

Valorization of Algerian Sand for Photovoltaic Application

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Extracting quartz from sand, as well as extracting silicon from quartz requires knowledge of the physical and chemical properties of quartz found in the sand. In this work the chemical composition, the crystallographic phase, crystal system, space group, unit cell parameters, the absorption bands, the granulometric analysis and the microscopic observations of quartz in the sand from Mostaganem (Algeria) region have been carried out using X-ray fluorescence, X-ray diffraction, infrared spectroscopy, sifting, optical and scanning electron microscopy in order to determine the rate and the nature the crystallinity of its various components and to discover a layer rich in silica, containing a sufficient reserve to feed a unit manufacturing pure silicon starting from silica. The study is driven by current economic importance of the silicon application in the field of photovoltaic solar cells. The X-ray fluorescence indicates that Mostaganem sand has got a very good purity (99.5% silica). The crystallographic parameters of Mostaganem sand have been determined through analysis of X-ray diffraction. The following parameters were found, hexagonal crystal system, space group P3221, unit cell parameters: $a = b = 4.9030 \text{ \AA}$, $c = 5.3999 \text{ \AA}$. The infrared absorption spectrum of studied sand exhibits absorption bands characterizing the SiO_2 compound, due to Si-O-Si and Si-O aggregates and others. The granulometric analysis determines the percentage of the various fraction of the grain. The microscopy observation gives the shape of the grain. The results show finally that Mostaganem sand has got good proprieties for the photovoltaic application.

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1. Introduction

Quartz is one of the most abundant compounds in the Earth's crust. It is a crystalline form of silica. Silica is most generally found in nature as quartz, as well as in various living organisms. In many parts of the world, silica is the major constituent of sand. Silica is one of the most complex and most abundant families of materials, existing in form of several minerals. It is the basic mineral of sedimentary rocks which are formed by the deposition of sand. It is also found in sand dunes.

Silicate minerals are the name given to a group of minerals composed of silicon and oxygen, the two most abundant elements in the earth's crust. Silica is found commonly in the crystalline state and rarely in the amorphous state. It is composed of one atom of silicon and two atoms of oxygen resulting in the chemical formula SiO_2 [1].

SiO_2 forms a network solid crystal (tectosilicates) in which each silicon atom is bonded to four oxygen atoms. It would, therefore, seem that the formula should be SiO_4 , but each oxygen atom is bonded to another silicon atom as well [2].

Therefore every silicon atom has four half-oxygen which means that silicon atom is bonded to two oxygen atoms Fig. 1.

Sand is a product of weathering processes, which causes the disintegration or decomposition of rock near the surface of the earth.

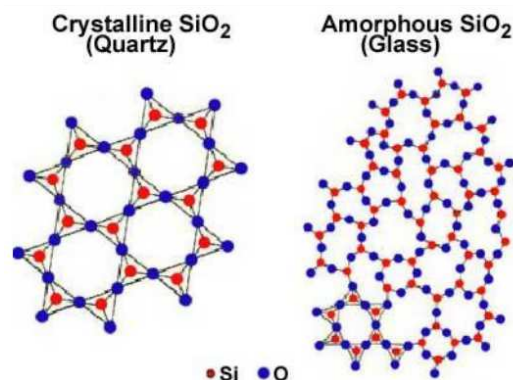


Fig. 1. Schematic of silica molecule.

Sand is considered as a clastic rock with a total absence of cement, whose size lies between 0.05 to 2 mm.

Although these grains may be of any mineral composition, the dominant component of sand is the mineral quartz, which is composed of silica (silicon dioxide). Sand can include other components like aluminium, sodium, calcium and potassium (feldspar minerals). Ferromagnesian minerals are silicate minerals in which cations of iron and magnesium form essential chemical components. The term is used to cover such minerals as the olivines, pyroxenes, amphiboles, and the micas biotite and phlogopite.

For a particular source of sand to be suitable for industrial application, it must not only contain a very high proportion of silica but it also should not contain more than strictly limited amounts of certain metallic elements such as iron, aluminium, titanium, etc.

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Silica sand is also normally required to be well-sorted, i.e. to have grains of an approximately uniform size. Industrial uses of silica sand depend on its purity and physical characteristics. Some of the more important physical properties are: grain size and distribution, grain shape and sphericity. Silica sands have a large number of uses depending on their characteristics [3]:

- Production of silicon and silicon carbide, production of glass.
- Foundry sand, ceramics.
- Sandblasting and other abrasives
- Building products, filler and extender
- Pigments, hydraulic fracturing and propping in the oil industry
- Ultra high silica products in the electronic and fiber optic industries, fused silica, silicone products.
- Water filtration.

