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Prospects and State of The Glass Industry in Saudi Arabia and a Preliminary Assessment of The Quality of Glass and Glass-Ceramics Fabrication

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Abstract
The current study presents a feasibility study of the fabrication of ordinary glass and glass ceramics from Saudi Arabian domestic raw materials. It discussed the glass industry in Saudi Arabia and the middle east region. It also gives a brief explanation of the sand geography in Saudi Arabia. Also, it represents experimental data about the fabrication of ordinary Glass and glass ceramics from Saudi raw materials. Firstly, ordinary transparent Glass without significant defects was fabricated with sand collected from the Ar-Rays region in Saudi Arabia. Four nanosized crystallization catalysts, namely Vanadium Carbide (VC), Tungsten Carbide (WC), Titanium Carbide (TiC), and Titanium Oxide (T_2O_3,) were added to the constituents of the Glass in 3% wt. For VC, the crystallization process was limited. The glass ceramics of WC consisted of multi-dimensional edges crystals that covered all of the matrices. The addition of TiC obtained gray crystalline whiskers. The Y_2O_3-glass ceramics consisted of multi-directionally rosette crystals. Finally, the microhardness values of the added crystallization catalysts in glass ceramics were much higher than in ordinary Glass.

1 Introduction

The Kingdom of Saudi Arabia lies between Africa and Asia, occupying about three fourth of the Arabian Peninsula. Most of the Saudi Arabian areas are mountains, valleys, forests, and the remaining parts of it (30%) are covered by vast sandy deserts [1], which consist mainly of silica and other oxides, which forms the primary raw materials of Glass [2]. The world's glass industries are vast in size and highly diverse in terms of the range of products made and the diversity of manufacturing techniques employed.

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The utilization of Glass ranges from banal windows or bottles to anti-nuclear radiation containers, from architectural and structural glasses to photosensitive glass devices used in machine controls, from food preparation tanks to the newest optical fibers [3]. The most commonly used glass composition by far is soda-lime Glass because it is cheap and easy to manufacture. The optimum glass composition comprises 72% silica, 15% soda, 10% lime and magnesia, 2% alumina, and 1% various oxides. Soda-lime Glass is used for windows, containers, bottles, jars, everyday tableware, and lamp envelopes. It accounts for about 90% of all tonnage manufactured [4,5].

On the other hand, glass-ceramics are fine crystalline materials formed when a glass that contains a small number of nucleating agent oxides or crystallization catalysts undergoes controlled heat treatment. However, many glasses are stable against crystallization. Therefore, the choice of specified compositions is essential to get a glass. Glass ceramics are used in a wide range of technical applications, including construction, domestic, military, and the microelectronics industry [6]. The majority of glass currently manufactured in Saudi Arabia is either sheet glass or glass molded into jars and bottles. 95% of sheet glass is used for glazing in houses and factories, with the remaining 5% being used for making mirrors or toughening for domestic appliances such as ovens [7].

This work is regarded as a seminal work in glass manufacturing in Saudi Arabia as there is a dearth of articles that deal with the glass industry in Saudi Arabia and an assessment of the quality of available sand. Many prospective researchers, manufacturing industry personnel, potential investors, and policymakers who wish to get an integrated view of the industry and its potential would appreciate such information gathered in one article to begin delving into possible project proposals in the glass industry. It gives an idea about the geography of the Saudi Kingdom, evaluation of sand quality in different areas, and the current status and future. Hence, it is trying to fill an important gap in the knowledge by providing a preliminary overview of the industry and evaluation of the resources available. Moreover, more information is being gathered through field studies, experimental tests, and economic evaluation.

1.1. Glass in the Middle East

Glass has been well known in the Middle Eastern region since the third millennium (Mesopotamia). It is historically accepted that the first manufactured Glass appeared about 5000 years ago in Egypt [8]. Before the 1st century BC, when blowing appeared, glass objects were mainly used to produce ornaments and small cosmetics containers. Soon afterward, Western Europeans learned about glass processes and started to develop them themselves. For the next 500 years, Egypt, Syria, and the other countries along the eastern shore of the Mediterranean Sea became glassmaking centers. Fragments constituted of plain Glass with a few decorated samples are usually blown or mold-blown; those could be of vessels, windows, bangles, beads, pins, or weights. Glass finds have been unearthed during excavations of coastal sites at Sharma, al-Shih. Others have been found in the south of the Arabian Peninsula, around Aden and Julfar in the Persian Gulf, and Bahrain and Kuwait. There have also been fragments found in Saudi Arabia, at Masafi and Yamama [9].

