ISSN : 0974 - 7486 Volume 8 Issue 1

Materials Science
An Indian Journal

Trade Science Inc.

Full Paper

MSAIJ, 8(1), 2012 [01-08]

Synthesis and characterization of leucite nano-crystalline extracted from Saudi clay for dental application

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Received: 15th May, 2011 ; Accepted: 21st November, 2011

ABSTRACT

Spherical leucite crystals having nanosize were prepared by heating a powder mixture of metakaolin, K_2SiO_4 and NaOH. The geopolymer thus obtained were fired at elevated temperature up to 1100 ^{0}C and were examined by XRD, DTA and XRF techniques. K-based geopolymer ($K_2O.\ Al_2O_3.\ 4SiO_2.\ 11H_2O$) was investigated due to its attractive refractory properties and its ability to convert to leucite ($KAlSi_2O_6$) on heating. The results show that metakaolin, K_2SiO_3 solution and KOH to regulate the PH form geopolymer, which may crystallize into cristoballite and lecuite, respectively, under thermal treatment. The geopolymer synthesized at alkaline PH, in turn, remains stable at temperatures until 1100 ^{o}C. A further increase in temperature to 1100 ^{o}C led to the formation of leucite crystals of two different diameters, approximately 40 μm and 10–50 μm. The thermal behavior of K-geopolymer was characterized using a variety of techniques in order to explore the details of dehydration, sintering, and crystallization. K-geopolymer was found to offer many of the benefits such as lower sintering temperatures and compositional control without high costs.

KEYWORDS

Metakaoline;
Geopolymer;
XRD;
SEM;
Thermal studies.

INTRODUCTION

Leucite ($KAlSi_2O_6$) has been used as an important crystal phase in dental porcelain/glass materials[1, 2] because of its tone, color appeal and excellent biocompatibility. Furthermore, due to its high melting point (1693 °C)[1, 3] and high thermal expansion coefficient ($31X10^{-5}\ K^{-1}$, at 600 ^{o}C)[1, 4], leucite has potential application in preparing functional coatings on metal substrates or reinforcing metal-based composites.

Leucite is generally synthesized by heating the mixture of raw materials at a temperature above its melting point and then slowly cooling the mixture to room temperature[1, 2, 4]. Recently, spherical leucite crystals with a controlled size of between several micrometers to approximately 100 mm have been synthesized at a much lower temperature at l000 ^{o}C[1, 5, 6], using reagent grade $Al_2(SO_4)_3$, SiO_2 and K_2SO_4 as starting raw materials.

Because of their spherical morphology, the synthesized leucite crystals could be well distributed in dental materials, allowing the materials (e.g. artificial teeth) to be rendered with substantially enhanced mechanical strength. In addition, the synthesized leucite crystals could be used as a raw material in the fabrication of bulk leucite ceramics or as an additive to silica glass due to having a near reflection coefficient. However, the present study is the first report of synthesis at a temperature below 1000 ºC using cheaper natural materials, such as kaolin.

Porcelain-Fused-to-Metal (PFM) for dental restorative purpose has been applied for more than half century[7, 8]. Leucite is an important component of the dental ceramics as it possesses high coefficient of thermal expansion, which boosts the coefficient of thermal expansion (CTE) of dental porcelain to be compatible with most metals used in prosthodontics[9]. Synthesis of leucite powders has always been an attractive subject and it was done by co-precipitation[10], salt bath[11], sol–gel[12, 13], hydrothermal[14, 15] and solid state methods[16, 17]. Though leucite has been synthesized by many ways, especially by chemical methods recently, the synthesis of pure leucite powder below 1000°C has not been reported yet. Leucite has a melting point of 1693°C[18], which makes the synthesis of pure leucite at relative low temperature difficult. Moreover, kasilite and glass phase are the common impurities of chemically derived leucite[12, 13] and sanidine can also crystallize from the leucite dental porcelain after multiple firing[19], which may cause a negative effect on the mechanical and esthetic properties of dental porcelain.

