

Phase separation in rare-earth-doped SiO_2 glasses

Vincent McGahay¹ and Minoru Tomozawa

Materials Engineering Department, Rensselaer Polytechnic Institute, Troy, NY 12180-3590, USA

Received 16 September 1992

Revised manuscript received 1 December 1992

Phase separation in the rare-earth silicates, which is closely related to the phenomenon of concentration quenching in laser glasses, is discussed in terms of the theory of corresponding states in charged particle systems. This theory has been previously shown to apply to related systems such as the alkali and alkaline-earth silicates. Literature values of the critical temperatures and concentrations of the rare-earth silicates are found to increase with decreasing rare-earth ion radius in agreement with the corresponding states theory. Reduced values of the critical parameters are in excellent agreement with those of other charged particle systems if it is assumed that the rare-earth ions are effectively divalent. This assumption is consistent with the high degree of association observed for charged particle systems at their critical points. The theory of corresponding states is used to estimate the Er_2O_3 – SiO_2 immiscibility boundary by rescaling data from the Nd_2O_3 – SiO_2 system.

1. Introduction

Oxide glasses have proven useful as host materials for rare-earth ions in solid-state lasers [1–3]. For a number of practical reasons [4] glasses doped with Nd^{3+} have found the widest application. Among other rare-earth-containing materials, Er^{3+} -doped glasses are currently generating much interest as fiber amplifiers in optical communications systems [3]. While the wavelength of laser radiation is primarily determined by the rare-earth ion employed, the glass used as host material has a considerable influence on the spectroscopic properties such as radiative lifetime, fluorescence lifetime, and laser cross-section [5–13] and dictates all of the material's bulk properties. With respect to the latter, vitreous SiO_2 is an outstanding candidate for a laser host

material because of its high transparency from the ultraviolet to the near infrared, its low coefficient of thermal expansion, high mechanical strength, and excellent chemical durability [14,15]. Use of pure vitreous silica as a laser host is hampered, however, by its inability to incorporate rare-earth oxides in amounts greater than a fraction of one mole percent and at the same time provide effective lasing. As the concentration of rare-earth oxide is increased beyond a certain amount, the fluorescence lifetime of the radiation begins to decrease, a phenomenon known as concentration quenching.

Concentration quenching results from interactions among rare-earth ions in the laser. Energy is transferred from one ion to another such that the two ions relax non-radiatively to the ground state [16]. The increase in extent of non-radiative decay with concentration indicates a connection with the relative proximities of rare-earth ions in the material. In addition to the increase in proximity which occurs with increasing concentration, a very strong thermodynamic probability of clustering in silica is expected [17–19] in the light of the extensive phase separation which occurs in its

¹ Present address: Z/47A, IBM Corporation, 1580 Route 52, Hopewell Junction, NY 12533-6531, USA.

Correspondence to: Dr M. Tomozawa, Materials Engineering Department, Rensselaer Polytechnic Institute, Troy, NY 12180-3590, USA. Tel: +1-518 276 6451. Telefax: +1-518 276 8554.

mixtures with rare-earth oxides [20]. Phase separation may be considered an extreme case of clustering and, conversely, clustering a small-scale or incipient phase separation.

There are a number of observations which attest to the close relationship between concentration quenching and phase separation tendency in rare-earth-doped silicate glasses [21]. For example, the extent of concentration quenching in single alkali glasses is observed [5,10] to increase in the order of K₂O, Na₂O, Li₂O which is identical to that of their phase separation tendencies in SiO₂. (The critical temperatures of the K₂O–SiO₂ [22], Na₂O–SiO₂ [23], and Li₂O–SiO₂ [23] immiscibility boundaries are 833, 1108 and 1274 K, respectively.) Furthermore, addition of Al₂O₃ to the pure SiO₂ host material is found to have a beneficial effect on concentration quenching by allowing the homogeneous dissolution of rare-earth oxides in amounts much higher than otherwise possible [19,24,25]. The ability of alumina to suppress immiscibility in oxide melts is well known and of great technological importance in conventional glass manufacture [26]. This effect has also been observed in one of the rare-earth-containing systems of interest here, Nd₂O₃–SiO₂ [27].

