Effect of rare-earth oxides on thermal behavior of alumina-silica glass sealants

N S Saetova1,2*, D A Krainova2 and A V Kuzmin2
1 Institute of High-Temperature Electrochemistry UB RAS, Yekaterinburg, 620137, Russia.
2 Vyatka State University, Kirov, 610000, Russia
*n.saetova@yandex.ru

Abstract. Thermal behavior of (62.92SiO2–4.71Al2O3–14.83Na2O–5ZrO2–12.54SrO)–5Re2O3 (Re = Y, La, Nd, Sm) glasses with superstoichiometric additives of rare-earth oxides has been investigated by scanning differential calorimetry, high temperature optical microscopy, and dilatometry. It is found out that an increase in characteristic temperatures (glass transition temperature and temperature of half-sphere formation) is caused by decreasing the ionic radius. The value of thermal expansion coefficient changes insignificantly.

1. Introduction
Glasses are believed to be the best choice for sealing of single units of solid oxide fuel cells (SOFCs). A significant attention in this area has been paid to alumina-silica glasses due to the possibility of varying their properties by changing the composition of modifying oxides and less complex crystallization process compared with barium-containing sealants.

As is known, rare-earth (RE) oxides positively affect the sealant properties decreasing the crystallization ability and stabilizing the values of the coefficient of thermal expansion (CTE) [1, 2]. Numerous studies are devoted to the study of Y2O3 and La2O3 effect on properties and crystallization of alumina-silica glass sealants [3-10]. It was shown that introduction of Y2O3 suppresses crystallization in glasses [4, 5-7] and La2O3 additive increases crystallization ability of glass sealants compared with Y2O3-containing glasses of similar composition [9].

The effect of other rare-earth oxides on properties of CaO–SrO–B2O3–Al2O3–SiO2 sealants was studied by Q. Zhang and co-workers [11-13]. They improved the stability of the mentioned glass in contact with 8YSZ by introduction of CeO2 and La2O3 [11], suppressed the growth of conductivity of CeO2-containing glass at crystallization by adding HfO2 [12], and established that Nb2O5 additive decreases the volatility of boron oxide [13].

However, in most of abovementioned studies one or several oxides were substituted by rare-earth ones which could affect the obtained results. In this work, the effect of superstoichiometric additive of RE oxides on thermal behavior of (62.92SiO2–4.71Al2O3–14.83Na2O–5ZrO2–12.54SrO)–5Re2O3 (Re = Y, La, Nd, Sm) glasses was studied.

Superstoichiometric additive was chosen to study the effect of RE oxides on system in general rather than the effect of partial substitution of any oxide in the composition of the system.
2. Experimental part
Glasses of \((62.92\text{SiO}_2–4.71\text{Al}_2\text{O}_3–14.83\text{Na}_2\text{O–5ZrO}_2–12.54\text{SrO})–5\text{Re}_2\text{O}_3\) \((\text{Re} = \text{Y}, \text{La}, \text{Nd}, \text{Sm})\) system were synthesized by high-temperature melting at 1480°C for 15 min. The melt was poured onto a glass carbon plate; the obtained glasses were annealed at a temperature \(T_r\) 50°C. Chemical composition was checked by atomic emission spectroscopy (AES) with inductively coupled plasma using an Optima 4300 DV (Perkin Elmer, USA) spectrometer with an accuracy of 2–3% (Table 1).

| Composition mark | SiO₂ | Al₂O₃ | Na₂O | ZrO₂ | SrO | Re₂O₃ |
|------------------|------|-------|------|------|-----|-------|
| Base (B) nominal | 62.92| 4.71  | 14.83| 5.00 | 12.54| 0.00  |
| real             | 59.58| 5.18  | 17.17| 4.17 | 13.31| 0.00  |
| B-Y₂O₃ nominal   | 59.77| 4.47  | 14.09| 4.75 | 11.91| 5.00  |
| real             | 60.01| 5.08  | 15.15| 3.74 | 11.66| 4.36  |
| B-La₂O₃ nominal  | 59.77| 4.47  | 14.09| 4.75 | 11.91| 5.00  |
| real             | 61.18| 5.09  | 14.33| 3.76 | 11.53| 4.11  |
| B-Nd₂O₃ nominal  | 59.77| 4.47  | 14.09| 4.75 | 11.91| 5.00  |
| real             | 58.11| 5.51  | 14.72| 5.18 | 11.59| 4.89  |
| B-Sm₂O₃ nominal  | 59.77| 4.47  | 14.09| 4.75 | 11.91| 5.00  |
| real             | 59.52| 4.81  | 14.60| 4.97 | 11.20| 4.9   |

Amorphous nature of as-synthesized glasses was confirmed by X-ray diffraction analysis using a D/Max 2200 diffractometer (Rigaku, Japan) with Cu-Kα-radiation \((\lambda=1.5418 \text{ Å})\) in a 2θ range of 15–60°.