As ultra-fine powder is beneficial for sintering, densification and mechanical properties of materials[20, 21], growing attention has been put onto fabrication of ultra-fine powders. High synthesis temperature and dehydration process in chemical method are the two primary obstacles for fabrication of ultra-fine powders[22-24]. Therefore, synthesis of pure leucite powders at low temperature is important and meaningful. Sol–gel method is an important method to prepare high purity inorganic materials at low temperature[25]. For leucite synthesis, Erbe and Sapieszko[12] prepared leucite at 1000°C with the impurity of kalsilite. Liu et al.[13] synthesized leucite at 900°C, which was a relatively low synthesis temperature, but there existed a large amount of glass phase.

Inorganic geopolymers are materials with ceramic like properties but which are synthesized and hardened by curing at ambient temperatures. Because of the low energy requirements of their production from common raw materials (clays) and their inflammability at high temperatures, these compounds are attracting increasing interest as ecologically friendly fireproof building materials[26-28], sound and heat insulators and materials for encapsulating hazardous wastes for storage or disposal.

The aim of the present study is to synthesize pure inorganic polymers from metakaolin at different batches, to obtain the lecuite crystal and study compositional and morphological changes in the geopolymer after heating to high temperatures. Synthesizing technique of nanometer-sized lecuite will be studied by the geopolymer technique in view of potential applications to ceramics.

EXPERIMENTAL

Starting materials

The clay locally named as white clay was used in this investigation. The white clay collected from gamgom queries, the west region in Jeddah. The characterization of clay included chemical composition in TABLE 1. Mineralogical composition are presented in TABLE 2 and Figures (1). Clay was used to make geopolymer compression sample after being calcined at 750 ºC for 1 h to obtain metakaolin. The details of the materials used are given in TABLE 3. Potassium– based geopolymers were made from 50 wt % solution of KOH diluted with ionized water and K_2SO_4 liquid at 50% solution, the H_2O / K_2O for these samples was not set at 11. In order to make the alkaline solution for KOH based geopolymers, KOH pellets from Fisher Scientific, USA were dissolved in de-ionized water.

Sample preparation

The materials used at molar oxide ratios were $SiO_2 /Al_2O_3 =4$, $K_2O/SiO_2 = 0.3$ and $H_2O /K_2O=11$. Geopolymer were prepared by mixing amorphous silica as K_2SO_4 liquid in a highly alkaline solution. Typical solution concentration ranged from 6-10 molar, resulting in a PH > 13. Metakaolin, i.e. kaolinite which was calcined at 750 ºC for 1 h, according to the method of

Rahier et al.,[29,30] was then mixed with the caustic silicate solution to initiate polymerization. After geopolymer suspensions have been prepared as described above, the suspensions are poured into plastic moulds and covered with either parafilm and left to cure between 40 ºC or 65 ºC. Curing of geopolymers was achieved by one of routes pressureless and warm curing. Covering of the geopolymer is necessary to prevent excessive water evaporation during curing which causes surface cracking of the samples. After demoulding, the geopolymer was dried at 65 ºC for 1 h. The cured samples were ground by using a gad mortar and sieved with a – 325 standard mesh (= 45 μm). The final green powder was sintered in a high temperature furnace from 800ºC, 900ºC, 1000ºC and 1100 ºC at a heating rate of 200 ºC/h, for soak time for 3 h and cooling rate of 10 ºC, then crushed and start characterization.

Characterization techniques

Chemical analysis

The chemical composition was determined by X-ray fluorescence spectroscopy using Philips PW 2400 equipment. The ignition loss was measured by calcinations at 1000 ºC.

X-ray diffraction

X-ray diffraction (XRD) analysis was performed using an automated (Philips type: PW1840) diffractometer equipment with Cu Kα radiation source and at a step size angle of 0.02 θ, scan rate of 2θ in 2h unit, and a scan range from 10 θ to 60 θ.

Thermal analysis (DTA/TGA)

Differential thermal analysis (DTA) and thermographmetric (TGA) were run with a coupled (SETARAM TG/DTA 92) DTA-TGA instrument. The geopolymer batches were heated with rate of 5 C/min at ambient atmosphere pressure and temperature, up to 1000 ºC.

Scanning electron microscopy

Morphology of the geopolymer samples were determined by SEM. The samples were previously coated with gold. The geopolymer samples were studied with a Philips®30 Analytical Scanning Electron Microscope. Particle images were obtained with a secondary electron detector.

