

The Microstructure and Translucency Investigation of Cellulose Containing Low Temperature Fritted Soft-paste Porcelain

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Abstract: Translucent porcelain with appropriate workability has been considered beneficial for light and shadow to be used in the production of ceramic artworks. In addition, using low firing temperature encourages more artists to use this body. The soft-paste cellulose composite porcelain is composed of similar amount of high borax/calcia leadless frit and kaolin with 3% Vee gum T as a plasticizer. In order to increase workability and green strength, five volume units of soft-paste porcelain (SP) slip was mixed with one volume unit bleached bagasse pulp of sugar cane slip and then cellulose containing soft-paste porcelain (CSP) slip was made. The samples were formed by hand, dried and then fired at the optimum temperature of 1120 °C for 5 hours. Results showed that the SP sample became self-glazed after firing. Adding 20% paper pulp by 1.4 g/cm³ density in volume to porcelain body slip (1.36 g cellulose fiber in 100 g SP) slightly increased transmission of light. Microstructural analysis showed large amount of glass phase, which improved translucency of the bodies. Moreover, mullite needle shaped crystals were formed with the reaction of clay and molten flux due to low melt viscosity. XRD results clearly showed that the fired soft-paste porcelain contained quartz, mullite, anorthite and albite in the fired state.

Keywords: Soft porcelain, Fritted porcelain, Translucency, Cellulose.

1. INTRODUCTION

Stonepaste, which is known as quartz-frit-clay paste, quartz-frit, frit ware, faience, artificial paste and kashi, was the earliest attempt to manufacture porcelain in the Middle East [1]. The composition was reported of some ten parts of quartz, one part of glass powder and one part of white clay in Egypt, Syria, Iran, Uzbekistan, and Turkey spanning the period from the eleventh to the seventh centuries AD. The low firing soft-paste porcelain prior to the discovery of sources of kaolin (china clay) began in Italy in the sixteenth century AD [2]. In France, soft-paste porcelain bodies were successfully produced at St Cloud, near Paris from the late of the seventeenth century. The formulation of French soft-paste porcelain bodies was constant, which was rich in silica (SiO₂=70-75%), alkalis (Na₂O+ K₂O= 6%) and lime (CaO = 14%). The body formulations are generally given in the notebooks of Jean Hellot (1685-1766) a French academician, chemist and technical director of the factory at Vincennes (which moved to Sevres

in 1756) and involved the production of an intermediate glassy frit from components including soda, sand, gypsum and lime. The first attempt in England was made to manufacture soft-paste porcelain body at about 1745. The early Chelsea formulation was clearly similar to the approach adopted in France. Based upon a glassy frit, and early English and French glassy porcelains were similar in composition with 60-75% silica (SiO₂) and 10-25% lime (CaO). However, they were different in minor components notably the alkalis soda (Na₂O) and potash (K₂O). The French bodies contained higher soda, which was a reflection of the raw material components employed in the crystal glass industries of the two countries. These were based on soda-rich plant ashes and potash in France and England, respectively. Higher alumina (Al₂O₃) in Chelsea porcelain may reflect a higher clay content but may equally reflect the use of alumina in the paste [3]. Optical microscopy, X-ray diffraction, X-ray fluorescence and scanning electron microscopy analyses were carried out on a typical soft (frit)

porcelain plate from 1781 that was made in Sevres, France. The body was detected rich in SiO₂ (73 mass %), CaO (16%) and alkali oxide (8%) and showed acicular wollastonite and tridymite crystals embedded in a glassy matrix consisting of SiO₂ (75%), K₂O (2%), and CaO (9%) [4].

There have been different parameters influencing translucency of unglazed porcelain bodies including: (a) total concentration of crystals; (b) relative proportions of quartz and mullite; (c) refractive indices of the glass phases; (d) degree of iron coloration; (e) content and size of voids. Results of the researches showed that translucency was improved by increasing the glass contents of the body, which led to lower firing temperature and poorer mechanical properties [5]. The decrease in the mullite/quartz ratio in the body would increase the translucency more effectively. On the other hand, the higher amount of the glass reflective index was a very promising mean for achieving high translucency. In addition, physical properties of the fired unglazed porcelain such as porosity content and size is significantly detrimental to the translucency of the body. As an example, the presence of voids in small quantities, even in size as large as 130 μm, is significantly detrimental to the translucency. The presence of pores has strong effect on the transmission of light through the ceramic body because the refractive index between the ceramic matrix and the pores is exceedingly different [5]. Moreover, increasing the porosity decreases the light transmission through the ceramic body. The light transmission is also minimized when the size of pores is near to the optical wavelength [6].

