2.3.3 Microhardness Measurement

Hardness tests were carried out with semi automatic micro hardness instrument (Emcotest M1C 010) under 0.5 kg. Vickers indenter was used and indentation was automatic with a 10 second dwell time. Both size of diagonals were measured by semi automatic and hardness results calculated automatically according to the $HV=0.1854\ P/d^2$ (P is loading force in N, d is the average of two diagonals in mm)

2.3.4 Glass Transition Temperature

T_g measurements were carried out in a NETZCH STA409PG thermogravimetry T_g/DTA test instrument. Samples of 30 mg were heated to 1200 °C at 10 °C/min in platinum crucible in flowing nitrogen atmosphere. Al_2O_3 was used as the reference material. The inflexion point of the endothermic drift on the DTA curve is reported as T_g.

3. RESULTS AND DISCUSSION

Simple visual observations showed significant differences between different glasses in terms of color. The color variations are due to the presence of different RE. These characteristics, CFS, density, hardness, T_g are summarized in Table 2.

3.1 XRD Test Results

X-Ray analysis shows no evidence of crystalline phase in the glass matrix. A typical XRD pattern for all the produced glasses is shown in Figure 3.

Figure 3. A typical XRD pattern for all producedglasses.

3.2 Density Results

Density increases proportionally to atomic weight and CFS of the lanthanide. This increase in density with increasing atomic number is primarily due to the increased atomic weight of modifying cation. However, it may also be due to the increasing cationic strength. Because attraction forces between anions increase (Menke et. al., 2000).

Density values were found between 2.89 – 2.97 g/cm^3 for RE-CaSiAlON glasses. Figure 4 and 5 show densities versus molecular weight and CFS respectively.

Figure 4. Increasing in density with different molecular weight

Figure 5. Increasing in density with CFS values of RE cations.

As shown in Figure 4 and 5, density increases were proved as proportionally to atomic weight of the RE element. A linear increase was obtained with increasing CFS. The CFS values increase along the series of $Nd^{3+}<Sm^{3+}<Eu^{3+}<Dy^{3+}<Er^{3+}<Yb^{3+}$.

3.3 Microhardness Measurement

For the (RE+Ca)SiAlON glasses, hardness increases fairly linearly with increasing CFS as shown in Figure 6. Highest hardness value of 7.55 GPa was obtained for Yb^{3+} containing glass. Density increases proportionally to atomic weight of the lanthanide and almost linearly with CFS. Figure 6 reveals 20 % enhancement in the hardness between glasses including Yb^{3+} and Nd^{3+}, respectively.

As known, hardness is directly related with bond hardness. This relationship was derived from atomic and ionic stiffness and proves an increase in bond hardness per unit area (KeYan et. al. 2009). As a result, it can be said that bond hardness increases with increasing CFS.

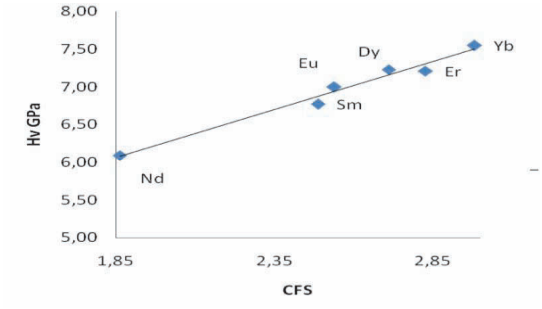

Figure 6. Changes in hardness with different values of-CFS.

Table 2. Summary of results

Glass Composition	Ionic Ratio	Color	RE CFS	Hv GPa	Tg °C	Density g/cm^3	Nature
Nd+Ca:Si:Al:O:N	1+27:56:16:95:5	Transparent	1.86	6,09	822	2.89	Amorphous
Sm+Ca:Si:Al:O:N	1+27:56:16:95:5	Transparent	2.49	6,77	837	2.90	Amorphous
Eu+Ca:Si:Al:O:N	1+27:56:16:95:5	Yellow	2.54	7,00	839	2.91	Amorphous
Dy+Ca:Si:Al:O:N	1+27:56:16:95:5	Blue	2.71	7,23	848	2.93	Amorphous
Er+Ca:Si:Al:O:N	1+27:56:16:95:5	Pink	2.83	7,21	854	2.95	Amorphous
Yb+Ca:Si:Al:O:N	1+27:56:16:95:5	Brown	2.98	7,55	858	2.97	Amorphous
Er+Y:Si:Al:O:N	3+25:56:16:100:0	Pink			856		Amorphous
Er+Y:Si:Al:O:N	3+25:56:16:95:5	Pink			866		Amorphous
Er+Y:Si:Al:O:N	3+25:56:16:90:10	Blurry Pink			873		Amorphous

3.4 Glass Transition Temperature

Two different experiments were performed to determine T_g results. First one was observing T_g results of (RE+Ca)SiAlON glasses and comparing them between each other. Figure 7 shows the change in T_g with increasing CFS. As seen from the figure, T_g increases approximately linearly. Nd^{3+} containing glass presents minimum T_g value (822°C) while Yb^{3+} containing one presents maximum (858°C). Cations with smaller ionic radius have higher CFS and tighten glass network, that is, rare earth with higher atomic number increases T_g (Lofaj et. al., 2004).

