# THE EFFECT OF LANTHANIDES AND NITROGEN ON MICROHARDNESS OF OXYNITRIDE GLASSES

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The investigation of microhardness of RE-Si-Mg-O-N glasses (RE = Y, La, Sm, Yb and Lu) containing 20–26 eq.% of nitrogen revealed a possibility of a control of the microhardness via modification of rare-earth element additives and by the control of nitrogen content. Lu-containing glasses exhibit hardness, which is almost of 15 % higher than that of La-glasses. Four-percent increase in nitrogen content would result in almost the same increase in microhardness. Microhardness of RE-containing glass follows linear dependence on ionic radius or cationic field strength (CFS) of the corresponding cation added in the glass network. Yttrium, which does not belong among lanthanides, does not fit into the linear dependence. Its deviation from linearity can be rationalized in terms of the change of the coordination number from CN = 6 to CN = 7 without change in valency.

Key words: microhardness, oxynitride glass, lanthanides, nitrogen

# VPLYV LANTANOIDOV A DUSÍKA NA MIKROTVRDOSŤ OXYNITRIDICKÝCH SKIEL

Štúdium mikrotvrdosti oxynitridických skiel typu RE-Si-Mg-O-N (RE = Y, La, Sm, Yb a Lu) s 20–26 ekv.% dusíka poukázalo na možnosť kontroly mikrotvrdosti pridávaním prvkov vzácnych zemín a zmenou obsahu dusíka. Mikrotvrdosť skiel s obsahom Lu bola takmer o 15 % vyššia ako pri sklách s obsahom La. Zvýšenie obsahu dusíka o štyri percentá malo za následok porovnateľné zvýšenie mikrotvrdosti. Mikrotvrdosť skiel s obsahom prvkov vzácnych zemín závisí lineárne od iónového polomeru, resp. sily katiónového poľa (CFS), pridávaného prvku. Mikrotvrdosť skla s obsahom ytria, ktoré nepatrí do skupiny lantanoidov, nie je v súlade s lineárnou závislosťou. Túto odchýlku od linearity možno vysvetliť zmenou koordinačného čísla z CN = 6 na CN = 7 pri zachovaní valentnosti.

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## 1. Introduction

Silicon nitride ceramics is a group of materials with excellent high-temperature mechanical properties. It is considered to be a candidate for replacement of superalloys in some structural components, e.g., blades in the high efficiency gas turbines [1].

Silicon nitride is produced from powder compacts containing powders of silicon nitride and sintering additives, usually, oxides of rare-earth elements. The additives react with the silica on the surface of silicon nitride particles at elevated temperatures to form a liquid phase [2]. Initial silicon nitride particles dissolve in the liquid which becomes an oxynitride liquid [3]. Upon cooling, oxynitride liquid phase remains as an intergranular glass at the grain boundaries and in the multigrain junction pockets among reprecipitated silicon nitride grains. Despite a possibility of full crystallization of the glass in the pockets, thin intergranular films (IGF) of the residual glass are always present at the grain boundaries in silicon nitride [4].

Mechanical properties of liquid phase sintered ceramics at high temperatures are controlled by the properties of the residual glass. The concept of grain boundary engineering introduced 20 years ago suggested using additives, which form more refractory secondary phases to improve high-temperature mechanical properties of vitreous bonded ceramics [5]. This approach combined with high purity powders and better densification technology resulted in remarkable improvements of silicon nitride ceramics [6, 7]. Basic condition for long-term use of ceramics for blades is the 1 % strain limit after 10 000 h at certain temperature and stress. This is equivalent to the steady state strain rate of $3 \times 10^{-10}$ s$^{-1}$. Silicon nitride with MgO additives under stress of 150 MPa could exist only at temperatures below 1050 °C. Silicon nitrides with $Y_2O_3$-$Al_2O_3$ additives were creep resistant to, approximately, 1100–1125 °C. The pure rare-earth oxide additives such as $Y_2O_3$ and $Yb_2O_3$ resulted in an increase of the corresponding temperature range up to 1300–1325 °C. The latest generation of materials is represented by SN 281 and SN 282 grades. These materials can operate up to around 1470 °C [7–9]. They exhibit 3 to 5 orders of magnitude greater creep resistance than the previous materials. The reason for greater creep resistance in SN 281 and SN 282 is related to the secondary phases since the primary phase, silicon nitride, is similar in all generations. Apparently, difference is due to the presence of Lu in the residual glass [7, 8]. Consequently, the properties of the residual glass at high, but also at room temperatures, are the key factor, and controlling chemistry of the residual glass is the principal way for development of better ceramics.