In the light of the correlation between concentration quenching and phase separation, it is interesting to examine clustering of rare-earth ions in vitreous silica laser hosts in terms of the inherent immiscibility tendency of rare-earth oxide–SiO₂ melts. As already mentioned, there exist extensive regions of immiscibility in these systems [21]. Ideally, one would like to extrapolate the liquid–liquid coexistence curves to sub-liquidus temperatures in order to obtain an estimate of the low-temperature solubilities of the rare-earth oxides in silica. The uncertainty in the immiscibility boundaries of the rare-earth silicates, which is related to the difficult experimental conditions associated with critical temperatures in the range 2200–2600 K, makes such an extrapolation unreliable, however. Thus it has been necessary to study the phase separation behavior at lower temperatures directly, but this appears to have been done only for the Nd₂O₃–SiO₂ system [27,28]. Because of the difficulties inherent in preparing homogeneous glasses with high silica content, it is

desirable to be able to estimate low-temperature solubilities by theoretical means. It is this possibility that we wish to explore here.

We have recently shown that the critical parameters of the alkali and alkaline-earth silicates [29,30], as well as a variety of other charged particle systems [30] follow certain scaling relations which point to Coulombic interaction as the source of the phase separation. In the next section we will show that the critical parameters of the rare-earth silicates obey the same scaling relations. The demonstration that the rare-earth silicates exist in corresponding states with this much larger class of charged particle systems makes it possible to estimate the composition of the silica-rich side of the immiscibility boundary for uncharacterized systems by rescaling available solubility data. This will be done for the Er₂O₃–SiO₂ system, which is currently of interest for laser amplifier devices.

2. Coulombic origin of phase separation in rare-earth silicates

According to the theory of corresponding states in coulombic fluids [31,32], the critical temperatures, T_c , and critical electrolyte concentrations, n_c , of systems which contain only one type of cation and one type of anion should scale according to the relations

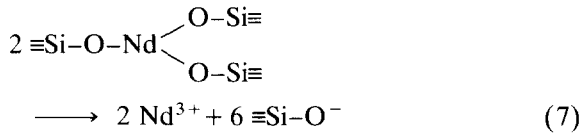
$$T_c = T_c^* |Z_+ Z_-| e_0^2 / 4\pi\epsilon_r \epsilon_0 k a \quad (1)$$

and

$$n_c = n_c^* / \nu a^3. \quad (2)$$

Z_+ is the valency of the cation, Z_- the valency of the anion, and e_0 the magnitude of the electronic charge (1.6×10^{-19} C). ϵ_r is the relative dielectric constant of the medium through which the ions interact, ϵ_0 the permittivity of vacuum (8.85×10^{-12} F/m), k is Boltzmann's constant (1.38×10^{-23} J/K), a the sum of the cationic and anionic radii, and ν the number of ions created per molecule of electrolyte. T_c^* and n_c^* are dimensionless constants which are, in effect, reduced critical parameters.

One might expect in further analogy with the alkali and alkaline-earth silicates that ions are created through the subsequent dissociation reaction



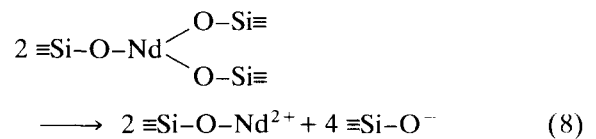
such that two trivalent rare-earth ions and six non-bridging oxygens with effective charge of -1 are created. Thus, $Z_+ = 3$, $Z_- = -1$ and $\nu = 8$. However, if these valencies are used with the relative dielectric constant $\epsilon_r = 3.8$ for SiO₂ and the values of a in table 1 to calculate the reduced critical temperature of the rare-earth silicate systems according to eq. (1), the values obtained are about 50% higher than expected.

