

Role of MgF₂ addition on high energy ball milled kalsilite: Implementation as dental porcelain with low temperature frit

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Abstract: Porcelain fused to metal (PFM) has received great attention over the last few years due to its importance in the dentistry. Kalsilite (K₂O·Al₂O₃·SiO₂) is a high thermal expansion porcelain, suitable for bonding to metals. However, kalsilite is a metastable phase which gets converted into crystalline leucite upon heating. In the current work feasibility of developing stable kalsilite phase, dispersion of MgF₂ in it as an additive and using mechanochemical synthesis are studied. Micro fine dental material has been formulated by mixing prepared kalsilite with low temperature frit (LTF) in different ratio. The crystalline phases evolved in fired powders are characterized by powder X-ray diffraction (XRD) technique. Kalsilite with different ratio of LTF has been cold pressed and heat treated to examine its coefficient of thermal expansion (CTE), flexural strength, apparent porosity (AP), bulk density (BD) and microstructure. Results indicate that MgF₂ addition and high milling duration help in kalsilite stabilization. Temperature also plays an important role in this stabilization, and at 1100 °C single phase kalsilite formation is observed. Present outcomes demonstrate that it is easily possible to synthesize a stable single phase kalsilite with desirable properties.

Keywords: kalsilite; porcelain fused to metal (PFM); dental ceramic; mechanochemical synthesis; thermal expansion; X-ray diffraction (XRD)

1 Introduction

Ceramic materials have been widely used in porcelain fused to metal (PFM) and all ceramic restoration systems over the last decade. They typically have high coefficient of thermal expansion (CTE) and high flexural strength. Kalsilite (KAlSiO₄) mineral has a network of tetrahedral Si and Al elements with charge balancing alkali metal ions [1]. CTE of kalsilite is 16×10⁻⁶ (°C)⁻¹ [2]. Kalsilite is a significant constituent

in PFM and ceramic restoration systems [3]. It is used as the precursor of leucite [4]. Becerro *et al.* [4] have previously reported that kalsilite being a high thermal expansion ceramic, is suitable for bonding to metals. Kalsilite however crystallizes as a metastable phase when synthesizing leucite [5,6].

Kalsilite has been synthesized previously by various techniques such as hydrothermal method [7], sol-gel method [8,9] and solid-state method [10,11]. Accompanying with other synthesis methods, mechanochemical process is economical and suitable to prepare pure materials with a micro fine particle size [12–14]. This synthesis involves chemical reactions of solids under the action of mechanical forces. Driving

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force for mechanochemical synthesis is the strain energy stored in the fine powders. The mechanical energy produces structural imperfections in the powder particles during grinding and increases the reactivity of ground materials.

There is lack of research in the stabilization and implementation of this material as PFM. So in order to produce fine stoichiometric kalsilite, mechanochemical synthesis was employed. The aim to improve the stability of kalsilite phase using 2 wt% MgF_2 as an additive has been studied in the present investigation. The ground powders were heat treated at different temperatures and characterized via powder X-ray diffraction (XRD) technique. Optimised kalsilite powders were then mixed with different weight ratio of low temperature frit (LTF) and characterized for CTE, flexural strength, apparent porosity, bulk density and morphology.

2 Experimental procedure

2.1 Materials

Analytical reagent (AR) grade aluminium oxide (Al_2O_3), potassium carbonate (K_2CO_3) and silica (SiO_2) were used as raw materials for kalsilite formulation. Sodium carbonate (Na_2CO_3), potassium nitrate (KNO_3), silica (SiO_2), potassium carbonate (K_2CO_3), borax ($\text{Na}_2\text{H}_3\text{BO}_4 \cdot 10\text{H}_2\text{O}$), feldspar ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$) and magnesium fluoride (MgF_2) were used for preparation of LTF. All materials were AR grade and procured from Loba Chemie Pvt. Ltd (Mumbai, India)