RESULTS AND DISCUSSION

Characteristics of the clay

TABLE 1 shows the chemical composition of the raw materials. The chemical composition of the clay is typical of kaolin -based material with low amount of silica oxide, low amounts of iron oxides and relatively low amount of Al_2O_3. The chemical composition of the clay, in addition to SiO_2 and Al_2O_3, shows a relatively low amount of iron oxides. Figure 1 presents the XRD patterns of the investigated clays. It could be noted that some clays have their major peaks associated with kaolinite (K) in TABLE 2. In addition, all clays exhibit minor contributions of quartz (Q), and

TABLE 1 : Chemical analysis of raw materials used

Material	Kaolin
SiO_2	51.67
TiO_2	0.95
Al_2O_3	23.55
Fe_2O_3	1.01
MnO	0.15
MgO	1.47
CaO	1.08
Na_2O	0.68
K_2O	1.82
P_2O_5	0.34
SO_3	0.08
Cl	0.14
L.O.I	12.52
Total	99.81

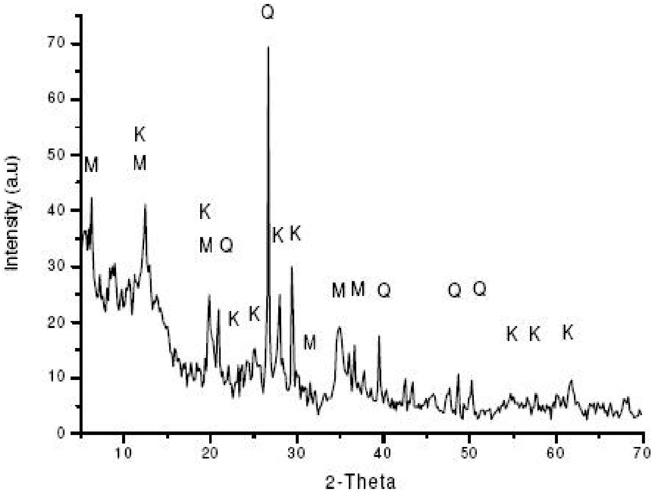

Figure 1 : XRD of the raw materials as kaolin in Saudi K=kaolin, M= montmorillonite, Q=Quartz

TABLE 2 : Mineralogical composition of kaolin

Phase	kaolinite	montmorillonite	quartz
%	83	5	10

montmorillonite (M).

Effect of temperature on the formation of leucite crystals

X-ray diffraction of the geopolymer samples showed an amorphous structure, consistent with diffraction patterns reported in literature. XRD patterns for batches L1 to L4 heated at different temperatures are shown in Figure 2-6 and SEM micrographs of the samples after heating the powder mixture at 800–1100 ºC for 3 h, respectively. At 800 ºC, only quartz (but no

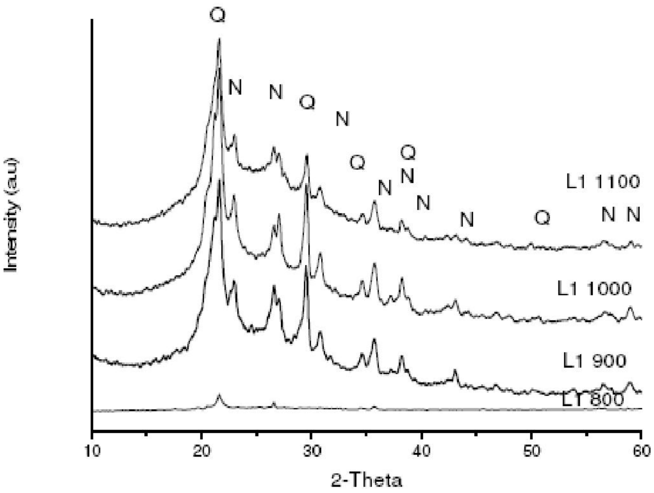

Figure 2 : XRD pattern of samples after heating the batch (L1) at 800-1100 ºC. Key: N= nepheline, Q= Quartz