Using oxides of lanthanides with high atomic number as sintering additives is a very productive approach in residual glass engineering because of so called “lanthanide contraction”: elements with higher atomic number have smaller ionic radii [10]. Smaller atoms can be more easily incorporated in the glass network and produce more tight structure with better rheological properties. High resolution transmission electron microscopy studies even revealed linear dependence of the IGF thickness on the ionic radius of corresponding element in silicon nitrides with different types of lanthanide-based additives [11]. Thinner boundaries occur in the glass containing Yb with smaller ionic radius than in the La-containing residual glass films. Number of other experimental studies confirmed similar correlation between ionic radius of the corresponding lanthanide and thermal expansion coefficients, viscosity, molar volume and softening temperatures in RE-Si-Al-O-N glasses (RE = rare-earth elements) [12–15].

Another important factor controlling rheological properties of glass and indirectly, properties of the vitreous bonded ceramics, is the presence of nitrogen in the residual glass since nitrogen acts as a network former [16–21]. Raman scattering [20] and infrared spectroscopy investigation [21] indicate that nitrogen is chemically or covalently bonded to silicon in the glass network and the substitution of oxygen also produces more tight and linked structure. It results in significant increase in viscosity, glass transition temperature, elastic moduli, hardness, fracture toughness, corrosion resistance, etc., compared to the standard glasses [17, 18]. For instance, the presence of 4.8 % of N in Y-SiAlON glass increases its viscosity at certain temperature by three orders of magnitude in comparison with the corresponding oxide glass [12]. Obviously, the increase in the refractoriness of the glass would have direct impact on high temperature creep behavior of ceramics containing glasses with similar composition. However, the correlation is not straightforward: glass transition temperatures in the bulk glasses are more than 200 ℃ lower than the transition temperatures in corresponding silicon nitride ceramics [13]. Despite that, detail studies of simultaneous effects of lanthanides and nitrogen on the room and high temperature properties of the corresponding bulk glasses are necessary for the understanding of behavior and development of new generations of silicon nitride ceramics.

The earlier studies on oxynitride glasses were focused mostly on the effects of several lanthanides on the pre-determined properties at one or two levels of nitrogen content [14–23]. Lutetium was not included and the concentration of nitrogen was usually below 20 %. Systematic data including Lu and high nitrogen levels are missing. Microhardness testing is the simplest and fast method for the investigation of the effects of chemistry on room temperature properties of the oxynitride glasses. Therefore the aim of the current work is to investigate load dependence of the microhardness on the oxynitride glasses with different lanthanides, including Lu, and several levels of nitrogen in the range above 20 eq.%. The following studies will include investigation of the elastic moduli, viscosity, transition temperature, and others to obtain comprehensive database for development of new ceramics.

## 2. Experimental procedure

### 2.1 Glass preparation

Fifteen glass formulations have been prepared at the University of Karlsruhe from the mixtures of powders of $SiO_2 + RE_2O_3 + \alpha - Si_3N_4 + MgO$, where RE denotes rare-earth elements including lanthanides La, Sm, Yb, Lu, and Y. The content of the rare-earth elements was kept constant at 20 eq.%. The amount of silicon nitride powder added was calculated in such a way that the resulting nitrogen content was 20, 22 or 24 eq.%. Magnesia powder was added to reduce the melting temperature and to prevent crystallization during cooling. The composition of the individual powder mixtures in equivalent %, molar % and weight % are summarized in Table 1. The corresponding powders were homogenized in a ball mill with 2-propanol and silicon nitride balls. The batches were subsequently dried and sieved. The portions of ∼10 g of powder were uniaxially pressed into pellets and then cold isostatically pressed at 400 MPa for 1 min. Green bodies after forming were placed into BN-containing powder bed in a BN crucible with the diameter of 3 cm and BN lid, which was enclosed in $SiO_2 + Si_3N_4$ powder bed. Melting was performed in a graphite-heated gas-pressure sintering furnace (Thermal Technology, Santa Rosa, CA) under 20 MPa of nitrogen. Heating rate was

