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Electrical Conduction and Corrosion Processes in Fast Ion Conducting Glasses

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ELECTRICAL CONDUCTION AND CORROSION PROCESSES IN FAST ION CONDUCTING GLASSES

Final Report

January 1990

by

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INTRODUCTION

Fast ion conductors (FIC) are of growing interest as components of advanced electrochemical energy conversion devices.[1] Amorphous FICs, known to exhibit a number of attractive characteristics,[1] including ease of fabrication and lack of grain boundaries, await extensive commercial application due to their often poor electrochemical stability. Our laboratory has focused, in the past, on glasses in the system Li_2O-LiCl-B_2O_3[2-4] as well as Na and K analogs.[5,6] Lithium chloride was found to markedly enhance the Li ion conductivity but also to degrade the chemical stability of glasses in contact with molten lithium.[7] Based on thermodynamic considerations, CaO additives are expected to improve the durability of such glasses. In an earlier preliminary study, we examined the influence of CaO on conduction in Li_2O-B_2O_3 based glasses[8] and found that it lowered the ionic conductivity. During this contract period, we examined lithium borate glasses with much higher CaO contents to which we simultaneously added LiCl in an attempt to maintain the conductivity at high levels. Below, we summarize the results of these studies and demonstrate that one can indeed prepare glasses with reasonably high Li ion conductivities even with substantial additions of CaO.

We have also completed both static and dynamic studies of the stability of these glasses in contact with lithium. We find that CaO additions do substantially decrease the growth rate of the passive reaction layers which form upon the contact of molten lithium with these glasses. We find that this is due to a

decrease in chemical diffusion through the layer which depends on minority electronic carriers. These findings are also discussed below.

EXPERIMENTAL METHODS

The two glass systems studied included the "boracites" 0.378 $((1-x-y)Li_2O + x(LiCl)_2 + yCaO)\cdot 0.622\ B_2O_3$ with x=0.25 and 0.415 designated as LCB15 and LCB25, respectively and the metaborates $0.49\ ((1-x-y)Li_2O + x(LiCl)_2 + yCaO)\cdot 0.49\ B_2O_3\cdot 0.02\ Al_2O_3$ with x=0.15 and 0.4 designated as LCM15 and LCM40, respectively. The CaO content varied between the limits $0.00 < y < 0.30$ while the O/B ratio was maintained constant, in an attempt to retain similar glass framework structures and thus isolate the effect of CaO doping on conductivity. Specimens were melted between 950-1050°C for 20-25 minutes and quenched between steel plates followed by annealing for 1.5 hours at T_g-75°C.

Conductivity measurements were performed on specimens with sputtered Pt electrodes as a function of temperature in a furnace chamber flushed with dry N_2 by complex impedance techniques. A representative plot is shown in Fig. 1. The bulk resistance is taken as the intercept of the high frequency semicircle with the real axis. Parts of a second semicircle, representative of interfacial impedance, are observed at lower frequencies.

Density measurements were made by a fluid displacement technique using a picnometer or adapting the ASTM method.[9] Toluene was substituted for the standard fluids due to the hygroscopic nature of the glasses.

Glass transition temperatures, T_g, were determined with the aid of a Perkin-Elmer DSC 4 Differential Scanning Calorimeter at temperatures between 250 and 500°C scanned at a heating rate of 10°K/min.

The chemical durability of glasses were studied by submerging glass specimens into a molten lithium bath for controlled periods of time and temperature. After removal from the lithium, the specimens were submerged in isopropyl alcohol to remove the lithium coating and cross sections were obtained by breaking the samples with a diamond tip while submerged in oil. The thickness of the reaction layers were determined by optical microscopy and SEM. The corrosion layers were also examined by x-ray diffraction.

Coulometric titration experiments were run on cells of the type LiAl/glass/Sn/glass/LiAl, in which the left-hand side of the cell is used to titrate Li into the initially pure Sn electrode and the right-hand side of the cell is used to monitor the change of lithium activity in the Li-Sn mixture with time by monitoring the Nernst emf generated across the right-hand glass electrolyte. The right-hand two-phase LiAl electrode is used as a reference electrode with well defined lithium activity. Barsoum and Tuller[10] showed that the time lag which develops between the predicted time to reach a predetermined lithium activity, assuming a faradaic efficiency of one, and the experimentally observed time which is longer due to lithium reaction with the glass, can be used to determine the chemical diffusivity in the reaction layer. For "short" times[10] the expression is given by

$$D = \frac{\pi}{t} \left(\frac{3 \delta \Delta t}{4t} \right)^2 \qquad (1)$$

where t is the time of the experiment and δ is the thickness of the tin electrode.

RESULTS

Physical Properties

The bulk dc conductivities of the glasses, obtained via a complex impedance analysis, are shown plotted versus reciprocal temperature in Fig. 2, 3, 4, and 5. The conductivities are observed to decrease monotonically with increasing CaO content in all cases.

The "metaborate" glasses are more conductive than the "boracite" glasses, which is a reflection of the higher Li ionic conductivity at higher Li_2O content. In each system, the glass series with the higher concentration of LiCl has the higher lithium ionic conductivity. These results are summarized in Fig. 6 as log σT at 150°C as a function of CaO.

As Fig. 7 demonstrates, the trend of decreasing conductivity with increasing CaO is tied to a near linear increase in activation energy, E_A, with CaO substitution for Li_2O. On the other hand, increasing LiCl content lowers E_A. The pre-exponential term in the conductivity appears to be little influenced by either substitution as illustrated in Fig. 8.

Based on the temperature and composition dependencies of the lithium ion conductivities in these systems, we observed three

important trends. First, CaO induces a systematic increase in activation energy, that being the major source of the decrease in conductivity with CaO addition. Second, within a given series, increasing LiCl content counteracts the affect of CaO by lowering the activation energy. Third, glasses with a lower fraction of network formers exhibit the lower activation energy and higher conductivity.

The measured density dependence on CaO additions for the four glass systems under study are shown in Fig. 9. The glasses increase in density in a near linear fashion with increasing y. In each system, Cl additions result in an apparent density decrease and the less-dense glasses have the higher conductivities, which seems to mirror the trend in activation energy reported above.

The dependences of glass transition temperature on y are reported in Figs. 10 and 11. Except for a small anomaly at low y in the boracites, T_g increases with increasing y in all cases.

Chemical Stability Studies

Static corrosion of the LCB25 series of glasses in molten lithium were examined at several temperatures. Fig. 12 shows the product layer thickness at 352°C after 25 hours as a function of CaO content. Following a small initial increase in thickness at y=0.05, the thickness of the reaction layer decreases monotonically with y up to y=0.3. In Fig. 13, we observe that the product layer thickness increases linearly with $t^{1/2}$ consistent with a parabolic growth mechanism found earlier by

Velez et al.[7] for CaO-free glasses. The parabolic rate constants for y=0 and 0.3 evaluated at 352 and 400°C are plotted versus 1000/T in Fig. 14. The apparent activation energy of 0.91 eV for y=0 is in close agreement with the value found earlier by Velez et al.[7] which was based on more extensive data. The corresponding activation energy for y=0.3 is only slightly larger at 0.96 eV. X-ray analysis of the reaction layer showed it to contain a mixture of $LiBO_2$, Li_2O and $Li_4B_7O_{12}Cl$.

Coulometric titration runs using the double-cell arrangement described above were performed at 344°C for LCB25 glasses as a function of y. Fig. 15 shows a typical EMF vs. relative titration time plot. The time represented by t=1 is the theoretical time it would take to reach an activity of lithium which corresponds to the liquidus composition in the Li-Sn system.[11] A value of t > 1 implies that some of the titrated lithium is consumed in the reaction layer. Fig. 16 shows, large error bars notwithstanding, that t_{rel} decreases systematically, for y values greater than 0.1, in concert with the above reported static results.

DISCUSSION

Ionic Conductivity

As in the ternary system, LiCl markedly increases the ionic conductivity in the quaternary system under investigation here. Thus, LCM40 with y=0.20 has nearly the same conductivity as LCM15

with y=0.05 (See Fig. 6). Thus, LiCl is observed to widen the tolerance to CaO additions which, as we have observed, leads to enhanced chemical stability.

It is of interest to consider the source of the depressing effect of CaO on conductivity. Obviously, the decreasing conductivity is linked to a corresponding increase in activation energy. Based upon our previous studies,[12] we might expect this to be a result of an increase in the strain energy component of the migration energy. To support such a hypothesis, we would expect a decrease in effective free volume for the carriers and/or an increase in the glass transition temperature. This does seem to be the case for the boracite system (See Fig. 17). At least from the standpoint of free volume, there appears to be an inverse relationship (See Fig. 17) in the metaborate system. It may be that the total free interstitial volume does not effectively represent the microscopic "doorway" size which is the key to ion migration,[12] and/or the change in modulus is the predominant factor influencing the migration energy.

It is of interest to briefly consider other possibilities. According to the weak electrolyte model,[13] the decrease in conductivity would be tied to a decrease in carrier density rather than mobility. Under those conditions, we would expect to see a variation in σ_o proportional to the square root of the concentration of Li ions associated with negative centers in the glass, i.e. BO_4^-, Cl^-, non-bridging oxygens.[14] Instead, we find a nearly constant σ_o. Minami et al.[15] emphasized that the key feature in such glasses is the fraction of alkali ions associated

with Cl. Since we maintain the LiCl molar concentration constant in each system, this would not explain the increase in E_A with CaO.

Another possibility is that Ca ions act as trapping sites for the more mobile Li ions. This would appear to be in concert with observations in mixed-alkali[16] and other mixed-cations[17] glasses. The source of the mixed-alkali effect however, remains controversial. We expect to examine these fundamental issues in greater detail in the near future.