The glass industry in the Arabian Gulf is currently undergoing rapid development. The rapid development of the construction industry dramatically stimulates the demand for flat and high-added-value glass products in the Arabian regions, especially in the United Arab Emirates (UAE) and Saudi Arabia. In recent years, the UAE and nearby regions have undergone unprecedented growth in the real estate and automobile industries, which causes continuous demand for glass products with high performance, environmental friendliness, and superior quality. In order to meet the growing demand, UAE and most countries in this region have to import a large quantity of glass from other countries. At the same time, the local glass enterprises also gained extensive and rapid development [10].

Fitch ratings expect the construction sector in the Arabian Gulf region will continue to be supported by government spending (about USD five trillion for the next decade). Particular emphasis will be placed on social and affordable housing to meet the needs of the growing indigenous populations. Moreover, growth in construction will be driven by high economic growth, the desire for diversification, and, in some cases, preparations for global sporting events. One of the main components of the infrastructure raw material is glass products [11]. Important facilitators of construction growth in the region are expected to include changes to mortgage laws in Saudi Arabia, driving residential construction, and more private sector participation in infrastructure investments across the region. The Arabian Gulf region is likely to continue to be a significant source of growth in the global construction market. Demographic factors, economic growth, and regional governments' pursuit of more balanced economies will serve as potent stimuli for construction demand [12]. A recent study has reported that several major construction and infrastructure projects have been awarded within six of the countries, which include: USD 119 billion in Saudi Arabia; USD 75 billion in UAE; USD 26 billion in Qatar; USD 30 billion in Oman; USD 25 billion in Kuwait; and USD 10 billion in Bahrain [13].

Fabricated flat glass demand will benefit from quick sales of energy-efficient products such as solar control, insulation, and low-E glass. The solar energy market, hurt by recent global economic weaknesses, is expected to take off gradually. It should be noted. However, the demand for flat Glass used in solar energy applications totalled just around 120 million square meters, which can be considered a niche market. The UAE has announced a planned USD 90 billion five-year spending spree on housing, schools, infrastructure, and leisure projects, making the capital the latest Gulf monarchy to unveil big new spending since the 'Arab spring' uprisings. The USD, 90 billion spending plan is aimed at the citizens and echoes the USD 130 billion investment program launched in Saudi Arabia. The Middle East container glass sector has three major consumer markets: the beverage sector, which accounts for around 56% of the total tonnage of glass packaging containers; the food sector, which makes up around 29%; and the perfumery, pharmaceuticals, and technical product containers (flacconage) sector, which accounts for about 15% of total tonnage [14].

A report by the Gulf Organization for Industrial Consulting on flat Glass stated that the Gulf countries are developing future markets due to the significant construction sector growth, which is supported by high oil prices and the increase in population. The report estimated the total investment in the construction sector in the Gulf countries at more than 180 billion dollars until 2022 [15]. The report also added that more than 75 companies are involved in the glass sector in the Gulf countries, most of which are concentrated in Saudi Arabia, which accounts for the production of 131 thousand tons annually. At the same time, the capacity of the primary industrial units reaches about 1.1 million tons annually. The report pointed out that the overall annual growth rate in flat glass consumption was 4%, compared to 8.2% for household consumption growth. It is also expected to increase by 10-12% during the next three years, and the prices of imported flat glass range between 450 and 600 dollars per ton, or between 6 and 8 dollars per square meter. It is noteworthy that the glass industry in the Gulf countries consists of a small group of companies producing glass and a larger group of glass manufacturers. The producers operate integrated plants that produce ordinary float glass [16]. Another report from the Gulf Industrial Knowledge Center revealed that the glass and glass products in the building materials industry represented about 7% of the total number of factories, 6.4% of the total investments, and 7.3% of the total number of workers.