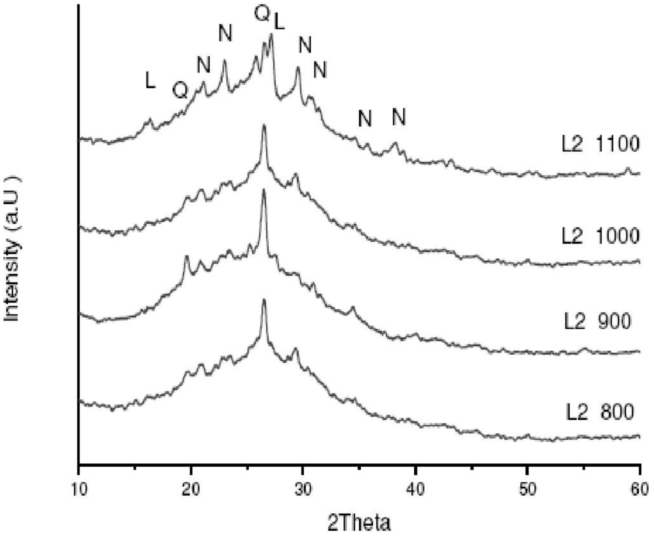

Figure 3 : XRD pattern of samples after heating the batch (L2) at 800-1100ºC. Key: L= Leucite, N= nepheline, Q= Quartz

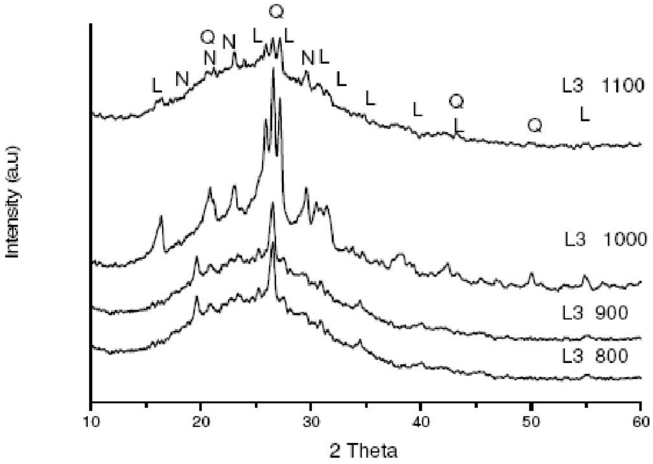

Figure 4 : XRD pattern of samples after heating the batch (L3) at 800-1100 ºC. Key: L= Leucite, N= nepheline, Q= Quartz

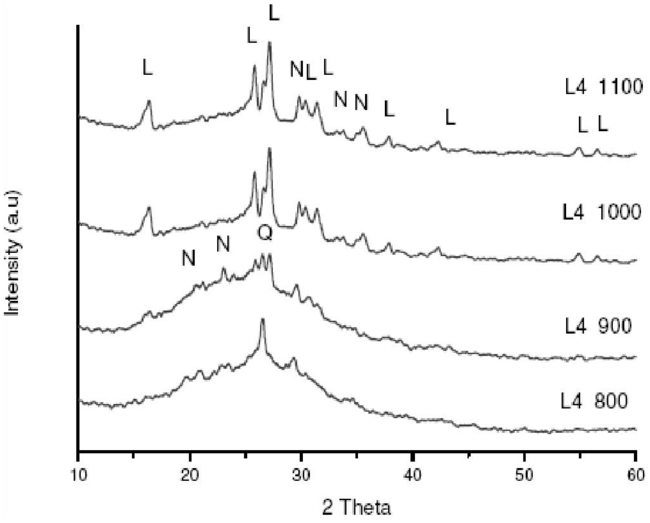

Figure 5 : XRD pattern of samples after heating the batch (L4) at 800-1100ºC. Key: L= Leucite, N= nepheline, Q= Quartz

TABLE 3 : Raw materials used and characteristics

Materials	Company	Purity
Kaolin	Break soudia company	83 % kaolin
Potassium silicate(liq.)	Hopkin & Williams, UK	55 %
KOH pellets	Sigma Aldrich	90% KOH, 10% H_2O

TABLE 4 : The different batches of composition of leucite preparation.