Chemical Stability

Phenomenologically, we find that the parabolic rate constant characterizing reaction layer growth of LCB25 glasses in contact with molten lithium decreases with y. This is presumably, in large part, determined by the chemical diffusivity in the reaction layer. Since we find the EMF plateaus in the titration experiments to conform with predicted values,[11] this proves that the reaction layers remain predominantly ionic conductors. Consequently, mass transport through the layer is limited by diffusion of the minority electronic defect.

Following Eq. (1), values for D are derived as a function of y and are plotted in Fig. 18. As expected, D decreases with y. In the following, we propose a mechanism for this decrease.

Consider the defect reactions summarized in Table 1, which are expected to apply in the reaction layer. From the reduction reaction, we can readily observe that

$$\sigma_{el} \approx n = (K_R a_{Li}/[Li_i^{\bullet}]) \qquad (2)$$

For heavy Ca doping, we can expect the neutrality equation to be approximated by

$$[V_{Li}'] = [Ca_{Li}^{\bullet}] \quad (3)$$

which, together with the frenkel product, results in

$$n = (K_R/K_F)a_{Li}[Ca_{Li}^{\bullet}] \quad (4)$$

The hole density is correspondingly given by

$$p = (K_e K_F/K_R)a_{Li}^{-1}[Ca_{Li}^{\bullet}]^{-1} \quad (5)$$

Since p decreases with increasing Ca, we propose that the key minority carrier in the reaction layer is, in fact, the electron hole. The decrease in diffusivity is then understood on the basis of the Ca acting as a donor impurity in the reaction layer. Further doping experiments would be useful in confirming this model.

CONCLUSIONS

Ca oxide additions to Li_2O-LiCl-B_2O_3 fast ion conducting glasses do lead to enhanced stability in lithium environments. To date, we have demonstrated, at least for "boracite"-like glasses, that the effect is primarily kinetic. The Ca additions apparently depress the minority hole concentration in the ionic reaction layer leading to a decreased chemical diffusivity. Although Ca additions do tend to depress the Li ion conductivity, relatively high values of conductivity can be retained in such systems by simultaneous additions of LiCl. The selection of optimum compositions must await further studies.

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REFERENCES

1. H.L. Tuller and P.K. Moon, Mat. Sc. Eng. B 1 171-91 (1988).

2. D. P. Button, R. P. Tandon, H. L. Tuller and D. R. Uhlmann, "Fast Li^+ Ion Conduction in Chloro-Borate Glasses," J. Non-Cryst. Solids 42, 297-306 (1980).

3. D. P. Button, R. P. Tandon, H. L. Tuller and D. R. Uhlmann, "Fast Li^+ Ion Conductance in Chloroborate Glasses, II: Diborates and Metaborates," Solid State Ionics 5, (1981), pp. 655-658.

4. D.P. Button, L.S. Mason, H.L. Tuller, and D.R. Uhlmann, "Structural Disorder and Enhanced Ion Transport in Amorphous Conductors," Solid State Ionics, 9 & 10, (1983), pp. 585-592.

5. F.A. Fusco and H.L. Tuller, "Effects of Halide Substitutions in Potassium Haloborate Glasses, in Proc. of NATO ASI on The Science & Technology of Fast Ion Conductors, Erice, Italy, July 1-15, 1987, eds. H.L. Tuller, and M. Balkanski, Plenum Press, in press.

6. H.L. Tuller and D.P. Button, "The Role of Structure in Fast Ion Conducting Glasses," in Transport-Structure Relations in Fast Ion and Mixed Conductors, eds. F.W. Poulson, N. Hessel-Anderson, K. Clausen, S. Skaarup, O.T. Sorensen, Riso National Lab, Roskilde, Denmark (1985), pp. 119-137.

7. M. H. Velez, H. L. Tuller and D. R. Uhlmann, "Chemical Durability of Lithium Borate Glasses," J. Non-Cryst. Sol. 49, (1982) pp. 351-362.

8. F.A. Fusco, H.L. Tuller, and D.R. Uhlmann, "Structure-Transport Relationships in Fast Ion Conducting Alkali Borate Glasses," in Defect Properties and Processing of High-Technology Nonmetallic Materials, (MRS Symp. Proc., Vol. 60) eds. Y. Chen, W.D. Kingery and R.J. Stokes, Pittsburgh, PA (1986), pp. 251-258.

9. ASTM, "Standard Test Method for Density of Glass by Buoyancy," Vol. 15:02 (1983).

10. M.W. Barsoum and H.L. Tuller, "In-Situ Determination of the Kinetics of Reaction Between Lithium and Fast Ion Conducting Lithium Borate Glasses," Solid State Ionics 18 & 19, (1986), pp. 388-392.

11. M.W. Barsoum and H.L. Tuller, "Thermodynamics of Molten Li-Sn Alloys," Met. Trans. 19A 637-44 (1988).

12. F.A. Fusco, H.L. Tuller, and D.P. Button, "Lithium, Sodium, and Potassium Transport in Fast Ion Conducting Glasses: Trends and Models," in Proc. Symp. Electro-Ceramics and Solid State Ionics, eds. H.L. Tuller and D.M. Smyth, The Electrochemical Society, Pennington, NJ, 1988, pp. 167-78.

13. D. Ravaine and H.L. Souquet, Phys. Chem. Glasses, 18 27 (1977).

14. H.L. Tuller, "Amorphous Fast Ion Conductors," in Proc. of NATO ASI on The Science and Technology of Fast Ion Conductors, Erice, Italy, July 1-15, 1987, eds. H.L. Tuller and M. Balkanski, Plenum Press, in press.

15. T. Minami, T. Shimizu, and M. Tanaka, Sol. St. Ionics, 9&10 577 (1988).

16. K. Matusita, S. Takayama, and S. Sakka, J. Non-Cryst. Solids 40 149-158 (1980).

17. S. Sakka, K. Matusita, and K. Kamitya, Phys. Chem. Glasses 20 25 (1979).

PUBLICATIONS RESULTING FROM THIS PROGRAM

1. F.A. Fusco, M. Massot, M. Oueslati, E. Haro, H.L. Tuller, and M. Balkanski, "Structural Changes in Fast Ion Conducting Chloride Doped Potassium Borate Glasses," Solid State Ionics, (MRS Symp. Proc. Vol. 135), Eds. G. Nazri, R.A. Huggins, and D.F. Shriver, Pittsburgh, PA (1989), pp. 189-198.

2. F.A. Fusco, "Effects of Halide Substitutions in Potassium Haloborate Glasses, in Science & Technology of Fast Ion Conductors, eds. H.L. Tuller, and M. Balkanski, Plenum Press, (1989), pp. 321-26.

3. H.L. Tuller, "Amorphous Fast Ion Conductors," in Science and Technology of Fast Ion Conductors, eds. H.L. Tuller and M. Balkanski, Plenum Press, New York, (1989), pp. 51-87. Invited review.

4. F.A. Fusco and H.L. Tuller, "Fast Ion Transport in Glasses," in Superionic Solids and Solid Electrolytes-Recent Trends, eds. A.L. Laskar and S. Chandra, Academic Press, San Diego, CA (1989), pp. 43-110. Invited Chapter.

5. H.L. Tuller, "Some Future Trends in Solid State Ionics," in Science and Technology of Fast Ion Conductors, eds. H.L. Tuller and M. Balkanski, Plenum Press, (1989), pp. 303-06.

6. S.L. Shue and H.L. Tuller, "Lithium Ion Transport in Li_2O-LiCl-CaO-B_2O_3 Glasses," in Proc. Int'l Conf. on Sol. St. Ionics, Hakone, Japan, Nov. 5-11, 1989, to be published in J. Sol. St. Ionics.

PREVIOUS YEARS

7. H. L. Tuller, D. P. Button and D. R. Uhlmann, "Fast Ion Transport in Oxide Glasses," J. Non-Cryst. Solids 40, 93-118 (1980).

8. D. P. Button, R. P. Tandon, H. L. Tuller and D. R. Uhlmann, "Fast Li^+ Ion Conduction in Chloro-Borate Glasses," J. Non-Cryst. Solids 42, 297-306 (1980).

9. M. W. Barsoum, M. Velez, H. L. Tuller and D. R. Uhlmann, "Reactions at Alkali Metal - Glass Interfaces," in Surfaces and Interfaces in Ceramic and Ceramic Metal Systems, eds. J. Pask and A. Evans, Plenum Press, NY (1981), pp. 567-577.

10. D. P. Button, R. P. Tandon, H. L. Tuller and D. R. Uhlmann, "Fast Li^+ Ion Conductance in Chloroborate Glasses, II: Diborates and Metaborates," Solid State Ionics 5, (1981), pp. 655-658.

11. M. H. Velez, H. L. Tuller and D. R. Uhlmann, "Chemical Durability of Lithium Borate Glasses," J. Non-Cryst. Sol. 49, (1982) pp. 351-362.

12. M.H. Velez, D.R. Uhlmann and H.L. Tuller, "Chemical Durability of Glasses," Latin American Journal of Metallurgy and Materials, 2, (1982), pp. 3-15, Invited Paper.

13. D. P. Button, R. P. Tandon, C. King, M. H. Velez, H. L. Tuller and D. R. Uhlmann, "Insights into the Structure of Alkali Borate Glasses," J. Non-Cryst. Sol. 49, (1982) pp. 129-142.

14. D.R. Uhlmann, H.L. Tuller, D.P. Button, And M.H. Velez, "Solid Electrolyte Batteries and Fast Ion Conducting Glasses; Factors Affecting a Proposed Merger," Wiss. Ztschr. Friedrich-Schiller-Univ. Jena, Math-Naturwiss.R., 32, (1983), pp. 285-300.

15. D.P. Button, L.S. Mason, H.L. Tuller, and D.R. Uhlmann, "Structural Disorder and Enhanced Ion Transport in Amorphous Conductors," Solid State Ionics, 9 & 10, (1983), pp. 585-592.