2.2 Preparation of kalsilite and LTF

Potassium carbonate, alumina and silica were weighed in stoichiometric ratio of kalsilite 1:1:1. Weighed mixtures of materials with and without the incorporation of 2 wt% MgF_2 were prepared in the same manner. These mixtures were then pulverized in a high energy planetary ball mill (supplied by V.B. Ceramics, Chennai, India) for 3 h and 6 h with the rate of 250 rpm. Milling was done in a 250 ml zirconia cylindrical jar. The grinding balls made of zirconia having diameter 10 mm were used as a hard grinding medium. Ball to powder weight ratio was kept 4:1. The milling operation of mixtures was carried out continuously at room temperature for 3 h and 6 h. The milled powders were heat treated in an electric furnace at 900–1100 °C at a heating rate of 6 °C/min and

soaked for 1 h. The furnace was equipped with SiC heating element and a program PID528 manufactured by Selectron Process Controls Pvt Ltd., India. This program has the temperature control accuracy of ± 1 °C. To prepare LTF, starting components were mixed in an agate mortar. The mixture was melt in an alumina crucible at 1350 °C for 60 min. The molten frit was quenched in deionized water, air dried and then ball milled to pass a 350 mesh BSS.

2.3 Preparation of samples

The samples prepared for characterization contained different weight percentage of kalsilite. Optimization in choosing the prepared kalsilite was based on its maximum phase formation. Different formulations are presented in Table 1. Rectangular test bars were prepared using a uniaxial hydraulic press under 200 MPa. These bars were heated in a VITA VACUMAT 40T according to a standard dental veneering firing cycle pre-programmed by VITA. It consists of five steps from room temperature to 800 °C. These five steps of firing cycle are: pre-heating at 500 °C for 2 min, heating from 500 °C to 800 °C for 6 min, 1 min soaking at 800 °C followed by cooling to 600 °C in 1 min.

2.4 Characterizations

The crystalline phases were identified by powder XRD technique. XRD patterns were observed using a portable XRD machine (Rigaku, Japan) using $\text{Cu K}\alpha$ radiation employing Ni filter operating at 30 mA and 40 kV. Phase identification was carried out by comparing the respective powder XRD patterns with the standard database stated by JCPDS (PDF-2 Database 2003).

The thermal expansion of the material was

Table 1 Batch composition of different weight percentage of kalsilite and LTF samples

Sample coding	Firing temperature (°C)	Kalsilite (wt%)	LTF (wt%)
K _{1000-20/80}	1000	20	80
K _{1000-25/75}	1000	25	75
K _{1000-30/70}	1000	30	70
K _{M1000-20/80}	1000	20	80
K _{M1000-25/75}	1000	25	75
K _{M1000-30/70}	1000	30	70

determined by dilatometer (supplied by VB Ceramic Consultants, India) in the temperature range 20–550 °C at 6 °C/min. The dilatometer was equipped with SiC heating element with a control accuracy of ± 1 °C. It had Nippon PID programmable digital temperature indicator cum controller. The samples for CTE measurement were cut and polished uniformly to the size of 45 mm \times 15 mm \times 10 mm.

Flexural strength measurements were done according to ASTM C78/C78M using universal testing machine Instron, 3344 (Germany). The specimens were bent in a three-point crossways fit with 20 mm span between the two supports (three-point bending). The load and the corresponding deflections were recorded. The flexural strength was calculated using the following equation:

$$F = \frac{3PL}{2bd^2} \quad (1)$$

where F is the flexural strength (kg/cm^2); P is the maximum applied load; L is the span length; b is the width of specimen; and d is the depth of specimen.

Apparent porosity (AP) and bulk density (BD) of all the kalsilite and LTF samples were determined according to ASTM C20-00. All specimens were polished using emery papers of grades 1/0, 2/0, 3/0 and 4/0 (Sia, Switzerland) followed by polishing on a velvet cloth using diamond paste of grade 1/4-OS-475 (HIFIN). These polished specimens were chemically etched with 40% hydrofluoric acid for 10 s and then washed with distilled water. Finally they were dried and gold sputtered. Micrographs were recorded with the help of a scanning electron microscope (INSPECT 50 FEI).