Batch No.	Kaolin (g)	$K_2O.SiO_2$ liquid (g)	KOH (g)	H2O (ml)
L1	50.0	30.0	11.5	20
L2	50.0	50.0	11.5	20
L3	50.0	70.0	11.5	20
L4	50.0	100.0	11.5	20

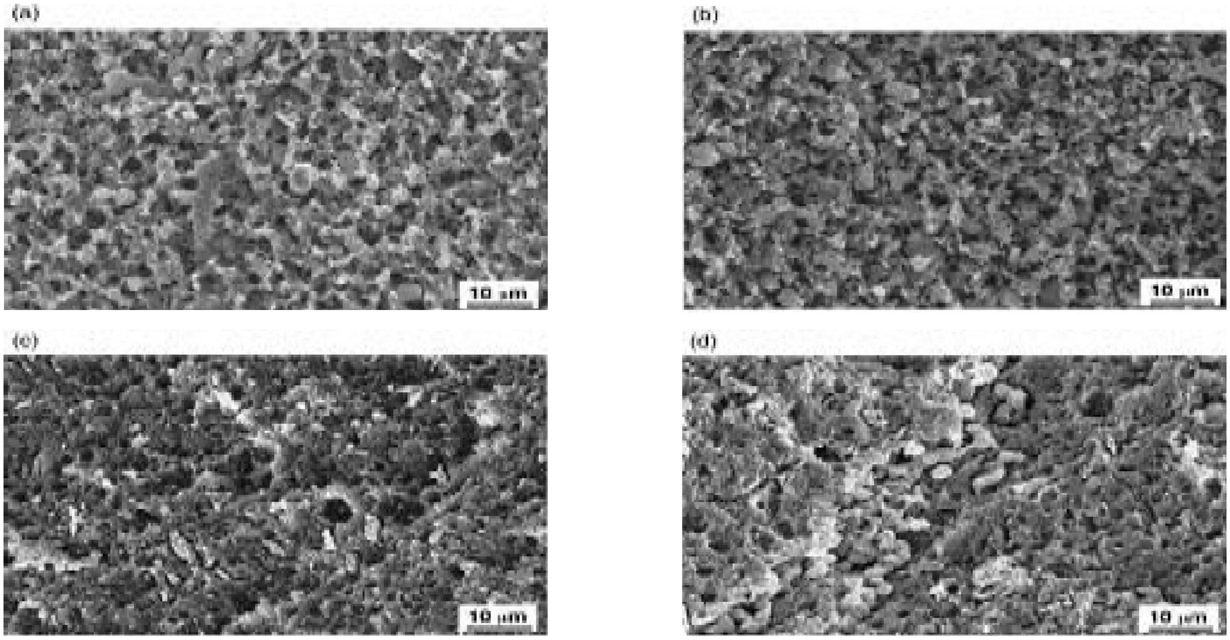

Figure 6 : Scanning electron microscopic of the lecuite (L4) after heating at (a) 800 ºC, (b) 900 ºC, (c) 1000 ºC, (d) 1100 ºC

leucite) was identified by XRD for each batch L1, L2, L3, and L4, the microstructure reveals an extensive formation of grains of less than 40 mm in diameter.

As the temperature increased to 900 ºC, the batches L1, L2 and L3, the quartz decrease or disappeared and appear small crystal for nepheline but in batch L4 appear nepheline, leucite and traceless of quartz at 900 ºC but increase the intensity of leucite at 1100 ºC. The batches L1 and L2 heated from 800 to 1100 ºC appear nephaline and quartz only but L2 traces of leucite at 1100C. Nevertheless, depending on the temperature, the formed leucite crystals showed different morphologies. The crystallization of leucite was obvious in samples L3 and L4 heated to 900-1100 ºC.

At 900 ºC, spherical leucite crystals having a diameter of approximately 10 μm were observed. However, at 1000 ºC, the leucite crystals began to lose their spherical morphology in (Figures 6(a) and (b)). A further increase in temperature to 1100 ºC led to the formation of leucite crystals of two different diameters, approximately 40 μm and 10–20 μm. At 900 ºC, the number of leucite nuclei formed in the sample decreased. Therefore, a comparatively small number of leucite crystals appeared to be responsible for the increase in the size of leucite crystals, which is thought to cause the formation of large monocrystals. In contrast, upon increasing the temperature to 1100 ºC, a large number of leucite nuclei formed, so that each of the leucite crystals became smaller and showed a tendency to form crystal agglomerations. Thus, these results indicated that when kaolin was used as the primary raw material, spherical leucite crystals of homogeneous size could be synthesized by heating the powder mixture at 900 ºC, which is lower than that (1000 ºC) reported in previous studies using reagent grade SiO_2 as a starting raw material[31, 32].