This discrepancy seems to indicate that the rare-earth silicates do not exist in corresponding states with systems such as the alkali and alkaline-earth silicates. There is, however, no reason to expect that the origin of phase separation in the rare-earth silicates should be different from that of the other silicates, since all evidence points to the contrary. For example, the general trend observed in table 1 is that the critical temperatures and concentrations increase with decreasing cation-oxygen separation as expected. In addition, alumina acts as a homogenizer in rare-earth silicate melts just as in the alkali- and alkaline-earth-containing systems. Moreover, it is unlikely that the reduced critical temperatures of the rare-earth silicates should be very different from those of the closely related alkali- and alkaline-earth silicates since the latter are almost identical to those of two very different types of systems, the optically excited semiconductors and molten salts [30]. These considerations suggest that the apparent discrepancy is due not to exceptional behavior on the part of the rare-earth silicates but to incorrect identification of the charged particles in these systems.

Phase separation in the optically excited semiconductors, molten salts and binary silicates is caused by the mutual attraction and consequent clustering of positively and negatively charged particles. It is possible, however, for ion clusters

to exist even in the single-phase region of the phase diagram. For example, the degree of dissociation of charged particle systems is only a few per cent near the critical point [30]. Most of the systems previously considered were symmetrical with cations and anions of equal and opposite charge. In such cases, the associated ions exist primarily as neutral pairs, although both charged and uncharged clusters of larger size may also be present. On the other hand, an associated cation-anion pair in an asymmetrical system results in a non-neutral species which can take part in the Coulombic interaction. The extent to which either the charged clusters or free ions determine the phase separation behavior depends on their relative concentrations. It is possible that the formation of highly charged free ions is energetically unfavorable and that the phase separation behavior is dictated instead by ion clusters with lower effective charge. For example, one would expect BiCl₃ to have a very high critical temperature compared with that of NaCl (~ 3400 K) [40] because of the highly charge bismuth ions, while the observed value (1178 K) [41] is considerably lower. It has been suggested on the basis of conductivity measurements [42] that BiCl₃ is almost completely associated at the critical point and that Bi³⁺ ions do not exist as free ions but in combination with Cl⁻ as charged clusters, in support of the above argument. It is likely that a similar situation exists in the rare-earth silicates, resulting in lower than expected critical temperatures.

If, in accordance with the above discussion, it is assumed that the rare-earth ions are unable to dissociate completely from the non-bridging oxygens, then the reduced critical temperatures can be brought into the expected range by requiring that the neodymium ions have an effective charge of $+2$ rather than the value $+3$ corresponding to the dissociation reaction in eq. (7). This situation may be realized by an association of the rare-earth ion with a single non-bridging oxygen:



so that $Z_+ = 2$, $Z_- = -1$ and $\nu = 6$. The reduced critical temperatures and concentrations for the rare-earth silicates calculated using these values of Z_+ , Z_- , ν and eqs. (1), (2) are listed in table 2. The reduced critical temperatures are in the range from 0.064 to 0.071 and the reduced critical concentrations in the range from 0.092 to 0.167, both in excellent agreement with values reported previously [30]. The agreement lends support to eq. (8) as the correct dissociation reaction.

3. Prediction of immiscibility boundaries

The fact that the rare-earth silicates have essentially identical reduced critical parameters suggests that they should also have the same reduced immiscibility boundaries. In other words, if the temperature and composition axes of the various phase diagrams are normalized in terms of the reduced variables

$$T^* = T / (|Z_+ Z_-| e_0^2 / 4\pi \epsilon_r \epsilon_0 k a) \quad (9)$$

and

$$n^* = n \nu a^3, \quad (10)$$

the immiscibility boundaries should coincide. This behavior has in fact been demonstrated [43,44] for a number of binary silicate systems. As a consequence of this corresponding states behavior, it is possible to predict the low-temperature immiscibility boundaries of uncharacterized systems (e.g. Er₂O₃-SiO₂) from that of characterized systems (e.g. Nd₂O₃-SiO₂). Let (n_A, T_A) denote points on the immiscibility boundary of a characterized system A. Then the predicted immiscibility boundary (n_B, T_B) for an uncharacter-