Differential scanning calorimetry (DSC) was performed using a STA 449 F1 Jupiter (Netzsch, Germany) calorimeter. The measurements were carried out in a platinum crucible in a temperature range of 35–1100°C in the air atmosphere with a heating rate of 10 °/min. Data were processed using the Netzsch Proteus software. To determine sealing temperature and study the glass behavior during heating, studies in heating microscope mode (HSM) were conducted using an ODP 868 optical dilatometric platform (TA Instruments, USA). A heating rate was 2 °/min, measurements were conducted in a temperature range of 20–1100°C on pressed from glass powder cylinders with a diameter of 2 mm.

Thermal expansion of samples cut from bulk glass was measured by a Tesatronic TT-80 (TESA, Switzerland) dilatometer with a TESAGT 21HP measuring probe in a temperature range from the room temperature to 650°C.

3. Results and discussion
Figure 1 presents XRD pattern of as-cast glasses after annealing. As it is seen, the glasses are generally amorphous, except a single peak on the XRD pattern of Sm₂O₃-containing composition. This peak is attributed to alumina and its presence might be caused by not complete dissolution of Al₂O₃ in the melt.
Temperatures of glass transition and crystallization are essential characteristics of sealing glasses since these temperatures determine the operating range and give a key to the temperature of beginning of crystallization processes which might change sealant properties. According to DSC results (Figure 2), no peaks corresponding to crystallization processes appear on the obtained curves. Therefore, these glasses might be expected to be non-crystallizing.

The sealing temperature was found by means of high-temperature optical microscopy based on the shape of glass drop. Figure 3 demonstrates changing the sample shape during heating on the example of Y$_2$O$_3$-containing glass. The given stages are typical, so the picture is similar for all studied samples.
The temperature of half-sphere formation is taken as the sealing temperature. Its values for all studied glasses are given in Table 2.

**Table 2.** Temperatures of glass transition ($T_g$, DSC) and half-sphere formation ($T_{HS}$, HSM), as well as CTE ($\alpha$) of glass samples in a temperature range of 50–500°C.

| Composition mark | $T_g$, °C | $T_{HS}$, °C | $\alpha$, $10^{-3}$K$^{-1}$ |
|------------------|-----------|--------------|--------------------------|
| Base (B)         | 566       | 898          | 11.3                     |
| B-Y$_2$O$_3$     | 601       | 924          | 11.3                     |
| B-La$_2$O$_3$    | 578       | 886          | 11.3                     |
| B-Nd$_2$O$_3$    | 580       | 896          | 10.9                     |

As it is seen, there is an increase in $T_{HS}$ value at introduction of Y$_2$O$_3$ to the glass composition. A small decrease is observed at transition of Y$_2$O$_3$ to La$_2$O$_3$, and the sealing temperatures of glasses containing La$_2$O$_3$, Nd$_2$O$_3$, and Sm$_2$O$_3$ gradually increase. Increasing $T_{HS}$ and $T_g$ from La$_2$O$_3$ to Sm$_2$O$_3$ can be explained by decrease in ionic radii [14]. The highest glass transition and half-sphere formation temperatures of B-Y$_2$O$_3$ glass are due to the smaller Y$^{3+}$ ionic radius compared with lanthanides.

As it is seen from Table 2, the values of coefficient of thermal expansion (CTE) do not change at the introduction Y$_2$O$_3$ and La$_2$O$_3$ and slightly decrease when Nd$_2$O$_3$ and Sm$_2$O$_3$ are added. As a rule, CTE of glasses depends on the degree of network polymerization and its strength. Since rare-earth oxides are considered as modifiers, they do not substitute the glass-forming units, but are located between glass chains near non-bridging oxygen atoms. Decreasing CTE correlates with the results of [14, 15] and it is caused by the growth of ionic field strength from La to Sm.

