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FORMATION OF LEUCITE CRYSTALS FROM METAKAOLIN-BASED GEOPOLYMER USING KAOLIN AND BENTONITE

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ABSTRACT

Inorganic polymerization of Al_2O_3- and SiO_2- containing materials in strong alkali environments often results in products generally referred to as geopolymers. A novel technique called the geopolymer technique will be studied. The geopolymer technique was initially applied for preparation of monolithic materials, starting from metakaolin and reactive silica under the presence of strong alkaline solutions. Leucite crystals having nanosize were prepared by heating a powder mixture of metakaolin, K_2SiO_4 and KOH. The geopolymer thus obtained were fired at elevated temperature up to 1100^0C and were examined by XRF, XRD and SEM techniques.

The results show that meta kaolin, K_2SiO_3 solution and KOH to regulate the pH to form geopolymer, which may crystallize into cristoballite and lecuite, respectively, under thermal treatment. K-based geopolymer ($K_2O.Al_2O_3$. $4SiO_2$. $11H_2O$) was investigated due to its attractive refractory properties and ability to convert to leucite ($KAlSi_2O_6$) on heating and the comparisons between clay and bentonite to obtain leucite at low potassium silicate solution. A further increase in temperature to 1100^oC led to the formation of leucite crystals. K-geopolymer was found to offer many of the benefits such as lower sintering temperatures and compositional control without the high costs.

Key words: Metakaoline, Geopolymer, XRD, SEM, Leucite.

INTRODUCTION

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[1-4]. Leucite ($KAlSi_2O_6$) has been used as an important crystal phase in dental

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porcelain/glass materials[1,2] because of its tone, color appeal and excellent biocompatibility. Furthermore, due to its high melting point (1693ºC)[1,3] and high thermal expansion coefficient (31 x 10^{-5} K^{-1}, at 600ºC)[1,4], leucite has potential application in preparing functional coatings on metal substrates or reinforcing metal-based composites. Recently, spherical leucite crystals with a controlled size of from several micrometers to approximately 100 mm have been synthesized at a much lower temperature (l000ºC)[1,5,6] by the present authors using reagent grade $Al_2(SO_4)_3$, SiO_2 and K_2SO_4 as starting raw materials.

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[7-9]. 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 handicaps 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].

Inorganic geopolymers are materials with ceramic like properties but these 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.

Present study was carried out to synthesize pure inorganic polymers from metakaolin (as clay and bentonite) at different batches, at chemical composition 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

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 and bentonite included chemical composition in Table 1. Clay and bentonite were used to make geopolymer compression sample after being calcined at 750ºC for 1 h to obtain metakaolin. The details of the materials used are given in Table 2. Potassium-based geopolymers were made from 50% wt. % solution of KOH diluted with deionized water and K_2SO_4 liquid at 50% solution. KOH pellets from Fisher Scientific, USA were dissolved in de-ionized water.

Table 1: Chemical analysis of raw materials used

Material	Kaolin	Bentonite
SiO_2	51.67	64.9
TiO_2	0.95	--
Al_2O_3	23.55	9.26
Fe_2O_3	1.01	2.52
MnO	0.15	--
MgO	1.47	1.80
CaO	1.08	0.83
Na_2O	0.68	4.03
K_2O	1.82	1.20
P_2O_5	0.34	--
SO_3	0.08	--
Cl	0.14	--
L.O.I	12.52	12.00
Total	99.81	99.54

Table 2: Raw materials used and characteristics

Materials	Company	Purity
Kaolin	Break Soudia company	83 % Kaolin
Bentonite	Egypt	80% Bentonite
Potassium silicate (liq.)	Hopkin & Williams, UK	55 %
KOH pellets	Sigma Aldrich	90% KOH, 10% H_2O

