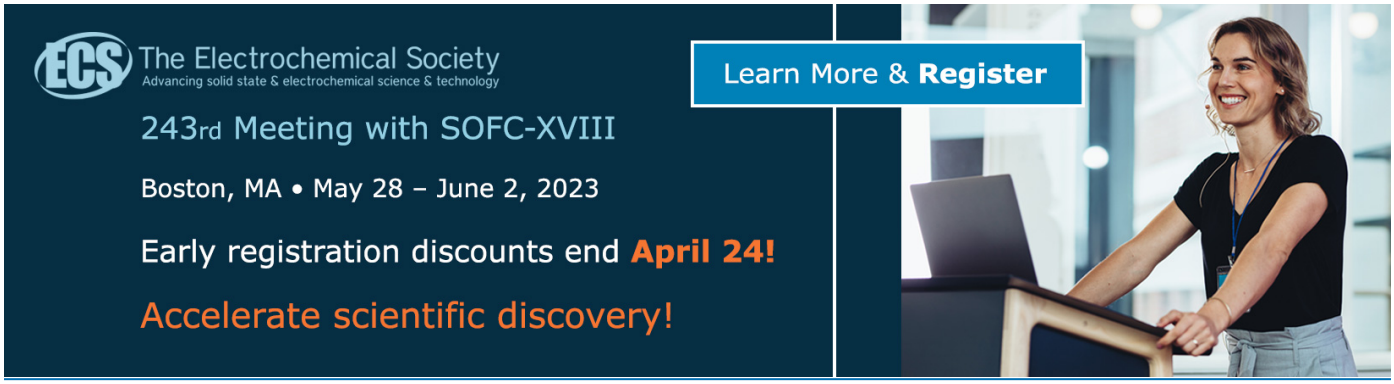
Synthesis of cristobalite from silica sands of Tuban and Tanah Laut



Synthesis of cristobalite from silica sands of Tuban and Tanah Laut

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Abstract. Synthesis of SiO_2 cristobalite powders has been successfully carried out by a coprecipitation method by making use of local silica sands from districts of Tuban and Tanah Laut, Indonesia. Cristobalite is a phase of SiO_2 polymorphs which can be used as a composite filler, a coating material, a surface finishing media, and structural ceramics. In the first stage of the synthesis, the as-received sands were processed by a magnetic separation, grinding, and soaking with HCl to increase the purity of silica content. X-ray fluorescence (XRF) spectroscopy showed that the atomic content of Si (excluding oxygen) in both powders reached 95.3 and 97.4%. A coprecipitation process was then performed by dissolving the silica powders in a 7M NaOH solution followed by a titration with 2M HCl to achieve a normal pH and to form a gel. Furthermore, the silica gel is washed, dried and then calcined at a temperature of between 950-1200 °C with a variation of holding time for 1, 4 dan 10 hrs to produce white powders. X-ray diffraction (XRD) data analyses showed that the powder with calcination temperature of 1150 °C for 4 hrs exhibited the highest cristobalite content of up to 95wt%. Its scanning electron microscopy (SEM) image showed that its grain morphology was relatively homogeneous.

1. Introduction

Crystalline silica (SiO_2) may have different polymorphic forms at room temperature, i.e. quartz, tridymite and cristobalite. Phase transitions between the last two phases into quartz occur at temperature above 1100°C but quartz is structurally stable [1–5]. Low cristobalite is a common silica polymorph with specific properties and applications. Its powder have a higher solubility than quartz and can be prepared in uniform particle size [6]. One of the applications of low cristobalite powder is for a microwave dielectric material [7]. Low cristobalite is also used to synthesize high-purity large quartz crystals and synthesis of uniform grain size of micro quartz crystals [6].

Cristobalite can be produced by several methods, e.g. sol-gel [8,9], microwave heating [10], coprecipitation [11]. The transformation to cristobalite structure from amorphous silica on a bacterial cell surface at a relatively low temperature was successes done [12]. Meanwhile, a new quantitative thermal analysis method based on differential scanning calorimeter was developed for determination of cristobalite phase [13]. Cristobalite as a single-product has, however, never been thoroughly studied and reported in the literature. Moreover, our local sands are rich of silica but has not been explored for

producing such phase. Therefore, it is interesting to investigate the potential of silica sands to synthesize cristobalite.

In this paper, we report the synthesis of cristobalite based on silica sands from two locals in Indonesia, i.e. Tuban, East Java and Tanah Laut, South Kalimantan.