16. D.P. Button, P.K. Moon, H.L. Tuller, and D.R. Uhlmann, "Structure-Transport Relationship in Oxide Glasses: Fast Ion Transport in Alkali Borate Glasses," Glastechnische Berichte, 56K, (1983), pp. 856-861.

17. H.L. Tuller and M. Barsoum, "Glass Solid Electrolytes Past, Present, and Near Future--the Year 2004," J Non-Cryst. Solids, 73, (1985), pp. 331-350, Invited Review.

18. H.L. Tuller and M.W. Barsoum, "Electrolytic Control and Detection of Ionic Species Using Fast Ion Conducting Glasses," in Proc. 1985 Int'l Conf. on Solid State Sensors and Actuators--Transducers '85, I.E.E.E., Piscataway, NJ (1985), pp. 256-59, Invited Paper.

19. H.L. Tuller and D.P. Button, "The Role of Structure in Fast Ion Conducting Glasses," in Transport-Structure Relations in Fast Ion and Mixed Conductors, eds. F.W. Poulson, N. Hessel-Anderson, K. Clausen, S. Skaarup, O.T. Sorensen, Riso National Lab, Roskilde, Denmark (1985), pp. 119-137, Invited Review.

20. M.W. Barsoum and H.L. Tuller, "In-Situ Determination of the Kinetics of Reaction Between Lithium and Fast Ion Conducting Lithium Borate Glasses," Solid State Ionics 18 & 19, (1986), pp. 388-392.

21. F.A. Fusco, H.L. Tuller, and D.R. Uhlmann, "Structure-Transport Relationships in Fast Ion Conducting Alkali Borate Glasses," in Defect Properties and Processing of High-Technology Nonmetallic Materials, (MRS Symp. Proc., Vol. 60) eds. Y. Chen, W.D. Kingery and R.J. Stokes, Pittsburgh, PA (1986), pp. 251-258.

22. M.W. Barsoum and H.L. Tuller, "The Reaction Kinetics and Electrochemical Stability of Lithium Fast Ion Conducting Glasses." In Proceedings: DOE/EPRI Beta Sodium-Sulfur Battery Workshop VI. (Ceramatec Report SPEC 8601), eds. J.C. Gordon and R.S. Gordon, September 1986, pp. 9-52 to 9-60.

23. F.A. Fusco, H.L. Tuller, and D.P. Button, "Lithium, Sodium, and Potassium Transport in Fast Ion Conducting Glasses: Trends and Models," in Proc. Symp. Electro-Ceramics and Solid State Ionics, eds. H.L. Tuller and D.M. Smyth, The Electrochemical Society, Pennington, NJ, 1988, pp. 167-78.

24. M.W. Barsoum and H.L. Tuller, "Thermodynamics of Molten Li-Sn Alloys," Met. Trans. 19A 637-44 (1988).

25. H.L. Tuller and P.K. Moon, "Fast Ion Conductors - Future Trends," Mat. Sc. Eng. B, B1 171-91 (1988), invited review.

Table I: Defect Relations: Donor-Doped Li_2O

Frenkel:	$Li_{Li} \longrightarrow Li_i^{\bullet} + V'_{Li}$;	$K_F = [Li_i^{\bullet}][V'_{Li}]$
Reduction:	$Li \longrightarrow Li_i^{\bullet} + e'$;	$K_R = \frac{[Li_i^{\bullet}]n}{a_{Li}}$
Electron-hole:	$null \longrightarrow e' + h^{\bullet}$;	$K_e = np$
Impurity:	$CaO \xrightarrow{Li_2O} Ca_{Li}^{\bullet} + V'_{Li} + O_o$;	
Electroneutrality	$n + [V'_{Li}] = p + [Li_i^{\bullet}] + [Ca_{Li}^{\bullet}]$	

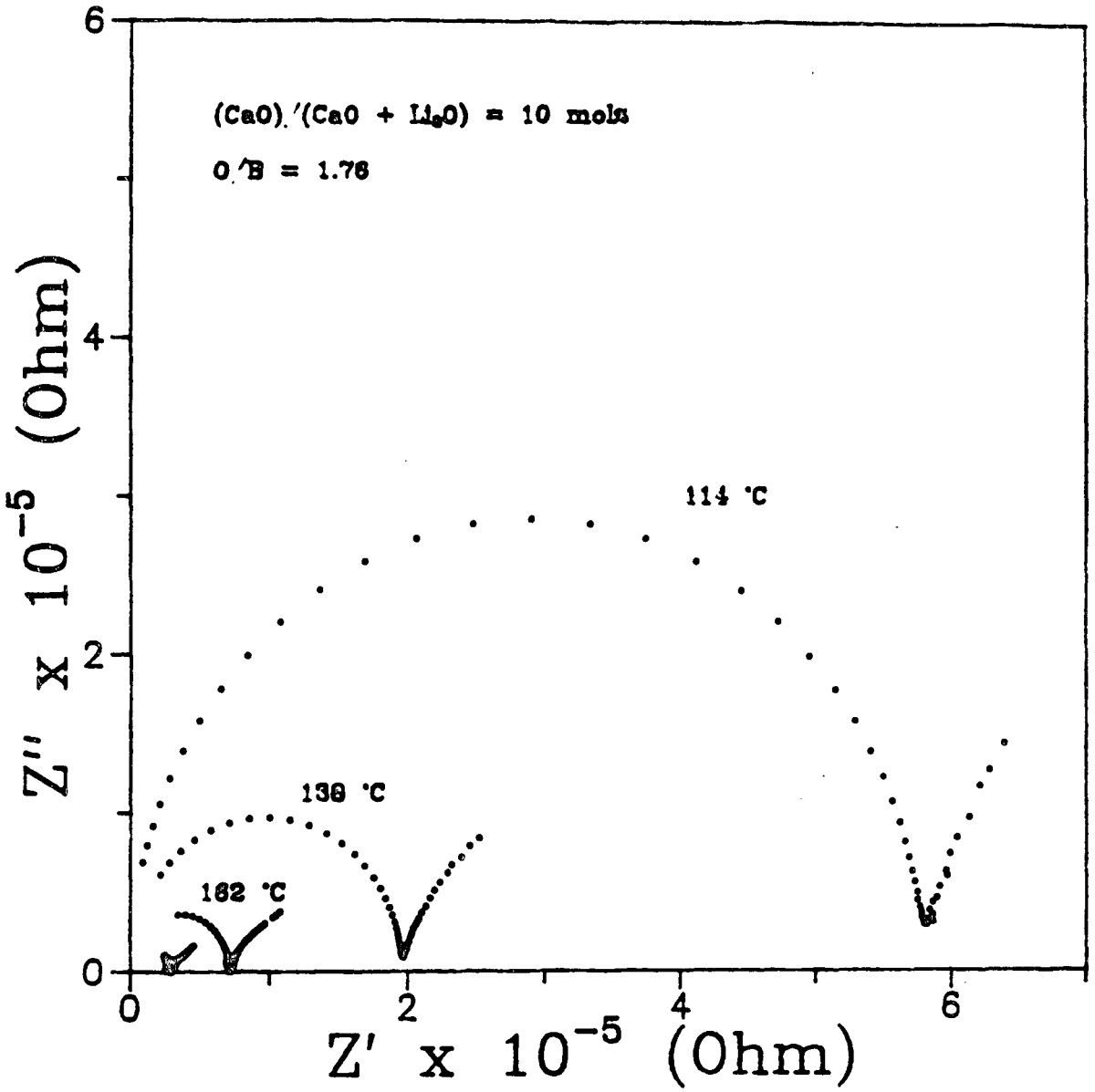

Figure 1: Complex impedance spectra are plotted for LCB15 at different temperatures