3 Results and discussion

3.1 Phase analysis of the ground kalsilite at different temperatures

Figure 1 shows the XRD patterns of the sample milled for 3 h at different firing temperatures. Diffraction peaks are well matched to JCPDS Card No. 87-1707. It can be seen that XRD pattern of precursor fired at 900 °C contains hexagonal kalsilite as a major phase alike to JCPDS Card No. 87-1707. As temperature increases from 1000 °C to 1100 °C, kalsilite is present as a major phase in addition to small amount of leucite phase. Unit-cell parameters are $a = b = 5.157$ Å and $c =$

8.706 Å and more similar to those given by Becerro *et al.* [4] ($a = 5.166$ Å and $c = 8.7123$ Å). Presence of broad peaks in XRD patterns shows the small crystallite size of the kalsilite.

Figure 2 shows the XRD patterns of the sample containing 2 wt% of MgF_2 milled for 3 h. It can be noted that XRD patterns of precursor fired at 900 °C and 1000 °C contains kalsilite as a major phase with hexagonal crystal structure. Furthermore when heat treatment is increased to 1100 °C, kalsilite occurs as a major phase with some peaks of leucite crystalline phase. It can be noted that formation of leucite crystalline phase occurs at high temperature. Formation of leucite phase is less in the sample containing MgF_2 in comparison to that of the sample without MgF_2 . It is probable that the presence of MgF_2 additive suppresses the crystallization of leucite.

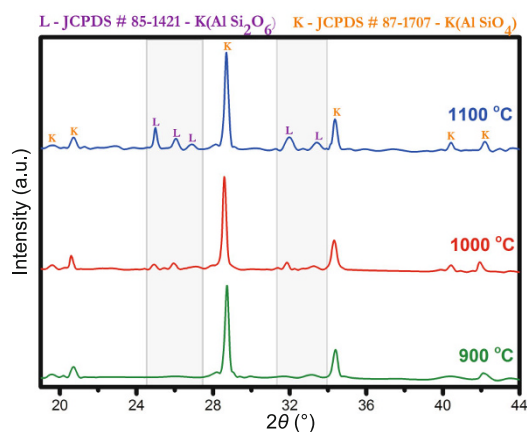


Fig. 1 XRD patterns of the sample milled for 3 h at different firing temperatures.

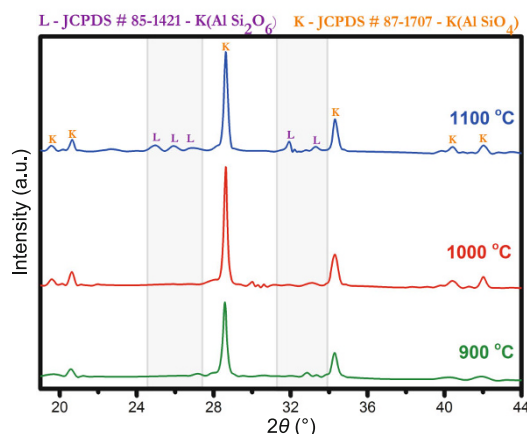


Fig. 2 XRD patterns of the sample containing 2 wt% of MgF_2 milled for 3 h at different firing temperatures.

Figure 3 shows the XRD patterns of the sample milled for 6 h. X-ray lines of the sample fired at 900 °C contain kalsilite as a major phase with small peaks of leucite phase. At temperatures 1000 °C and 1100 °C, leucite is present as a main phase with small peaks of kalsilite crystalline phase. It might be due to high surface energy of ground sample. The smaller the particle size is, the larger the surface area and hence the higher the surface energy will be. Therefore, it can be concluded that the heat for formation of leucite is higher than that of kalsilite. It has also been previously reported by Zhang *et al.* [5] that activation energy for formation of leucite is higher than that of kalsilite. Kalsilite, therefore, crystallizes first as a metastable phase and then reacts with SiO₂ tetrahedra, which leads to formation of leucite phase. In the present work, the sample milled for 6 h has very fine particles in comparison to sample milled for 3 h. In former case therefore, most of the kalsilite converts into leucite at higher temperatures.