1.2. Glass in Saudi Arabia

The glass industry in Saudi Arabia is an industry whose raw materials are available naturally in abundance. It is an industry that branches out and overlaps with many other industries such as automobiles, buildings, electricity, packing bottles and utensils, etc., reaching economically viable levels. Many glass factories have been constructed in different regions: Obeikan Glass Co., located in Yanbu, produces clear floating glass of different thicknesses. Saudi Arabian Glass CO (SAGCO), located in the Red Sea port of Jeddah, produces flint, green and amber glass. Arabian United Float Glass Company (UFG), located in Yanbu, produces clear float, light green, mirror glass, and patterned glass. Mahmood Saeed Glass Industry Company in Jeddah produces glass bottles, jars, and glass food containers. Al-Andalus Glass, located in Riyadh, produces insulated glass, double glass, laminated glass, and tempered glass [17,18].

On the other hand, Saudi Arabia imports a considerable amount of glassware. Unfortunately, there is no available data about the import of glass goods in 2020. The only available data reported that Saudi Arabia spent 2,076 million Saudi Riyals in the fourth quarter of 2020 for importing construction materials, including glass and glassware. Saudi Arabia spent 2018 almost one billion Saudi Riyals in importing about 280 992 tons of glass from many countries in Europe (France, Italy, Germany, Poland, Belgium, and Spain), Asia (China, India, Japan, Taiwan, and South Korea), Middle East (United Arab Emirates, Egypt, Bahrain), USA, Turkey, Switzerland and Peru [19].

1.3. Sand geography in Saudi Arabia

In this section, it is essential to have an idea about the geography of the Saudi Kingdom, the evaluation of sand quality in different areas, the current status, and the future. Hence, we are trying to fill an important gap in the knowledge by providing a preliminary overview of the industry and evaluation of the resources available. Sand is defined as loose granular material which ranges in size from 62.5 to 2000 micrometers derived from weathering and natural disintegration of rocks, minerals, and other materials on the earth's surface [7]. The sand is found in four central regions in Saudi Arabia, comprising one-third of the Saudi Arabian area, 780,000 km^2: The Al Nafud desert, the Dahna desert, the Empty Quarter desert, and the Al-Jafouda desert. Al-Nafud desert is a big sand sea in the northwest of the kingdom. It has an estimated area of about 64,630 km^2 and consists of longitudinal and transverse dunes [20]. In the southeast, there is the Empty Quarter desert, which is the largest continuous sandy desert in the world, with an area of more than 600,000 km^2. Between them, two longitudinal regions begin to extend in the form of arcs [21]. The first sandy area is located to the east and is called the Dahna desert. Its length is 1,200 km, and its width ranges between 20 and 80 km. It is noted that the sand areas in the kingdom are concentrated in areas with low terrain, often in narrow, rectangular plains, and confined between a mountain edge in the east and a slope inclined towards the east in the west or large basins with low terrain. Sand is also concentrated in the Najd plateau in the form of Sebai veins, extending north to south. Its length is 176 km, and its width varies between 30 and 50 km. Among the areas of concentration of sand is also the Nafud Alsura, which extends in a direction from northwest to southeast, with a length of 177 km and ranges between 4 and 10 km in width, and covers an area of about 548 km^2 [22].

One of the critical questions to be asked is what would be the potential feasibility of utilizing these sand deposits as the raw materials for manufacturing glass? Would they prove to be suitable, and to what extent would the quality of glass which will be produced? To answer this question, laboratory experimentation in manufacturing glass was carried out from samples collected from several sites. This paper also reports on the experiment carried out as part of this research work and gives an indicative assessment of their sand quality. The experimental methods and results are given in the following section.

2 Experimental Methods

Six Sand samples were collected from different Saudi regions located in the map shown in Figure 1. The sand samples were analyzed using X-ray Fluorescence (XRF) to ensure the quality of the sands, and the results are shown in Table 1. A quantity of 70% wt of the sand from Area 3 (Ar-Rays) was chosen as the main constituents to fabricate the glass products due to the high percentage of silica. Soda ash with 15 % wt was the second added ingredient. Limestone comprises almost 12 % of the weight of the produced glass. Firstly, the sand was washed and dried before the weighing process. Then, 15 % wt soda ash and 12 % wt Limestone were added. All components were mixed manually to be sure that it is mixed homogeneously. 3 % wt of each of (Titanium carbide) TiC, (yttrium oxide) Y_2O_3, (vanadium carbide) VC, and (Tungsten carbide) WC were added as nano-size powders to the ingredients as a crystallization catalyst to promote the formation of glass ceramics. To the best of our knowledge, there are so far no reports regarding the fabrication of glass ceramics using such powders. The added powders were summarized in Table 2. The mixed ingredients were packed in a graphite mold and melted in an electric furnace. The temperature of the furnace was adjusted to 1150 ^oC. The furnace takes about three hours to reach this temperature. Then, the soaking time was adjusted to three hours to remove any gas porosities.

