Journal of Alloys and Compounds 504 (2010) 273–276

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Viscosity and thermal expansion of rare earth containing soda–lime–silicate glass

Wang Mi-tang [a,b,*], Cheng Jin-shu [a]

[a] Key Laboratory for Silicate Materials Science and Engineering of Ministry of Education, Wuhan University of Technology, Wuhan 430070, China
[b] School of Material and Metallurgy, Inner Mongolia University of Science and Technology, Baotou 014010, China

ARTICLE INFO

Article history:
Received 4 April 2010
Received in revised form 12 May 2010
Accepted 21 May 2010
Available online 2 June 2010

Keywords:
Thermal expansion
Viscosity
Silicate glass
Rare earth

ABSTRACT

Viscosity, coefficient of thermal expansion, glass transition temperature and dilatometric softening temperature of soda–lime–silicate glass doped with rare earth oxides (La_2O_3, CeO_2, Nd_2O_3) were investigated by the rotating crucible viscometer and dilatometry, the melting temperature and activation energy for viscous flow of the studied melt were derived on the basis of Arrhenius equation, in order to reveal the effects of rare earth elements on the behavior of soda–lime–silicate glass. The results show that introduction of rare earth oxides increases the coefficient of thermal expansion, decreases viscosity of soda–lime–silicate glass, and Nd_2O_3 is an exception in viscosity. The glass transition temperature, dilatometric softening temperature, melting temperature and activation energy for viscous flow of soda–lime–silicate glass doped with rare earth oxides increase with increasing cationic field strength of corresponding rare earth ions.

1. Introduction

Physical properties of elevated temperature melts is a cornerstone of high temperature related industries, such as iron and steelmaking, glass melting, ceramics sintering, controlling the rate of various reactions and the fluid flows. Thus, numerous measurements of the physico-chemical properties have been investigated in the last half a century [1]. Glass-viscosity is one of the key properties for melt, fining, condition processing optimization, glass formulation and annealing process [2].

The rare earth composites were praised as the treasury of materials due to their special optical, electric and magnetic properties that were given by the specific 'f' electron of rare earth elements [3]. Because the ionic radii of the lanthanide elements decrease continuously with their increasing atomic number, which is known as lanthanide contraction, their cationic field strength (CFS = Z/r^2, Z is the valence of the corresponding element, r its ionic radius) also continuously changes with their atomic number. This causes consequent variations in the various properties, such as glass transition temperature, softening temperature, density, microhardness, elastic modulus, refractive index, and the coefficient of thermal expansion, etc., of rare earth containing oxide and oxynitride glasses [4–7]. However, to our best knowledge, there are very little reports on the effect of rare earth on the physical properties of silicate melts. Therefore, the aim of this paper is to focus on the effect of some light rare earth additives on the thermal expansion, characteristic temperature and viscosity of soda–lime–silicate glass.

2. Experimental

2.1. Glass preparation

Batch compositions (71.52 SiO_2, 12.99 Na_2O, 0.31 K_2O, 8.87 CaO, 0.58 Al_2O_3, 5.73 MgO, expressed in mol%) were added different light rare earths (La_2O_3, CeO_2, Nd_2O_3) of 1 mol% respectively, and ground. Fusion was carried out in corundum crucibles by means of an electric furnace in the 1500–1580 °C temperature range for 3 h. The part of melt was poured into a pre-heating stainless steel model to form, and then annealed for 1 h at below 50 °C the glass transition temperature T_g determined by dilatometry. Regular bulk glass samples were prepared for test of dilatometry. The residual melt was poured into water and dried for 24 h at 120 °C in the oven to obtain glass frit for testing viscosity. The glass samples were labeled with a short word (FG, FGL, FGC and FGN), the FG indicates the soda–lime–silicate glass without doping rare earth, FGL, FGC, FGN the glasses doped with La_2O_3, CeO_2, and Nd_2O_3 respectively.