Figure 4 shows the XRD patterns of the sample containing 2 wt% of MgF₂ milled for 6 h. It shows hexagonal kalsilite as a major phase with small peaks of leucite at 900 °C, 1000 °C and 1100 °C. Diffraction peaks are well matched to JCPDS Card Nos. 87-1707 and 85-1421. It can be concluded that MgF₂ promotes the formation of kalsilite. Zhang *et al.* [6] studied the effect of addition of CaF₂ on the crystallization of leucite. They found that CaF₂ decreases the crystallization temperature of leucite. Ionic radius of F⁻ ion (1.33 Å) is very close to radius of O²⁻ ion (1.4 Å); therefore, it replaces the O²⁻ ion and forms the Si–F or Al–F bonds [6]. Due to strong electrostatic attraction between Ca²⁺ and O²⁻ ions, network becomes loose. It

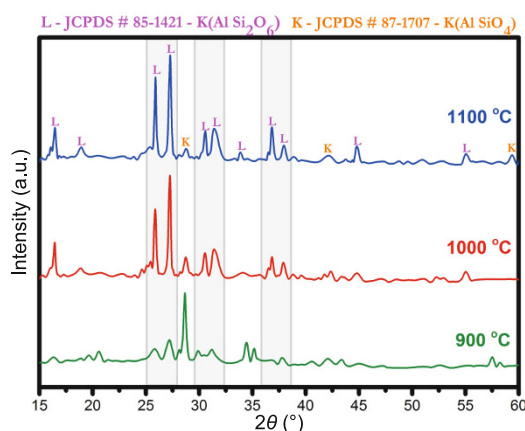


Fig. 3 XRD patterns of the sample milled for 6 h at different firing temperatures.

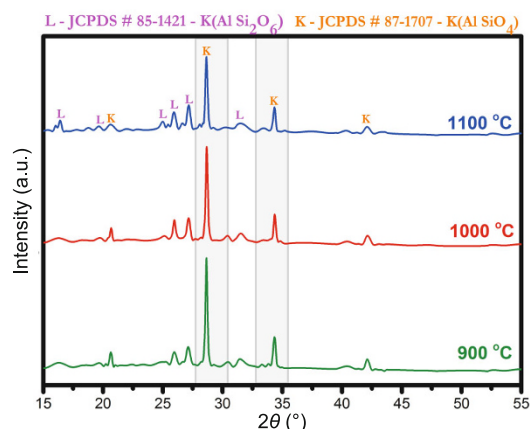


Fig. 4 XRD patterns of the sample containing 2 wt% of MgF₂ milled for 6 h at different firing temperatures.

helps the conversion of metastable kalsilite phase into stable leucite phase at low temperature.

In the present work, whereas, MgF₂ inhibits the formation of leucite phase and stabilizes the kalsilite metastable phase. It may be due to small amount of free silica present in the matrix. When F⁻ ion replaces O²⁻ ion in K⁺, free Mg²⁺ reacts with free silica forming low temperature eutectic phase, enstatite (MgO·SiO₂). It decreases any silica present around grain boundary around the kalsilite and hence suppresses the formation of leucite.

3.2 Coefficient of thermal expansion

Thermal compatibility of PFM from room temperature to the glass transition temperature can be assessed by measuring the average expansion coefficient of metal and porcelain in the range of 20–550 °C. Its thermal expansion is essential to assure good bonding of the ceramic to metal. Figure 5 shows the CTE curves of kalsilite with different weight percentage of LTF, K_{1000-20/80}, K_{1000-25/75} and K_{1000-30/60}. It is found that the addition of kalsilite to LTF increases the CTE of the whole matrix. It may be due to formation of leucite crystalline phase which has high CTE. Glass transition temperatures (T_g) of K_{1000-20/80}, K_{1000-25/75} and K_{1000-30/70}, are determined to be 415 °C, 425 °C and 440 °C, respectively.