Algeria is a very large sunny country which makes it an important reservoir of solar energy. This solar radiation can be converted to electricity using photovoltaic solar panels. These are, mainly, manufactured of silicon cells, which are quite expensive. There are huge quantities of quartz (SiO_2), which is found in the sands although there are no producers of silicon in Algeria.

To our knowledge, the amount of quartz, that has a great economic importance, in the sand of Mostaganem has not been evaluated up to now. The main aim of this work is to evaluate several proprieties of the Mostaganem sand required for production of photovoltaic-grade silicon.

2. Materials and methods

2.1. Geological setting

Mostaganem is located in the in northwest Algeria. The area of the city is about 2.269 km^2 . Its geographical coordinates are: latitude of $35^\circ 55' 57''$ North, longitude of $0^\circ 05' 21''$ East, Fig. 2. The city of Mostaganem is lo-

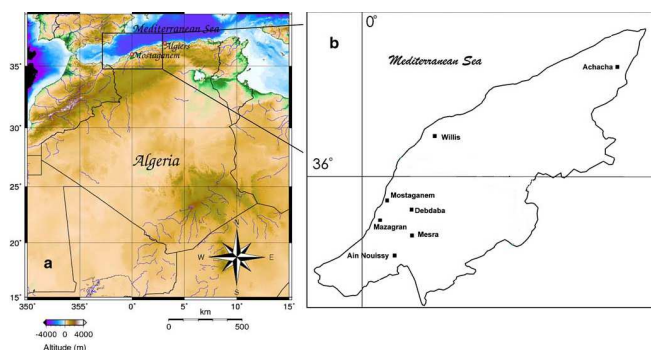


Fig. 2. Location of Mostaganem in Algeria [5, 6].

cated in the vicinity of Chlef in the east, of Relizane in the southeast, of Oran in the west, and of Mascara in the southwest. Mostaganem city is a littoral town. The climate is semi-arid, mild in winter and slightly humid at elevations greater than 500 m [4].

Our six sand (SM1, SM2, SM3, SM4, SM5 and SM6) samples were collected in this city.

The stratigraphy of the site is presented in Fig. 3.

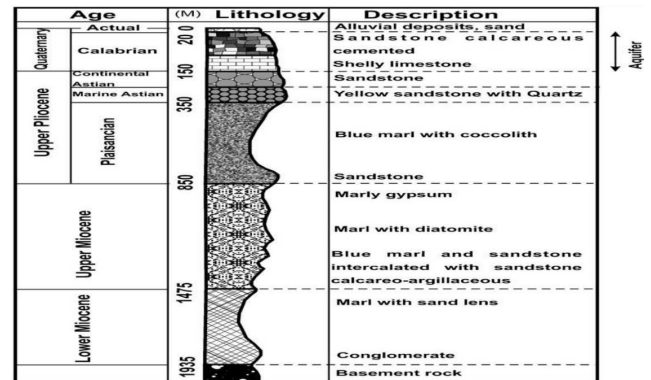


Fig. 3. Schematic stratigraphic section of the Mostaganem area [5].

2.2. X-ray fluorescence analysis

Chemical composition of the six samples, in their oxide form, was determined by employing an Axios Panalytical X-ray fluorescence instrument in the department of geology of the National Office of Research in Geology and Mineralogy (ORGM, Boumerdes, Algeria)

Samples were first milled in a laboratory disc mill to approximately $40 \mu\text{m}$ before pressing into pellets (approx. 5 g of sample material) and analyzed.

2.3. X-ray diffraction analysis

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions.

Knowledge about crystallinity is highly relevant, as a crystalline form is usually preferred in development. In contrast to amorphous material, the crystal has well-defined properties (melting point, solubility), parameters that should be known in order to control the final product. The result from an XRD analysis is a diffractogram showing the intensity as a function of the diffraction angles.

Our results of XRD analysis were obtained by means of Siemens D500 analyzer in the Department of Materials Science of the University of Biskra, Algeria.