The crystallization process for the formed glasses was performed using two steps. First, the glass samples were heated to 630 °C for 2 hours and at a heating rate of 10 ℃ /min to promote nucleation. The temperature was then raised to 920 °C for six hours to promote crystal growth. The microstructures of the resulting materials were examined using optical microscopy after etching by 1% HF + 1% HNO_3 solution in 20 seconds. For hardness measurements, a Vickers microhardness tester was used according to the ASTM standard for Vickers indentation hardness of advanced ceramics [23]. The testing load was 9.8 N with a loading time of 15 s for all measurements of glass and glass-ceramic samples. 5 indentation readings were done for each sample.

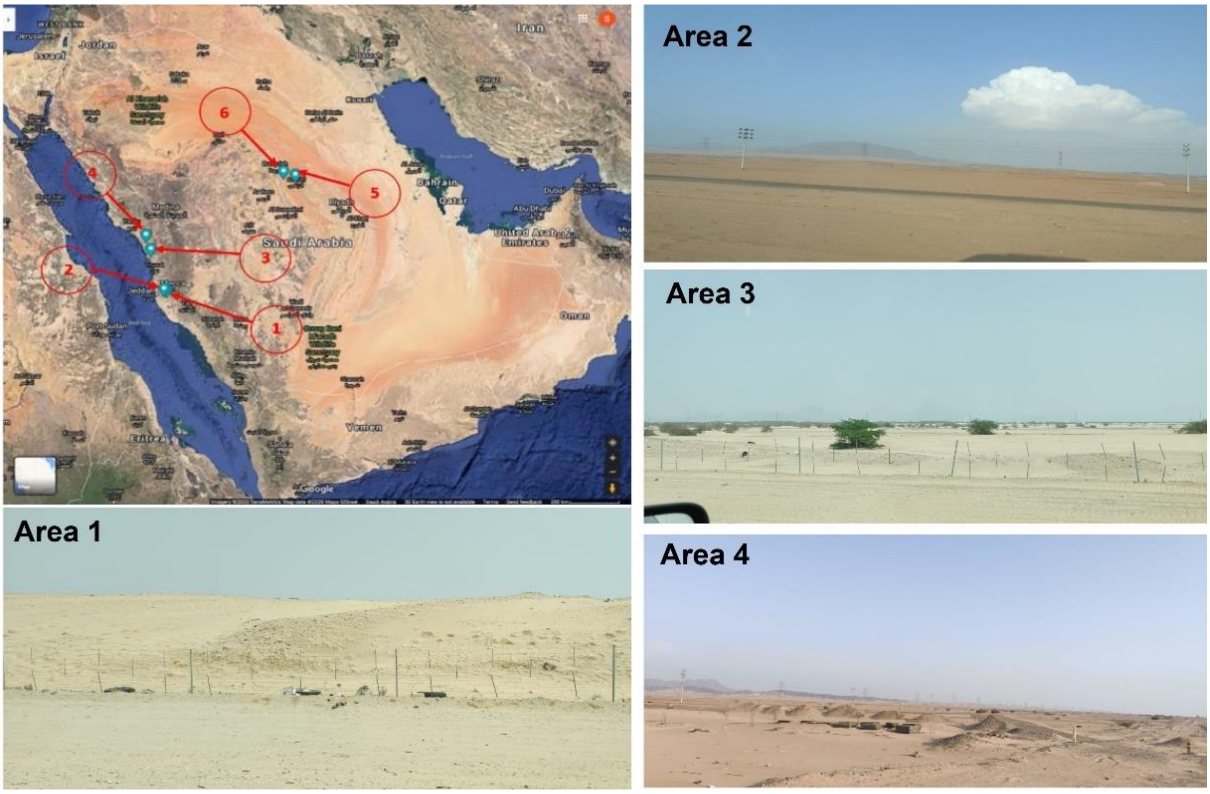

Figure 1. Location of collected samples in Saudi Arabia

Table 1. The compositions of six grains of sand from six different arias of Saudi Arabia obtained by the XRF analysis