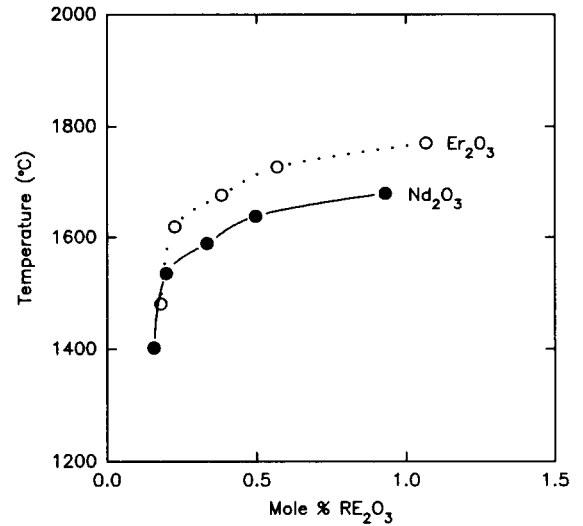


Fig. 1. Immiscibility boundaries of the Nd₂O₃-SiO₂ and Er₂O₃-SiO₂ systems. The boundary of the Nd₂O₃-SiO₂ system is experimental data from ref. [28]. The boundary of the Er₂O₃-SiO₂ system was calculated by rescaling the Nd₂O₃-SiO₂ immiscibility boundary using eqs. (11) and (12).

ized system B may be determined using the relations

$$n_B = (a_A/a_B)^3 n_A \quad (11)$$

and

$$T_B = (a_A/a_B) T_A, \quad (12)$$

where a_A and a_B are the minimum cation-anion separations of the systems A and B, respectively. Figure 1 shows the experimental immiscibility boundary of the Nd₂O₃-SiO₂ system [28] and the boundary predicted for the Er₂O₃-SiO₂ system by applying eqs. (11) and (12) to the data of the former. The rare-earth oxide concentrations were assumed to be simply proportional to mole fraction for the calculations.

4. Discussion

The theoretical prediction of the Er₂O₃-SiO₂ immiscibility boundary is interesting in several respects. First, it appears that the low-temperature solubility of Er₂O₃ in SiO₂ is not very different from that of Nd₂O₃ in SiO₂. As the tempera-

Table 2
Reduced critical parameters of the rare-earth silicates

System	$10^2 T_c^*$	$10^2 n_c^*$
La ₂ O ₃ -SiO ₂	6.81	13.86
Nd ₂ O ₃ -SiO ₂	6.40	14.46
Sm ₂ O ₃ -SiO ₂	6.90	13.56
Gd ₂ O ₃ -SiO ₂	7.10	15.58
Dy ₂ O ₃ -SiO ₂	7.06	16.70
Er ₂ O ₃ -SiO ₂	6.85	16.24
Yb ₂ O ₃ -SiO ₂	6.54	9.20

ture increases, however, incorporation of Er₂O₃ into silica is predicted to be more difficult than that of Nd₂O₃. For example, the solubility of Nd₂O₃ in SiO₂ at 1675°C is more than twice that predicted for Er₂O₃. It is expected from the corresponding states analysis that, with the exception of La₂O₃, the solubility of all lanthanide oxides in silica should be less than that of Nd₂O₃ for temperatures above 1600°C since only La³⁺ is larger than Nd³⁺.

A natural consequence of erbium oxide's lower solubility in silica compared with that of neodymium oxide is that the minimum temperature at which a single phase exists increases for a given rare-earth oxide content. Thus to obtain a homogeneous glass containing 0.75 mol% Nd₂O₃, it is necessary to quench the melt quickly from above 1650°C. For a glass containing the same amount of Er₂O₃, it is predicted from fig. 1 that the quench must be made from above 1750°C.

