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Oxygen self-diffusion in a cordierite glass

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Abstract

Oxygen self-diffusion measurements determined below and above the glass transition temperature in a cordierite glass are reported. The diffusion experiments were performed by the solid–gas isotope exchange method using ^{18}O as a tracer in $\text{H}_2\text{--H}_2^{18}\text{O}$ and $\text{Ar}/^{18}\text{O}_2$ atmospheres. The ^{18}O diffusion profiles were established by secondary ion mass spectrometry (SIMS) after appropriate diffusion annealing. The oxygen diffusion coefficients changed at the glass transition temperature as expected. The atmosphere affected the oxygen diffusivity in agreement with other studies. The diffusion data were useful for comparisons with diffusion controlled process in the same glass. There is a difference between the activation enthalpies for crystal growth, viscous flow, and oxygen self-diffusion. Hence, bond-breaking and molecular reorientation required for crystallization and the atomic transport mechanism involved in viscous flow are not correlated in any obvious way to oxygen diffusion in cordierite glass. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The study of physical and chemical properties of cordierite glasses ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$) has gained interest in the last few years. Most research has been motivated by the use of cordierite based compositions in the production of glass–ceramics because of the chemical and physical properties, when used as dielectric substrates in a number of electronic applications. Due to these uses, a cordierite glass was chosen by the Nucleation, Crystallization & Glass–Ceramics Committee of the

International Commission on Glass (TC-7 Committee of the ICG) for a world-wide round-robin study of crystallization.

The TC-7 members have determined several issues regarding the crystallization properties of cordierite glasses and were looking for auxiliary data (e.g., diffusion data) to aid in the interpretation of crystallization kinetics. In oxide glasses, the O^{2-} ion is one of the network-forming ions; therefore, data about oxygen diffusion are essential for understanding diffusion controlled processes, such as viscous flow and crystallization. In addition, as far as we know, there are no data about oxygen diffusion available in the literature for cordierite glass. This communication deals with the experimental determination of oxygen

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self-diffusion in an almost stoichiometric cordierite glass. We also test if there is any obvious correlation between oxygen diffusion, viscous flow and crystal growth kinetics in the same glass.

2. Experimental

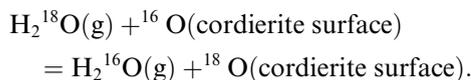
The composition of the cordierite glass samples was 52.3 wt% SiO₂, 33.2 wt% Al₂O₃ and 14.6 wt% MgO (the stoichiometric composition is 51.3 wt% SiO₂, 34.9 wt% Al₂O₃, 13.8 wt% MgO). This commercial glass (GM-30870) was obtained from Schott Glaswerke, Germany. For the diffusion experiments, 1 × 5 × 5 mm samples were cut and polished to an optical finish with diamond paste.

The oxygen diffusion coefficients were determined by using the gas–solid isotope exchange method. Two different series of experiments were performed.

2.1. Determination of the oxygen diffusion coefficient above and below the transition temperature in H₂/H₂O atmosphere

The diffusion experiments were performed in a range of temperatures, between 650°C and 800°C; that is, below the glass transition temperature ($T_g \sim 820^\circ\text{C}$), by using the gas–solid isotope exchange method. Some experiments were also performed at temperatures above T_g , between 832°C and 930°C. The atmosphere used in these experiments was a gaseous mixture of 98.4% N₂:1% H₂:0.6% H₂O. The oxygen partial pressure in these experiments was ca 3.0×10^{-13} Pa at 860°C. For annealing, the water vapor in the atmosphere was supplied by natural water (H₂¹⁶O), while in the diffusion treatments the source of vapor was water enriched with the ¹⁸O isotope (H₂¹⁸O). The (H₂¹⁸O) rich oxygen had about 40% ¹⁸O.

In the exchange isotope method, the introduction of the tracer and the diffusion treatment is simultaneous. The incorporation of ¹⁸O in the surface of the sample may be schematically described by



After being incorporated into the sample surface, ¹⁸O diffuses into the material. Details of the experimental arrangement used in the diffusion experiments are described in Ref. [1].

The diffusion profiles of the oxygen were determined by secondary ion mass spectrometry (SIMS-Cameca 4F-CNRS/Meudon/France). The analyses were made using 10 keV Cs⁺ primary ions. Since cordierite is an insulator, it charges during SIMS analysis. This problem was eliminated by depositing by evaporation a gold film on the specimen surface.