No.	Region	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O
1	Madinah	76.21	10.52	2.32	2.26	3.1	1.13
2	Jeddah	93.5	2.61	0.72	0.21	0.19	0.01
3	Ar-Rayis	97.02	1.6	0.62	0.18	0.12	0.11
4	Rabigh	75	11.2	4.53	3.42	2.51	1.54
5	Al Majma’ah	95.6	1.42	0.79	0.32	0.22	0.092
6	Unayzah	94.5	1.25	0.72	0.65	0.37	0.55

Table 2. Glass and glass-ceramics fabricated samples

Sample No.	Catalyst Type	Purity, %	Particle size	% wt
1	Plain glass without any crystallization catalyst addition			
2	VC	99	<100 nm	3
3	WC	99.95	30 nm	3
4	TiC	99.9	30 nm	3
5	Y_2O_3	99.9	40 nm	3

3 Results and Discussion

The microstructure of the formed plain glass sample 1 (without crystallization catalyst addition) is an opaque brown color. It looks like a featureless amorphous microstructure, homogenous, dense with a slight presence of porosity, as shown in Figure 2. The glasses fabricated with the addition of crystallization catalyst show significantly different topography and contain inhomogeneities. All the samples were less transparent in dark brown color. For sample 2 of VC, the structure appeared as a glassy matrix with a limited amount of crystallization. The formed crystals take the form of randomly distributed single dots as shown in Figure 3. This may be due to the large particle size of VC. The mixing can enhance the topological and chemical short-range order, forming a dense packing structure and enhancing the stability of the undercooled liquid against crystallization. On the other hand, the fine grain size particles have a positive heat of mixing, which tend to segregate to form clusters (nucleation) inside the glassy phase upon undercooling.

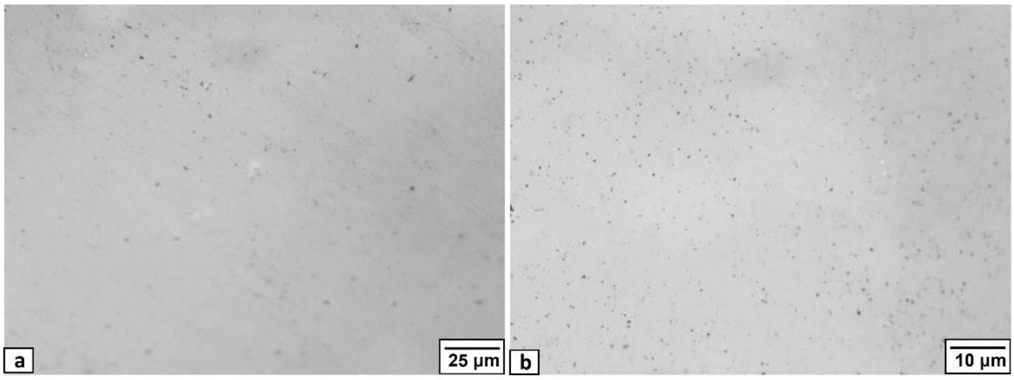

Figure 2. Micrographs of the plain glass

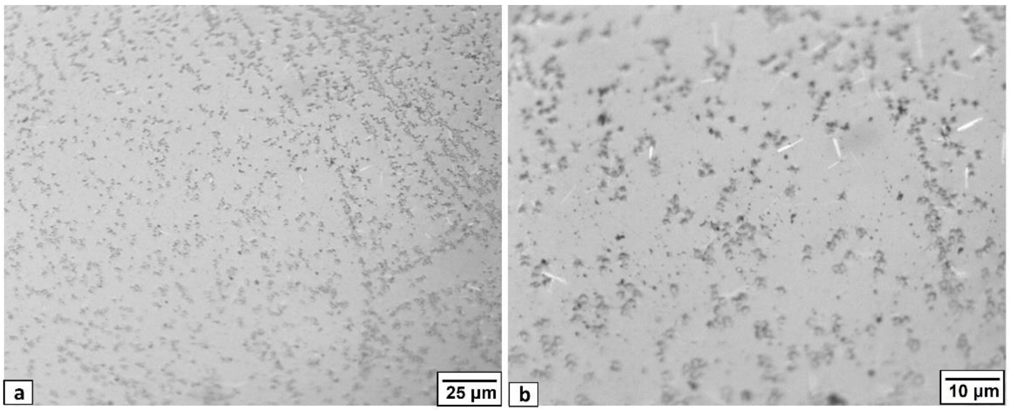

Figure 3. Micrographs of the glass ceramics with the addition of VC as crystallization catalyst show a glassy matrix with single dots crystals