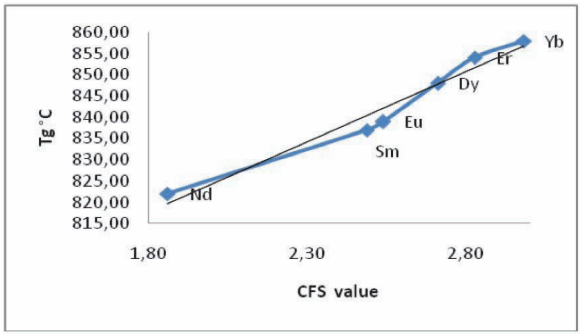

Figure 7. T_g values of CaSiAlON glasses.

The second study is comparing T_g values of (Er+Y)SiAlON glasses **[**(3+25):56:16:O:N (O:N = 100:0 , 95:5, 90:10)**]** between each other according to increasing nitrogen content.This experiment has proved that the amount of nitrogen affects the T_g values. It is observed that

higher nitrogen addition was shifts the T_g to higher values. Figure 8 shows T_g results with different nitrogen content. Minimum T_g was obtained with nitrogen free glass while the maximum T_g was obtained by 10 eq% nitrogen containing glass.

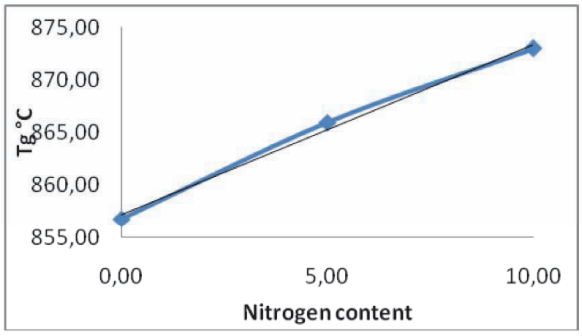

Figure 8. T_g values for different nitrogen content in ErYSiAlON glasses.

T_g values of glasses with same cation ratios exhibited a fairly linear increase with increasing nitrogen content.

Moreover, T_g in silicates is related to the energy required to break up and re-form covalent bonds in an amorphous lattice and T_g is directly proportional to bond strength (Ojovan, 2008).

Additionally, T_g values of (Er+Y):Si:Al:O:N [(3+25):56:16:95:5] and (Er+Ca):Si:Al:O:N [(1+27):56:16:95:5] glasses were compared. According to the experimental results, T_g of ErYSiAlON was observed higher than that of (Er+Ca)SiAlON glasses.

There are two basic differences between these glasses as elemental. First one is the amount of Er^{3+}, second one is different cation contents (Y^{3+} and Ca^{2+}). Because of these, it's very hard to talk about the reason why (Er+Y)SiAlON glasses have higher T_g values. If the reason can be related with covalency difference between CaO and Y_2O_3, the result is not contrary to the relationship between T_g and covalency (Ojovan, 2008). According to electronegativity (χ), lower electronegativity difference is indicating higher covalency (χO- χY=2.22 and χO- χCa=2.44) (Pauling, 1932). And as mentioned before, covalency is affecting the T_g directly.

Different amounts of Er^{3+} cations may also be considered to explicate the reason. This study is another research topic about structural characterization that will be investigated in future. Figure 9 shows the comparison of (Er+Ca)SiAlON and (Er+Y)SiAlON glasses and the other two results mentioned before.

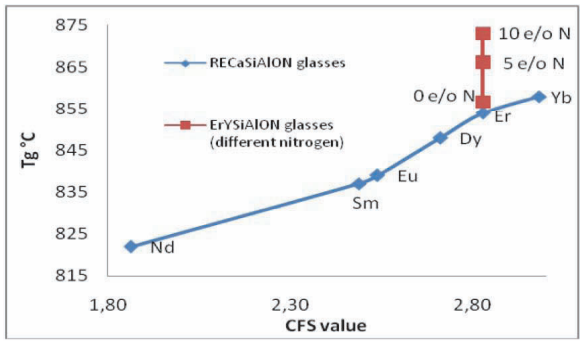

Figure 9. Comparing T_g values according to different RE in CaSiAlON and different nitrogen content in (Er+Y)SiAlON.

4. CONCLUSIONS

In this paper, all the presented results were achieved parallel to other similar published papers (Pomeroy et. al., 2008; Hampshire et. al., 2004 ; Ramesh et. al., 1997 ; Lofaj et. al., 2004 ; Becher et. al., 2002 ; Pomeroy et. al., 2005 ; Iftekhar et. al., 2011). Density, T_g and hardness showed a linear increase with increasing CFS. It is clear that these properties can be adjustable with different RE and nitrogen content. For (RE+Ca)SiAlON system, linearity was associated with CFS values of RE cations.

The amount of nitrogen also affected the structure. Nitrogen additive makes the structure stiffer. Glasses including 0, 5 and 10 e/o nitrogen showed fairly linear increase in T_g.

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