In general, kaolin is used in porcelain bodies but the plasticity of kaolin is not sufficient for many manufacturing methods or may cause cracks in the bodies during working and drying. To solve this problem, some materials such as ball clays can improve the strength of porcelain bodies. On the contrary, these additives caused other problems like undesirable effects on the molding and increasing the production time of the piece [7]. In the last few decades, artists have been working to increase the workability and strength of porcelain body by adding cellulose.

The first attempt was made by Jean-Pierre Beranger in 1987 introducing paper Porcelain [8]. A combination of the translucent porcelain

was also made using pulp, which was designed as bending, twisting and printing pages. The contraction of the porcelain and the pulp of paper were considered very similar, and thin plates of the combination showed the potential of light transmission as well.

The translucent porcelain bodies such as bone china have not commonly shown a good workability in plastic forming. Steve Harrison and coworkers performed an effort in order to resolve the problems associated with the workability of these bodies in 1998 [9]. On the other hand a special cellulose containing porcelain was used to make thin-walled ceramic plates measuring from 60 to 90 cm in the thickness of 1.5-1.1 mm, which reported it easily transferred light. The firing temperature of the bodies was 1250 °C, with dwelling of 4 to 8 hours depending on the size of the engraving [9]. In 1999, Angela Mellor and Owen Rey also were looking for a way to cast a bone china slip using cellulose fibers to improve plasticity of the bodies [10]. In 2006, Kim Jeoung-Ah studied aesthetic and experimental aspect of cellulose fibers containing porcelain body [11]. She developed a hard porcelain body by adding two types of paper pulps and the properties and microstructures of the samples were characterized by XRD and SEM [12]. Aesthetic aspects of this research considering slip casting of different tableware models showed less crazing, bending and deformation of the porcelain containing cellulose fibers in comparison with the main porcelain [13]. There are many aspects to be considered by the creative maker, the first being the nature of the clay and the quality of light coming from within the form. It is embracing for the artist to consider all of these aspects and to create his own way of expressing thoughts and feelings. Artists like Margaret O' Roke, Inkeri Leivo, Mia Göransson, Una Lee, Jeremy Cole, Lilach, Ron Lotan, Chris Wight, and Angela Mellor have worked on the translucent paper composite porcelain for creative ceramic artworks [14].

Generally different cellulose compounds are being used in ceramic industry [15]. For example sodium carboxy methyl cellulose (Na-CMC) may be used as the electrolyte in the production of many ceramics due to its good adhesion, suspension, deagglomeration, and water retention. Also its addition into ceramic glaze

slurries which play a bonding role to increase the strength of raw glaze, can control the drying shrinkage of the green glaze layer as well as avoiding glaze falling off the ceramic body [16]. Nowadays many researchers focused on clay cellulose composites in engineering and bio ceramic industries. Komar and Singh [17] Developed a novel hybrid nano composite of clay cellulose into thermoplastic polymer. They found improvement in material properties such as mechanical, thermal, and water absorption in cellulose-reinforced clay composite.

However, high firing temperature and weak workability make many artists unwilling to work with this type of bodies. Working with a translucent body is very attractive for artists in ceramic area. In the present study, the main focus is to make low temperature soft-paste porcelain frit and study the properties such as translucency and plasticity behavior by adding cellulose.

2. EXPERIMENTAL PROCEDURES

2.1. Materials

A high Borax/calcia leadless frit with melting range of 1500-1700 °F (815-926 °C), Zettlitz kaolin, Vee gum T and cellulose were used for preparation of the samples. Chemical analysis of the frit and Zettlitz kaolin are given in tables 1.

Table 1. The chemical analysis of Zettlitz kaolin and leadless High borax/calcia frit (wt. %).