The oxygen diffusion profiles were established from the ¹⁶O⁻ and ¹⁸O⁻ signals through the following expression:

$$C({}^{18}\text{O}) = \frac{I({}^{18}\text{O}^-)}{I({}^{18}\text{O}^-) + I({}^{16}\text{O}^-)}. \quad (1)$$

2.2. Determination of the oxygen diffusion above the glass transition temperature in O₂/Ar atmosphere

We have repeated the diffusion experiments at temperatures above the transition temperature. This second series of experiments was also performed by the gas–solid isotope exchange method, but using an Ar + O₂ (98% ¹⁸O) atmosphere. The heat-treatment arrangement used in these experiments are described elsewhere [2]. The diffusion annealings were performed from 826°C to 880°C, and the oxygen pressure was equal to 2.1×10^4 Pa. To avoid crystallization or thermal etching, the annealings were performed for short times. The correction for heat up and cool down of the temperatures was performed using a method described by Rothman [3].

Concentration profiles were established by secondary ion mass spectrometry (SIMS) (Vacuum Generators time-of-flight instrument), using a 10 keV Ga⁺ ion source.¹ During these analyses, charge neutralization was obtained by means of an electron flood gun. The oxygen concentration was determined from the ¹⁶O⁻ and ¹⁸O⁻ signals using Eq. (1).

¹ The analysis were performed at the Center for Advanced Materials/University of Lowell (USA).

The penetration depths were obtained assuming a constant sputtering rate and measuring the depth of the crater by means of a profilometer (Dektak).

3. Results

The ^{18}O concentration at the sample surface was less than that in the atmosphere in all experiments. Consequently, the oxygen diffusion coefficients were determined by using a solution of the diffusion equation for the case of diffusion controlled by a surface exchange reaction. That solution is given by the following expression [4]:

$$\frac{C - C_{\infty}}{C_g - C_{\infty}} = \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) - \exp(hx + h^2Dt) \operatorname{erfc}\left(\frac{x + 2hDt}{2\sqrt{Dt}}\right), \quad (2)$$

where C_{∞} is the natural concentration of ^{18}O in the sample, C_g is the concentration of ^{18}O in the atmosphere, erfc is the inverse error function, D is the diffusion coefficient, t is the time of the diffusion treatment, x is the penetration depth and $h = \alpha/D$. The parameter α is the exchange coefficient given by the boundary condition [4]:

$$-D \frac{\partial C(0, t)}{\partial x} = \alpha [C_g - C(0, t)]. \quad (3)$$

Eq. (2) has two fitting parameters, D and h . These parameters were determined by fitting Eq. (2) to the depth profiles obtained for ^{18}O diffusion in cordierite glass. It was performed by nonlinear fitting using the software Origin [5]. In this software, the fitting is achieved by minimizing the Chi-squares using the Levenberg–Marquardt algorithm [5].

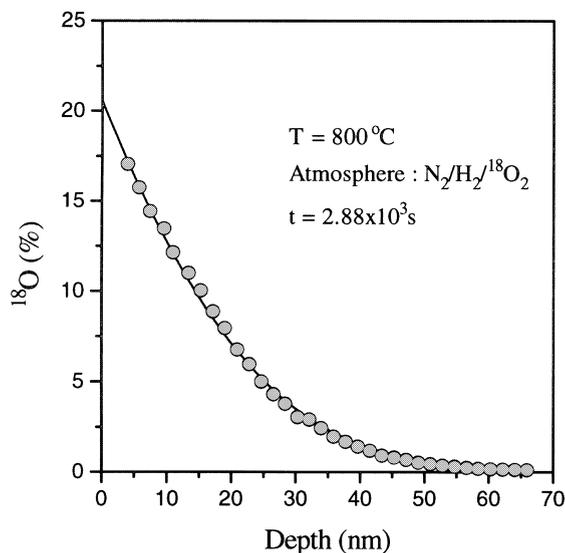


Fig. 1. (●) Penetration plot for ^{18}O diffusion in cordierite glass at 800°C , in $\text{N}_2/\text{H}_2/\text{H}_2\text{O}$ atmosphere, and (—) non-linear fitting giving $D = (1.18 \pm 0.03) \times 10^{-15} \text{cm}^2/\text{s}$, $h = (4.24 \pm 0.10) \times 10^5 \text{cm}^{-1}$, and correlation coefficient = 0.998.

