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ARAŞTIRMA MAKALESİ / **RESEARCH ARTICLE**

INVESTIGATION ON THE EFFECT OF RARE EARTH (RE) CATION TO THE (RE+Ca)SiAlON GLASSES

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ABSTRACT

The main purpose of this study was to determine the change in density, glass transition temperature (T_g) and hardness as a result of compositional modifications in the (RE+Ca)SiAlON oxynitride glasses (RE= Er, Nd, Sm, Eu, Dy, Yb) with a cation ratio in eq% of (1+27):56:16 = (RE+Ca):Si:Al. The amount of nitrogen was kept constant (N=5 eq %).

Additionally other series of the (Er+Y):Si:Al:O:N glasses with cation composition (3+25):56:16 were prepared with different amount of nitrogen (where N= 0, 5, 10 eq %) to observe the effect of nitrogen to glass transition temperature. X-Ray diffraction patterns proved that all produced glasses were amorphous.

T_g and hardness results of (RE+Ca)SiAlON glasses were revealed that there is a linear relationship between cation field strength (CFS). Density results versus molecular weight and CFS were presented. Additionally, glass transition temperatures of the (Er+Y)SiAlON glasses were further increased with the increasing nitrogen content in the structure. These results are also compared with (RE+Ca)SiAlON glass series.

Keywords: Oxynitride glass, Rare earth effect, Nitrogen effect, Cation field strength (CFS).

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NADİR TOPRAK ELEMENTİ KATYONLARININ (RE+Ca)SiAlON CAMLARINA ETKİSİNİN İNCELENMESİ

ÖZ

Bu çalışmanın ana amacı katyon oranı eşdeğer yüzdece (eq %), (1+27):56:16=(RE+Ca):Si:Al olan (RE+Ca)SiAlON oksinitrür camlarında yoğunluk, cam geçiş sıcaklığı ve sertlik değişimlerinin bileşimsel değişikliklere bağlı olarak incelenmesidir. (RE+Ca)SiAlON camlarının azot değerleri sabit tutulmuştur (N=5 eq %).

Ayrıca, katyon bileşimi (3+25):56:16 olan (Er+Y):Si:Al camlar, azotun T_g'ye etkisini gözlemlemek amacıyla farklı azot oranlarıyla hazırlanmıştır (N= 0, 5, 10 eq %).

(RE+Ca)SiAlON camlarının T_g ve sertlik sonuçları katyon alan mukavemeti (CFS) değerlerine bağlı olarak lineer bir ilişkiyle açıklanmıştır. Yoğunluk sonuçları ise moleküler ağırlık ve CFS değerlerine karşı sunulmuştur. Ayrıca, (Er+Y)SiAlON camlarının cam geçiş sıcaklıkları artan azot miktarına göre artış göstermiştir. Bu sonuç (RE+Ca)SiAlON serisiyle kıyaslanmıştır.

Anahtar Kelimeler: Oksinitrür cam, Nadir element etkisi, Azot etkisi, Katyon alan mukavemeti.

1. INTRODUCTION

Oxynitride glasses were found firstly as grain boundary phases within silicon nitride based structures and they are aluminosilicate glasses where some oxygen atoms were substituted by nitrogen. These glasses are located as an intergranular film approximately 1 – 1.5 nm thickness between Si_3N_4 grains interface (Becher et. al., 2000). In microstructure, grains and grain boundaries have a key role to identify the properties of Si_3N_4 based ceramics. For instance, under high temperature fracture resistant, hardness is determined by grain and grain boundary characteristic (Kleebe et. al., 1999). Property determination of such glasses is important to bring them application areas or to help improving the SiAlON based ceramics.

The best way to understand the structure of these intergranular films is to produce them at macro scale to implement tests and to obtain meaningful data. Within the number of written articles, rare earth and nitrogen effects are the one of the most attractive subjects.

RE cations affect the density, glass transition temperature, hardness and viscosity in order to their CFS values (Hampshire et. al., 2004 ; Lofaj et. al. 2004). CFS values of RE cations with the same coordination number (CN) and the valence are inversely proportional to ionic radius (CFS= Z/r^2 where Z=valance r=ionic radius). RE cations act as a network modifier which is incorporated in the space between Si-(O,N)x tetrahedra (Lofaj et. al., 2004). RE cation with smaller radii (higher CFS) brings a tighter structure to glass.