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	K ₂ O	Na ₂ O	L.O.I
Zettlitz kaolin	47.35	37	0.83	0.2	0.65	0.6	0.5	12.6
High Borax/ Calcia Frit	48.35	11.98			11.36		5.69	

The Vee gum T (which is a commercial ceramic binder containing bentonite,) was used in the body supplied from Axner Pottery supply of Laguna Clay Co.

Table 2. The qualification of VGum T.

Density (mg/m ³)	Viscosity (after shear mixing, 5% dispersant)	Moisture PH
2.6	250 cps ± 25%	8% Max 8.5

In order to increase the workability and green strength of fritted soft-paste porcelain, bagasse¹ pulp of sugar cane (Pars Paper Industrial Group, Iran) was selected because of its short fibers and whiteness. The typical analysis of cellulose are shown in table 3.

Table 3. Typical analysis of bleached bagasse pulp.

Cook Species	Fiber length	Ash	ISO Brightness
Soda Bagasse	0.75 mm	≤1%	≥ 75 ± 4

2.2. Sample Preparation

Two different samples were made. The slip formulation of reference sample of soft porcelain (SP) was shown in table 4. The slips were aged for 2 days and mixed for 6 hours. After pouring the slip on a plaster plate, the sample kneaded until the mix plasticity approach to Atterberg limit. Test samples were made by hand in the thickness of 0.75 mm and dried for 24 h at room temperature, then the prepared samples were dried in an oven for 24 h at 110 °C.

Table 4. Slip formulation of fritted soft-paste porcelain (wt. %).

Materials	Zettlitz Kaolin	Frit	Vee gumT	Water
SP	50%	50%	3%	38%

For the preparation of cellulose fibers slip, 30 g of dry bagasse pulp of sugar cane was soaked in 533 cc water for 1 day and blended by a mixer. For making CSP, 5-unit soft-paste porcelain slip (based on Table 4) mixed with 1 unit volume of cellulose fiber slip in order to increase the workability and green strength.

Firing was carried out in an electric kiln (Atbin, Iran) at different temperatures from 1060 °C to 1160 °C by 20 °C interval. The samples were heated up to the peak temperature within 5h. After that, the temperature was decreased to 1140 °C and soaked at this temperature for 30 minutes. Then the kiln was turned off.

2.3. Characterization Techniques

The open and closed porosities, water absorption, bulk density, the true and apparent densities of the fired samples were determined according to ASTM standard C 200.

For phase analysis DRON-8 X-ray diffractometer was used. The X-ray scan was made over a range of 2θ values of 5–100° with data acquisition for

¹ The dry pulpy residue left after the extraction of juice from sugar cane.

2.0 s at intervals of 0.05°. This was performed using a Siemens D5000 diffractometer operating the X-ray intensities were recorded using a computer system and commercial software Diffract AT. Crystalline phases were identified by comparison with standard reference patterns from the Powder Diffraction File PDF-2 database sets 1–52, maintained by the International Centre for Diffraction Data (ICDD).

Microstructural examination of surfaces were carried out using the VEGA3. Silver coating of the specimens was carried out using a Nano-Structure Coating (Model: DSR1).

The Contrast Ratio is the ratio between the reflectance of a specimen on a black background to that on a white background of a known reflectance. The CR values are calculated according to the equation $CR = Y_b/Y_w$, in which Y_b represents the spectral reflectance of the light of the specimen on a black background and Y_w on a white background. The CR is a direct measure of opacity and decreases as translucency increases. The value of perfectly transparent material is 0, while the value of a completely opaque material is 1. Contrast Ratio was carried out by spectrophotometer model CE 7000A and Propalette software.

3. RESULTS AND DISCUSSION

3.1. Firing Temperature

The samples fired at 1100 °C and less did not show signs of vitrification while other samples deformed at 1140 and 1160 °C. But the samples fired at 1120 °C showed a well vitrified texture without any deformation. Therefore, the firing temperature of 1120 °C with 30 min soaking time was selected as the optimum firing temperature. In some of the previous work, the optimum firing temperature for translucent porcelains have been considered as 1250 °C and higher. For example, Angela Mellore worked with bone china considering the firing

temperature of 1250 °C [18] and Kim Jeoung-Ah studied on the hard porcelain, which became vitreous in 1300 °C. The decrease in optimum firing temperature of the translucent porcelain to 1120 °C which is attractive for ceramic artists can be considered as an important aspects of this research.