Table 1. The composition of the powder mixtures used for the preparation of the glasses. The designation of the samples indicates type of rare-earth element used and nitrogen content

| Glass | Eq.% | | | | | Mol.% | | | | Wt.% | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| system | Si | RE | Mg | O | N | $RE_2O_3$ | $SiO_2$ | MgO | $Si_3N_4$ | $RE_2O_3$ | $SiO_2$ | MgO | $Si_3N_4$ |
| YN20 | 60 | 20 | 20 | 80 | 20 | 13.4 | 39.7 | 40.1 | 6.8 | 37.8 | 30.2 | 20.2 | 11.7 |
| YN22 | 60 | 20 | 20 | 78 | 22 | 13.5 | 38.2 | 40.6 | 7.6 | 37.9 | 28.8 | 20.3 | 13.0 |
| YN24 | 60 | 20 | 20 | 76 | 24 | 13.7 | 36.6 | 41.2 | 8.4 | 38.1 | 27.4 | 20.4 | 14.2 |
| LaN20 | 60 | 20 | 20 | 80 | 20 | 13.4 | 39.7 | 40.1 | 6.8 | 46.7 | 25.9 | 17.3 | 10.1 |
| LaN22 | 60 | 20 | 20 | 78 | 22 | 13.5 | 38.2 | 40.6 | 7.6 | 46.9 | 24.6 | 17.4 | 11.1 |
| LaN24 | 60 | 20 | 20 | 76 | 24 | 13.7 | 36.6 | 41.2 | 8.4 | 47.0 | 23.4 | 17.4 | 12.1 |
| LaN26 | 60 | 20 | 20 | 74 | 26 | 13.9 | 35.0 | 41.8 | 9.3 | 47.1 | 22.2 | 17.5 | 13.2 |
| SmN20 | 60 | 20 | 20 | 80 | 20 | 13.4 | 39.7 | 40.1 | 6.8 | 48.4 | 25.0 | 16.8 | 9.7 |
| SmN22 | 60 | 20 | 20 | 78 | 22 | 13.5 | 38.2 | 40.6 | 7.6 | 48.6 | 23.8 | 16.8 | 10.7 |
| SmN24 | 60 | 20 | 20 | 76 | 24 | 13.7 | 36.6 | 41.2 | 8.4 | 48.7 | 22.7 | 16.9 | 11.8 |
| YbN20 | 60 | 20 | 20 | 80 | 20 | 13.4 | 39.7 | 40.1 | 6.8 | 51.5 | 23.6 | 15.8 | 9.2 |
| YbN22 | 60 | 20 | 20 | 78 | 22 | 13.5 | 38.2 | 40.6 | 7.6 | 51.6 | 22.4 | 15.8 | 10.1 |
| YbN24 | 60 | 20 | 20 | 76 | 24 | 13.7 | 36.6 | 41.2 | 8.4 | 52.4 | 21.4 | 15.9 | 10.3 |
| LuN20 | 60 | 20 | 20 | 80 | 20 | 13.4 | 39.7 | 40.1 | 6.8 | 51.7 | 23.4 | 15.7 | 9.1 |
| LuN22 | 60 | 20 | 20 | 78 | 22 | 13.5 | 38.2 | 40.6 | 7.6 | 51.9 | 22.3 | 15.8 | 10.1 |

20 K/min and melting of the glass was performed at 1710 ℃ for 0.5 h to achieve homogeneous melts. Then, furnace was cooled down at the rate >50 ℃/min above 1200 ℃. The resulting glass samples were rounded pellets with a diameter of 3 cm, flat from the bottom and with slightly rounded top. The pellets were cut by a low speed diamond saw, embedded in epoxy and one side polished for microstructure observation.