2. Methods

The natural silica sands from Bancar and Tanah Laut were first purified. There was a gradually steps for purification of the sands: cleaning & sieving, magnetic separation, milling, another magnetic separation and soaking with hydrochloric acid prior to a hydrothermal treatment. The previous steps would produce cleaned sands which were ready for coprecipitation. The cleaned silica sands were dissolved in a 7M NaOH and then was stirred in a hydrothermal process to obtain Na_2SiO_3 powders. A 2M hydrochloric acid was then added by titration to form silicic acid ($Si(OH)_4$). This gel was then dried at 100°C to obtain SiO_2 amorf powder. After a DSC/TG assessment, the powders were calcined at temperature of 950 to 1200°C for 1, 4, 8 and 10 hr. XRD and SEM measurements were conducted to reveal the phase composition and the microstructure respectively.

3. Result and discussion

Table 1 presents the elemental content of the silica sands after several purification processes. The as-received silica sands have different Si content, being Bancar sand has much lower Si content than the Tanah Laut one. The purification process has improved the Si content. Although the content for Bancar has improved significantly, that for Tanah Laut is higher, i.e. up to 98%.

Table 1. XRF elemental content of the silica sands from Bancar and Tanah Laut after purification steps.

Steps	Quantity Si (wt%)	
	Bancar	Tanah Laut
Washing	74.70	95.58
Milling	78.70	97.70
HCl Soaking	91.60	97.42
Coprecipitation	95.30	98.02

The coprecipitated powder was then checked for phase analysis. The typical XRD pattern for the powder is given in Figure 1 and it shows amorphous phase.

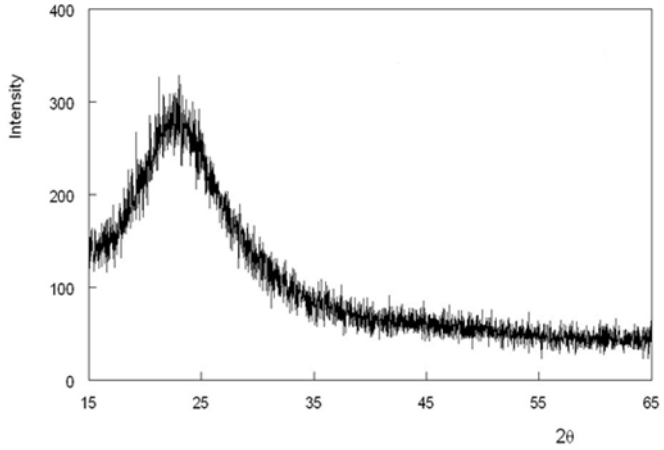


Figure 1. Typical XRD pattern (radiation CuKα) of the amorphous silica powder, represented by Bancar powder.

To determine the calcination temperature for cristobalite formation, the coprecipitated powder was thermally examined using TGA/DSC system. Both thermal and mass change effect were measured concurrently on the same sample. Figure 2 shows phase transitions in the amorphous powder. The associated peak for formation of cristobalite is observed around 950-980°C. Therefore the calcination temperature was set in a constant heating rate at 10 ˚C/min at various temperatures between 1100-1200 °C.

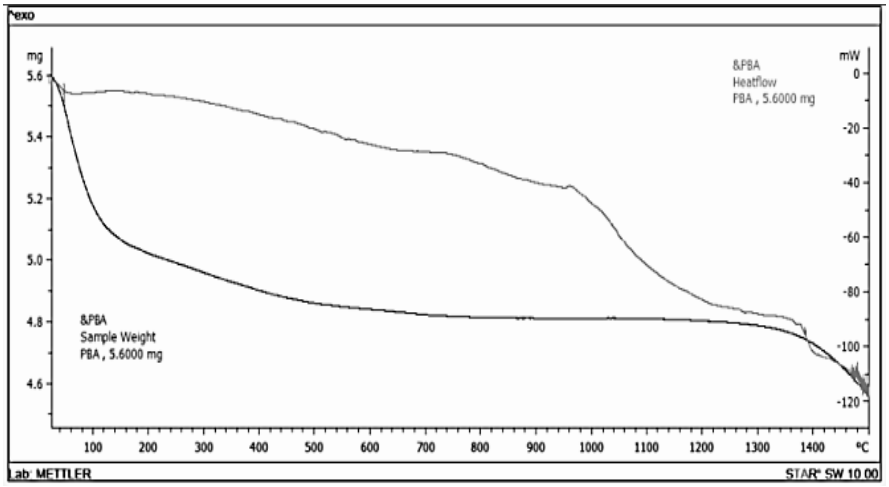
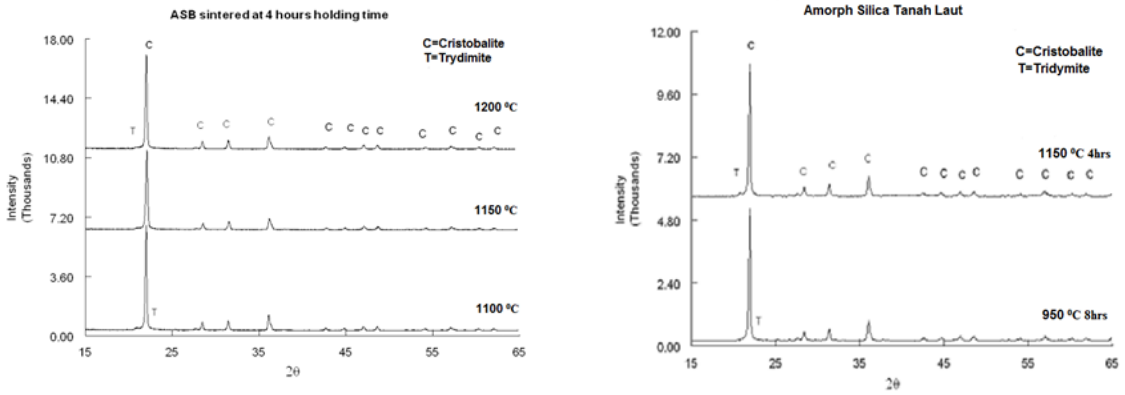