After the XRF analysis, we conclude that our sand is very rich in silica so that the concentration of other minerals is almost the same. This is why the analysis was carried out only for sample SM1. For the analysis, sample SM1 was milled in a laboratory disc mill to approximately $63 \mu\text{m}$.

2.4. Infrared absorption spectroscopy

Infrared spectroscopy (FTIR) is one of the most interesting ways to study materials. It can be used to obtain the material structure without affecting its properties. Infrared spectroscopy exploits the fact that molecules absorb light with specific frequencies that are characteristic of their structure. It is often used to identify structures because functional groups give rise to characteristic bands both in terms of intensity and frequency. Infrared spectroscopy is a simple and reliable technique widely used in both organic and inorganic chemistry, in research and industry.

Sample SM1 was first milled in a laboratory disc mill to approximately 40 μm and then formed into a KBr-etch pellet for spectroscopic examination using a Bruker spectrometer in the laboratory of FTIR analysis of the Research Center of semiconductors for Energetic Application CRTSE, Algiers Algeria.

About 1.5 mg of carefully ground sand was mixed with 100 mg of dried KBr powder and then the mixture was further ground using a mortar and pestle. The mixture was then pressed in a hydraulic press to make a pellet, which was subsequently used for recording of the FTIR spectrum.

2.5. Grain size analysis

In this analysis we have used the sifting method, because it can separate sand from gravel and clay [7].

For this purpose we have used a mechanical sifter with ten sieves. We have used a dry-sieve analysis to determine the particle size distribution [8], or grading, of the sample. To obtain a grading, the aggregate is shaken through a series of sieves, nested one above the other

in order of increasing opening size. The sieve with the largest openings is on top and the one with the smallest openings is on the bottom. A pan placed beneath the sieves catches material passing through the smallest sieve. Coarse and fine aggregate usually are sieved separately.

There are various indices which can be measured using this technique. In this work we have just measured the concentration in several sieves.

The grain size analysis was carried out at the metallurgy laboratory of the national company of the industrial vehicles (SNVI) in Rouiba (Algiers Algeria), using mechanical sifter RETSCH-AS 200.

2.6. Microscopy observations

In order to determinate the shape of the sand grain, scanning electron micrographs of the sand samples were obtained using JSM-5500LV/JSM-5500 in the Department of Materials Science of the University of Biskra, Algeria.

Optical micrographs of the sand samples were obtained using Nikon Eclipse E600 at the metallurgy laboratory of the national company of the industrial vehicles (SNVI) in Rouiba (Algiers Algeria).

3. Results and discussion

3.1. X-ray fluorescence analysis

According to Table I, we show that Mostaganem sand is very rich in silica 99.5%. This sand has a small concentration of alumina and hematite and even smaller concentration of other oxides, such as the pyrite, the free rutile, the ilmenite, limonite and magnetite, which were also found in the raw material.

Chemical analysis of the content of Mostaganem sand [%].

TABLE I

Oxides	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅
SM1	99.5	0.20	0.23	0.06	0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
SM2	99.4	0.20	0.28	0.011	0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
SM3	99.48	0.20	0.25	0.06	0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
SM4	99.52	0.20	0.23	0.08	0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
SM5	99.55	0.20	0.28	0.06	0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
SM6	99.45	0.25	0.23	0.06	0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05

3.2. X-ray diffraction analysis

In order to determine the parameters and the structure of the crystal lattice of our sand samples, we have used the X-ray diffraction which turns out to be the only technique for the determination of these parameters. The XRD spectrum of Mostaganem sand is shown in Fig. 4.

In Table II, we observe the appearance of all peaks related to the presence of alpha-quartz in our sand sample, confirming the high crystallinity.

According to these results, we attest the absence of other phases than quartz, which confirms the results found by XRF.

When we compare between the results found by the XRD and those presented in the jcpds 46-1045 card (ASTM card), also shown in Table II, we certify that there is a very good similarity between the measured parameters and those present in this card.

The software used for data analysis and for the Rietveld refinement was HighScore Plus from PANalytical.

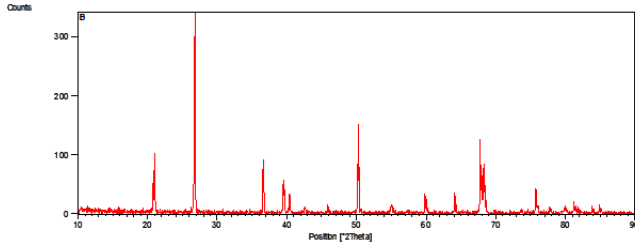


Fig. 4. XRD spectrum of Mostaganem sand.