The nanosized WC modified sample 3 to be a glass ceramics structure, as shown in Figure 4. The structure consisted of edged crystals which covered all of the matrices. Some clusters appeared in bright color in Figure 4 (b), which is probably WC. For the added TiC (sample 4), gray crystalline whiskers (Figure 5) were observed within the glassy matrix. The length of the whiskers was excellent and reached about 30 nm. This is due to the smaller particle size of the TiC particles. Carbides are present in the early stages of crystallization treatments and presumably push the sillimanite ($Al_2O_3.SiO_2$) to nucleate.

Moreover, some non-crystalline glassy lakes appeared in some parts, as shown in Figure 5 (d). This is maybe due to the lack of homogeneity of the raw materials, which allows some local areas to be depleted from the TiC particles. Also, the formed crystalline phase is stable and has high bonding energy. The non-crystalline glassy remained after the crystallization treatment. Figure 6 shows the significant crystalline phases distributed in the glassy matrix in sample 5 of Y_2O_3. The microstructure exhibited multi-directionally rosette crystals around the nucleating agent particles, ranging from ~ 4 to ~ 20 µm. The crystals start on these particles and then grow in different directions. The oxides, especially nanosized, are considered solid catalysts for crystallization. It served as heterogeneous nucleation sites for the crystals to be nucleated. Y_2O_3 plays a vital role in crystal nucleating as it induces liquid-liquid phase separation in the glass. The Y_2O_3-rich liquid will then start to be crystallized.

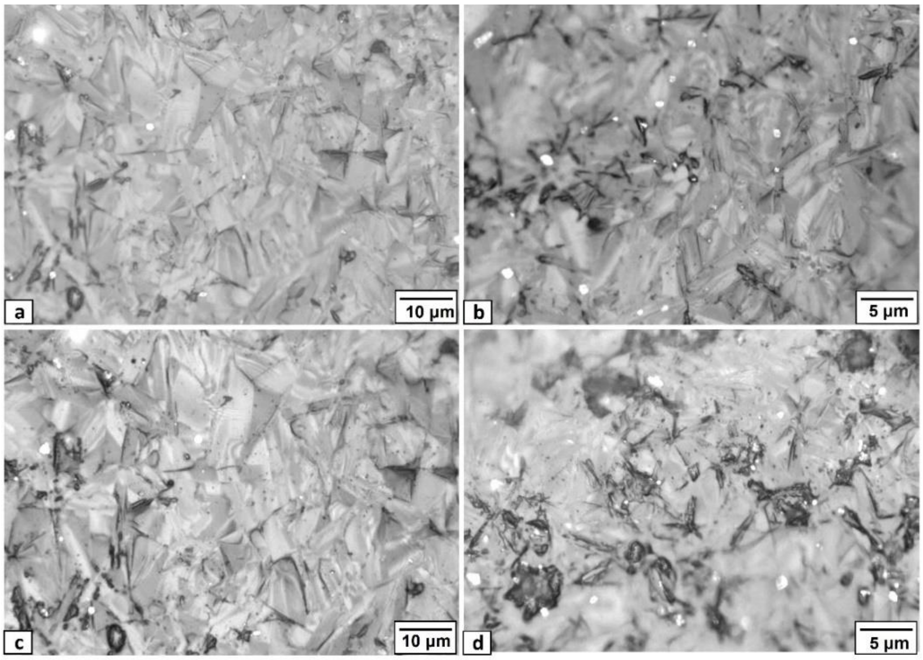

Figure 4. Micrographs of the glass ceramics with the addition of WC as crystallization catalyst show edged crystals covering all the glass matrix