Nitrogen acts as a network former and directly bonds to silicon in the structure (Hampshire, 2008). If nitrogen was substituted with oxygen, structure becomes stiffer because of triple bonding ability of nitrogen (Becher et. al., 2011). Triple bonding ability is related to higher valance of nitrogen (Lofaj et. al., 2004). The strength of Si-N bonds and substitution ability of nitrogen in SiO_4 tetrahedral units have led to the development of oxynitride glasses with significantly modified properties.

In this study glasses were produced under laboratory conditions. Mixing time, mixing media, pressing conditions, raw materials were exactly the same for all recipes. The only difference of glass production techniques is melting temperature for ErYSiAlON and RE-CaSiAlON. To melt the ErYSiAlON and RE-CaSiAlON glasses, 1700 and 1600 °C were applied respectively. For all recipes Si_3N_4 were used as nitrogen source. Recipes were calculated in order to equivalent percent calculation of anions and cations (Hampshire, 2009).

2. EXPERIMENTAL PROCEDURE

Nine glass formulations were prepared from mixtures of powders. Powder qualities and brands were shown in Table 1. RE cations which have 3+ valances were chosen from lanthanide series (Nd, Sm, Eu, Dy, Er, Yb).

2.1 Glass Production

Batches were prepared by mixing them in isopropanol alcohol. Then they were dried and shaped. Shaping process was carried out by pressing technique under 30 MPa as cylindrical shape (40 mm diameter – ~10 mm height). An intensive care had been paid to clean the surface impurities coming from mold. After shaping, melting process was carried out in flowing nitrogen atmosphere. All recipes were calcined at 800 °C for 1 hour to remove volatiles or chemically absorbed water. Produced glasses were shown in Figure 1.

Table 1. Raw materials used

Materials	Company	Purity %
SiO_2	Fluka analyti-	99,5
Y_2O_3	Alfa aesar	99,99
Al_2O_3	Sigma Aldrich	99,7
Si_3N_4	UBE SN 10	
Er_2O_3	Alfa aesar	99,9
CaO	Aldrich chem-	99,9
Nd_2O_3	Aldrich	99,9
Sm_2O_3	Aldrich	99,9
Eu_2O_3	Aldrich	99,5
Dy_2O_3	Aldrich	99,5
Yb_2O_3	Aldrich	99,5

2.2 Sample Preparation

Some samples were prepared in the bulk form for hardness and density measurements while others were prepared as powder form for T_g and XRD tests.

Figure 1. Some produced glasses in this study.

For hardness and density tests, glasses were cut approximately to 1.5 mm slices, then thinned, and polished by 0.05 µm aluminum suspension to 1.2 mm (±0.01 mm). A sample, obtained by melting and polishing, was shown in Figure 2.

Figure 2. Thinned and polished glass sample (below) obtained from a big piece (above).

2.3 Measurement Methods

2.3.1 Density Measurements

Bulk density was measured by the Archimedean displacement technique using distilled water as working fluid.

2.3.2 X-Ray Diffraction

X-Ray analysis was carried out between 20 – 70 degrees on a Rigaku Rint 2000 XRD difractometer. X-ray diffraction analysis was undertaken to detect the presence of any crystalline phases and only materials free of crystalline phases were used for further measurements of glass properties.

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.

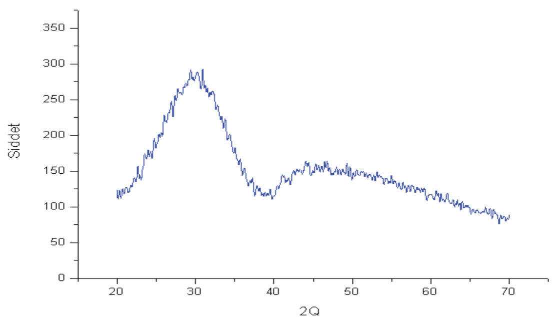

Figure 3. A typical XRD pattern for all producedglasses.