### 2.2 Microstructure observation

Simple microstructure observations were performed using direct optical observation and conventional inverted optical microscope on the polished surfaces of each glass prior to indentation tests at the magnification up to 500. The purpose of the observation was to investigate the homogeneity of different glasses and to determine the possibility of partial glass crystallization. Simultaneously, the homogeneous regions were chosen for microhardness tests.

### 2.3 Microhardness

The microhardness for each of the glass systems studied was measured using semi-automatic microhardness tester (Model LM 700AT, LECO Inc., USA) at the loads of 50, 100, 200, 300, 500, and 1000 g using a Vickers indentor. Indentation was automatic with the pre-determined dwell time of 10 s. The size of both diagonals was measured semi-automatically using adjustable digital micrometer with the hair-cross. The absolute values were calculated automatically according to the well-known formula and expressed in conventional units HV,

$$\mathrm{HV} = 0.189\, P/d^2,$$

where $d$ is the average of two indentation diagonals in mm, and $P$ is the loading force in N. The coefficient for the conversion of the conventional units into GPa is $10.19 \times 10^{-3}$. At least 10 indents were used to get the mean value of microhardness and corresponding standard deviation. In several cases, 10 more measurements were added to assure that the measured microhardness is not affected by local variations in chemical composition.

## 3. Results

Optical observations revealed significant differences between different glasses in terms of transparency, color and color homogeneity. La-containing glasses with 20–24 eq.% of N were colorless, transparent with a black layer at the bottom of the pellet whereas the glass with 26 eq.% of N was non-transparent and grey. All Sm-containing glasses were homogeneously black. Yb-containing glasses were also

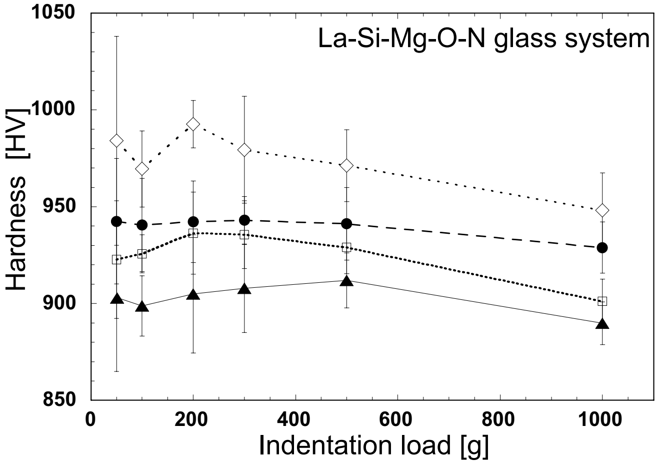

Fig. 1. Comparison of the effect of nitrogen content on the load dependence of the microhardness of La-Si-Mg-O-N glasses (▲ – 20 eq.% of N, □ – 22 eq.% of N, ● – 24 eq.% of N, ◊ – 26 eq.% of N).

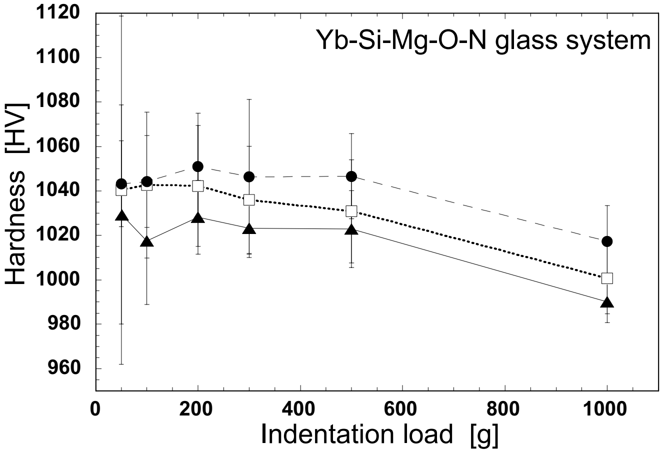

Fig. 2. Effect of nitrogen on the load dependence of the microhardness in Yb-Si-Mg-O-N glasses with 20 eq.% of N (▲), 22 eq.% of N (□), and 24 eq.% of N (●).