Figure 6 shows the CTE curves of kalsilite–2 wt% MgF₂ with different weight percentage of LTF, K_{M1000-20/80}, K_{M1000-25/75} and K_{M1000-30/70}. It is found that the addition of MgF₂ to kalsilite decreases the CTE of final mixture. These CTE values are about 40% less than that of samples without MgF₂. This may be due to

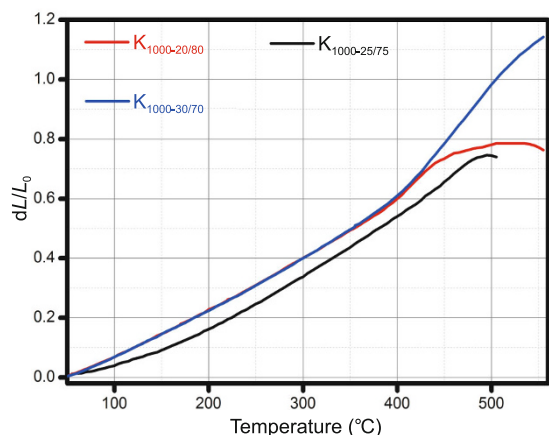


Fig. 5 CTE curves of the samples with different weight percentage of kalsilite and LTF.

the formation of low CTE major kalsilite phase. These results are in conformity with the results of XRD where the sample with MgF_2 has kalsilite as a major phase, i.e., MgF_2 suppresses the formation of leucite. The glass transition temperatures (T_g) of $\text{K}_{\text{M}1000-20/80}$, $\text{K}_{\text{M}1000-25/75}$ and $\text{K}_{\text{M}1000-30/70}$ are determined to be 415 °C, 425 °C and 430 °C, respectively. These prepared materials are suitable for PFM, as their CTE values of 14.0×10^{-6} – 14.8×10^{-6} ($^\circ\text{C}$) $^{-1}$ are close to standard CTE of nickel–chrome alloy (13.9×10^{-6} ($^\circ\text{C}$) $^{-1}$).

3.3 Flexural strength

Figure 7 shows the flexural strength of K_{1000} and $\text{K}_{\text{M}1000}$ with different weight percentage of kalsilite in LTF. Flexural strength increases with increasing the micro fine kalsilite in matrix. Homogenous dispersion of micro fine kalsilite grains within the glassy matrix leads to enhance the mechanical strength. $\text{K}_{\text{M}1000}$ has higher flexural strength than K_{1000} . Subsequently the synthesised samples show better sinterability, low

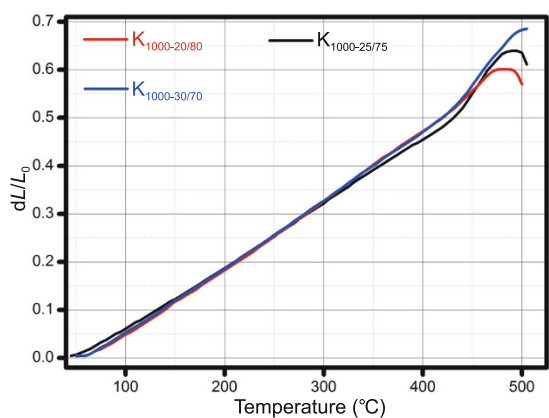


Fig. 6 CTE curves of the samples with different weight percentage of kalsilite–2 wt% MgF_2 and LTF.