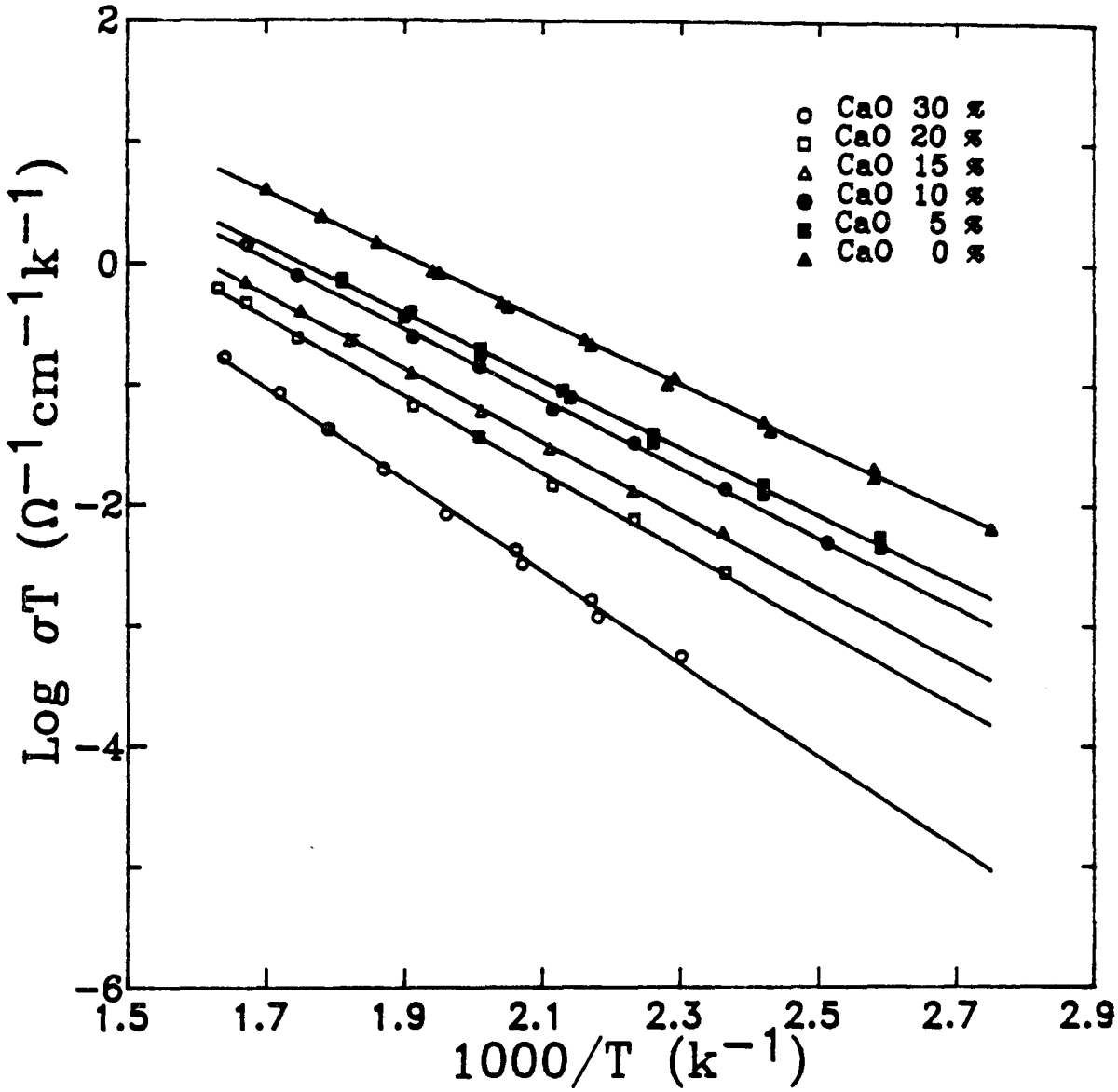

Figure 2: Arrhenius plot of σ for lithium boracite glasses of LCB25.

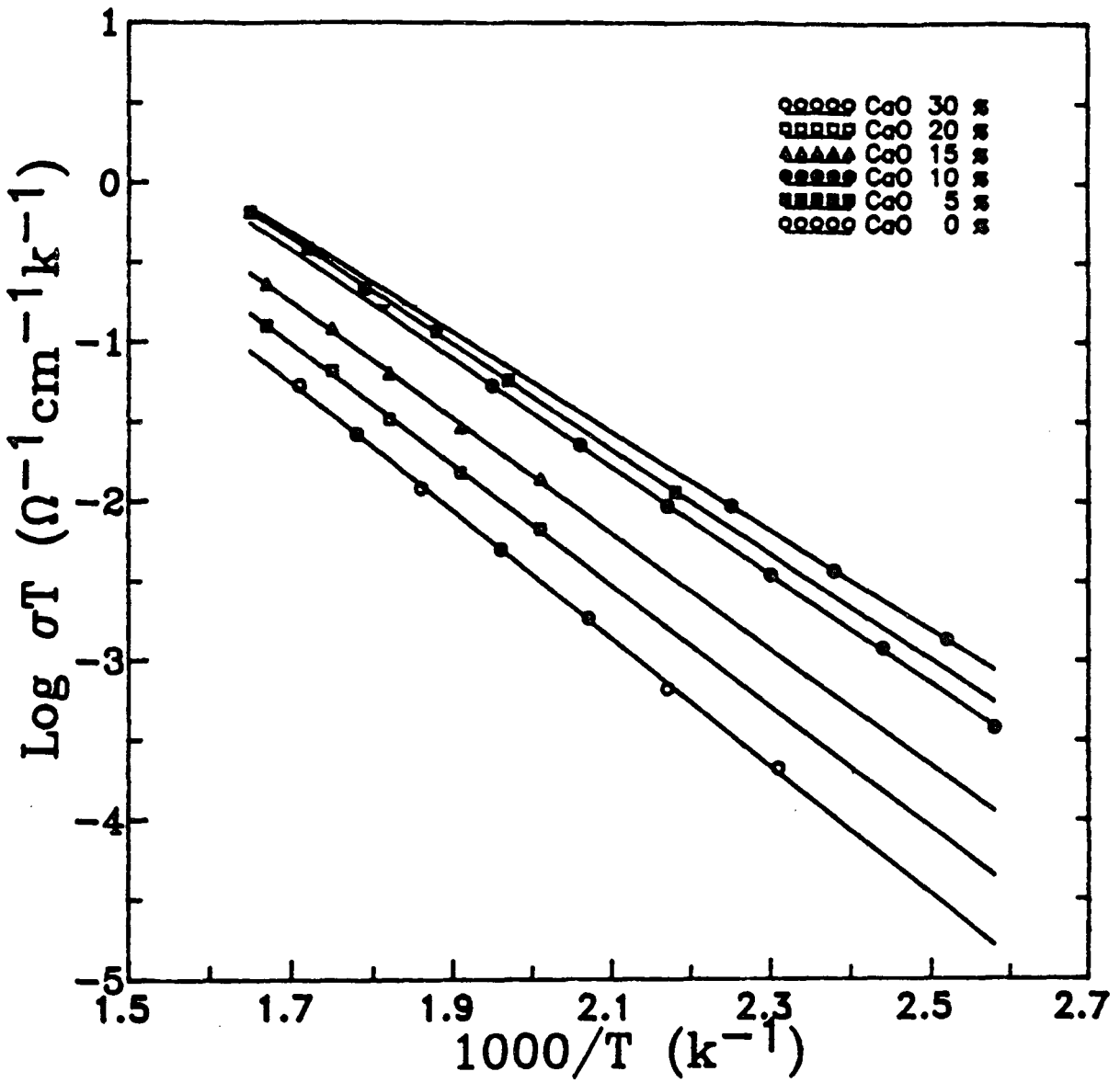

Figure 3: Arrhenius plot of σ for lithium boracite glasses of LCB15.

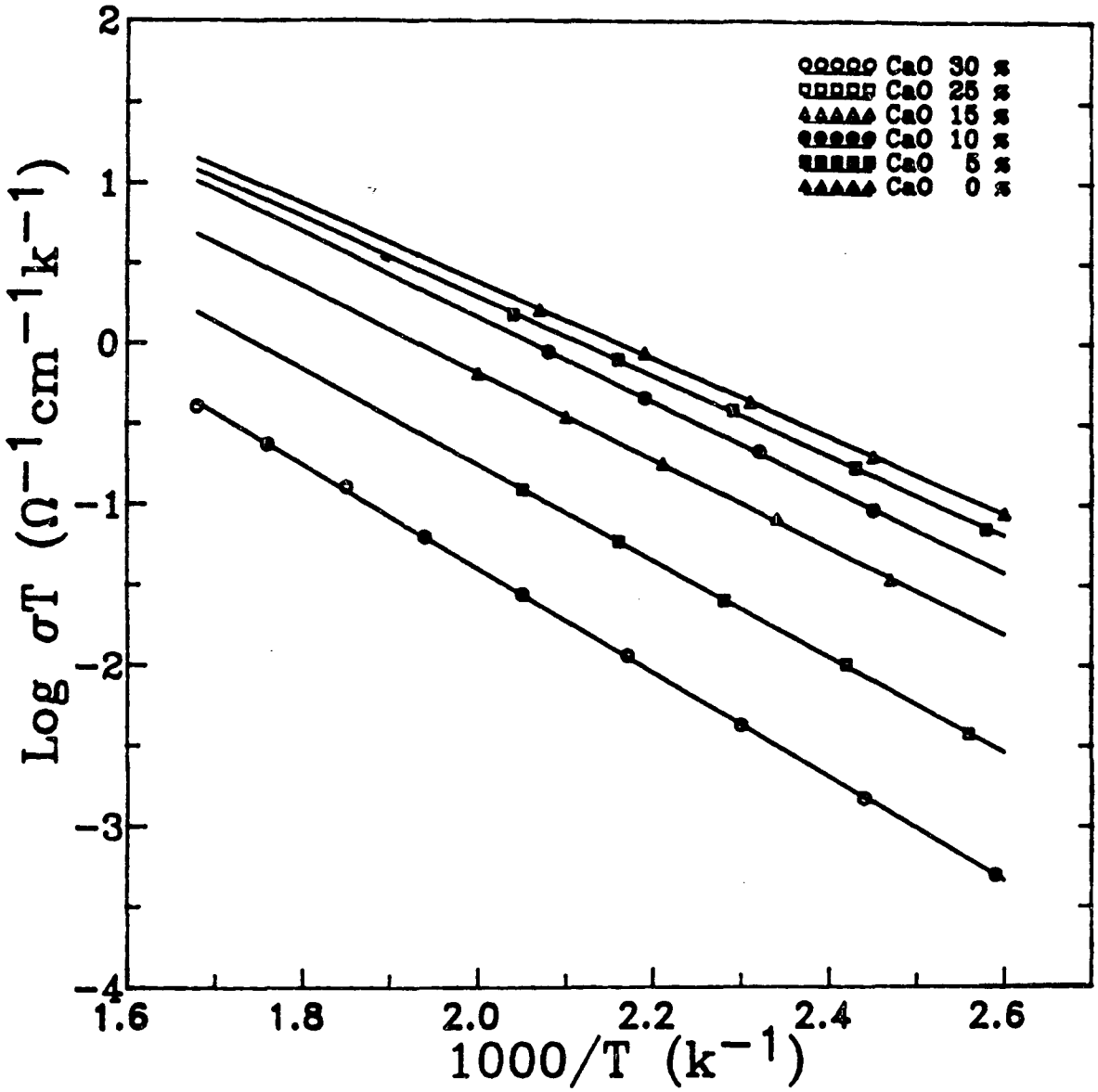

Figure 4: Arrhenius plot of σ for lithium boracite glasses of LCM40.