2.2. Viscosity measurement

The viscosity of glass frit quenched in water was measured with a rotating crucible viscometer (Model Rheotronic II). About 100 g of glass frit was added into a Pt crucible and placed into the furnace set at 1500 °C. The viscometer spindle was placed in the center of the crucible with the lower end of the rod at 5.1 mm above the bottom of the crucible. The furnace was set to the required ramp/soak schedule, and digital data collection and recording began. The viscometer was calibrated for 5 times with a standard quartz glass before testing. The standard measurement error is less than 0.05 log units.

---

* Corresponding author at: Key Laboratory for Silicate Materials Science and Engineering of Ministry of Education, Wuhan University of Technology, Wuhan 430070, China. Fax: +86 027 87860801.
E-mail address: btwmt@126.com (W. Mi-tang).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.05.111

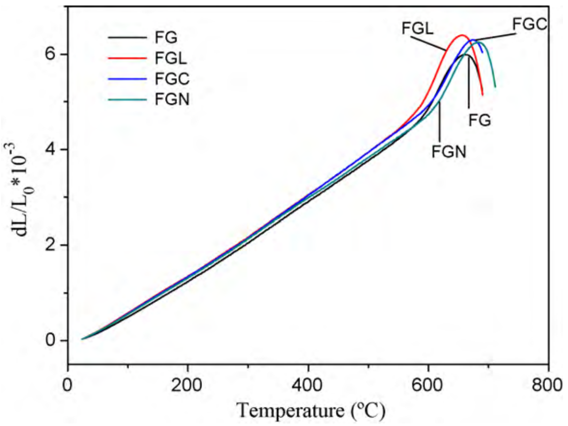

Fig. 1. The thermal expansion curves of glasses doped with different rare earths.

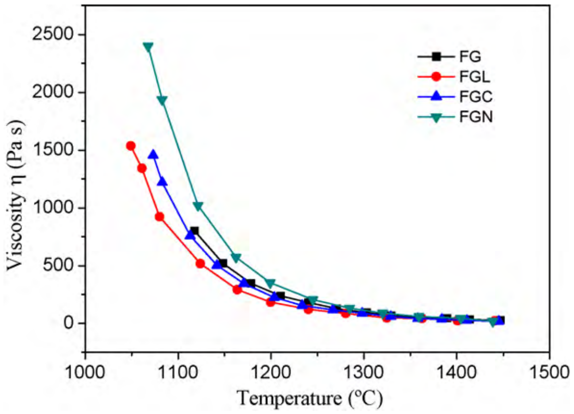

Fig. 2. Viscosity as a function of temperature for glasses doped with different rare earths.

2.3. *Dilatometry*

The dilatometric experiments were performed in a horizontal dual-rod dilatometer (Model DIL 402) at heating rate of 1 °C/min and quartz glass standard. The experiments on as-prepared samples were carried out to estimate the T_g, the annealing temperature of each glass was determined. The dilatometric experiments of the pre-annealed samples were performed to yield final values. The coefficient of thermal expansion (CTE), α, were determined from the experimental curves for temperature difference between room temperature (25 °C) and 400 °C. T_g was determined as the intersection of the linear extrapolation of the slope of thermal expansion curve of the solid glass and that of the glass "melt". The dilatometric softening point T_f can be determined from the maximum of the dilatometric curve. These values seem to be more reliable for estimation of the effects of chemical compositions, although these determination procedures are subjective to some extent.

3. Results

3.1. *CTE, T_g and T_f*

The coefficient of thermal expansion, glass transition, dilatometric softening temperature, determined from the thermal expansion curves (see Fig. 1), of containing different rare earths (La, Ce, Nd) glasses and cationic field strength of the corresponding rare earth elements are summarized in Table 1. As shown in Table 1, in the case of glass FG without doping rare earths, the coefficient of thermal expansion, $\alpha_{(25\text{–}400\,^\circ\mathrm{C})}(\times 10^{-6})$, glass transition temperature, T_g, and dilatometric softening temperature, T_f are 7.67 $^\circ\mathrm{C}^{-1}$, 594.0 and 662.5 °C respectively. When the rare earth oxides (La_2O_3, CeO_2 and Nd_2O_3) are introduced into the glasses, all the coefficients of thermal expansion of glass FGL, FGC and FGN are greater than that of glass FG without containing rare earths. The glass transition temperature and dilatometric softening temperature of glass FGC and FGN are higher than that of glass FG, however, the corresponding values of glass FGL are lower than that of glass FG.