It should be kept in mind that the prevention of phase separation by means of a rapid quench does not guarantee absence of the clustering which leads to degradation of lasing properties. Clustering will occur even in the single-phase region by means of composition fluctuations. Theoretically, the mean square concentration fluctuation, $\langle \Delta n^2 \rangle$, is related to the immiscibility tendency through the relation [45]

$$\langle \Delta n^2 \rangle = kT/V(\partial\mu/\partial n)_{T,V} \quad (13)$$

where $(\partial\mu/\partial n)_{T,V}$ is the derivative of the chemical potential with respect to concentration at temperature, T , and volume, V . This derivative is zero at the spinodal line, which intersects the immiscibility boundary at the critical point but in general lies below it. The derivative is positive in sign above the spinodal, its magnitude increasing with increasing distance from the spinodal. From this behavior and eq. (13) it follows that the extent of concentration fluctuations increases as the spinodal is approached. Therefore, the clustering which leads to degradation of lasing properties becomes more extensive the closer the glass is brought to the immiscibility boundary. A practical consequence of this behavior for erbium and neodymium silicate glasses with equal silica contents is that the extent of clustering at a given

temperature will always be more severe for the Er-containing glasses because of their inherently greater phase separation tendency.

5. Summary

Fused silica is an attractive material for use as a laser host because of its outstanding physical properties. Unfortunately, the phenomenon of concentration quenching, which leads to degradation of lasing properties, is very severe in the rare-earth silicates. This behavior was discussed in terms of the phase separation tendency of these systems. Corresponding states analysis showed the origin of the immiscibility to be ionic interaction in the manner of the alkali and alkaline-earth silicate systems.

Of the several rare-earth silicates, only the immiscibility of the Nd₂O₃–SiO₂ system has been carefully determined at low temperatures. A method of predicting the immiscibility boundaries of uncharacterized systems based on the principle of corresponding states was presented. The immiscibility boundary of the Er₂O₃–SiO₂ system, which is of current technological interest for use in laser amplifier devices, was predicted as an illustration. The solubility of Er₂O₃ in SiO₂ is expected to be lower than that of Nd₂O₃ except at temperatures below 1600°C where the solubilities are predicted to be approximately equal. The inherently greater tendency for Er-containing glasses to exhibit concentration quenching was discussed in terms of the theory of composition fluctuations.

This research was supported by NSF Materials Research Group Grant DMR-8801004.

References

- [1] E. Snitzer, *Proc. IEEE* 54 (1966) 1249.
- [2] C.G. Young, *Proc. IEEE* 57 (1969) 1267.
- [3] Y. Asahara, *J. Ceram. Soc. Japan* 99 (1991) 903.
- [4] D.W. Harper, *Phys. Chem. Glasses* 5 (1964) 11.
- [5] C. Hirayama and D.W. Lewis, *Phys. Chem. Glasses* 5 (1964) 44.
- [6] K. Hauptmanova, J. Pantoflíček and K. Patek, *Phys. Status Solidi* 9 (1965) 525.