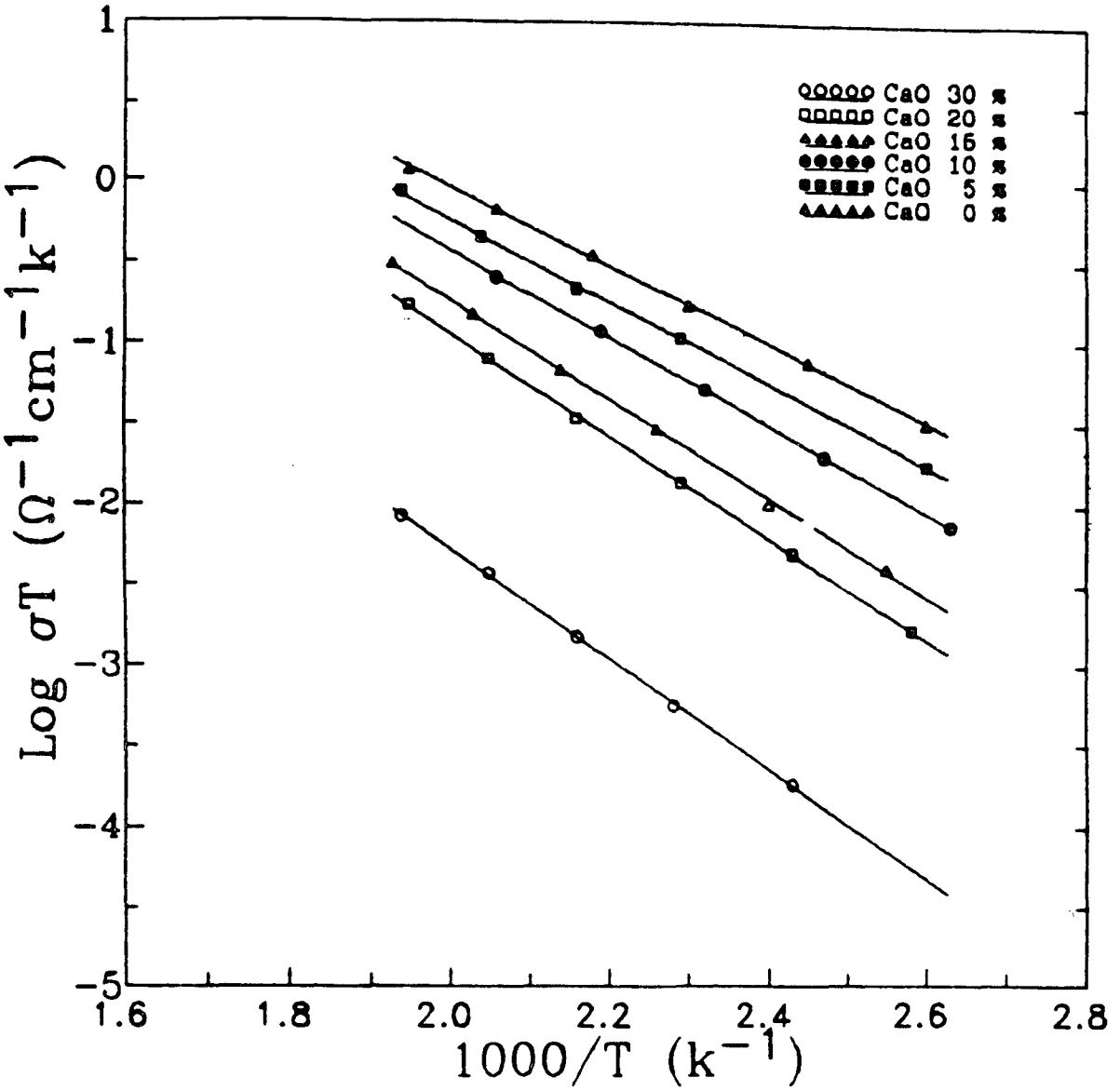

Figure 5: Arrhenius plot of σ for lithium boracite glasses of LCM15.

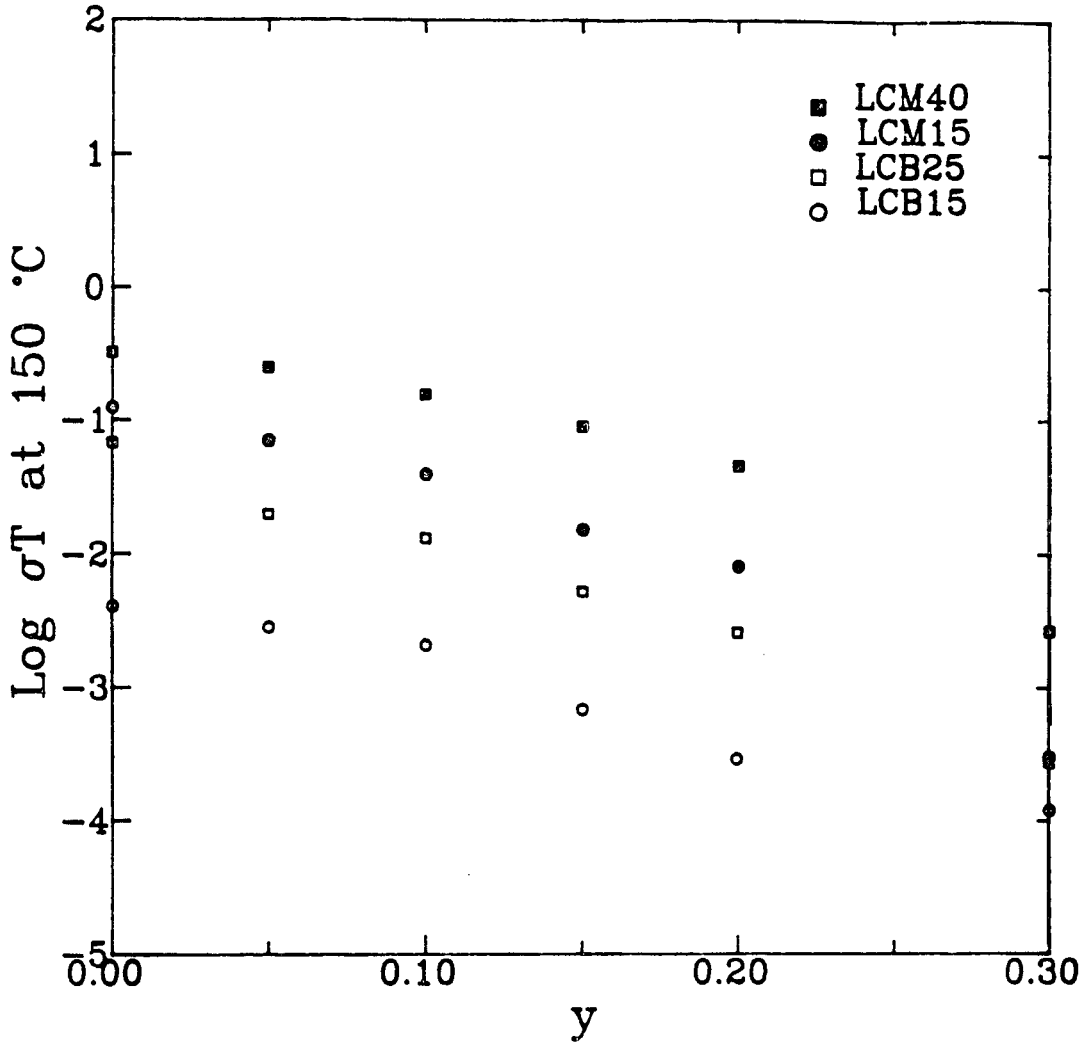

Figure 6: Log σ at 150 °C versus calcium substitution for Li.