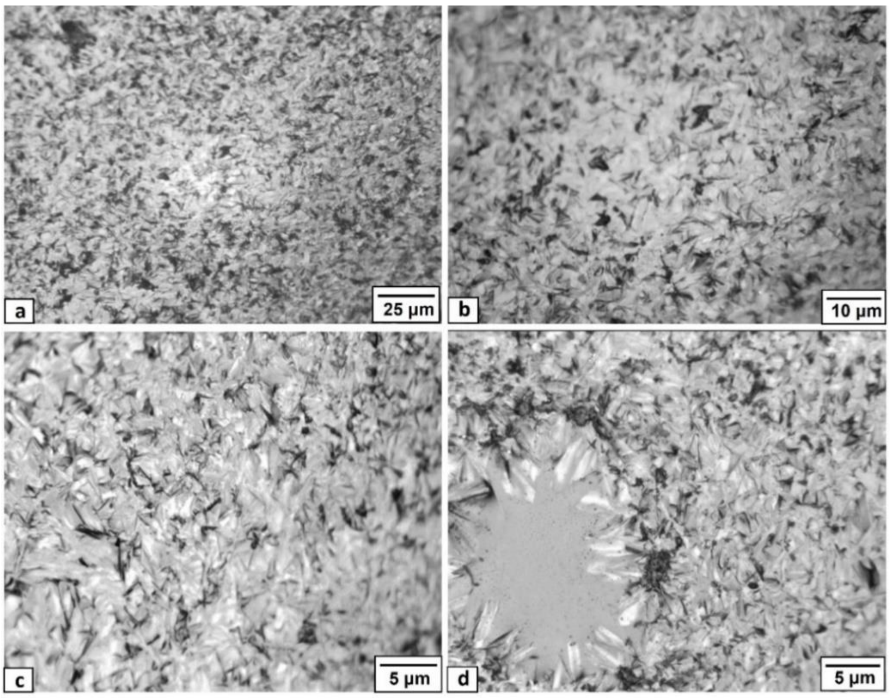

Figure 5. Micrographs of the glass ceramics with the addition of TiC as crystallization catalyst show crystalline whiskers within a glassy matrix.