3.2. *Viscosity*

In Fig. 2, the viscosities (in Pa s) for glass FG, FGL, FGC and FGN at high temperature are reported as a function of the temperature. It can be observed that the viscosity of all glasses decrease with increment of temperature. Besides, the viscosity of glass FG, FGL, FGC and FGN is seen to increase in the order: FGN > FG > FGC > FGL, namely, the addition of La_2O_3, CeO_2 into soda–lime–silicate glass decreases the viscosity, conversely, Nd_2O_3 increases the viscosity.

Table 1
The coefficient of thermal expansion, transition, softening temperature of glasses doped with different rare earths and cationic field strength of the corresponding rare earth elements.

Samples	$\alpha_{(25\text{–}400\,^\circ\mathrm{C})}(\times 10^{-6}\,^\circ\mathrm{C}^{-1})$	T_g (°C)	T_f (°C)	CFS (A^{-2})
FG	7.67 ± 0.03	594.0 ± 2.5	662.5 ± 0.5	–
FGL	8.03 ± 0.01	590.2 ± 1.2	655.4 ± 0.3	2.665
FGC	8.01 ± 0.01	607.5 ± 1.5	674.0 ± 0.6	2.806
FGN	7.88 ± 0.02	611.5 ± 1.8	682.9 ± 0.2	3.030

4. Discussions

4.1. *Dilatometry*

The thermal expansion of solid glasses is controlled by the asymmetry of the amplitude of thermal vibrations in the glass. It decreases as the rigidity of glass network increases. An increase of the number of non-bridging bonds would weaken the structure and increase the coefficient of thermal expansion, whereas the changes in coordination number of network former cation may cause either its increase or decrease depending on the effect on glass structure [6]. Moreover, the infrared and Raman spectra of silicate glasses containing rare earth ions have demonstrated that rare earth ions behave as glass network modifiers rather than as network formers [8]. Therefore, doping of rare earth oxides into glass may lead to broadening of Q_n (n = 4, 3, 2, 1) distribution, increasing of the numbers of NBO and Si–O_B bonding length [9]. These are the reasons for the coefficient of thermal expansion of glass FGL, FGC and FGN are greater than that of glass FG (Table 1). The other important observation can be also made from Table 1, the coefficients of thermal expansion of glass FGL, FGC and FGN are decreased with cationic field strength. The smaller lanthanide cation (corresponding to the higher cationic field strength) tighten glass network, therefore, lanthanides with higher cationic field strength reduce the coefficient of thermal expansion. As anticipated, the T_g and T_f of glass FGL was lower than that of FG, however, the introduction of CeO_2 and Nd_2O_3 not only increased the coefficient of thermal expansion but also increased the corresponding T_g and T_f of glass FGC and FGN, which seems to be incompatible, although varying trend of T_g and T_f of glass FGL, FGC and FGN with increasing of cationic field strength of corresponding rare earth elements is reasonable. The same enhanced effect of Nd on the coefficient of thermal expansion, α, glass transition temperature, T_g, and dilatometric softening temperature, T_f, was also observed in oxynitride glass [6]. Therefore detailed structure investigations are necessary to reveal the reason for enhanced effect of Ce and Nd on α, T_g and T_f of glass.

4.2. *Viscosity*

Viscosities of the glasses FG, FGL, FGC and FGN are plotted against testing temperature (°C) in Fig. 2 and log viscosity vs. $10^3/T$ (K) are illustrated in Fig. 3. The viscosity data displayed in Fig. 3

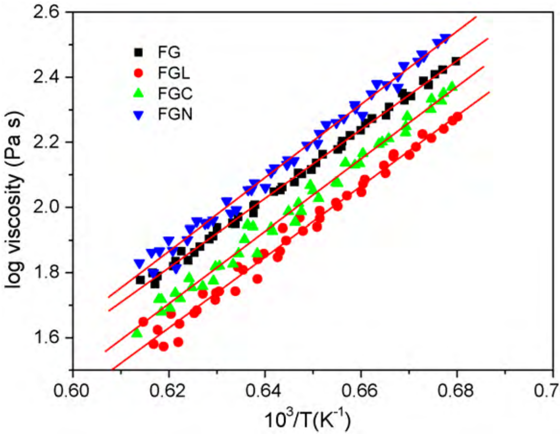

Fig. 3. Log viscosity vs. $10^3/T$ for glasses doped with different rare earths.