3.2. Porosity, Water Absorption and Density

The porosity, water absorption and density of the fired samples are given in Table 5.

The cellulose addition decreased apparent density from 2.13 to 1.356 and increased water absorption from 0.7 to 4.957% as well as open porosity from 1.637% to 6.237% and total porosity from 9.96% to 46.54%.

3.3. Phase Analysis

XRD patterns of the samples are illustrated in Fig. 1. The major crystalline phases in the porcelain fired at 1120 °C are mullite ($3Al_2O_3 \cdot 2SiO_2$), α -quartz (SiO_2), anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$), albite ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$) and amorphous silica-rich phase. Kim Jeoung-Ah found mullite, α -quartz, and anorthite phases in the fired paper composite porcelain [11]. In this body, albite formation can be attributed to the presence of 5.69 wt% Na_2O in frit composition used for SP and CSP samples.

3.4. Microstructural Analysis

Microstructural analysis showed size and level of the porosities within SP and CSP (Fig. 2). The pores are round shaped and isolated which can be related to characteristics of over firing of the specimens [19]. Large amount of glassy phase in the fritted samples improved sintering at low temperature and formed round and isolated pores in the matrix. Although CSP was more porous due to cellulose content but microstructure of the samples showed maximum sizes of pores that are about 100 μm in both samples. Cellulose has increased the number rather than the sizes of the pores in the matrix.

Table 5. The porosity, water absorption and density of the fired samples.

Test property	Apparent Density	True Density	Water Absorption, %	Open Porosity, %	Total Porosity, %
SP	2.13	2.32	0.7	1.637	9.96
CSP	1.356	2.38	4.9	6.6237	46.54

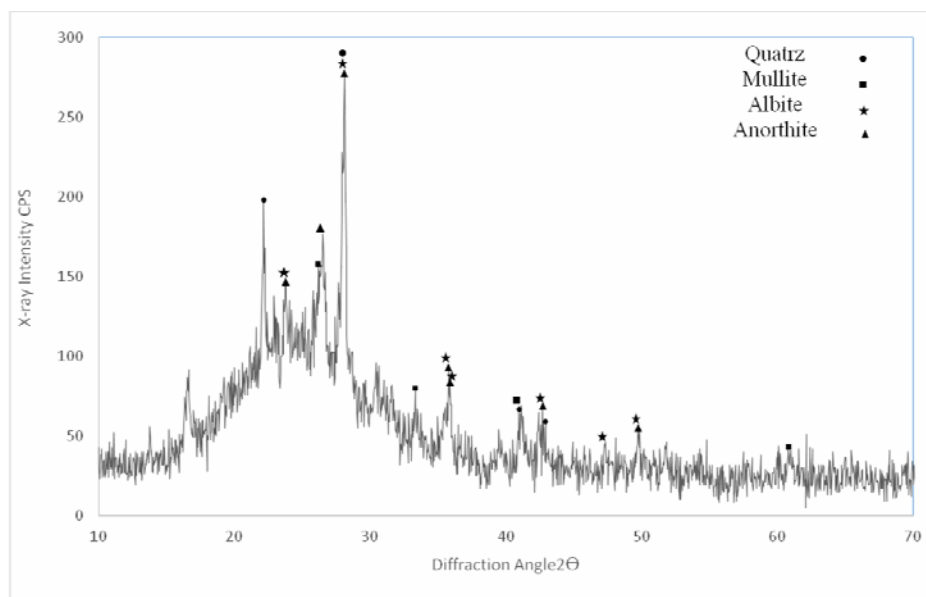


Fig. 1. X-Ray diffraction pattern of high borax/calcia soft-past porcelain fired at 1120 °C.

