0.50 wt. %, Darvan C-N from 0 to 0.86 wt. %, and citric acid from 0 to 0.30 wt. %, at ashear rate of 50 s^{-1}.

Mixing dispersants B and C also shows a synergistic effect on the reduction of viscosity, which can be deduced from the negative value of the regression coefficient with the product of their weight fractions. However, the combined effect of dispersants B and C on the viscosity reduction is not statistically significant, because the *p*-value of the product of their weight fractions is higher than 0.05. The antagonistic effect of the mixture of dispersants was obtained after adding small amounts of the Darvan C-N and the citric acid to the Tiron with increasing viscosity up to 20 mPa·s.

The addition of only one dispersant to the Al_2O_3 aqueous suspension reduces the viscosity of the suspension, but only for certain values of the weight fraction of the dispersant with small variations of the values around the optimal content. The simultaneous addition of two or three dispersants results in a reduction of the apparent viscosity with a wider allowable range of variation around the range of optimum dispersant proportions.

Table 4. Estimated regression coefficients in the linear model of apparent viscosity (η, mPa·s) of 70 wt. % alumina suspensions dependent on added dispersants.

Term	Coefficient	Sum of error of coef.	*p*-value
x_A	23.42	1.807	
x_B	14.28	1.807	
x_C	15.00	1.807	
$x_A \cdot x_B$	−30.61	8.326	0.021
$x_A \cdot x_C$	5.32	8.326	0.557
$x_B \cdot x_C$	−8.66	8.326	0.357

Based on equation (1) and Figure 5 the combination of dispersants can be optimized by looking for the combinations resulting in a minimum apparent viscosity of high-concentrated Al_2O_3 suspension suitable for slip-casting.

4. Conclusions

The focus of this research was on the influence of three different dispersants on the apparent viscosity of highly concentrated alumina suspensions with 70 wt. % of dry Al_2O_3 powder. The simplex lattice mixture design was used to evaluate the effect of different amounts of dispersants (Tiron, Darvan C-N, and citric acid) on viscosity. When analysing the rheological test results, the synergistic effect of decreasing the 70 wt. % alumina suspension viscosity was found for mixtures of dispersants Tiron and Darvan C-N (0.3 wt. % Tiron, 0.8 wt. % Darvan C-N), as well as for Darvan C-N and citric acid (0.8 wt. % Darvan C-N, 0.2 wt. % citric acid). The mixture of all three dispersants in the weight content: 0.16 wt. % Tiron, 0.86 wt. % Darvan C-N, and 0.13 wt. % citric acid also resulted in an acceptably low viscosity of the suspension. A linear regression model is proposed for the optimisation of the dispersant content, which is estimated on the basis of the statistical analysis of rheological measurements.

Acknowledgements

This work has been fully supported by the Croatian Science Foundation under the project IP-2016-06-6000: “Monolithic and composite advanced ceramics for wear and corrosion protection” (WECOR).

References

[1] Ćurković, L., Majić Renjo, M., Ciglar, D., Effects of cold isostatic pressing and granule size distribution on the densification of alumina ceramics. *Mater Test*, 57(6), 1–4 (2015).

[2] Greenwood, N.N., Earnshaw, A., Chemistry of the Elements. Oxford, Butterworth-Heinemann. (2012).

[3] Žmak, I., Ćorić, D., Mandić, V., Ćurković, L., Hardness and Indentation Fracture Toughness of Slip Cast Alumina and Alumina-Zirconia Ceramics. *Materials*, 13, 1–17 (2020).

[4] Gutiérrez, A.V., Cuevas, J.L., Ángeles, A.G., Pilalua, N., Addition of ceramics materials to improve the corrosion resistance of alumina refractories. *SN Applied Sciences*, 1(7), 1–7 (2019).

[5] Vukšić, M., Žmak, I., Ćurković, L., Ćorić, D., Effect of Additives on Stability of Alumina—Waste Alumina Suspension for Slip Casting: Optimization Using Box-Behnken Design. *Materials*, 12, 1–16 (2019).

[6] Sever, I., Žmak, I., Ćurković, L., & Švagelj, Z., Stabilization of highly concentrated alumina suspensions with different dispersants. *Transactions of FAMENA*, 3(72), 61–70 (2018).

[7] Ćurković, L., Kumić, I., Grilec, K., Solid particle erosion behaviour of high purity alumina ceramics, *Ceram Int*, 37, 29–35 (2011).

[8] Lóh, N.J., Simão, L., Jiusti, J., De Noni Jr., A., Montedo, O.R.K., Effect of temperature and holding time on the densification of alumina obtained by two-step sintering *Ceram Int*, 43(11), 8269–8275 (2017).

[9] Tian, Q., Dai, J., Xu, L., Wang, X., Advance of Sintering Methods of High Purity Alumina Ceramics. *Key Eng Mater*, 703, 76–80 (2016).

[10] Ćurković, L., Veseli, R., Gabelica, I., Žmak, I., Ropuš, I., Vukšić, M., A review of microwave-assisted sintering technique, *Transactions of Famena*, 45, 1–12 (2021).

[11] Landek, D., Ćurković, L., Gabelica, I, Kerolli Mustafa, M., Žmak, I., Optimization of Sintering Process of

Alumina Ceramics Using Response Surface Methodology, *Sustainability*, 13, 6739 (2021).

[12] Yuan, C.S., Wang, Z.J., Zhi, Q., Zhang, Y.M., Wang, X.D., Yang, J.F., The preparation and properties of alumina ceramics through a two-step pressureless sintering process, *Mater. Sci. Forum*, 922, 47–54 (2018).

[13] Boch, P., J Niepce, C., Ceramic Materials: Processes, Properties, and Applications., ISTE Ltd, London, UK, (2010).

[14] Souza, L.P.F., Mansur, H.S., Production and characterization of ceramic pieces obtained by slip casting using powder wastes, *J Mater Process Technol*, 145, 14–20 (2004).

[15] Tsetsekou, A., Agraotis, C., Milias, A., Optimization of the rheological properties of alumina slurries for ceramic processing applications Part I: Slip-casting, *J Eur Ceram Soc*, 21, 363-373 (2001).

[16] Majić Renjo, M., Lalić, M., Ćurković, L., Matijašić, G., Rheological properties of aqueous alumina suspensions, *Materwiss Werksttech*, 43, 979–983 (2012).

[17] Wu, L., Huang, Y., Liu, L. Meng, L., Interaction and stabilization of DMF-based alumina suspensions with citric acid, *Powder Technol*, 20, 477–481 (2010).

[18] Singh, B.P., Bhattacharjee, S., Besra, L., Sengupta, D.K., Evaluation of dispersibility of aqueous alumina suspension in presence of Darvan C, *Ceram Int*, 30(6), 939–946 (2004).

[19] Tsetsekou, A., Agrafiotis, C., Leon, I., Milias, A., Optimization of the rheological properties of alumina slurries for ceramic processing applications Part II: Spray-drying, *J Eur Ceram Soc*, 21(4), 493–506 (2004).

[20] Gulicovski, J.J., Čerović, L.S., Milonjić, S.K., Rheology of alumina suspensions stabilized with Tiron, *Korea Aust Rheol J*, 20(2), 65–71 (2008).

[21] Mohanty, S., Das, B., Dhara, S., Poly(maleic acid) - A novel dispersant for aqueous alumina slurry, *J Asian Ceram Soc*, 1(2), 184–190 (2013).