TABLE II

Parameters of XRD peaks of Mostaganem sand and reference parameters.

Measured parameters				jcpds 46-1045			
Peak	2θ	D hkl	Intensity [%]	2θ	D hkl	Intensity [%]	HKL
1	21.0283	4.22482	6.34	20.859	4.2550	16.0	(100)
2	26.8635	3.31891	100.00	26.639	100.0	3.3435	(101)
3	36.6860	2.44971	11.28	36.543	2.4569	9.0	(110)
4	39.4900	2.28200	4.35	39.464	2.2815	8.0	(10 2)
5	40.3841	2.23351	2.55	40.299	2.2361	4.0	(111)
6	42.4300	2.13043	0.80	42.449	2.1277	6.0	(200)
7	46.1200	1.96821	0.08	45.792	1.9799	4.0	(201)
8	50.2382	1.81610	11.45	50.138	1.8180	13.0	(11 2)
9	50.6800	1.80130	0.21	50.621	1.8017	< 1	(003)
10	54.7600	1.67635	0.08	54.873	1.6717	4.0	(20 2)
11	55.2700	1.66209	0.16	55.323	1.6592	2.0	(10 3)
12	57.1900	1.61077	0.15	57.234	1.6083	< 1	(2 10)
13	59.8582	1.54519	3.46	59.958	1.5415	9.0	(21 1)
14	63.9100	1.45665	0.13	64.034	1.4529	2.0	(11 3)
15	65.8300	1.41874	0.08	65.784	1.4184	< 1	(30 0)
16	67.7892	1.38243	13.45	67.742	1.3821	6.0	(21 2)
17	68.2976	1.37338	6.08	68.142	1.3750	7.0	(20 3)

The crystallographic parameters of Mostaganem sand have been determined through analysis of X-ray diffraction. These parameters were found to be as follows: hexagonal crystal system, space group P_3221 , unit cell parameters: $a = b = 4.9030 \text{ \AA}$, $c = 5.3999 \text{ \AA}$.

3.3. Infrared absorption spectroscopy

The experimental FTIR absorption spectrum of studied sand is shown in Fig. 5.

TABLE III

The main bands of IR absorption and associated bond vibration of Mostaganem sand.

Frequency [cm^{-1}]	Vibration kind
459.75	Si–O–Si
693.25	Si–O vibration
778.34	Si–O vibration
790.90	Si–O vibration
1080.72	stretching vibrations Si–O–Si
1163.53	stretching Si–O–Si bond
1616.37-1876.23-3349.23	Stretching H–OH

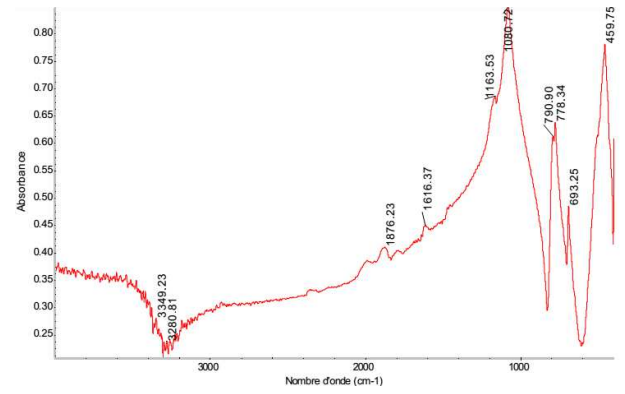


Fig. 5. FTIR absorption spectrum of Mostaganem sand.

The main bands of absorption obtained from Fig. 5, are shown in Table III [9–11].

3.4. Granulometric analysis

Sand samples were dried at 120°C for one hour and a half in an oven. After this the sieving operation was carried out. After studying the grain size distributions of the six samples, we have concluded that they are almost similar and for this reason here we present only the results of the grain size analysis of sample SM1. The results of granulometric analysis are shown as histogram in Fig. 6.