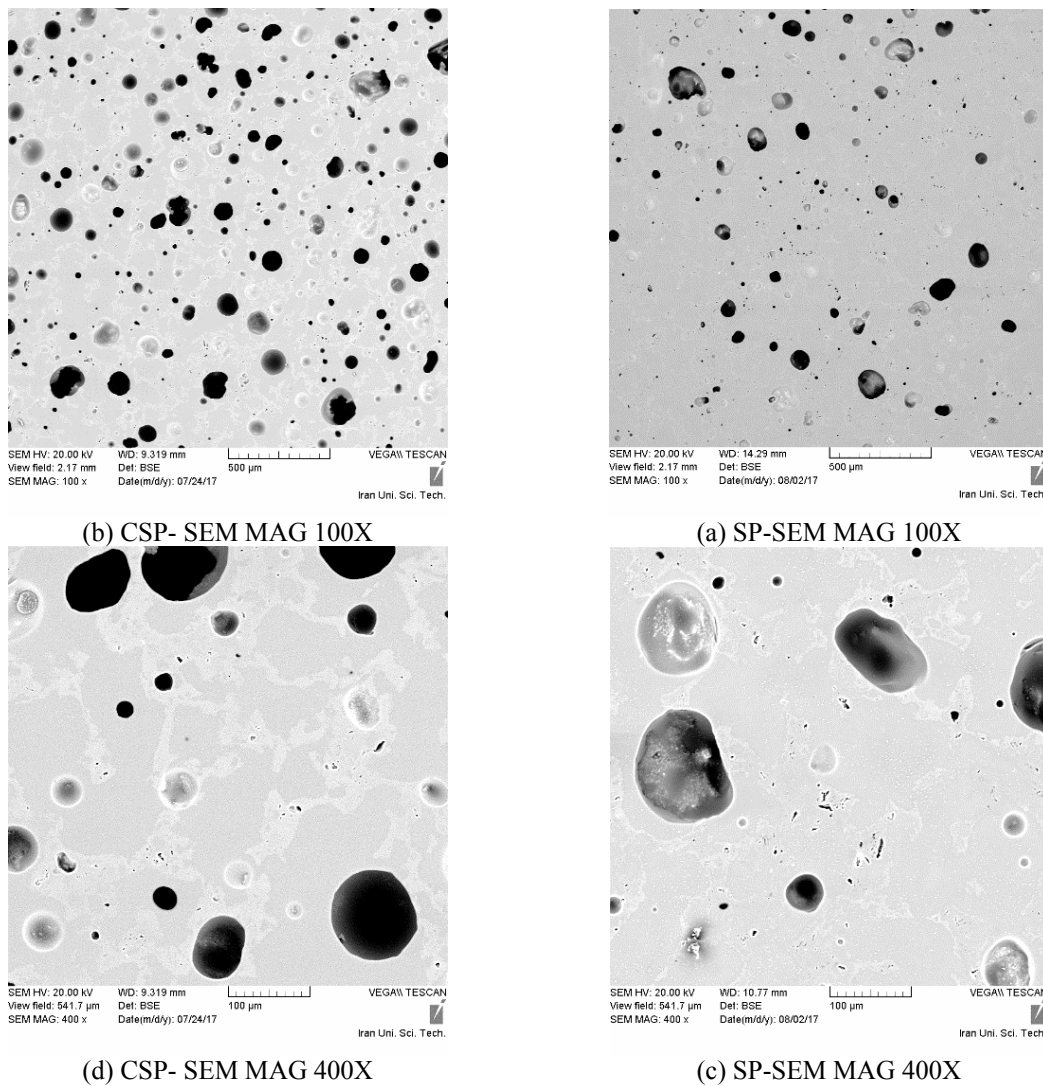


Fig. 2. Pores in SEM electro micrographs of the samples SP and CSP.

The comparison of SP and CSP microstructures showed higher number of pores with nearly similar sizes were shown on CSP sample based on high magnification micrographs in Fig. 2 (C and D) confirming results of Table 5. Backscattered images of the polished surfaces of the samples are given in Fig. 3. Using 50 wt% high borax/calcia frit in the samples as well as XRD result and microstructure analysis showed a large amount of glass phase in both samples. Also needle-shaped crystals, which mullite phase confirmed by phase analysis result, were detected in the matrix of the samples are clearly shown in the micrograph (b). Iqbal Y and Lee WE [20] proposed these mullite needle shaped crystals derived from flux-penetrated clay relicts. Generally the mullite needles form easier in less viscous molten body matrix. The needles achieve a high aspect ratio when their growth is easier. Moreover, SEM micrographs show anorthite and albite in Fig. 4. Both calcium and sodium aluminum silicates morphologies are nearly similar, but the phases formation were identified can recognized by the EDS analysis.

