POREUS MATERIAL SINTERED FROM QUARTZ NANOPARTICLES

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ABSTRACT

Nanoquartz is defined as quartz in nanometric scale, and usually presents crystalline structure similar to the bulk α-quartz. Samples obtained by milling of natural quartz in a ball mill were submitted to ultrasound treatment, and then pressed and sintered. Four quartz powder samples were analyzed in a pycnometer, and it was found that the average density was 2.55 g/cm³. 28 samples of nanoquartz were pressed under 30 MPa and sintered in temperatures under ~1000°C, and then tested for density and SEM analyzes. The average apparent density was 0.96 ± 0.03 g/cm³, with average porosity of 0.62 ± 0.01. It was concluded that this methodology is effective for obtaining a material with high porosity and probably high superficial area. The density of the pressed material is considerably lower than the density of bulk quartz.

Keywords: nanoquartz, density, porosity.

INTRODUCTION

Nanoquartz is defined as quartz particles in nanometric scale, and usually presents crystalline structure similar to the α-quartz[14]. It is possible to manufacture a
porous material from nanoquartz by pressing and sintering its powder, and this material has a significantly lower apparent density. It can be obtained by several routes, like the milling of bulk quartz or precipitation from siliceous brines. Such particles, in theory, could be used in ceramic technology, being pressed and sintered, in order to produce a material with engineered porosity.

It is known that the pressing and compaction processes involves the distribution of stresses throughout the powder, by sliding, rotation, particle deformation, and rupture\[1\]. The sintering process is defined by Hausner\[8\] as the bounding of particles in a powder mass, granted to the atomic or molecular attraction in the solid state, and both the movement of particles and the mass transfer occur after the application of heat, making the material densified\[9\]. Such statements show that the sintering and the pressing processes have a great influence in the density and porosity of the obtained material obtained.

The porosity of a solid material is can be defined as the fraction of empty space in its volume\[6\]. It can be calculated by Equation (A), (presented in Materials and Methods section). The porosity is important for several possible applications for the material. If it could be used as a filter, for example, the porosity will be a key parameter in the equipment design\[4,6\]. If it will be used as a heterogeneous catalyst for a chemical reaction, it will be relevant in calculating the mass transfer taxes from the medium to the catalyst surface\[3,11\].

The dimensions of the pores are also relevant, because they can retain materials, for size-exclusion mechanisms\[16\], and they can affect the mass transfer taxes and the flow pressure drop\[2,3,4\].

For some industrial applications, it is important to transport ceramic slurries across pipes, from one equipment to another\[4\]. If a ceramic slurry is intended to be transported, separated or purified, it is important to know both the density of the ceramic solid particles and the density of the slurry\[4,6\]. The density of the bulk material is also a parameter for study the compression process, making it possible to verify if the pressed material has a great fraction of empty space\[12\].

It is clear that physical properties such as the porosity and the density of the ceramic material are of great relevance for ceramic industrial and economical applications. This work presents a study of the nanoquartz properties, making the contribution for researchers and engineers who intend to use this material in their
researches and for those who need to design equipment for nanoquartz industrial applications.

**MATERIALS AND METHODS**

The nanoquartz powder was produced by the milling of natural quartz, obtained from the *Santa Maria Eterna* formation in Belmonte, Brazil. The powder was separated in two portions: the first was analyzed in the scanning electron microscope and submitted to the picnometry test, and the second was submitted to the pressing and sintering processes, in order to manufacture the porous ceramic materials studied. A sample of this manufactured material is shown in Figure 1. The analytical studies are described in details in this section.

![Figure 1: A sample of the ceramic material obtained after the pressing and sintering processes.](image)

In order to analyze the nanoquartz powder bulk density, four nanoquartz samples were submitted to a picnometry test: the mass of the empty pycnometer is quantified in an analytical balance, it is filled with powder, and the sum of the pycnometer and powder masses is verified. Finally, the pycnometer is completely filled with deionized water, all the air is carefully removed and the total mass is verified, in order to verify the mass of water. By subtracting the volume of water, calculated from the available data of water density, from the volume of the pycnometer, the volume of the powder mass is determined. The picnometry test is schematically shown in Figure 2.
The pressed material was prepared by submitting the powder to the pressure of 30 MPa, using an hydraulic press, Maekawa Testing Machine MFG CO. Briquetting Press BR E-32. It was then sintered in temperatures under ~1000°C, in a tubular electric furnace, manufactured by Ikoma Co., Japan, with a refractory chamber made of silicon carbide, able to reach the temperature of 1460°C. The mass of the sample of material was verified in the analytical balance and its thickness was measured with a caliper rule. After the measurements, the sample was broken into four pieces, and every part was then submitted to another picnometry test. The average density of the four pieces was taken as the density of the sample.

The porosity of the material can be obtained from Equation (A), using the calculated density\[^6,12\]:

\[
\varepsilon = 1 - \frac{V_s}{V_T}
\]  

(A)

Where \(\varepsilon\) is the porosity, \(0 \leq \varepsilon \leq 1\), \(V_s\) is the volume occupied by the solid material and \(V_T\) is the total volume of the sample\[^6\].