The batches L2 and L3 after heating at 900-1100 ºC, leucite was observed to form, but SiO_2 quartz and nephaline were still present, and spherical grains were still not formed in the microstructure. However, the batch L4 after heating at 900-1100 ºC, the quartz and nephaline had almost disappeared and only leucite was identified by XRD, and the microstructure reveals the formation of spherical grains having a diameter of approximately 30 μm. All samples contained a large number of small 1–5-mm-sized leucite crystallites, which increased slightly in size in samples fired at higher temperatures. This observation is thought to be indicative of a nucleation-rich environment and the results indicated when the increase of the amount of K_2SO_3 liquid from batch L1 to L4 the leucite crystal was formed. It is believed that in samples heated to 1000 or 1100 ºC (Figures 6(d) and (e)), the crystals reached a large enough size to have some level of connectivity, and was therefore less likely to fall out.

Thermal analysis

Preliminary observations are presented in Figures 7 and 8, which are TGA and DSC plots, respectively. The TGA data shows a decrease in weight between 25 ºC and 600 ºC, with a more rapid decrease beginning at ˜ 150 ºC. The DSC data of sample L1 shows an exothermic at ˜ 325 ºC as well as a small possible transition at ˜ 1000 ºC.

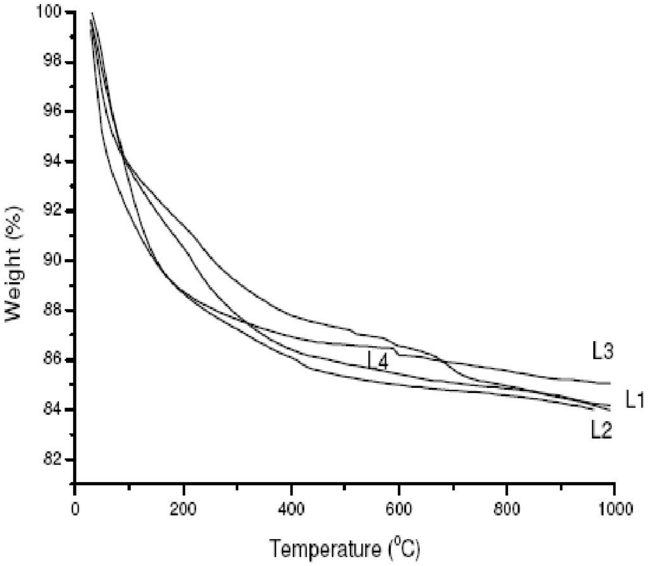

Figure 7 : TGA of K crosslinked, poured and 40 ºC cured, geopolymer sample.

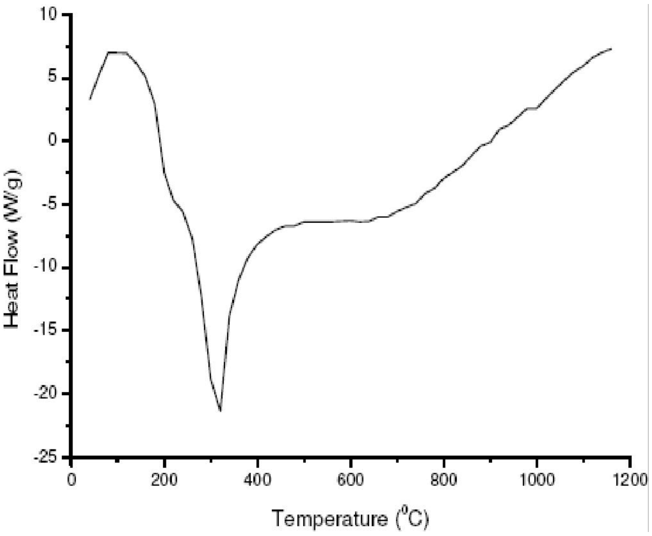

Figure 8 : DSC of K crosslinked, poured and 40 ºC cured, geopolymer sample (L1).

As shown in Figure 8 the DSC pattern for K-geopolymer heated at 10 ºC/ min had an exotherm centered at ˜1072 ºC due to leucite crystallization over the range of 1080º–1150ºC. This was in agreement with the expected crystallization temperature observed from X-ray results. Zhang et al.[36] observed an exotherm due to leucite crystallization from the range of approximately 1000º–1200ºC, with the peak centered at 1170ºC. Duxson et al.[33] did not observe a substantial leucite crystallization exotherm for K-geopolymers with a Si/Al5 = 1.9 or 2.15. This was consistent with the small amount of leucite formed. A large endotherm was present over the range of 251–400 ºC and had a minimum value at ˜ 82 ºC (Figure 8). TG data indicated that a dramatic weight loss occurred over this temperature range and was attributed to evaporation of free water.