- [7] C. Hirayama, *Phys. Chem. Glasses* 7 (1966) 52.
- [8] C. Hirayama, F.E. Camp, N.T. Melamed and K.B. Steinbruegge, *J. Non-Cryst. Solids* 6 (1971) 342.
- [9] P.H. Sarkies, J.N. Sandoe and S. Parke, *J. Phys. D4* (1971) 1642.
- [10] T. Komiyama, *Yogyo-Kyokai-Shi* 82 (1974) 637.
- [11] W.F. Krupke, *IEEE J. Quantum Electron.* QE-10 (1974) 450.
- [12] H.G. Lipson, J.R. Buckmelter and C.O. Dugger, *J. Non-Cryst. Solids* 17 (1975) 1.
- [13] R.R. Jacobs and M.J. Weber, *IEEE J. Quantum Electron.* QE-12 (1976) 102.
- [14] J. Stone and C.A. Burrus, *Appl. Phys. Lett.* 23 (1973) 388.
- [15] H. Namikawa, K. Arai, K. Kumata, Y. Ishii and H. Tanaka, *Jpn. J. Appl. Phys.* 21 (1982) L360.
- [16] L.G. van Uitert and S. Iida, *J. Chem. Phys.* 37 (1962) 986.
- [17] A.V. Amosov, V.K. Zakharov, G.T. Petrovskii, T.I. Prokhorova and D.M. Yudin, *J. Appl. Spectrosc.* 11 (1969) 1261.
- [18] E.I. Galant, Yu.N. Kondrat'ev, A.K. Przhnevskii, T.I. Prokhorova, M.N. Tolstoi and V.N. Shapovalov, *JETP Lett.* 18 (1973) 372.
- [19] K. Arai, H. Namikawa, K. Kumata, Y. Ishii, H. Tanaka and I. Iida, *Jpn. J. Appl. Phys.* 22 (1983) L397.
- [20] M.K. Reser, ed., *Phase Diagrams for Ceramists 1969 Supplement* (American Ceramic Society, Columbus, OH, 1969).
- [21] A.V. Dmitryuk, G.O. Karapetyan and L.V. Maksimov, *J. Appl. Spectrosc.* 22 (1975) 119.
- [22] Y. Kawamoto and M. Tomozawa, *J. Am. Ceram. Soc.* 64 (1981) 289.
- [23] W. Haller, D.H. Blackburn and J.H. Simmons, *J. Am. Ceram. Soc.* 57 (1974) 120.
- [24] Y. Ishii, H. Namikawa, K. Arai, A. Noda, A. Negishi and T. Handa, *Yogyo-Kyokai-Shi* 93 (1985) 22.
- [25] E.I. Gallant, B.S. Gorovaya, E.L. Demskaya, Yu.N. Kondrat'ev, M.P. Golubovskaya, A.K. Przhnevskii, T.I. Prokhorova and M.N. Tolstoi, *Fiz. Khim. Stekla* 2 (1976) 438.
- [26] E.M. Levin, in: *Phase Diagrams*, Vol. 3, ed. A.M. Alper (Academic Press, New York, 1970) p. 143.
- [27] F.Ya. Galakhov, B.S. Gorovaya, E.L. Demskaya and T.I. Prokhorova, *Fiz. Khim. Stekla* 6 (1980) 46.
- [28] F.Ya. Galakhov, E.L. Demskaya, T.I. Prokhorova and M.V. Rogozovets, *Fiz. Khim. Stekla* 1 (1975) 52.
- [29] V. McGahay and M. Tomozawa, *J. Non-Cryst. Solids* 109 (1989) 27.
- [30] V. McGahay and M. Tomozawa, *J. Chem. Phys.* 97 (1992) 2609.
- [31] H.L. Friedman and B. Larsen, *J. Chem. Phys.* 70 (1979) 92.
- [32] K.S. Pitzer, *J. Phys. Chem.* 88 (1984) 2689.
- [33] N.A. Toropov, I.A. Bondar and F.Ya. Galakhov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* No. 5 (1961) 740.
- [34] V.B.M. Hageman and H.A.J. Oonk, *Phys. Chem. Glasses* 27 (1986) 194.
- [35] N.A. Toropov and I.A. Bondar, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* No. 8 (1961) 1372.
- [36] N.A. Toropov, F.Ya. Galakhov and S.F. Konvalova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* (4) (1960) 541.
- [37] N.A. Toropov, F.Ya. Galakhov and S.F. Konvalova, *Izv. Akad. Nauk SSSR, Ser. Khim.* (8) (1961) 1368.
- [38] N.A. Toropov, F.Ya. Galakhov and S.F. Konvalova, *Izv. Akad. Nauk SSSR, Ser. Khim.* (8) (1961) 1370.
- [39] J.F. Shackelford, *Introduction to Materials Science for Engineers*, 2nd Ed. (Macmillan, New York, 1988).
- [40] A.D. Kirshenbaum, J.A. Cahill, P.J. McGonigal and A.V. Grosse, *J. Inorg. Nucl. Chem.* 24 (1962) 1287.
- [41] M. Buback and E.U. Franck, *Ber. Bunsenges, Phys. Chem.* 76 (1972) 350; 77 (1973) 1074.
- [42] G. Treiber and K. Tödheide, *Ber. Bunsenges, Phys. Chem.* 77 (1973) 540.
- [43] Y. Kawamoto and M. Tomozawa, *Phys. Chem. Glasses* 22 (1981) 11.
- [44] Ding Yong and Jiang Zhonghong, *Phys. Chem. Glasses* 30 (1989) 202.
- [45] L.D. Landau and E.M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, MA, 1969).