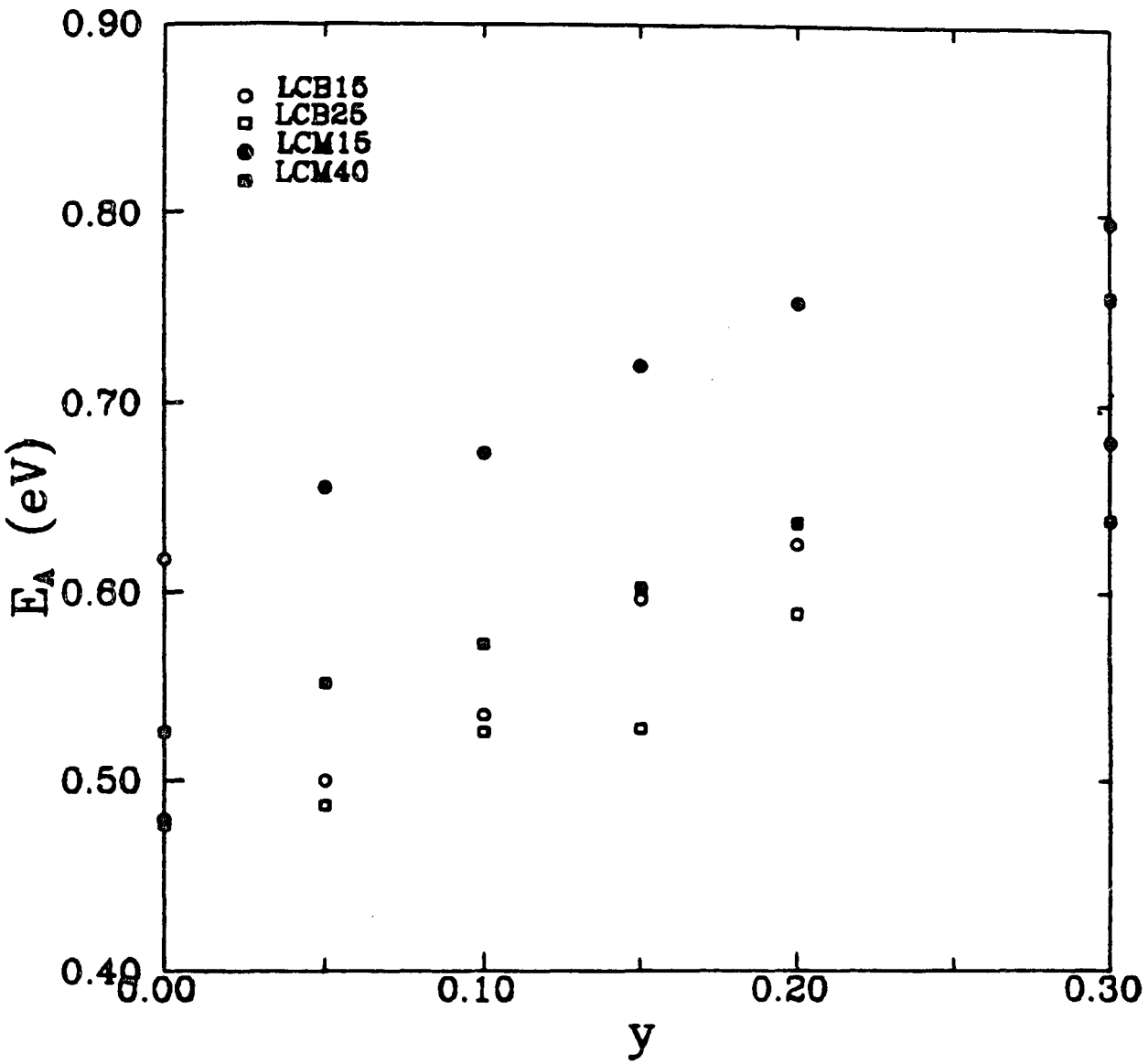

Figure 7: Activation energy as a function of calcium substitution.

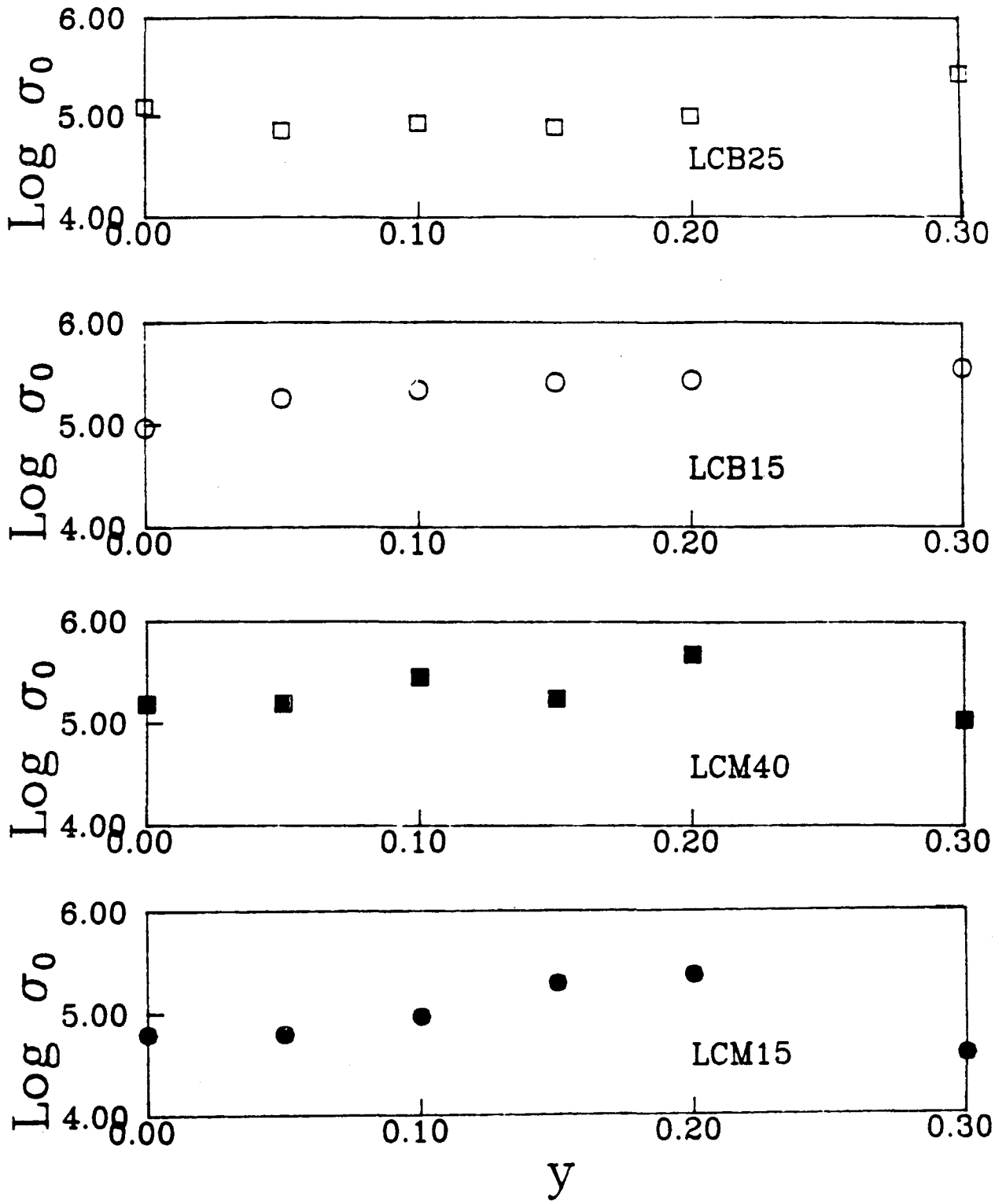

Figure 8: Pre-exponential constant σ_0 as a function of calcium substitution.

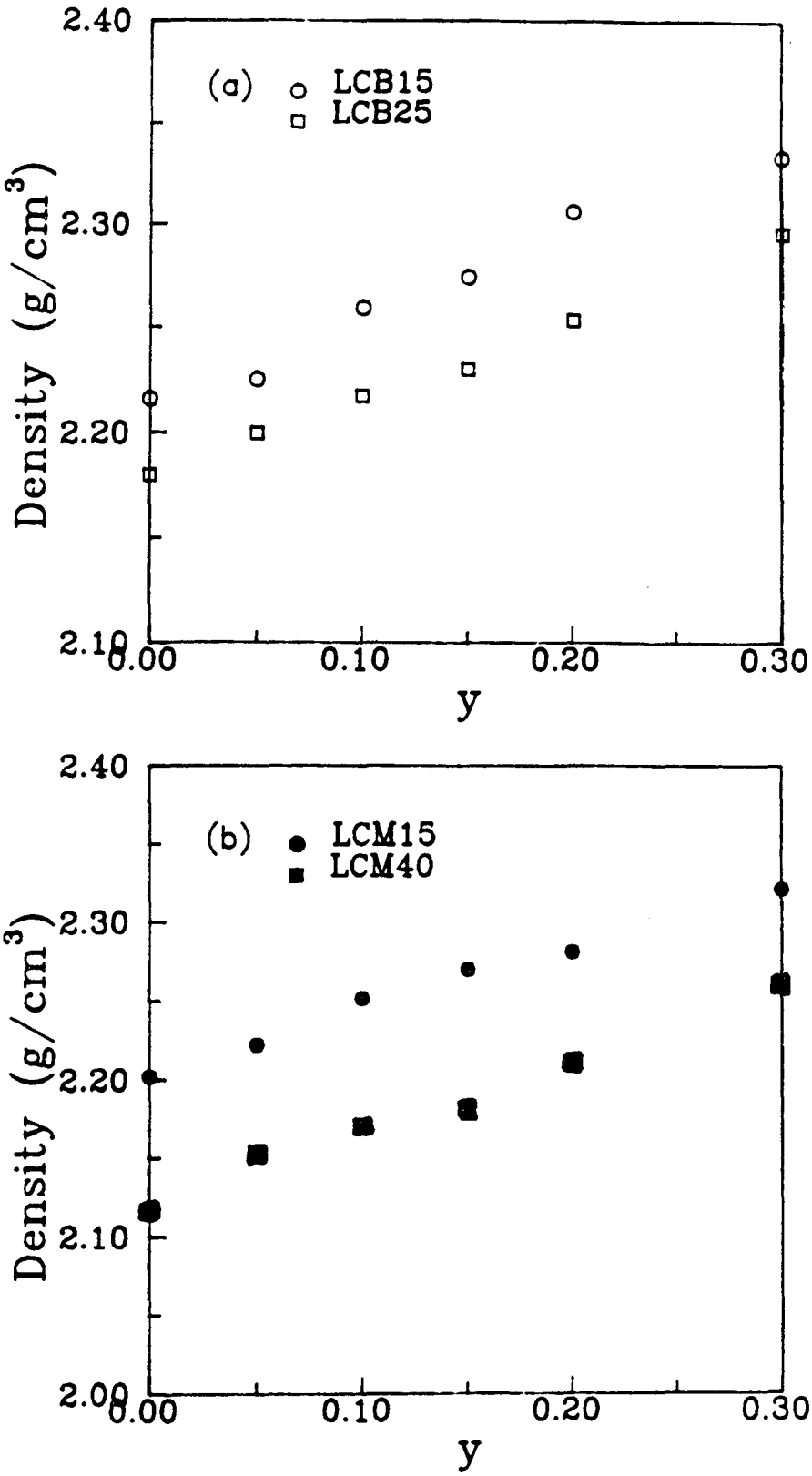

Figure 9: Density as a function of calcium substitution.