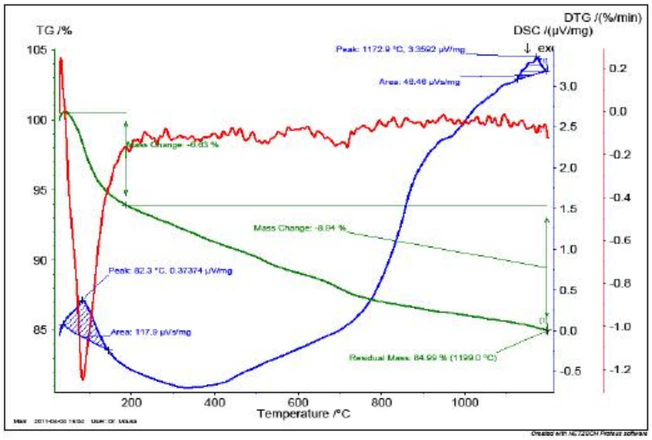

Figure 9 : DSC/TG, the derivative thermal shrinkage of samples (L4) were heated at 10 ºC/min up to 1200 ºC in air.

In this work, the endotherm minimum value was centered at ˜82 ºC for K-geopolymer. The results have been observed in a variety of geopolymers, regardless of alkali choice (K and Na) or Si/Al ratio.[34-36, 37] Little shrinkage was observed for K-geopolymer on heating from room temperature to 100 ºC (Figure 8). However, there was substantial weight loss due to water evaporation from large pores and surfaces. In this region, K-geopolymer had a lower extent of densification and weight loss. Since K-geopolymer had a lower starting surface area, there was expected to be less freely evaporable water from surfaces. Additionally, the L4 ion has a larger hydration energy compared with L1 and is therefore less likely to dehydrate at lower temperature. A similar trend was observe when comparing Na- and K-based geopolymers[33].

Over the range of 100 º–300 ºC, the shrinkage and weight loss in region II was due to capillary contraction created as water was desorbed from small pores. As shown in Figure 8, the maximum rate of shrinkage occurred at ˜175ºC. In this region, there was a larger relative mass loss, shrinkage, and surface area reduction for KGP. Above 100 ºC, the intrinsic geopolymer gel structure is expected to play a larger role than cation hydration[38]. Because K-geopolymer has a lower initial surface area and extent of water loss in region I, more water was expected to be bound within the gel pores on surfaces.

Application

Dental technicians are usually familiar with this technique, commonly used to cast dental alloys. In addition, the equipment needed to heat-press dental ceramics is relatively inexpensive. So, k-geopolymer was found to offer many of the benefits such as lower sintering temperatures and compositional control without high costs.

CONCLUSIONS

1- Geopolymers are increasingly being considered in a variety of refractory applications and as precursors to ceramic formation. Despite this, little work has been done to systematically characterize their X-rays and microstructural evolution on heating.
2- The chemical composition of the clay is typical of kaolin -based material with low amount of silica oxide, low amounts of iron oxides and relatively low amount of Al_2O_3.
3- As the temperature increased to over 800 ºC as 900–1100 ºC, the quartz disappeared, naphaline and leucite remained. Nevertheless, depending on the temperature, the formed leucite crystals showed different morphologies.
4- A further increase in temperature to 1100 ºC led to the formation of leucite crystals of two different diameters, approximately 40 μm and 10–20 μm.
5- The thermal behavior of K-geopolymer was characterized using a variety of techniques in order to explore the details of dehydration, sintering, and crystallization. On heating above 1000 ºC, K-geopolymer crystallized into leucite and a minor amount of nephaline.
6- In terms of leucite formation, K-geopolymer was found to offer many of the benefits such as lower sintering temperatures and compositional control without the high costs associated with expensive precursors

ACKNOWLEDGEMENTS

The financial support provided by Taif University Grant # 724/431/1 is gratefully acknowledged. The authors would also like to thank national research center (Egypt).

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