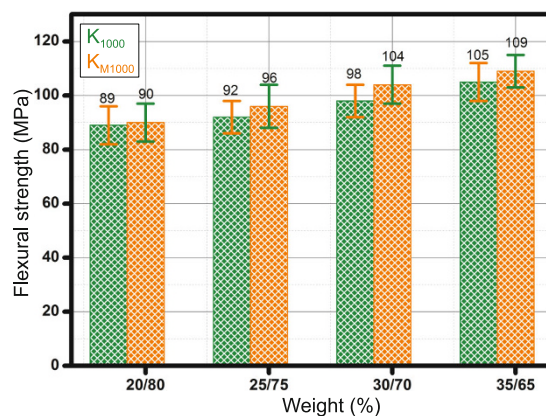


Fig. 7 Flexural strength of K_{1000} and $\text{K}_{\text{M}1000}$ with different weight percentage of kalsilite and LTF.

porosity and high flexural strength. The flexural strength is more or less similar for all samples. However, the mixed samples with 20 wt%, 25 wt%, 30 wt% and 35 wt% kalsilite expressly result in higher flexural strength. This is due to presence of micro fine particles, i.e., larger surface area and hence less porosity.

3.4 Bulk density and apparent porosity

Figure 8 shows the variation of BD and AP with different weight percentage of kalsilite and LTF. It can be noted from Fig. 8 that BD increases with increasing the content of kalsilite followed by a continuous decrease of AP. Micro fine kalsilite particles dispersed throughout the glassy matrix help in improvement of packing density of the samples.

3.5 Microstructure evaluation through SEM

The microstructures of kalsilite with ($\text{K}_{\text{M}1000}$) and without (K_{1000}) MgF_2 with different weight percentage

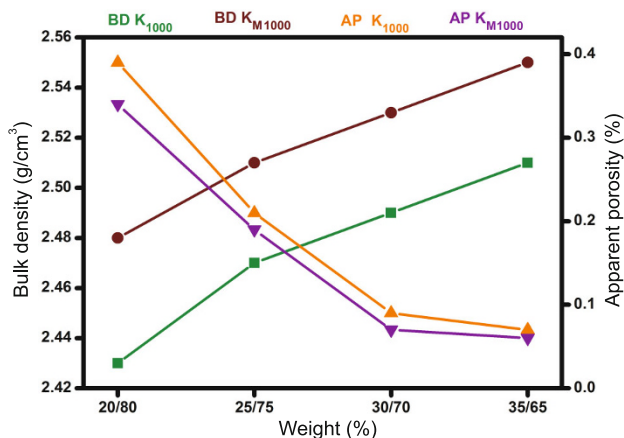


Fig. 8 BD and AP of the samples with different weight percentage of kalsilite and LTF.

of LTF are shown in Fig. 9. There is no visible micro-crack appearance due to phase transformation. Micrographs show a very dense structure which is also

in conformity with the AP and BD plots. This also results in the high flexural strength.