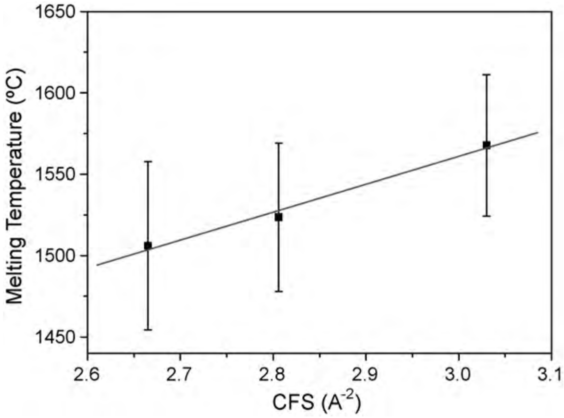

Fig. 4. Variation in melting temperature of soda–lime–silicate glass with cationic field strength of rare earth ions.

show nearly linear trends and can therefore be fitted over the investigated temperature ranges using the approximation of Arrhenius equation [1,2,10]:

$$\eta = A \exp\left(\frac{E_\eta}{RT}\right)$$

where A, E_η, R and T are the pre-exponential factor, activation energy of viscous flow, the gas constant and absolute temperature. Over the temperature interval between the glass transition temperature and the glass fining temperature, the viscosity spans 12 orders of magnitude. Fortunately, the viscosity range of glass processing, i.e., melting, fining, and conditioning, is relatively short, spanning approximately 3 orders of magnitude ($1\text{–}10^3$ Pa s). For this range, the relationship between viscosity and temperature is sufficiently well represented by the Arrhenius equation [2]. The fitting results are reported in Table 2. The melting temperature of soda–lime–silicate glass was obtained by extrapolating the viscosity to 10 Pa s according to the Arrhenius equation. The incorporation of rare earth oxides (La_2O_3, CeO_2 and Nd_2O_3) increases all the activation energy of viscous flow and decreases the melting temperature T_m of glass FGL and FGC while the T_m of FGN is equal to that of glass FG, indicating that rare earth ions behaves as a network modifier of complex silicate anions in high temperature melts, which is in agreement with results of infrared and Raman spectra of silicate glasses containing rare earth ions [8]. From Fig. 2, it can be seen that the addition of Nd increases the viscosity of the investigated glass in the testing temperature ranges, however, two melting temperatures of glass FG and FGN are also same, therefore, one can presume that the viscosity of glass FGN is lower than that of glass FG at above melting temperature. These tendencies are quite similar with the addition effect of alkaline-earth oxides on the viscosity of binary or ternary silicate melts [11].

The variation in melting temperature of soda–lime–silicate glass as a function of the cationic field strength of corresponding rare earth ions was demonstrated in Fig. 4. It can be obviously observed that the melting temperature of soda–lime–silicate glass doped with rare earth oxides linearly increases with increment of cationic field strength of corresponding rare earth ions. Namely, the viscosity of soda–lime–silicate glass doped with rare earth oxides at same temperature increases linearly with increasing cationic field strength of corresponding rare earth ions. The similar phenomena were also observed in the effect of cationic field strength of rare earth ions on the glass transition temperature, T_g, dilatometric softening temperature, T_f (see Table 1), and activation energy of viscous flow, E_η (see Table 2). These observations are consistent with the results reported by Fumiyuki et al. [1], Hampshire et al. [7] and Lofaj et al. [6,12] in studied oxide and oxynitride glasses.

Table 2
The Arrhenius parameter A, activation energy E_η and melting temperature T_m of glasses doped with different rare earths.