Fig. 1 shows a fit of Eq. (2) to an experimental diffusion profile after a diffusion treatment at 800°C . The nonlinear fitting analysis, indicated by the solid line in Fig. 1, yields $D = (1.18 \pm 0.03) \times 10^{-16} \text{cm}^2/\text{s}$, and $h = (4.24 \pm 0.10) \times 10^5 \text{cm}^{-1}$.

The diffusion coefficients (D) and the exchange coefficients (α) obtained for oxygen diffusion in cordierite glass at temperatures below and above T_g , in $\text{N}_2/\text{H}_2/\text{H}_2\text{O}$ atmosphere, are listed in Table 1.

Below the transition temperature ($T_g \sim 820^\circ\text{C}$), in $\text{N}_2/\text{H}_2/\text{H}_2\text{O}$ atmosphere, the diffusion coefficients of oxygen in cordierite glass can be represented by the following Arrhenius relation:

Table 1
Results for oxygen diffusion in cordierite glass in $\text{N}_2/\text{H}_2/\text{H}_2\text{O}$ ^{18}O

Sample	T ($^\circ\text{C}$)	t (s)	D (cm^2/s)	α (cm/s)
1	650	9.90×10^3	$(1.42 \pm 0.13) \times 10^{-16}$	$(5.50 \pm 0.92) \times 10^{-11}$
2	700	7.92×10^3	$(2.25 \pm 0.04) \times 10^{-16}$	$(7.00 \pm 0.28) \times 10^{-11}$
3	750	3.60×10^3	$(4.00 \pm 0.22) \times 10^{-16}$	$(1.70 \pm 0.19) \times 10^{-10}$
4	800	2.88×10^3	$(1.18 \pm 0.03) \times 10^{-15}$	$(5.00 \pm 0.25) \times 10^{-10}$
5	832	3.60×10^3	$(7.52 \pm 0.26) \times 10^{-15}$	$(3.30 \pm 0.28) \times 10^{-9}$
6	860	7.08×10^3	$(7.43 \pm 0.31) \times 10^{-14}$	$(2.90 \pm 0.40) \times 10^{-8}$

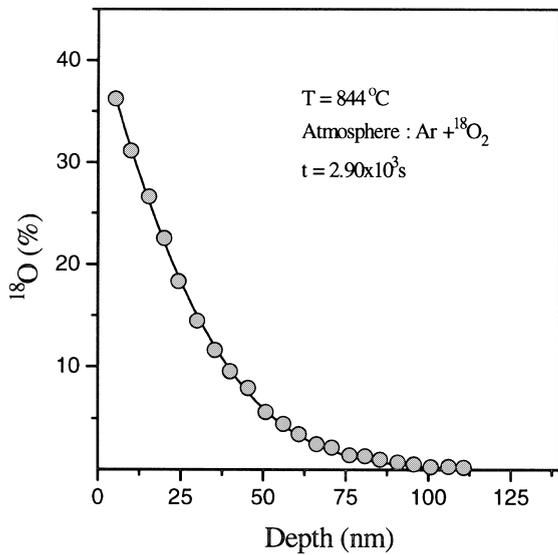


Fig. 2. (●) Penetration plot for ^{18}O diffusion in cordierite glass at 844°C , in $\text{Ar} + \text{O}_2$ atmosphere, and (—) non-linear fitting giving $D = (2.70 \pm 0.04) \times 10^{-15} \text{cm}^2/\text{s}$, $h = (2.15 \pm 0.04) \times 10^5 \text{cm}^{-1}$, and correlation coefficient = 0.998.

$$D (\text{cm}^2/\text{s}) = 2.97 \times 10^{-10} \exp \left[-\frac{(113 \pm 21) \text{kJ/mol}}{RT} \right] \quad (4)$$

obtained by linear regression of the diffusion coefficients measured from 650°C to 800°C , with a correlation coefficient = 0.969.

An Arrhenius relation for the oxygen diffusion coefficients obtained above T_g , in $\text{N}_2/\text{H}_2/\text{H}_2\text{O}$, is not proposed because there are only two data points at 832 and 860°C . In fact, we have also performed diffusion experiments at 905 and 930°C , however these were discarded due to surface crystallization, as shown by X-ray diffraction.