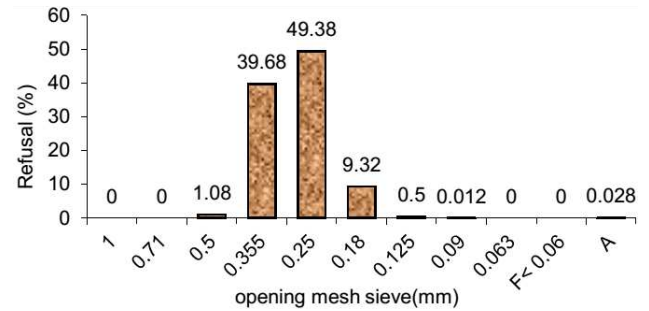


Fig. 6. Histogram representation of granulometric analysis of Mostaganem sand.

TABLE IV

Granulometric analysis.

Opening size of sieve [mm]	Refusal [%]
1.4	0
1	0
0.71	0
0.5	1.08 (corse sand)
0.355	39.68 (corse to medium)
0.25	49.38 (medium to fine)
0.18	9.32 (fine sand)
0.125	0.5
0.09	0.012
0.063	0
$F < 0.06$	0
A	0.028

After the analysis of the obtained results, we notice that in the size distribution of Mostaganem sand prevail grains in the class of 0.25 mm and 0.355 mm. These classes represented almost 50 to 40% of the overall mass of the sand.

In the particle size class of 0.18 mm we find almost 9%, while the concentration is insignificant in the remaining sieves.

3.5. The microscopy observations

3.5.1. Optical microscopy observation

The micrographs at lower magnifications in Fig. 7 reveal the presence of somewhat rounded, angular edged, elongated and irregular grains.

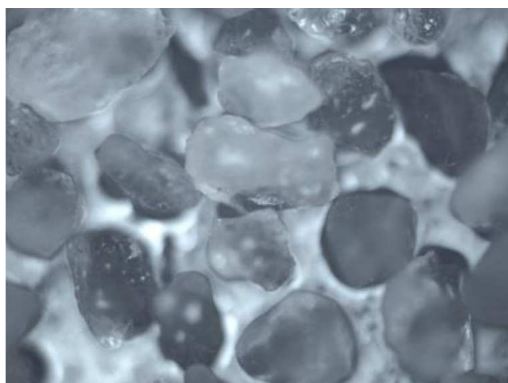


Fig. 7. Mostaganem sand micrograph.

3.5.2. Scanning electron microscopy observations

The observation under the scanning electron microscope confirms the irregular shape of sand. Figure 8a confirms the rounded shape of sand and that the grain dimensions are about 200 μm in average.

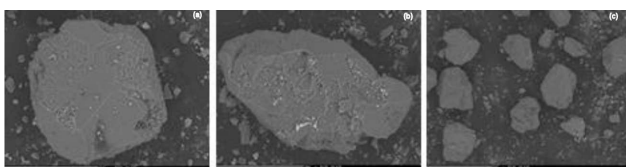


Fig. 8. Scanning electron micrographs of Mostaganem sand.

Figure 8b confirms the elongated shape of sand grains and that their dimensions are about 400 μm in average.

Figure 8c shows several shapes of sand, including somewhat elongated, rounded and angular shape with various dimensions.

4. Conclusions

The present work has been carried out using several characterization techniques in order to assess applicability of Mostaganem sand for photovoltaic applications.

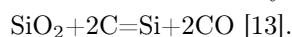
According to X-ray fluorescence analysis, we certify that Mostaganem sand is very rich in silica 99.5%. The X-ray diffraction reveals that Mostaganem sand

has a high crystallinity. The crystallographic parameters were found to be as follows: hexagonal crystal system, space group P_3221 , unit cell parameters: $a = b = 4.9030 \text{ \AA}$, $c = 5.3999 \text{ \AA}$. The FTIR spectrum of this sand indicates that the majority of chemical bonds were Si–O bonds, with different kinds of vibrations. Especially the double absorption at 790 and 7798 cm^{-1} indicates that the sand is in α -quartz phase.

The granulometric analysis shows that in the size distribution of Mostaganem sand prevail grains with the size of 0.25 mm and 0.355 mm.

Using the optical microscopy and the scanning electron microscopy, we observed that the sand grains are rounded, angular edged, elongated and irregular.

After the study of several proprieties of the Mostaganem sand, we conclude that this sand can be used in photovoltaic applications by the reduction of silica with carbon in an electric arc furnace [12] at temperatures higher than 2000 $^{\circ}\text{C}$ in the hottest parts, by a reaction that can be written ideally as:



We confirm that Mostaganem silica can be used as the raw material for production of silicon.

Acknowledgments

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