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.

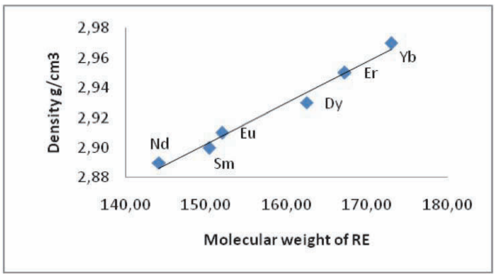

Figure 4. Increasing in density with different molecular weight

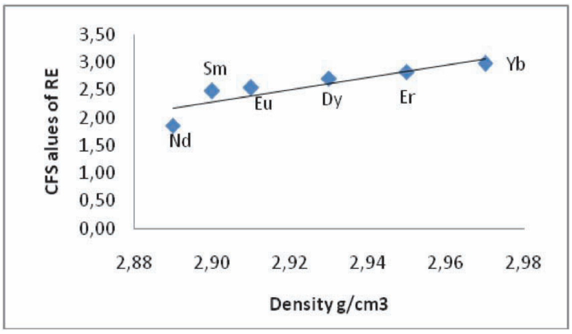

Figure 5. Increasing in density with CFS values of RE cations.

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.

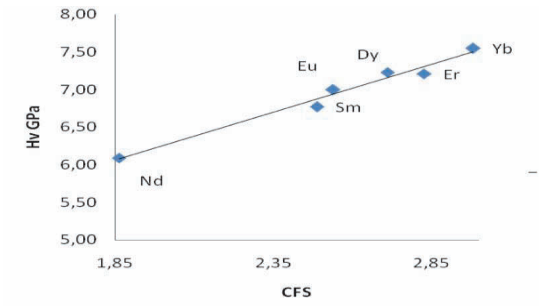

Figure 6. Changes in hardness with different values of-CFS.

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).

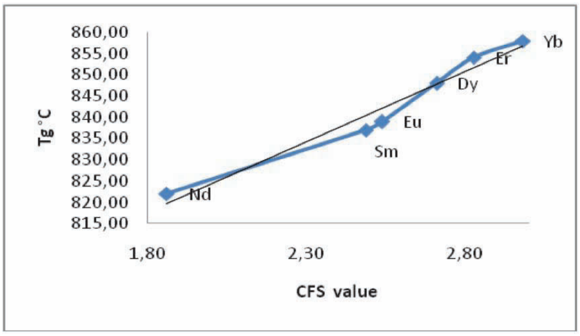

Figure 7. T_g values of CaSiAlON glasses.

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.

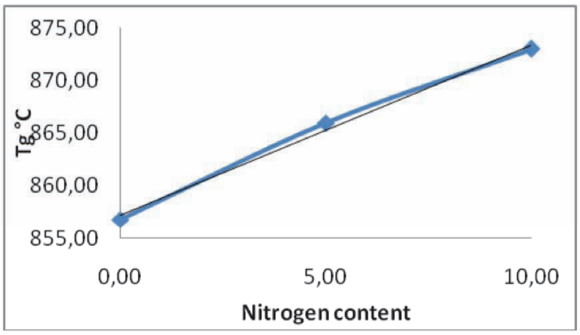

Figure 8. T_g values for different nitrogen content in ErYSiAlON glasses.

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.

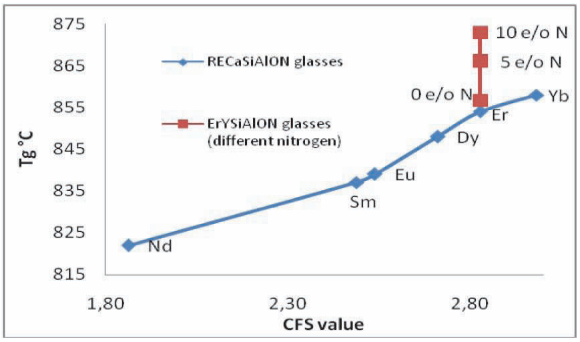

Figure 9. Comparing T_g values according to different RE in CaSiAlON and different nitrogen content in (Er+Y)SiAlON.

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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