Fig. 2 shows a depth profile for oxygen diffusion at 844°C , in Ar/O_2 atmosphere. Again, the ^{18}O concentration at the sample surface was much less than that in atmosphere (98%). Thus, the diffusion coefficients were also determined by using Eq. (2). The non-linear fitting analysis, shown as the solid line in Fig. 2, yields $D = (2.70 \pm 0.04) \times 10^{-15} \text{cm}^2/\text{s}$, and $h = (2.15 \pm 0.04) \times 10^5 \text{cm}^{-1}$.

The oxygen diffusion coefficients and the exchange coefficients obtained for oxygen diffusion in cordierite glass, above T_g , in $\text{Ar} + \text{O}_2$ atmosphere, are shown in Table 2.

From 826°C to 880°C , the diffusion coefficients can be described by the following Arrhenius relation:

$$D (\text{cm}^2/\text{s}) = 7.9 \times 10^7 \exp \left[-\frac{(481 \pm 36) \text{kJ/mol}}{RT} \right]. \quad (5)$$

Relation (5) was obtained by linear regression of the data given in Table 2, with a correlation coefficient = 0.988.

4. Discussion

Fig. 3 shows an Arrhenius plot of the oxygen diffusion coefficients (D) measured above and below the transition temperature, in $\text{N}_2/\text{H}_2/\text{H}_2\text{O}$ atmosphere.

The diffusion coefficients measured below the transition temperature, extrapolated to temperatures above T_g by Eq. (4) are less than those obtained experimentally above T_g . This difference indicates a change of the diffusion coefficients through the transition temperature, which has been observed by other authors in other silicate glasses [6,7], and also in metallic glasses [8].

Table 2
Results for oxygen diffusion in cordierite glass in $\text{Ar} + ^{18}\text{O}_2$

Sample	T ($^\circ\text{C}$)	t (s)	D (cm^2/s)	α (cm/s)
1	826	7.28×10^3	$(1.30 \pm 0.03) \times 10^{-15}$	$(3.30 \pm 0.22) \times 10^{-10}$
2	830	6.97×10^3	$(1.10 \pm 0.06) \times 10^{-15}$	$(1.60 \pm 0.23) \times 10^{-10}$
3	844	2.90×10^3	$(2.70 \pm 0.04) \times 10^{-15}$	$(5.80 \pm 0.19) \times 10^{-10}$
4	862	3.34×10^3	$(7.35 \pm 0.18) \times 10^{-15}$	$(8.00 \pm 0.42) \times 10^{-10}$
5	869	1.41×10^3	$(7.92 \pm 0.28) \times 10^{-15}$	$(1.60 \pm 0.12) \times 10^{-9}$
6	880	1.67×10^3	$(1.21 \pm 0.04) \times 10^{-14}$	$(1.58 \pm 0.09) \times 10^{-9}$

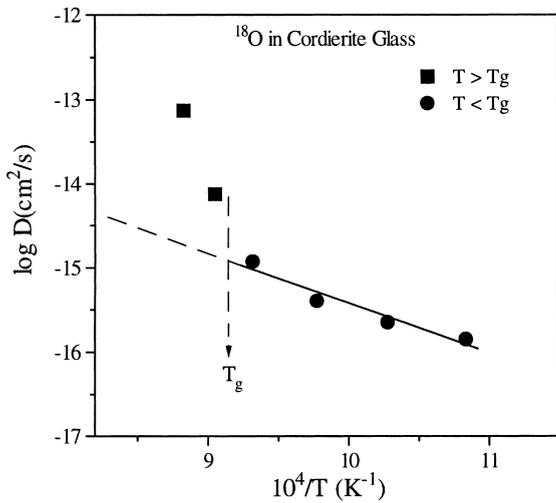


Fig. 3. Arrhenius plot for oxygen diffusion in cordierite glass above and below the transition temperature, in $\text{N}_2/\text{H}_2/\text{H}_2^{18}\text{O}$ atmosphere.

Fig. 4 compares the oxygen diffusion coefficients obtained in $\text{Ar} + \text{O}_2$ and $\text{N}_2/\text{H}_2/\text{H}_2\text{O}$ atmospheres, above T_g . The larger diffusion coefficients in a water rich atmosphere were also expected and have been observed in previous studies of oxygen diffusion in other silicates [9,10].