Preparation and formation of lecuite

Geopolymers were prepared by mixing amorphous silica as K_2SO_4 liquid in a highly alkaline solution. The materials used at molar oxide ratios were $SiO_2/Al_2O_3 = 4$, $K_2O/SiO_2 = 0.3$ and $H_2O/K_2O = 11$. Typical solution concentration ranged from 6-10 molar, resulting in a pH > 13. Metakaolin, i.e. kaolinite and bentonite, which was calcined at 750ºC for 1 h, according to the method of Rahier et al.[29,31] was then mixed with the caustic silicate solution to initiate polymerization. Curing of geopolymers was achieved by one of routes pressureless and warm curing. 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 40ºC or 65ºC. After demoulding, the geopolymer was dried at 65 C for 1 h. The cure samples were ground by using a gad mortar and sieved with a (– 325) standard mesh (≤ 45 µm). The batches composition in Table 3 were sintered in a high temperature furnace from 800ºC, 900ºC, 1000ºC and 1100ºC at a heating rate of 200ºC/h, for soak time for 3 h and cooling rate of 10ºC. It was then crushed and characterized.

Table 3: The different batches of composition of leucite preparation

Batch No.	Kaolin (g)	Bentonite (g)	$K_2O.SiO_2$ liquid (g)	KOH (g)	H_2O (mL)
L5	-	50.0	50.0	11.5	20
L6	50.0	-	50.0	11.5	20
L7	50.0	-	100	11.5	20

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 1000ºC.

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 2 θ in 2 h unit, and a scan range from 10 θ to 60 θ.

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 and bentonite

The chemical composition of raw materials can be used as shown in Table 1. The chemical composition of the clay is typical of kaolin-based material with low amount of silica oxide, iron oxides and relatively low amount of Al_2O_3. The chemical composition of the bentonite is high amount of silica oxide & iron oxide and low amount of Al_2O_3. In addition to SiO_2 and Al_2O_3, it shows a relatively low amount of iron oxides.

Formation of leucite and comparisons from clay and bentonite

XRD patterns for batches L5 to L7 heated at different temperatures are shown in Fig. 1-3 and SEM micrographs of the samples after heating the powder mixture at 800-1100ºC for 3 h, respectively.

At 800ºC, only quartz (but no leucite) was identified by XRD for each batch L5 to L7. As the temperature was increased to 900ºC, the batches L6 and L7, the quartz decrease or disappeared and small crystal for nepheline appeared but in batch L5, leucite appears and traceless of quartz at 900°C but increase in the intensity of leucite at 1100ºC appeared. In the batch L6 heated to 1100ºC, nephaline, quartz and traces of lecuite appeared. As the temperature was increased to over 800ºC as 900–1100ºC, the quartz disappeared, but naphaline and leucite remained. Nevertheless, depending on the temperature, the formed leucite crystals showed different morphologies. The crystallization of leucite was obvious in samples L5 and L7 heated to 1100ºC.

At 1000ºC, the leucite crystals began to lose their spherical morphology. A further increase in temperature to 1100ºC led to the formation of leucite crystals. At 900ºC, 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 1100ºC, 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 and bentonite were used as the primary raw material, spherical leucite crystals of homogeneous size could be synthesized by heating the powder mixture at 900ºC, which is lower than that (1000ºC) reported in previous studies using reagent grade SiO_2 as a starting raw material[5,6].

Fig. 4 presents XRD patterns and SEM micrographs of the samples after heating the powder mixture at 1100ºC for various time periods and further treating with hot hydrochloric acid. Leucites was detected by XRD in the sample that was heated at 1000ºC. No spherical grains but many bar shape barrel were seen in the corresponding microstructure.

In the batches L5 and L7 after heating at 900-1100ºC, leucite was observed to form, but little nephaline were still present L5, and spherical grains were still not formed in the microstructure. However, the batch L7 after heating at 900-1100ºC, the quartz and nephaline had almost disappeared and only leucite was identified by XRD in L7,[31] and the microstructure reveals the formation of spherical grains having a diameter of approximately 30 μm in L7 but L5 appear bar shape barrel.

The comparison between batches L5 and L6 was different only in clay and bentonite. In L5 lecuite was formed at 900ºC and high crystal forms at 1100ºC but in L6, nepheline and traces of lecuite are formed at 1100ºC. So, L5 is better than L6 in forming lecuite crystal.