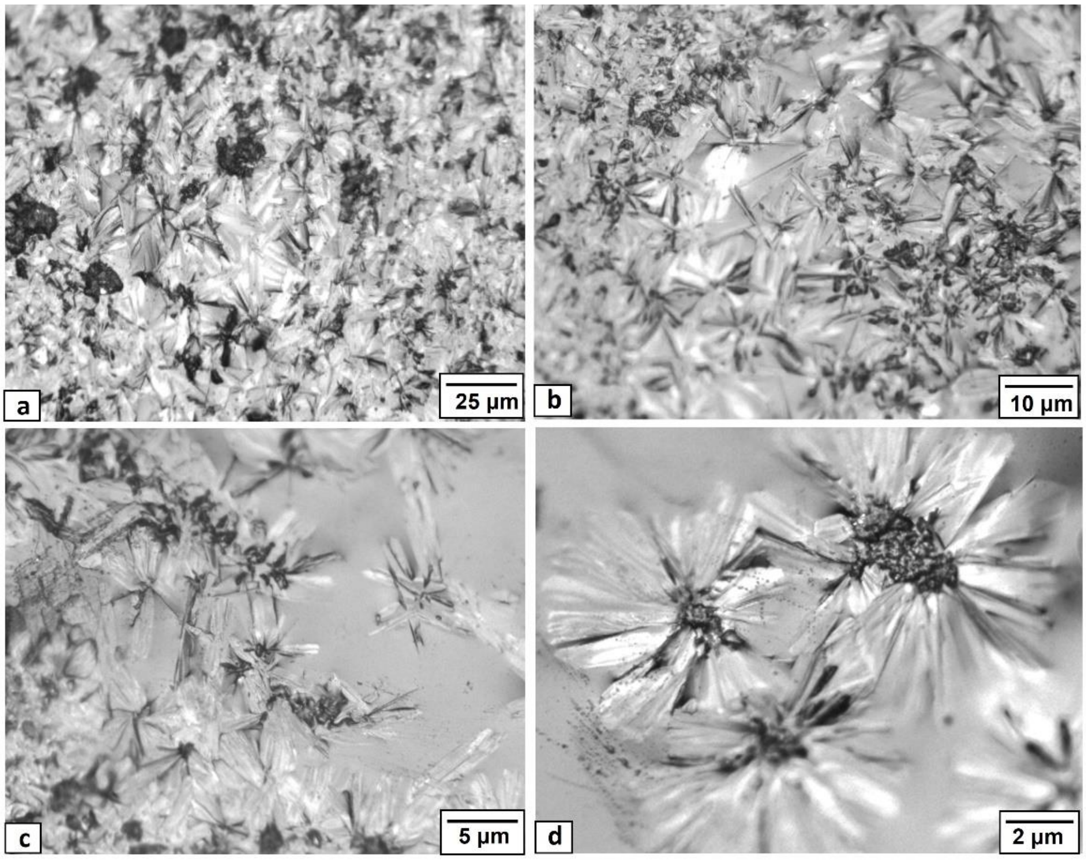

Figure 6. Micrographs of the glass-ceramics with the addition of Y_2O_3 as crystallization catalyst show multi-directionally rosette crystals within a glassy matrix

As shown in Table 3, Vickers microhardness values for crystallized samples are much higher than that of regular plain glass. The hardness values of the crystallization catalyst samples are almost twice that of the corresponding ordinary glass. The higher crystallinity can be the explanation for higher hardness. The crystalline phases play an important role in preventing cracks and slipping propagation during indentation, which improves the hardness values [24]. The relatively lower hardness values of the standard glass samples may be attributed to microvoids and other defects in the glassy structure. The difference in the crystalline fraction and the phases present in each sample might explain the different behavior of Vickers hardness. The lower values of these mechanical properties may indicate lower crystallinity of the new composition. The relatively lower hardness values in samples with lower values of crystallized phases may be attributed to the occurrence of voids, cracks, and point defects in the crystalline phases. Also, it may be due to active slipping at the glass-crystal interfaces. During loading, in the structure of the mixed crystalline phase and amorphous glass matrix, the discordance of the elastic limit between them led to the deformation mismatch between the two different phases. In this case, dislocations began accumulating in the interface, resulting in stress concentration. Moreover, the small size of the formed crystal phase tended to increase the stress concentration, as mentioned by Xu et al. [25] and Liu et al. [26], as they found that the crystalline materials have fine crystals shares in higher hardness.

The main conclusions from this study showed that it is possible to produce good quality ordinary glass without large voids from the sites. Also, it was possible to produce good quality glass ceramic with twice the hardness of ordinary glass from raw materials gathered from these sites. This would greatly interest potential investors seeking to invest in glass making factories in the regions above Saudi Arabia.

Table 3. Microhardness of the fabricated samples

Sample No.	Hardness kg/mm^2
Plain glass	312
2 (VC)	417
3 (WC)	640
4 (TiC)	710
5 (Y_2O_3)	687

4 Conclusions

This paper has reviewed the current state of the art in the glass-making industries in Saudi Arabia. It has also reviewed the present and future demand for glass products in the Saudi and Gulf Areas. The results show that the current local industries cannot meet the growing demand for all glass and glass related products by the local construction industries and the other country's consumers. Hence, Saudi Arabia will still have to import large glass products to compensate for the shortfall. This represents a significant challenge and a major business opportunity for the country. The readily available amount of ample indigenous raw materials resources has also been highlighted, yet to be fully explored or researched. This paper has also reported on experimental research carried out in the same project to ascertain the sand quality material from one of the sample sites.

The research results have confirmed that it was possible to produce ordinary glass and glass ceramics with superior qualities. Ar-Rayis area showed the best sand quality among the six chosen areas in Saudi Arabia. This bodes well for the sustainability and future of the glass industry in Saudi Arabia because the exploitation of this infinitely sizeable natural resource will not only satisfy the local markets but also extend the possibility of Saudi Arabia being a major glass exporter to the Gulf and beyond in line with Saudi Vision 2030.

The research results have confirmed that it was possible to produce ordinary glass and glass ceramics with superior qualities. Adding different crystallization agents to the sand gradients helps in glass-ceramics formation. The crystals appear as fine single dots in the case of VC, while it appears as edged crystals in the case of WC. The addition of TiC results in the formation of tiny crystalline whiskers, while the addition of Y_2O_3 helps in nucleating multi-directionally rosette crystals. Moreover, the hardness values of the glass-ceramics were much higher than ordinary glass.

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