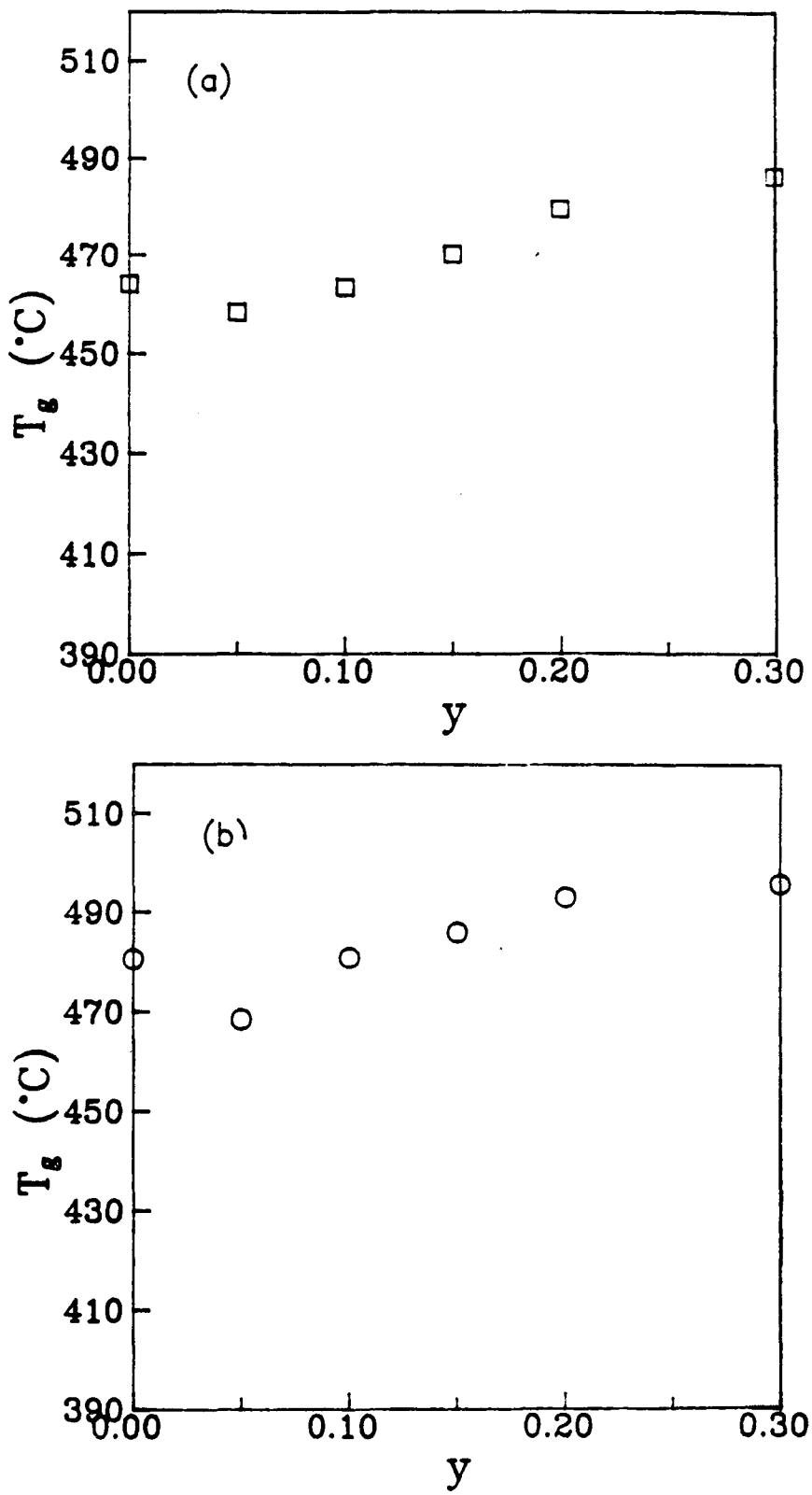

Figure 10: Transition temperature dependence on calcium content plot of "boracite" (a) LCB25 (b) LCB15 glass series.

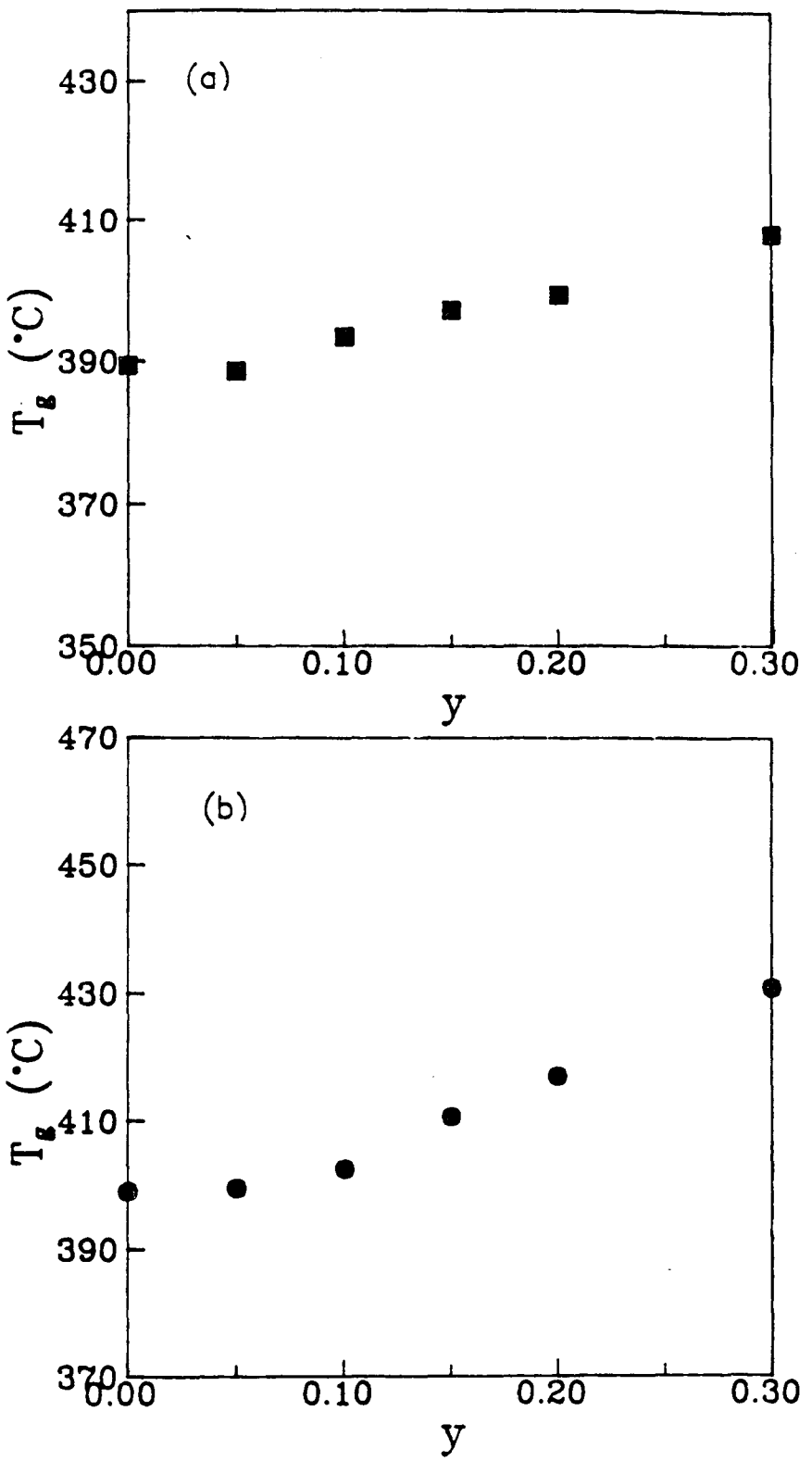

Figure 11: Transition temperature dependence on calcium content plot of "metaborate" (a) LCM40 (b) LCM15 glass series.