After etching the samples in 3 wt. % HF acid, the glassy phase dissolved away and leucite crystals could be observed (Fig. 4-6). The heated leucite contained a polydisperse distribution of leucite crystals, a glassy matrix, and pores left behind from leucite crystals that fell out during etching. All samples contained a large number of small 1–5-mm sized leucite crystallites, which increased only slightly in size in samples fired at higher temperatures. This observation is thought to be indicative of a nucleation-rich environment. It is believed that in samples heated to 1000 or 1100ºC (Figs. 6), the crystals reached a large enough size to have some level of connectivity.

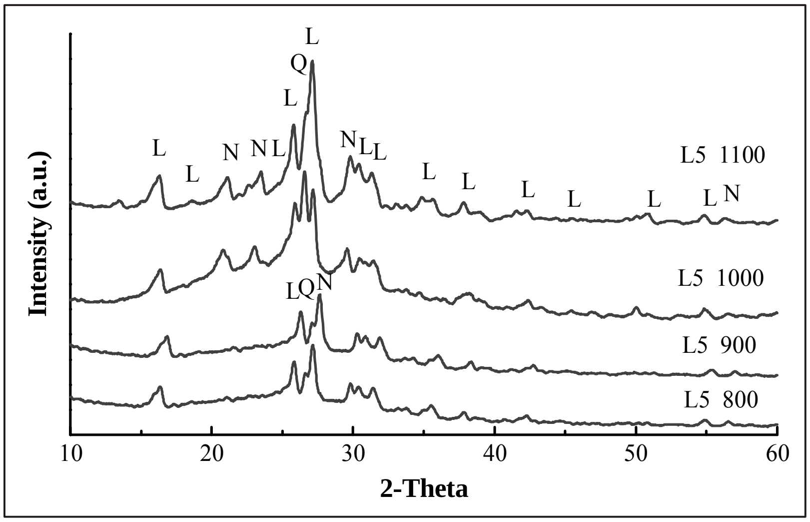

Fig. 1: XRD pattern of samples after heating the batch (L5) at 800-1100ºC (Key: L = Leucite, N = Nepheline, Q = Quartz)

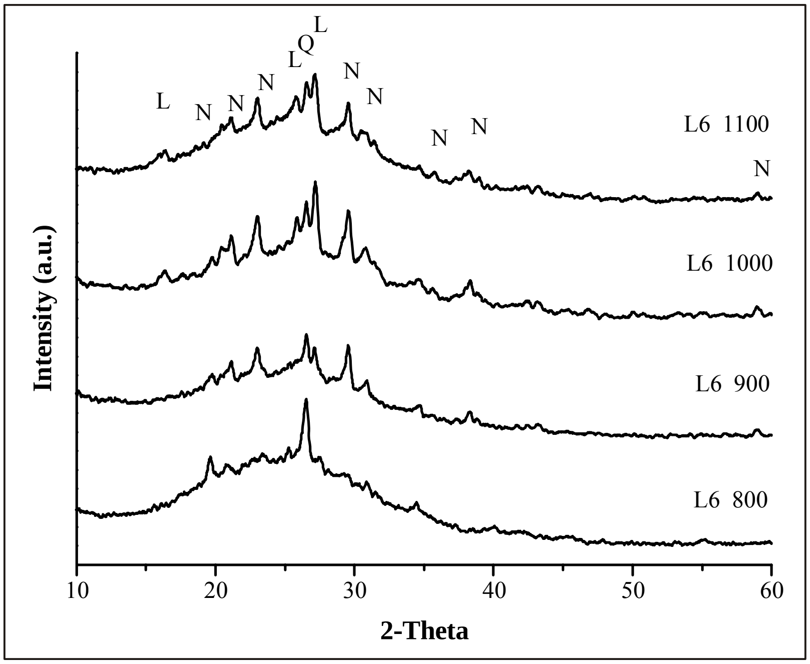

Fig. 2: XRD pattern of samples after heating the batch (L6) at 800-1100ºC (Key: L = Leucite, N = Nepheline, Q = Quartz)