homogeneously black except several yellow regions in Yb-Si-Mg-O-20 eq.% N material. Lu-Si-Mg-O-20 eq.% N was transparent and colorless, while the glass with 22 eq.% N was translucent with several white regions. Y-containing glasses were color-

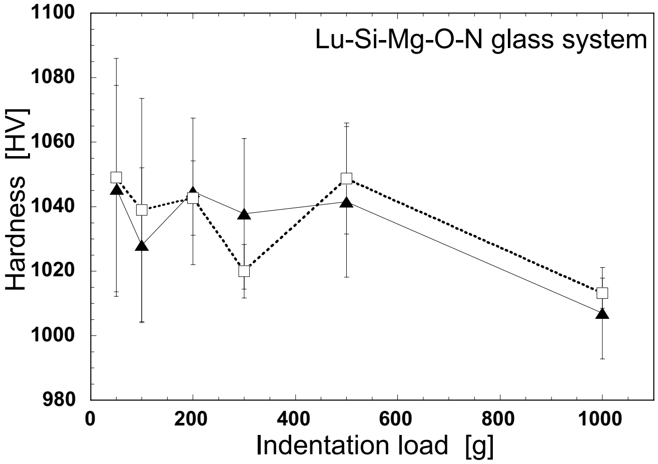

Fig. 3. Comparison of the microhardness of Lu-Si-Mg-O-N glasses with 20 eq.% (▲) and 22 eq.% of nitrogen (□) at different loads.

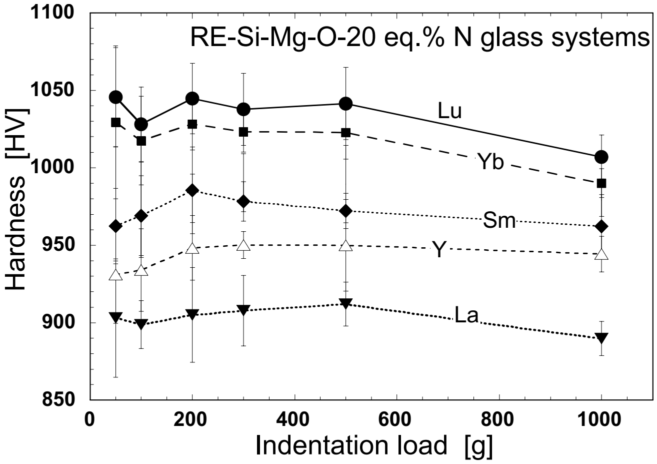

Fig. 4. Comparison of load dependence of microhardness in different RE-Si-Mg-O-N glass systems containing 20 eq.% of nitrogen.

less and transparent but the glass with 24 eq.% of N was non-homogeneously grey with brown layers. The regions with non-homogeneous color were avoided during the indentation tests.

Table 2. The results of the microhardness measurements in the glasses with different rare-earth elements and nitrogen contents