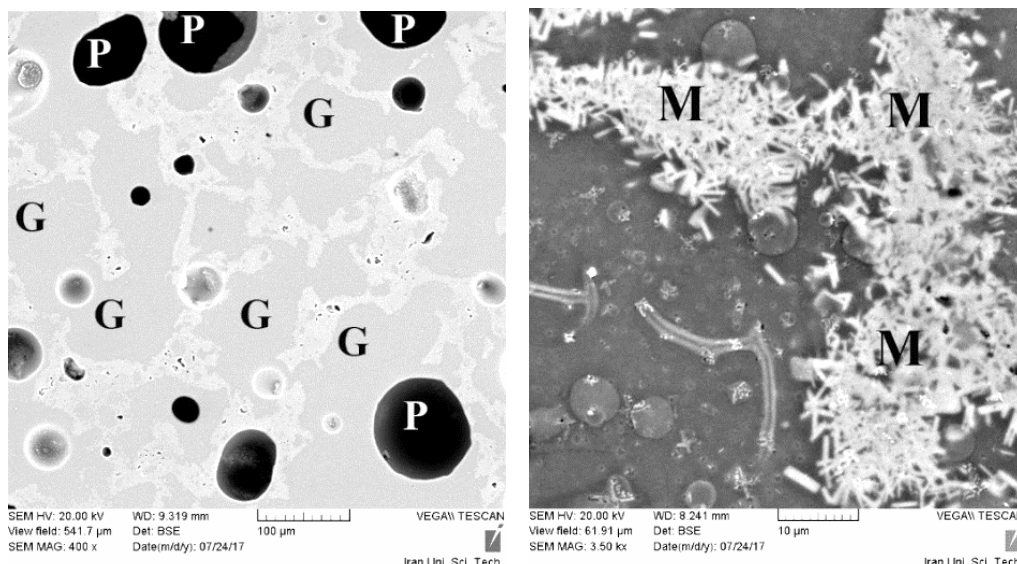
3.5. Translucency Measurement

Recently, optical properties, including the translucency of ceramic bodies have been the focus of many studies because esthetics is increasingly important. Translucency is a

property that cannot be accurately measured [21]. Among the laboratory methods for measuring the percentage of passing light through a material, there is still not a specific method for measuring translucency. A definition of the level of translucency can be provided by contrast ratio method and comparison of the porcelain body with a perfectly transparent material (CR=0%) and a completely opaque one (CR=100%). In order to study the effect of cellulose on the translucency of body, a specimen with cellulose (CSP) and a cellulose-free specimen (SP) were prepared and fired as mentioned. After firing thickness of the specimen was 0.7 mm and translucent-glass (glass slide) was used as a reference. The results of contrast ratio are shown in Table 6.

Results showed that adding 20% volume paper pulp with the density of 1.4 gr/cm³ to porcelain body slip (1.36 g cellulose fiber in 100 g SP) slightly increased transmission of light.

In the present study, cellulose addition increased total porosity as well as the open porosity. The slight improvement in transparency of the cellulose containing sample can be attributed to the differences in total porosity and open pores as well as the probable change in pore size distribution of the cellulose containing fritted soft-paste porcelain.



a) Porosity and glass phase

b) Mullite

Fig. 3. SEM photomicrographs of the sample.