4. Conclusions

The effect of superstoichiometric additive of rare-earth oxides on thermal behavior of (62.92SiO$_2$–4.71Al$_2$O$_3$–14.83Na$_2$O–5ZrO$_2$–12.54SrO)–5Re$_2$O$_3$ (Re = Y, La, Nd, Sm) glasses was studied by differential scanning calorimetry, high-temperature optical microscopy and dilatometry. It was found out that characteristic temperatures (glass transition temperature and temperature of half-sphere formation) strongly depend on the ionic radius of the rare-earth element. At the same time, the value of the coefficient of thermal expansion changes insignificantly. The values of CTE and sealing temperatures of the obtained glasses, as well as the absence of crystallization peak on DSC curves, make the studied sealants promising candidates for application in solid oxide fuel cells operating at decreased temperatures, for example, based on proton-conducting electrolytes.

5. Acknowledgment

This work was supported by the Council of the President of the Russian Federation (scholarship no. SP-1942.2019.1). The research was partially performed using the facilities of the Shared Access Centre “Composition of Compounds” of IHTE UB RAS.

6. References

[1] Kaur G 2016 Solid Oxide Fuel Cell Components (Springer International Publishing: Cham, Switzerland) pp. 43-78
[2] Liu H, Du X, Yu Z, and et al. 2016 The phase evolution, electrical stability and chemical compatibility of sealing glass-ceramics for solid oxide fuel cell applications: effect of La$_2$O$_3$ or CeO$_2$. *RSC Advances, 6* 17151-7
[3] Kang J, Wang J, Lou X, and et al. 2018 Effect of Y$_2$O$_3$ content on the crystallization behaviors and physical properties of glasses based on MgO-Al$_2$O$_3$-SiO$_2$ system. *J. Non-Cryst. Solids.* 497 12-8
[4] Mahdy E A and Ibrahim S 2012 Influence of Y$_2$O$_3$ on the structure and properties of calcium magnesium aluminosilicate glasses. *J. Mol. Struct.* 1027 81-6
[5] Singh K, Gupta N and Pandey O P 2007 Effect of Y$_2$O$_3$ on the crystallization behavior of SiO$_2$--
MgO–B₂O₃–Al₂O₃ glasses. J. Mater. Sci. 42 6426-32

[6] Wang M, Fang L, Li M, et al. 2019 Glass transition and crystallization of ZnO-B₂O₃-SiO₂ glass doped with Y₂O₃, Ceram. Int. 45 4351-59

[7] Krainova D A, Saetova N S, Kuzmin A V, et al. 2020 Non-crystallising glass sealants for SOFC: Effect of Y₂O₃ addition, Ceram. Int. 46 5193-200

[8] Kaur M, Kaur G and Kumar V 2019 Impact of La₂O₃/Y₂O₃ ratio on crystallization kinetics of CaO based alumino-borosilicate glasses and compatibility with Crofer and 8YSZ for SOFCs. J. Non-Cryst. Solids. 521 119539

[9] Abdoli H, Alizadeh P and Agersted K 2014 Fabrication and sealing performance of rare-earth containing glass–ceramic seals for intermediate temperature solid oxide fuel cell applications. Ceram. Int. 40 7545-54

[10] Kumar V, Singh K and Pandey O P (2011). Study on the formation of crystalline phases in lanthanum borosilicate glass. T. Indian Ceram. Soc. 70 17-22

[11] Zhang Q, Tan S, Ren M, , et al. 2018 Effect of Gd₂O₃ doping on structure and boron volatility of borosilicate glass sealants in solid oxide fuel cells – A study on the La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃₋δ (LSCF) cathode. J.Power Sources. 383 34-41

[12] Liu H, Huang J, Zhao D, et al. 2016 Improving the electrical property of CeO₂-containing sealing glass–ceramics for solid oxide fuel cell applications: Effect of HfO₂. J. Eur. Ceram. Soc. 36 917-23

[13] Zhang Q, Chen K, Tang D, et al. 2017 Effects of Nb₂O₃ and Gd₂O₃ doping on boron volatility and activity between glass seals and lanthanum-containing cathode. J. Eur. Ceram. Soc. 37 1547-55

[14] Sasmal N, Garai M and Karmakar B 2016 Influence of Ce, Nd, Sm and Gd oxides on the properties of alkaline-earth borosilicate glass sealant. J. Asian Ceram. Soc. 4 29-38

[15] Zhang L, Qu Y, Wan X, et al. 2020 Influence of rare earth oxides on structure, dielectric properties and viscosity of alkali-free aluminoborosilicate glasses. J. Non-Cryst. Solids. 532 119886