| Glass system | MHV 50 g HV | MHV 100 g HV | MHV 200 g HV | MHV 300 g HV | MHV 500 g HV | MHV 1 kg HV |
|---|---|---|---|---|---|---|
| YN20 | 931.0 ± 31.4 | 935 ± 26.6 | 948.3 ± 20.9 | 950.1 ± 8.7 | 949.9 ± 29.6 | 944.3 ± 11.4 |
| YN22 | 958.8 ± 17.9 | 964.6 ± 14.5 | 961.4 ± 19.6 | 964.9 ± 20.2 | 961.8 ± 12.2 | 968.6 ± 7.3 |
| YN24 | 965.2 ± 37.4 | 974.8 ± 21.7 | 969.5 ± 14.4 | 973 ± 41.4 | 987.2 ± 13 | 975.6 ± 26.3 |
| LaN20 | 903.1 ± 38.2 | 898.8 ± 15.5 | 905 ± 30.6 | 907.8 ± 22.7 | 912 ± 14.2 | 889.9 ± 11 |
| LaN22 | 922.7 ± 30.4 | 925.7 ± 9.9 | 936.3 ± 21.2 | 935.6 ± 17.5 | 929 ± 13.6 | 901.8 ± 11.4 |
| LaN24 | 942.5 ± 32.4 | 940.6 ± 24.1 | 942.2 ± 21.1 | 943 ± 12.3 | 941.2 ± 18.8 | 928.9 ± 13.2 |
| LaN26 | 984.1 ± 53.9 | 969.5 ± 19.6 | 992.6 ± 12.2 | 979.4 ± 27.6 | 971.2 ± 18.6 | 948.2 ± 19.3 |
| SmN20 | 962.4 ± 24.3 | 969.1 ± 25.8 | 985.5 ± 28 | 978.3 ± 12.7 | 972.2 ± 11.4 | 962.3 ± 20.3 |
| SmN22 | 965.6 ± 30.4 | 972.7 ± 17.6 | 985.5 ± 25.4 | 974.8 ± 21 | 974.5 ± 20.9 | 963.5 ± 6.6 |
| SmN24 | 970.2 ± 45.9 | 972.4 ± 31.9 | 994.6 ± 16.9 | 987.4 ± 26.3 | 983.8 ± 21.6 | 969.6 ± 13.5 |
| YbN20 | 1029.4 ± 49.3 | 1017.5 ± 28.6 | 1028.1 ± 16.6 | 1023.2 ± 13.1 | 1022.8 ± 17.3 | 990.1 ± 9.4 |
| YbN22 | 1040.3 ± 78.4 | 1042.6 ± 32.8 | 1042.2 ± 27 | 1036 ± 24.1 | 1030.8 ± 23.2 | 1000.7 ± 16 |
| YbN24 | 1043.2 ± 19.3 | 1044.3 ± 20.7 | 1050.9 ± 24.1 | 1046.3 ± 34.8 | 1046.6 ± 19.2 | 1017.3 ± 16 |
| LuN20 | 1045.6 ± 32 | 1028.1 ± 24 | 1044.7 ± 22.7 | 1037.8 ± 23.3 | 1041.5 ± 23.3 | 1007 ± 14.2 |
| LuN22 | 1049.1 ± 36.9 | 1039 ± 34.6 | 1042.7 ± 11.0 | 1020 ± 8.3 | 1048.7 ± 17.2 | 1013.2 ± 4.7 |

Table 3. Comparison of the average microhardness in the glasses with different additives and nitrogen content in the range of indentation loads from 50 up to 1000 g

| Glass system | La-Si-Mg--O-N | Y-Si-Mg--O-N | Sm-Si-Mg--O-N | Yb-Si-Mg--O-N | Lu-Si-Mg--O-N |
|---|---|---|---|---|---|
| 20 % N | 902.7 ± 7.7 | 943.0 ± 8.4 | 971.6 ± 9.1 | 1018.6 ± 14.5 | 1034.1 ± 14.7 |
| 22 % N | 925.1 ± 12.9 | 963.0 ± 3.4 | 972.8 ± 7.8 | 1032.1 ± 16.0 | 1035.4 ± 15.2 |
| 24 % N | 939.7 ± 5.4 | 974.2 ± 7.4 | 980.7 ± 9.9 | 1041.4 ± 12.1 | – |
| 26 % N | 974.2 ± 15.3 | – | – | – | – |

The results of the microhardness tests are summarized in Table 2. The data for La-, Yb- and Lu-containing glasses are plotted in dependence on indentation load and nitrogen content in Figs. 1–3, respectively. The scatter of the microhardness at 50 and 100 g loads is greater than that at higher loads due to larger relative error of the measurement of the diagonal length in the case of small indents (see Figs. 1–3). Microhardness values reach saturation at approximately 200 g load and remain approximately constant. Small decrease of microhardness at 1000 g load in some cases seems to be a consequence of intensive crack formation during indentation rather than a true microhardness decrease. The average microhardness obtained for each material over the whole load range is summarized in Table 3.