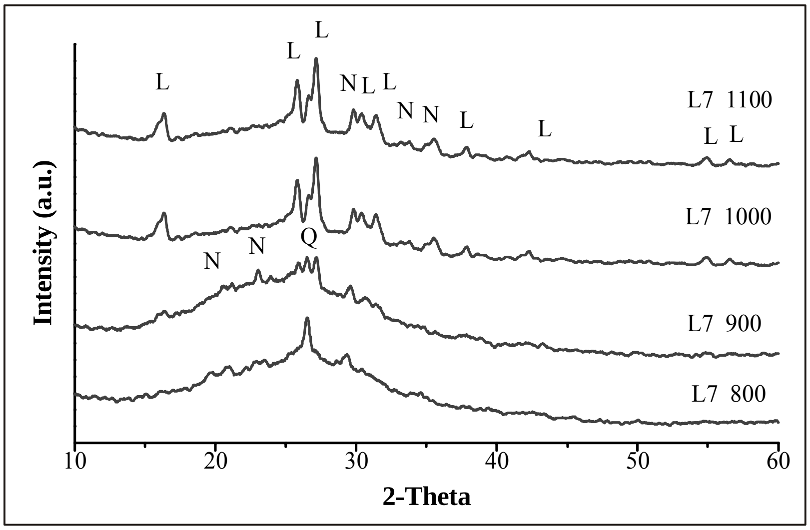

Fig. 3: XRD pattern of samples after heating the batch (L7) at 800-1100ºC (Key: L = Leucite, N = Nepheline, Q = Quartz)

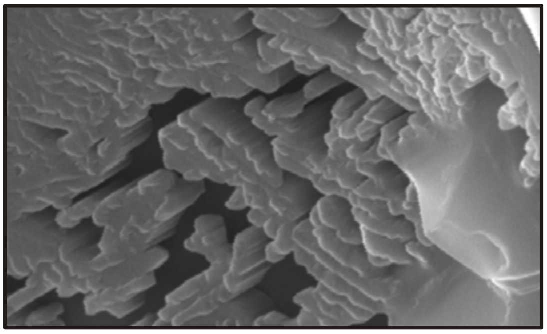

Fig. 4: Scanning electron microscopic of the sample (L5) sintered at 1100ºC

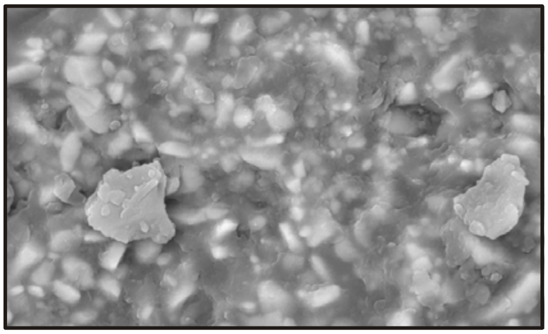

Fig. 5: Scanning electron microscopic of the sample (L6) at 1100ºC

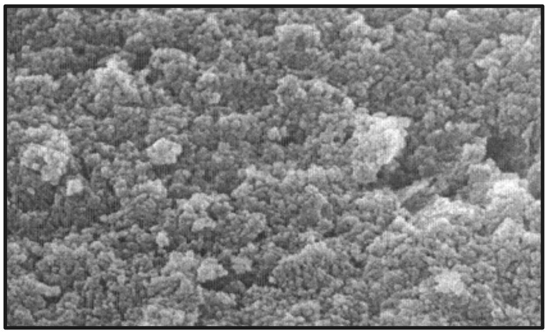

Fig. 6: Scanning electron microscopic of the sample (L7) at 1100ºC

CONCLUSION

(i) Geopolymers are increasingly being considered in a variety of refractory applications and as precursors to ceramic formation.

(ii) The temperature increased to over 800ºC as 900-1100ºC, the quartz disappeared, nepheline and leucite remained. Nevertheless, depending on the temperature, the formed leucite crystals showed different morphologies.

(iii) 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.

(iv) The comparison between batches L5 and L6 was different only in clay and bentonite. So, L5 is better than L6 in formed in lecuite crystal.

(v) In this study, K-based geopolymer ($K_2O.Al_2O_3.\ 4SiO_2.11H_2O$), deemed K-geopolymer, was investigated due to its attractive refractory properties and ability to convert to leucite ($KAlSi_2O_6$) on heating.

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