It is also important to evaluate the crystalline structure of the material after the sintering process, because it can possibly suffer phase transitions. A sample of the pressed material was submitted to the X-ray diffraction (XRD) analysis, using a X-ray diffractometer Rigaku DMAX 2200, equipped with a copper tube “fine focus” (\(\lambda = 1,54\) Å), submitted to a tension of 40 kV and an electric current of 20 mA. This technique allows identifying and quantifying materials phases, as well as constructing their respective phase diagrams\[^6\].
The pressed material was then submitted to the scanning electron microscope (SEM) analysis, in order to verify its morphological aspect and the dimensions of the superficial pores. It was used, for the analysis, a Zeiss EVO MA15 microscope, equipped with LaB$_6$ thermoionic cannon. The SEM analysis has many applications in the study of the ceramic materials, allowing the researcher to directly observe the material’s surface characteristics, like the presence of pores, fractures and some crystalline defects\cite{13}.

RESULTS AND DISCUSSION

The picnometry analysis of quartz powder revealed an average density of (2.55 ± 0.02) g.cm$^{-3}$ for the bulk material, which is quite similar to the values reported in literature for the macroscopic quartz crystal. Schmalz has reported an average density of 2.65 g.cm$^{-3}$ for macroscopic quartz crystals\cite{15}, but the quartz’ physical properties depend on the geological origin, for example\cite{7}. The SEM image obtained for the powder, before being submitted to the pressing and sintering processes, is shown in Figure 3. It is possible to observe grains in different sizes and shapes, with diameter in the order of 300 nm.

![Figure 3: Scanning electron microscopy of the nanoquartz powder, before being pressed and sintered.](image)

The measurements of the 28 pressed and sintered samples revealed an average mass of (1.59 ± 0.07) g and an average thickness of (2.4 ± 0.1) mm. It was then verified an average density of (0.96 ± 0.03) g.cm$^{-3}$ for the pressed and sintered
material. Applying Equation (A), it was obtained that the average porosity - the fraction of empty volume in the total volume of the sample - is equal to \((0.62 \pm 0.01)\). Table 1 shows a comparison between these density values.

**Table 1**: Comparison between nanoquartz density, pressed and sintered ceramic apparent density and macroscopic quartz density reported in literature.

<table>
<thead>
<tr>
<th></th>
<th>Nanoquartz</th>
<th>Pressed and sintered ceramic (apparent value)</th>
<th>Macroscopic quartz (reported in literature(^{[15]}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g.cm(^{-3}))</td>
<td>2.55 ± 0.02</td>
<td>0.96 ± 0.03</td>
<td>2.65</td>
</tr>
</tbody>
</table>

It was concluded that the process of pressing and sintering the nanoquartz is able to manufacture a material with high porosity and with the density considerably lower than the bulk nanoquartz – the density is about 62% lower. More precise analysis, like the BET test, should be done in the future, in order to obtain a more precise measurement\(^{[10]}\).

The X-ray diffractogram of the material is shown in Figure 4. It shows the characteristic pattern of \(\alpha\)-quartz, showing that the material does not change its phase during the sintering process, and is crystalline.

**Figure 4**: X-ray diffractogram of nanoquartz after pressing and sintering processes.
The SEM analysis is shown in Figure 5 and in Figure 6. Figure 5 presents the material surface in a scale of 1 μm, and it is possible to observe pores of dimensions varying from 1 to 3 μm. Figure 6 has a greater resolution, and shows that there are pores even smaller. The circle is rounding a pore with diameter in the order of 200 nm.

**Figure 5**: Scanning electron microscopy of the surface of the pressed and sintered material.

**Figure 6**: Scanning electron microscopy of the surface of the pressed and sintered material. The circle is rounding a pore with diameter in the order of 200 nm.

The small dimensions of the pores and the high porosity calculated suggests a big value of superficial area for this material. In order to verify it, it will be done, in the future, the BET analysis\textsuperscript{10}. Another important study that will be done, in a future
work, is the calculus of the sphericity of the nanoquartz particles, using the SEM images. This study presents a great relevance for engineering applications of the powder\textsuperscript{[4,6]}.

**CONCLUSION**

The nanoquartz powder is a material which can be used for manufacturing a pressed powder with high porosity and low density. After being pressed and sintered, the density of the material goes from (2.55 ± 0.02) g.cm\(^{-3}\) to an apparent value of (0.96 ± 0.03) g.cm\(^{-3}\). The porosity calculated for this material is of (0.62 ± 0.01), meaning that about 62% of the total volume is empty, filled with atmospheric air.

The XRD analysis shows that these changes are not related to phase changes, since the material maintains its crystalline pattern, characteristic of the α-quartz, and the SEM images reveal pores varying from ~200 nm to about 3 μm.

The small pore dimensions and the high value of porosity strongly suggests a big contact surface area inside the pores of the material, and more precise studies will be done in order to verify this parameter. With such data, it will be possible for researchers and engineers to use this material as an alternative to other ceramics used in industrial applications, and they will be able to design equipment which are supposed to work with and transport it with more precision and better performance.

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