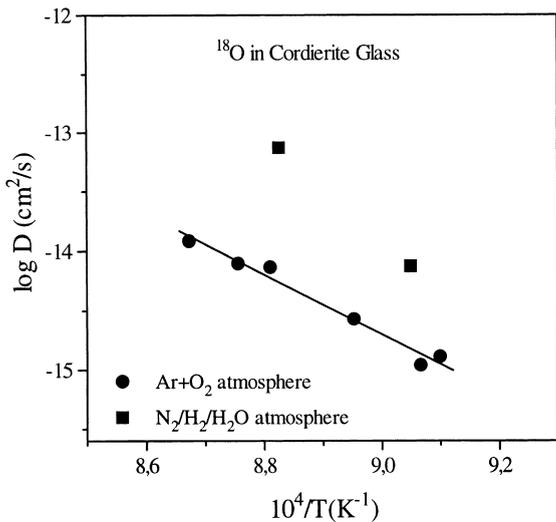


Fig. 4. Comparison between the oxygen diffusion coefficients measured in $\text{Ar} + ^{18}\text{O}_2$ and $\text{N}_2/\text{H}_2/\text{H}_2^{18}\text{O}$ atmospheres, above T_g .

As far as we know, there are no previous data available on oxygen diffusion in cordierite glass for comparison.

In oxide glasses such as cordierite, the ion O^{2-} is one of the network-forming ions and its diffusion may play an important role in diffusion-controlled processes, such as viscous flow and crystallization. Using the data determined in this work, a correlation of oxygen self-diffusion with viscous flow and crystallization kinetics determined in the same glass [11] will be discussed.

In a previous publication, Diaz-Mora et al. [12] investigated the activation enthalpies and energies for crystal growth (ΔH_u , ΔG_u) and viscous flow (ΔH_η , ΔG_η) in the same cordierite glass, by using experimental growth rates and viscosity data. They found that ΔG_u is similar to ΔG_η in magnitude, however, their temperature dependencies are not equal, leading to different activation enthalpies, thus $\Delta H_u \neq \Delta H_\eta$. This conclusion was confirmed by an analysis of literature data for six other glasses.

Fig. 5 shows ΔH_u and ΔH_η (from [12]) and the activation enthalpy for oxygen diffusion, ΔH_D , obtained in this work above T_g , in $\text{Ar} + \text{O}_2$ atmosphere. There is a difference between these quantities indicating that there is no obvious relationship among them. Hence, bond-breaking and atomic reorientation required for crystalliza-

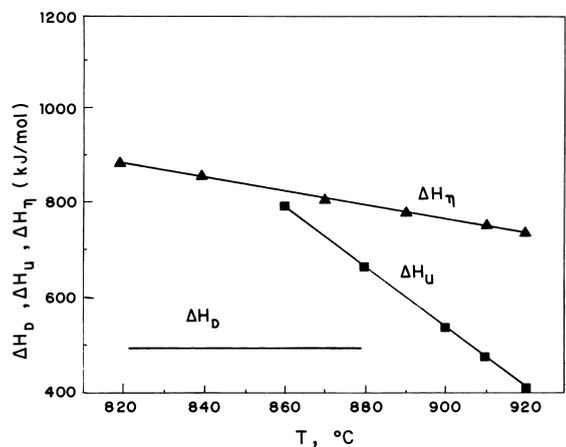


Fig. 5. Activation enthalpies for crystal growth, ΔH_u [12], viscous flow, ΔH_η [12], and oxygen diffusion, ΔH_D , in a cordierite glass.

tion and the atomic transport mechanism involved in viscous flow are not correlated directly to oxygen diffusion in cordierite glass.

5. Conclusion

Oxygen diffusion in cordierite glass changes at the glass transition temperature and is dependent on atmosphere. These results confirm previous studies with other glass systems and have been used for comparison with viscous flow and crystal growth kinetics. There is a difference among the activation enthalpies for crystal growth, viscous flow and oxygen self-diffusion. Hence, bond-breaking and atomic reorientation required for crystallization and the atomic transport mechanism involved in viscous flow are not correlated in any obvious way to oxygen diffusion in cordierite glass.

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