1. INTRODUCTION

Glasses are important optical materials that are used as transparent for visible spectrum applications. Since they are amorphous, they don’t show anisotropic properties which is characteristic of crystalline materials. Glasses absorb light in ultraviolet region because of electronic transitions and are infrared absorber as a result of their molecular vibrations. By addition of titanium in silicate glass, spectrum can be changed significantly, therefore it is a good candidate material to investigation of glass structure[1].

2. EXPERIMENTAL PROCEDURE

A series of glass samples were prepared with different amounts of TiO$_2$. Glasses were prepared from following composition: $x$TiO$_2$ -3SiO$_2$ -Na$_2$O that ($8\leq x\leq40$) (molar). SiO$_2$, Na$_2$CO$_3$ and TiO$_2$ were used, all as 5N grade materials. Glasses melted at air using electric furnace in alumina crucibles. The melting temperature is 1400-1600 °C based on composition. Melting time is 1 hour after finishing the last trace of the batch. After gaining complete uniformity, molten glass was poured into the stainless steel mold and then samples were annealed at 450-500 °C for 45 minutes. In order to doing tests, samples were polished to diminish thickness. The thickness of the samples is 3±0.2 mm. For measuring the amount of light transmission, UV-VIS spectrophotometer camspec double beam uv-vis 350 m was used. Resolution power and wavelength delay are 0.2 nm and 2 nm respectively. Spectrum range is 200-1100 nm. Some samples were tested by XRD (Siemens-d500) in order to investigate the formation of crystals in glass. Cu Kα (λ=1.540598 nm) and 40.00 kv voltage were used for radiation in XRD. In order to taking some images from glasses and investigating the formation of crystals, SEM VEWGA//TESCAN

Abstract: Glassy samples with $x$TiO$_2$ -3SiO$_2$ -Na$_2$O composition that ($8\leq x\leq40$) (molar) were casted in refractory steel molds after melting at air as parallel palates. After polishing and getting to desire thickness, UV-VIS spectrometry in 200-1100 nm was measured on samples. Glass density was measured by a sensitive micro balance and was found that by increasing titanium dioxide of glasses, glass density increases. Results from UV-VIS spectroscopy show that increase of titanium dioxide decreases light transmission and this value reaches zero for sample with 40 molar percent of titanium dioxide. One reason of this reduction is formation of crystalline phase in glass, in which, by increasing titanium content crystalline phase will be increased, results of X-ray diffraction and electron microscopy confirm this claim.

Keywords: glass, spectroscopy, titanium dioxide, optical transmission.
was used. The samples were fractured and sputtered with a thin film of gold as coat. The voltage used is 15.00 kv. Eventually glass density was measured using archimedes technique with precise electronic microbalance(HF-300GD).

3. RESULTS AND DISCUSSION

3.1. Density

Since density is composition sensitive, it is used routinely for industrial investigations. Density also can be used for glass optical measurements and volume characteristic calculations. Changing of density can change some optical properties of glass. For instance, refraction is a result of interaction between electromagnetic waves and electrons of a material. Increasing of atoms (ions) polarization or electronic density can increase refractive index, on the other words, when the amount of material is increased in the definite volume, interaction between material constituents and light will be increased[6]. Glass density was measured using archimedes technique with precise electronic microbalance. The results of density are shown in figure 1.

As can be seen from figure 1, glass density increases with increasing TiO$_2$ [7,8]. Titanium dioxide density is higher than silica and soda, therefore increasing TiO$_2$ results in increasing of density and this trend is linear, so the last sample with 40% of TiO$_2$ has the highest density (around 3g/cm$^3$).

3.2. UV_Vis spectroscopy

The results obtained from UV-Vis spectroscopy have been shown in figure 2.

Sample5 (40% TiO$_2$) has no transmission in this region (200-1100 nm) or transmission is zero. It might be a result of crystal formation in glass. As can be seen from fig 2, increasing of TiO$_2$ results in increasing the absorption edge of samples that has confirmed before with many researchers[9-15]. With increasing TiO$_2$ content, the number of non-bridging oxygen increased and then absorption edge increased (see figure 3). In addition, there is a strong absorption in UV region as can be found from deep steep of the curve in all samples. The mechanism of absorption is charge transfer from O$_2$ ligand to central ion Ti$^{4+}$ as $L\rightarrow M$. The orbital structure of Ti$^{4+}$ is $3d^0$. So there is not any electron to transfer to oxygen ligand. That is why the main absorption mechanism is charge transfer as $L\rightarrow M$, not ligand field transition. Since there is
not any electron in \(3d^0\), this ion is eager to gain electron from ligand and the incident light supply this transfer energy.

If glass contains sufficient \(Ti^{+3}\), and under strong reduction atmosphere, glass will not be colorless. According to figure 2, glass samples are colorless. That's why all these glasses contain only \(Ti^{+4}\) as a major ion. Ionic radius of \(Ti^{+4}\) is 0.61 Å. In oxidation atmosphere, even neutral, it can replaced with \(Si^{+4}\), but titanium atoms are surrounded with more oxygen because titanium radius is bigger than silicon radius. In fact, titanium is in competition with silicon for bonding with oxygen, and coordination number of titanium atoms depends on it’s concentration in glass.

3.3. XRD Results

Results obtained from XRD were shown in figure 4. As can be seen from figure 4, increasing \(TiO_2\) leads to increasing crystalline phase in
samples with high proportion of titanium dioxide.

Light transmission decreased in UV-Vis region as TiO$_2$ content increased. In sample 5 (40% TiO$_2$) transmission was zero. In sample 4 (32% TiO$_2$), titanium dioxide act as nuclei agent and crystals were grown in the glass matrix. As TiO$_2$ content increased to 40%, the amount of crystal phase increased. It must be said that since the TiO$_2$ contents we chose is very broad, it might be possible to form new crystals even in samples with lower TiO$_2$ contents. It needs of course choosing more samples to investigate the exact composition that start crystallization. According to figure 4, sample 4 is not completely glass and XRD pattern shows mutual behavior of glass and crystal that can be seen in SEM where presence of crystals in glass matrix is observable. But in sample 5, as can be seen, crystal phase is dominant. As crystal phase increased, the light transmission decreased. SEM results confirm this statement.

3.4. SEM Results

SEM is used as a powerful instrument to investigate of glass to glass-ceramic transformation process. SEM images were shown in figure 5.

There are 3 images from sample 3, sample 4 and sample 5.
and sample 5 as a, b and c respectively. Sample 3(24% TiO2) is completely amorphous and there are not any trace of crystals in it. Crystals are forming in sample 4(32% TiO2) results in more attraction with light and therefore light transmission decreased that can be seen from UV_vis spectroscopy results. With increasing TiO2 in glass (sample5) light transmission acquired zero. This result is compatible with XRD results showed completely crystalline phase in sample 5.

CONCLUSIONS

1. Glass density increased as TiO2 content increased at constant silica soda ratio.
2. There were a shift in absorption edge of samples toward lower energy with increasing TiO2.
3. Light transmission decreased in samples with increasing TiO2 and at sample 5 reached zero (not transparent) which is related to crystal formation in glass and XRD and SEM results confirmed this opinion.
4. Charge transfer is a main mechanism of absorption as ligand to metal (L → M ).

REFERENCES