Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 7067–7072

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Synthesis and characterisation of gel-derived mullite precursors from rice husk silica

Simon Sembiring[a], Wasinton Simanjuntak[b], Posman Manurung[a], Dwi Asmi[a], I.M. Low[c,*]

[a]Department of Physics, Faculty of Mathematics and Natural Sciences, University of Lampung, Bandar Lampung 35145, Indonesia
[b]Department of Chemistry, Faculty of Mathematics and Natural Science, University of Lampung, Bandar Lampung 35145, Indonesia
[c]Department of Applied Physics, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

Received 6 September 2013; received in revised form 9 December 2013; accepted 9 December 2013
Available online 18 December 2013

Abstract

The sol–gel synthesis and characterization of mullite precursor derived from rice husk silica and aluminum nitrate hydrate [$(Al(NO_3)_3 \cdot 9H_2O$] has been investigated. The samples were characterized using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) coupled with Rietveld analysis, and scanning electron microscopy (SEM). FTIR results showed the presence of Si–O–Si, Al–O–Al, and Si–O–Al functional groups, which were associated with mullite, corundum, quartz, and cristobalite, as verified by XRD analysis. It is concluded that mullite formation started at 1150 °C, and its abundance increased rapidly with an increase in temperature from 1150 to 1350 °C, resulting in increased phase content from 30.9 to 67.7 wt%. Although mullite was formed at a low temperature, the complete reaction between corundum and silica to form mullite was not achieved. This finding demonstrated that rice husk silica is a potential alternative raw material for the production of mullite ceramic.

Keywords: B. Sol–gel growth; C. Electron microscopy; C. Fourier transform infrared spectroscopy (FTIR); C. X-ray scattering; D. Phase transitions

1. Introduction

Mullite ($3Al_2O_3 \cdot 2SiO_2$) is a refractory aluminosilicate material that belongs to the Al_2O_3–SiO_2 system. This ceramic is an interesting material because of its various attractive properties which include high thermal stability, low thermal expansion and conductivity, high melting point and chemical stability, and high thermal shock resistance [1–5]. For these reasons, mullite has been widely used as an advanced structural or functional ceramic in various applications such as components in reinforced composites [6], microelectronic packaging and substrates [7], and optical component of infrared windows [8].

In general it is well established that the method of synthesis and raw material play an important role in determining the mullitization temperature and the homogeneity of the product. The method used for the synthesis of mullite is an important factor because it determines the degree of mixing of aluminum and silicon in the precursor, which in turn influences the mullitization temperature. Many methods to synthesize mullite have been developed, however, the sol–gel approach is acknowledged as the most attractive because it enables good mixing to promote uniformity of the starting materials, resulting in very homogeneous distribution of elements at the atomic level to produce mono-phasic gels [9]. As a result, the formation of mullite from gels could be achieved at temperatures in the range of 1000–1250 °C [10–12], which are lower than those required in the solid state (i.e., powder mixture) method, in which the temperatures range from 1240 to 1350 °C [13]. In addition to the synthesis method, types of precursors have been reported to strongly influence the mullitization temperature. For example, crystalline mullite can be produced at ~1000 °C from aluminosiloxanes [14], and at ~1350 °C using kyanite and alumina powder [15]. Production of mullite from alumina and silica sols indicated that amorphous mullite forms at around 600 °C and can be sintered into dense mullite at 1600 °C [16]. Previous study by Cividanes et al. [17] revealed that mullitization lies at the

*Corresponding author.
E-mail address: j.low@curtin.edu.au (I.M. Low).

0272-8842/$ - see front matter
http://dx.doi.org/10.1016/j.ceramint.2013.12.038

interface between liquid phase and crystalline corundum (α-Al_2O_3) and the subsequent growth of the mullite phase was generated by Al^{3+} and Si^{4+} interdiffusion. In another study [18], it was found that by atomic scale mixing of metal salts and metal alkoxides, mullite, spinel and silica segregation can occur simultaneously at 980 °C. In another study using kaolinite and alumina [19], it was reported that both mullite and spinel were detected in the sample sintered at 980 °C, while Chen et al. [20] reported the formation of spinel, alumina and silica at 980 °C, followed by mullite formation at 1100 °C. Fully densified mullite was obtained at 1300 °C using raw wastes containing high silica (slate rock) and aluminum hydroxide (aluminum sludge) [21].