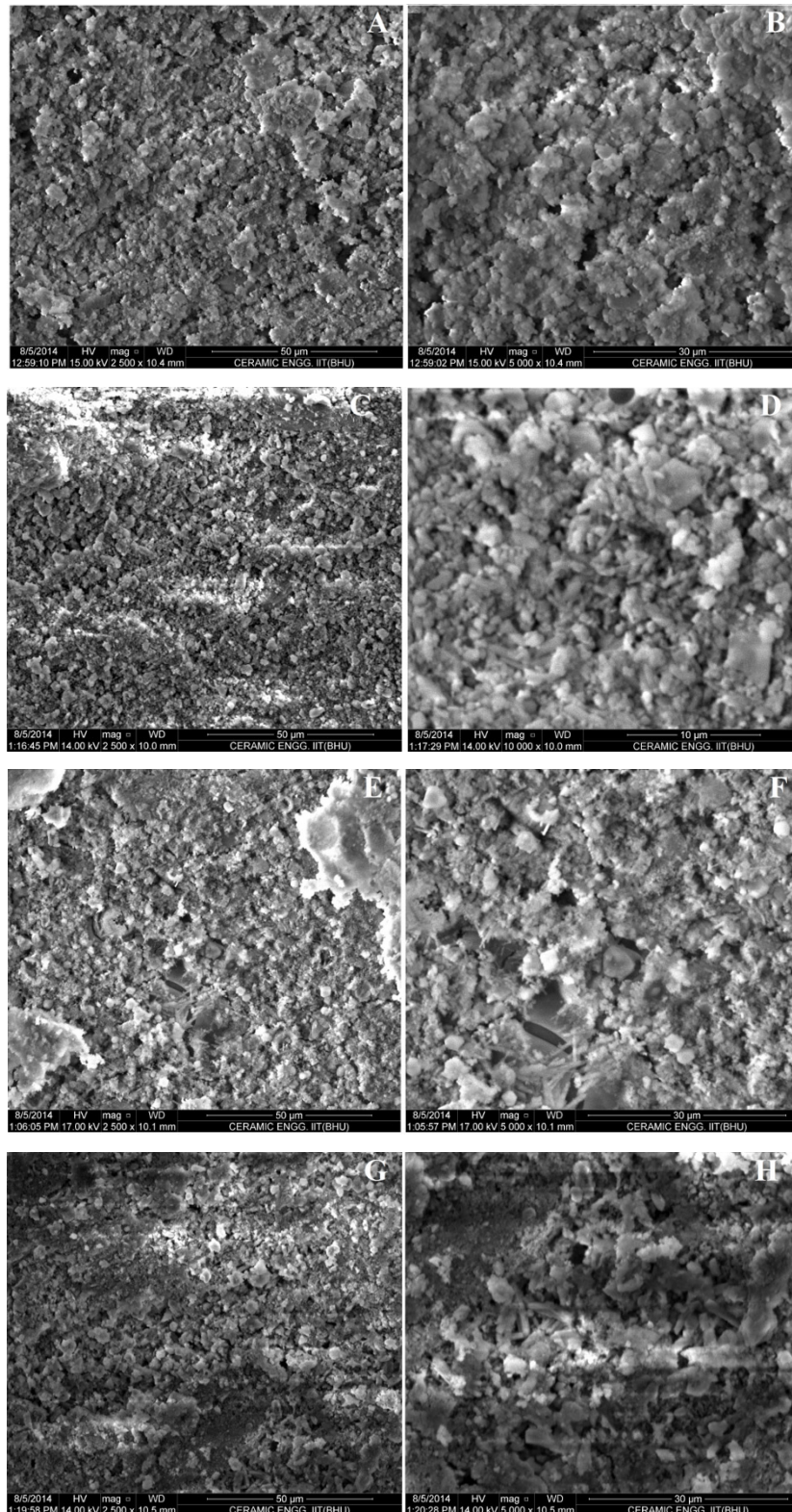


Fig. 9 Scanning electron micrographs of kalsilite with (K_{M1000}) and without (K_{1000}) MgF_2 with different weight percentage of LTF in different magnification: (a, b) $K_{M1000-25/75}$; (c, d) $K_{M1000-30/70}$; (e, f) $K_{1000-25/75}$; (g, h) $K_{1000-30/70}$.

4 Conclusions

Micro fine kalsilite has been successfully synthesised by high energy ball milling. Addition of MgF_2 suppresses the formation of leucite phase and stabilizes the kalsilite phase. Kalsilite–2 wt% MgF_2 with different weight percentage of LTF, shows the CTE value of $14.0 \times 10^{-6} (\text{°C})^{-1}$ to $14.8 \times 10^{-6} (\text{°C})^{-1}$. This value is close to standard CTE of nickel–chrome alloy ($13.9 \times 10^{-6} (\text{°C})^{-1}$). Samples with 20 wt%, 25 wt% and 30 wt% kalsilite have higher flexural strength due to presence of micro fine kalsilite particles in the matrix. Micrographs show very dense structure with no visible cracks. This makes present material suitable for application in porcelain fused to metal.

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