Samples	A	E_η(kJ mol^{-1})	T_m (°C)
FG	−4.76 ± 0.06	203.06 ± 1.68	1568.02 ± 23.77
FGL	−5.11 ± 0.13	208.07 ± 3.96	1506.03 ± 51.68
FGC	−5.18 ± 0.12	212.70 ± 3.50	1523.58 ± 45.62
FGN	−5.12 ± 0.11	215.75 ± 3.27	1567.75 ± 43.52

5. Conclusions

The thermal expansion and viscosity of rare earth oxides (La_2O_3, CeO_2 and Nd_2O_3) bearing soda–lime–silicate glass were investigated, the conclusions can be drawn as follows:

(a) The addition of rare earth oxides into the soda–lime–silicate glass increases the coefficient of thermal expansion, the coefficient of thermal expansion decreases with increment of cationic field strength of corresponding rare earth ions.
(b) The doping of La_2O_3 and CeO_2 decreases the melting point and viscosity of soda–lime–silicate glass, however, Nd_2O_3 additives increases the viscosity of glass while has the same melting point.
(c) The glass transition temperature, dilatometric softening temperature and activation energy of viscous flow of soda–lime–silicate glass increase with increasing cationic field strength of rare earth ions.
(d) The reason for enhanced effect of Ce and Nd on the coefficient of thermal expansion, glass transition temperature and dilatometric softening temperature of glass is not clear, detailed structure investigations are necessary.

References

[1] S. Fumiyuki, T. Hirofumi, S. Noritaka, Nakashima, Kunihiko, Viscosity and surface tension measurements of RE_2O_3–MgO–SiO_2 (RE = Y, Gd, Nd and La) melts, ISIJ Int. 46 (2006) 388–393.
[2] P. Hrma, Arrhenius model for high-temperature glass-viscosity with a constant pre-exponential factor, J. Non-Cryst. Solids 354 (2008) 1962–1968.
[3] M. Li, Z.G. Liu, Y.H. Hu, Z.X. Shi, H.Q. Li, Effects of the synthesis methods on the physicochemical properties of cerium dioxide powder, Colloids Surf., A 301 (2007) 153–157.
[4] M. El-Okr, M. Ibrahem, M. Farouk, Structure and properties of rare-earth-doped glassy systems, J. Non-Cryst. Solids 69 (2008) 2564–2567.
[5] J. Johnson, R. Weber, M. Grimsditch, Thermal and mechanical properties of rare earth aluminate and low-silica aluminosilicate optical glasses, J. Non-Cryst. Solids 35 (2005) 1650–1655.
[6] F. Lofaj, R. Satet, M.J. Hoffmanna, A.R. de Arellano Lopez, Thermal expansion and glass transition temperature of the rare-earth doped oxynitride glasses, J. Eur. Ceram. Soc. 24 (2004) 3377–3385.

[7] S. Hampshire, M.J. Pomeroy, Effect of composition on viscosity of rare earth oxynitride glasses, J. Non-Cryst. Solids 344 (2004) 1–7.

[8] R.A. Condrate Sr., Infrared and raman spectra of glasses containing rare earth ions, Key Eng. Mater. 94–95 (1994) 209–232.

[9] M.S. Gaafar, S.Y. Marzouk, Mechanical and structural studies on sodium borosilicate glasses doped with Er_2O_3 using ultrasonic velocity and FTIR spectroscopy, Physica B 388 (2007) 294–302.

[10] D. Giordano, M. Potuzak, C. Romano, D.B. Dingwell, M. Nowak, Viscosity and glass transition temperature of hydrous melts in the system $CaAl_2Si_2O_8$–$CaMgSi_2O_6$, Chem. Geol. 256 (2008) 203–215.

[11] L.M. Zhang, X.H. Huang, X.L. Song, Fundamentals of Materials Science, Wuhan University of Technology Press, Wuhan, 2004, pp. 173–176.

[12] F. Lofaj, S. Deriano, M. LeFloch, T. Rouxel, M.J. Hoffmann, Structure and rheological properties of the RE–Si–Mg–O–N (RE = Sc, Y, La, Nd, Sm, Gd, Yb and Lu) glasses, J. Non-Cryst. Solids 344 (2004) 8–16.