Figure 2. DSC-TGA pattern Amorf Silica Bancar

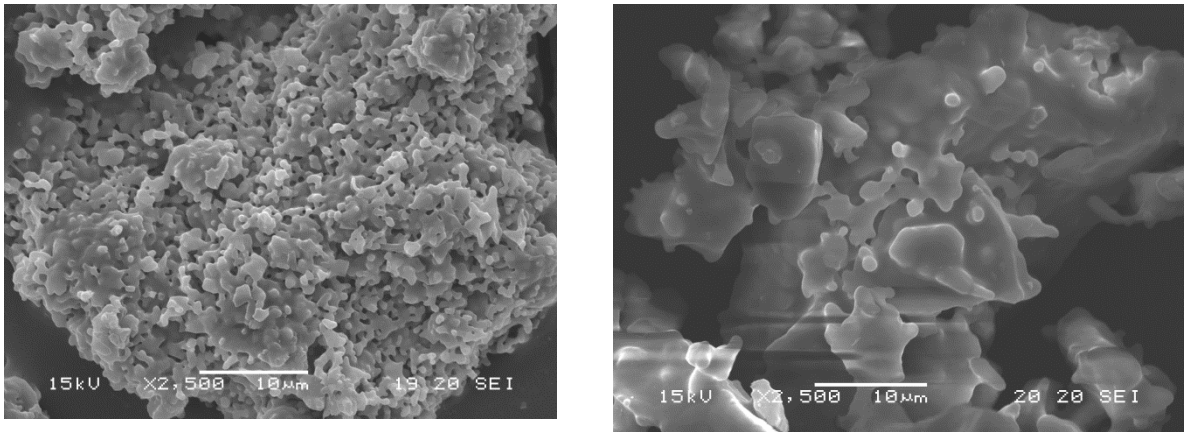
The XRD patterns of all powder samples after calcination are shown in Figure 3a (Bancar) and 3b (Tanah Laut). All powder samples showed that low cristobalite (ICSD No 9008110) become the dominating phase while tridymite (ICSD No 2104422) is the only minor phase. Applying Rietveld refinements for all XRD patterns using the Rietica software, it was found that all calcined samples contains more than 90 wt.% cristobalite and less than 10 wt% tridymite.



(a) (b)

Figure 3. XRD patterns (radiation CuKα) for the calcined amorphous silica from a) Bancar sand at various temperatures d) Tanah Laut at 950°C for 8hrs.

Figure 4 shows the SEM images of the calcined Bancar and Tanah Laut cristobalite powder. Both images show the presence of grains indicating that the powders contain crystallites, as claimed from the XRD data.



(a) (b)

Figure 4. SEM images of calcined cristobalite powders from a) Bancar and b) Tanah Laut

4. Conclusions

Low cristobalite powders have been successfully synthesized from local silica sands from Bancar and Tanah Laut. The results showed that nearly pure cristobalite can be obtained by the coprecipitation method and calcination at temperature above 1100°C. The optimized amount of cristobalite was obtained for calcination at 1150˚C for 4 hours.

Acknowledgments

We are indebted to BPPDN DIKTI for the fellowship programs. The research work was supported by "Hibah Unggulan Perguruan Tinggi (PUPTN)" ITS Research Grant, No. 003246.105/IT2.11/PN.08/2015 and "Hibah Disertasi Doktor (PDD) 2017" .

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