Figure 4 illustrates the effects of different rare-earth elements on the microhardness of glasses with 20 eq.% of nitrogen. Similar behavior was observed in the glasses with 22 eq.% and 24 eq.% of nitrogen. La-containing glasses have always the lowest microhardness of around HV 900. The replacement of La by another lanthanide results in an increase of the microhardness in dependence on the atom number. The highest values of around HV 1035 were obtained in the case of Lu--containing glasses.

## 4. Discussion

The results of the measurements clearly indicate that microhardness can be controlled by both different rare-earth element addition and nitrogen. Nitrogen content increase is the most effective in the case of La- and Y-containing glasses whereas smaller increase was observed in Yb-, Sm- and Lu-containing glass systems. Adding 4 % of nitrogen from 20 eq.% to 24 eq.% in La-Si-Mg-O-N resulted in 4.1 % increase in microhardness (and 7.8 % for 26 eq.% of nitrogen). The increase was 3.3 % in Y-, 2.2 % in Yb-, and 0.9 % in Sm-containing glass. Two percent increase of nitrogen content in Lu-Si-Mg-O-N glass produced only very small change. The effect of lanthanides follows from Fig. 4. Maximum increase obtained from replacement of La by Lu resulted in an increase of microhardness by 14.5 %. When both effects of nitrogen and rare-earth elements are combined, the maximum increase in microhardness obtained is almost 14.6 %. This is the limit of the microhardness increase via chemical composition variations in terms of rare-earth elements and nitrogen in the range of nitrogen content studied.

Y-containing glasses deserve special attention since yttrium, although being an element from the third group in the periodic table of elements, does not belong among lanthanides. However, its electron structure is very similar to that of lanthanum, and yttria is common sintering additive in earlier grades of silicon nitride ceramics. Including Y-containing glasses in the study is important for understanding potential of different commercially used elements in the control of the glass properties and silicon nitride ceramics as well. As expected from the similarities between Y and La, microhardness of Y-Mg-Si-O-N glasses was approximately 4.5 % greater than that of La-containing glass. Thus, ranking of the effectiveness of rare-earth elements on the microhardness of the oxynitride glasses is La, Y, Sm, Yb, and Lu.

Microhardness is a physical property, which indirectly reflects the strength of the bonds in the material. Hardness data are therefore often related to the cationic field strength (CFS), which is determined as

$$\mathrm{CFS} = Z/r^2,$$

where $Z$ is the valence of the corresponding element in the oxide compounds and $r$ is the ionic radius. The most often used for calculation of CFS are the values of ionic radii reported by Shannon [20]. Figure 5 summarizes ionic radii in oxides for all lanthanides and Y at various $Z$ values possible. Lanthanide contraction is clearly

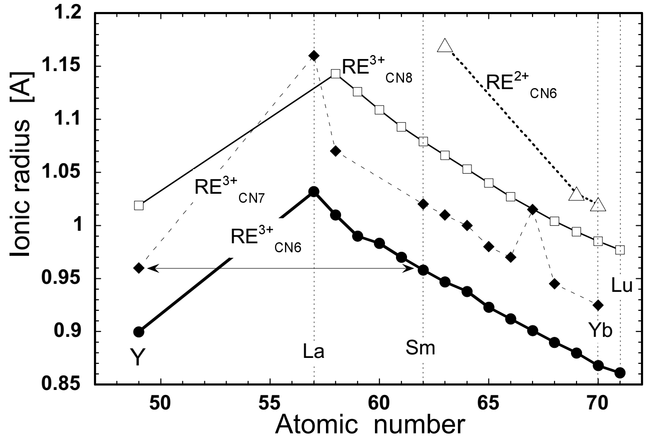

Fig. 5. Ionic radii of lanthanides and Y in oxides with different valency and coordination numbers according to the data by Shannon [24].