Rice husk is currently being considered as an important and competitive resource for the production of high purity and amorphous silica [22], which is essential for the synthesis of various materials such as iron/silica catalyst [23], cordierite [24,25], silicon carbide [26], magnesium–aluminum–silica [27], lithium–aluminum–silica [28], borosilicate [29], and silica aerogel [30]. Utilization of rice husk is attractive because of the possibility of removing impurities to produce active silica with high specific surface area at relatively low cost. In addition, active silica from rice husk is naturally amorphous but can be transformed into crystalline phases, such as cristobalite and tridymite, by thermal treatment at between 700 and 1400 °C [31]. To take advantage of the availability and suitable properties of rice husk silica, the present study utilized this silica as a raw material for the synthesis of mullite precursor using the sol–gel technique. The main purpose of this study was to evaluate development of mullite as a function of sintering temperature, based on the changes in the functionality, structure, and microstructure of the samples. The functionality change as a function of heat treatment was investigated using FTIR spectroscopy, the structure was characterized by XRD coupled with Rietveld analysis, and the microstructure was examined using SEM. Rietveld refinement of the XRD data was carried out to ascertain the quantitative phase compositions of the samples.

2. Experimental methods

2.1. Materials

Raw materials used for the synthesis of mullite were rice husk silica and [($Al(NO_3)_3 \cdot 9H_2O$] (Merck, Germany) as a source of alumina. KOH and HCl used were reagent grade obtained from Merck.

2.2. Procedure

Rice husk silica was obtained using an alkali extraction method previously reported [29]. In this procedure, 50 g dried husk was mixed with 500 ml of 5% KOH solution in a beaker glass. The mixture was boiled for 30 min, and then allowed to cool to room temperature and left for 24 h. The mixture was filtered through a Millipore filter to separate the filtrate which contained silica (silica sol). To obtain solid silica, the sol was acidified by additing 5% HCl solution until the sol was converted into gel. The gel was aged for three days, and then rinsed repeatedly with deionised water to remove the excess acid. The gel was then oven dried at 110 °C for eight hours and then ground into powder. A specified amount of silica powder was redissolved in 5% KOH solution to obtain a silica sol for the synthesis of mullite. Alumina sol was prepared by dissolving 44 g of $Al(NO_3)_3 \cdot 9H_2O$ in 100 ml ethanol under magnetic stirring for 1 h and then kept in a tightly covered conical flask. The preparation of mullite precursor was carried out by slow addition of appropriate volume of Al $(NO_3)_3 \cdot 9H_2O$ solution into the specified volume of silica sol to give the mol ratio of alumina to silica of 3:2 [32]. The mixture was then magnetically stirred, during which HCl solution was added slowly to produce a gel. The gel was then aged for three days, rinsed repeatedly with deionised water to remove excess acid and alkali, and then oven dried at 110 °C for 12 h. Dry gels were heat-treated in a ventilated furnace at the peak temperatures of 800, 950, 1050, 1150, 1250, and 1350 °C with 6 h dwell time at each peak temperature. The heating rate used was 5 °C/min.

2.3. Characterisation

A Perkin Elmer FTIR spectrometer was used for the investigation of functional groups of mullite. The sample was mixed with KBr, and scanned in the spectral range of 4000–400 cm^{-1}. XRD patterns were recorded to analyze mullite formation and the effect of sintering temperature on mullite abundance. The samples were examined using an automated Shimadzu XD-610 X-ray diffractometer at the Agency of Nuclear Energy National (BATAN), Serpong—Indonesia. The operating conditions used were Cu$K\alpha$ radiation ($\lambda = 0.15418$ Å), produced at 40 kV and 30 mA, with a 0.15° receiving slit. Patterns were recorded over goniometric (2θ) ranges from 5 to 100° with a step size of 0.02, counting time 1 s/step, and using post-diffraction graphite monochromator with a NaI detector. The diffraction data were analyzed using the JADE software after subtracting background and stripping the Cu$K\alpha_2$ pattern [33] and the refinements were performed using the Rietica program for Windows 95/98/NT version 1.70 [34]. Microstructural examination on polished and thermally-etched samples was carried out using a Philips-XL scanning electron microscope.

3. Results and discussion

3.1. Characteristics of rice husk silica

In our previous study [29], we described the functionality of rice husk silica as determined from the FTIR technique. Briefly, the FTIR spectrum is marked by the presence of several functional groups associated with silica, including Si–OH, Si–O–Si, and O–Si–O groups. No absorption bands associated with the organic functional groups were detected, indicating that high purity rice husk silica could be obtained using alkali extraction followed by the sol–gel method. Other basic characteristics of rice husk silica we investigated previously [35] were phase structure using X-ray diffraction