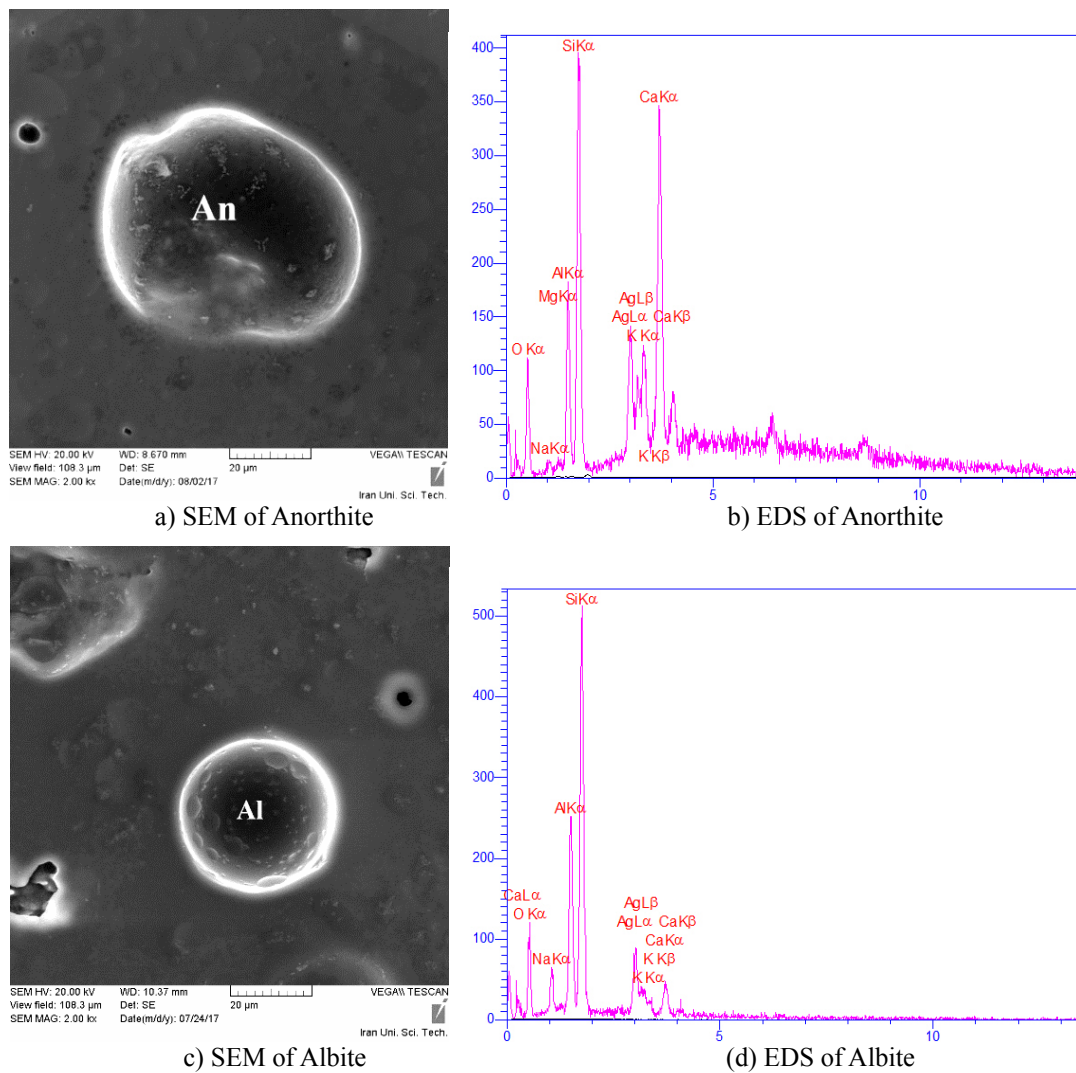


Fig. 4. SEM and EDS of Anorthite (An) and Albite (Al).

Table 6. Contrast ratio.

SP	CSP	Sample
77.8%	77.2%	Contrast Ratio

4. CONCLUSION

Using 50 wt% high borax/calcia frit in the body led to a decrease in the firing temperature to 1120 °C. Cellulose fibers gave a higher green strength and better working characteristics in the green state than that of porcelain. SEM and EDS studies showed the formation of a large amount of glass phase, which was responsible for the translucency in the body. XRD clearly showed that the fritted soft -paste porcelain body in the fired state consists of quartz, mullite, anorthite and albite. This porcelain body with the composition of half

high Borax/Calcia frit and half Kaolin led to the formation of mullite phase at low temperature. Furthermore, adding cellulose to porcelain body improved the workability, green strength and translucency to some extent.

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