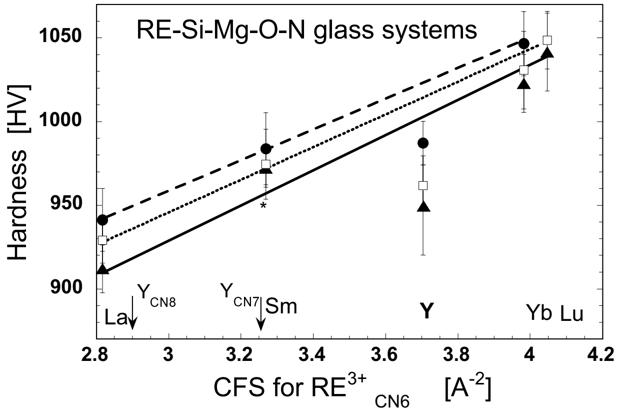

Fig. 6. Linear dependence between microhardness and cationic field strength (CFS) in the RE-Si-Mg-O-N glasses (RE = La, Sm, Yb, Lu or Y) with 20 eq.% of N (▲), 22 % of N (□) and 24 % of nitrogen (●) when valency $Z = 3+$ and coordination number CN = 6 are assumed. Yttrium does not fit into this dependence unless change of the coordination number to CN = 7 is assumed.

visible with the increase of the atom number from 57 to 71. Obviously, smaller lanthanides form more tight structure and greater hardness can be expected than in the glasses with larger atoms and more loose structures. This figure also suggests that ionic radii depend on $Z$ and CN. Typical state in oxides is $Z = 3+$ and the coordination number is 6, however, $Z = 4+$ and $Z = 2+$ are possible simultaneously with the coordination numbers CN = 7 and CN = 8 in the case of Y.

Figure 6 shows the dependence of the microhardness on CFS in the glasses with different nitrogen content at 500 g load. CFS values were calculated assuming that RE element valency is 3+ and the coordination numbers for all elements are CN = 6. The dependences agree with the expectations and literature data [14–15]. Microhardness increases approximately linearly with the increase of CFS of the lanthanides, except yttrium-containing glasses. These are softer than predicted from the linear dependence for lanthanides. Ramesh reported similar deviation in RE-Si-Al-O-N glasses [14]. Deviations from linearity were reported also for other properties, such as density, glass transition temperature, $T_g$, and thermal expansion coefficient in the case of Eu-, Y-, Gd-, Dy- and Er-containing SiAlON glasses [14, 15]. They were explained in several different ways: purely by the ionic radius, by the change of valency or by the change of coordination number of the corresponding rare-earth element. Ramesh argues that the structures of RE-Si-Al-O-N glasses are not significantly changed by rare-earth substitution and linear property changes depend purely on the modified CFS resulting from the change of the ionic radius [14]. However, Menke in more recent work concluded that substitution of the lanthanides changes overall glass structure and linear or non-linear behavior of some properties depends on CFS via valency, coordination number and ionic radius, as well [15]. Nonlinearity in Y-glass microhardness could be explained within this approach by the change in coordination number. Arrows in Fig. 6 show CFS for $Y^{3+}$ with the CN = 7 and CN = 8, respectively. Using CFS for CN = 7 would shift microhardness data for Y-glass exactly on the lines fitted to other lanthanides. Thus, the current results support the approach proposed by Menke.

## 5. Conclusions

The investigation of the microhardness on RE-Si-Mg-O-N glasses revealed a possibility of the control of the microhardness via modification of rare-earth element additives or by the control of nitrogen content. Lu-containing glasses exhibit hardness, which is almost 15 % higher than that of La-glasses. Four percent increase in nitrogen content would result in almost the same increase in microhardness. Microhardness of RE-containing glass follow linear dependence on ionic radius or CFS of the corresponding cation added in the glass network. Y does not fit into linear dependence and the deviation can be rationalized in terms of the change of the coordination number from CN = 6 to CN = 7 without change in valency (3+).

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