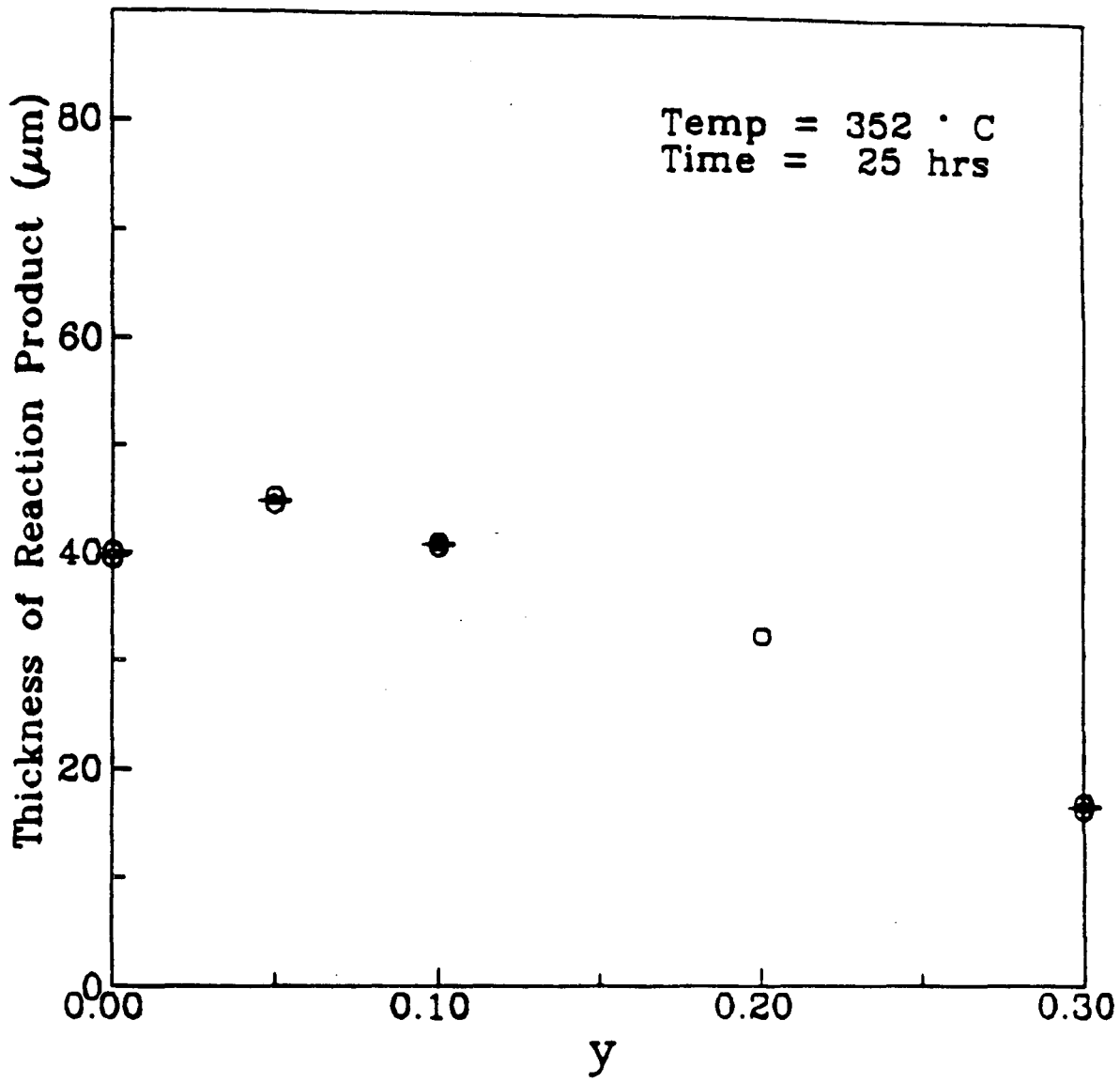

Figure 12: Product layer thickness at 352 °C with m/o CaO content in boracite system: $(LiCl)_2/B_2O_3$ = 25 mol %.

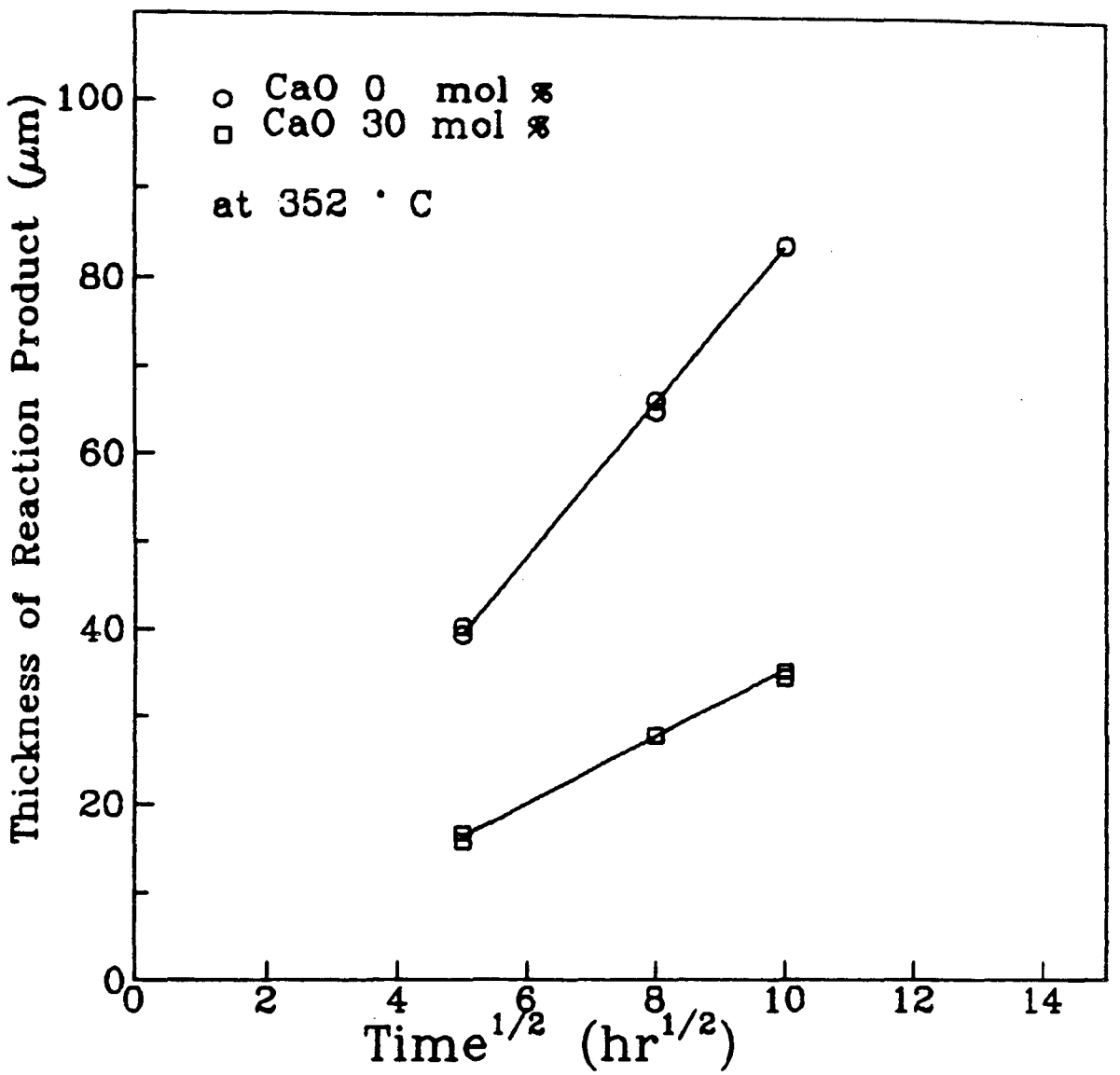

Figure 13: Time dependence of product layer thickness at 352 °C in boracite system: $(LiCl)_2/B_2O_3$ = 25 mol %.

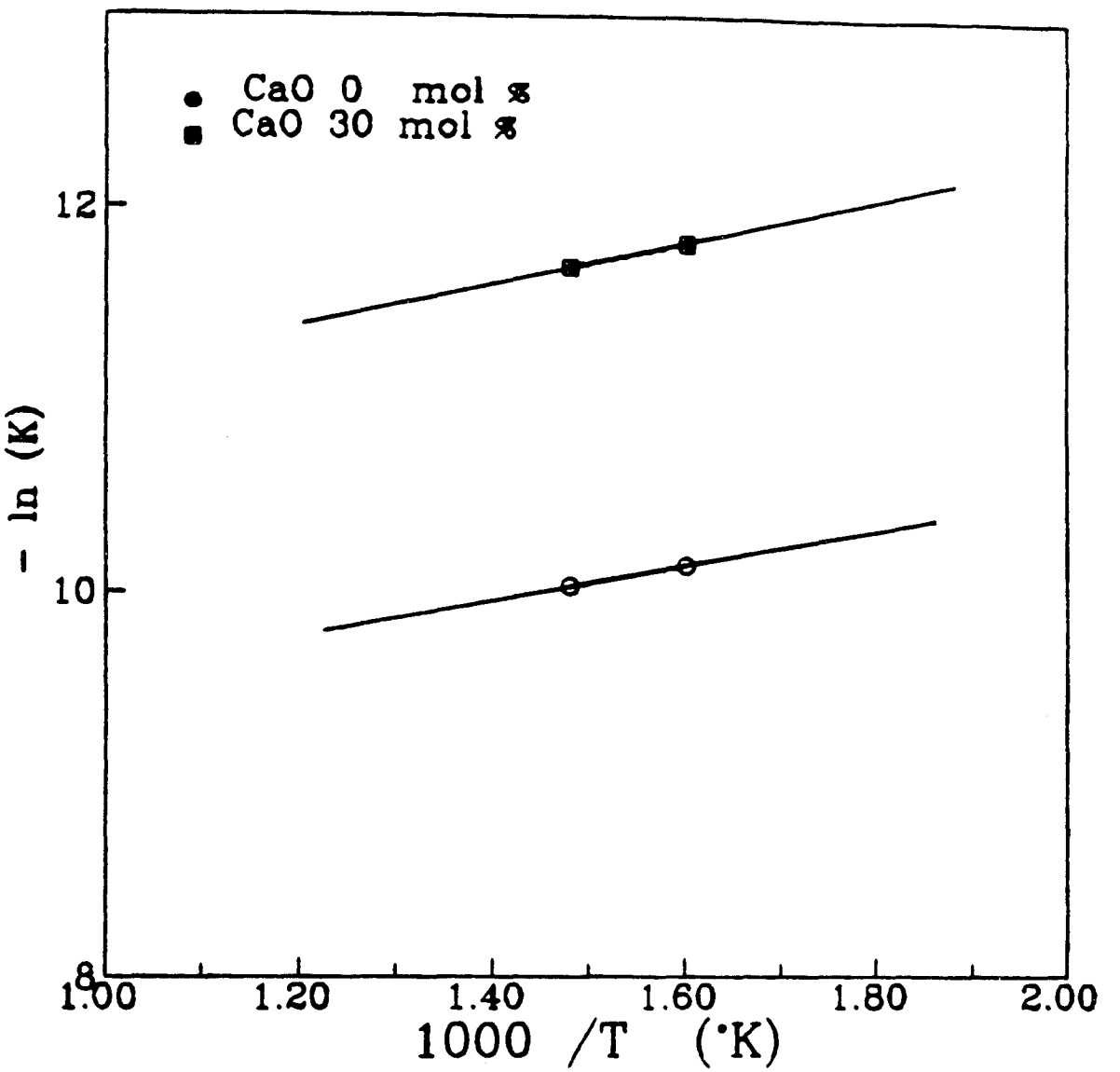

Figure 14: Corrosion rate for $B_2O_3 - Li_2O - (LiCl)_2$ glasses in contact with molten Li with this work point. After [4].

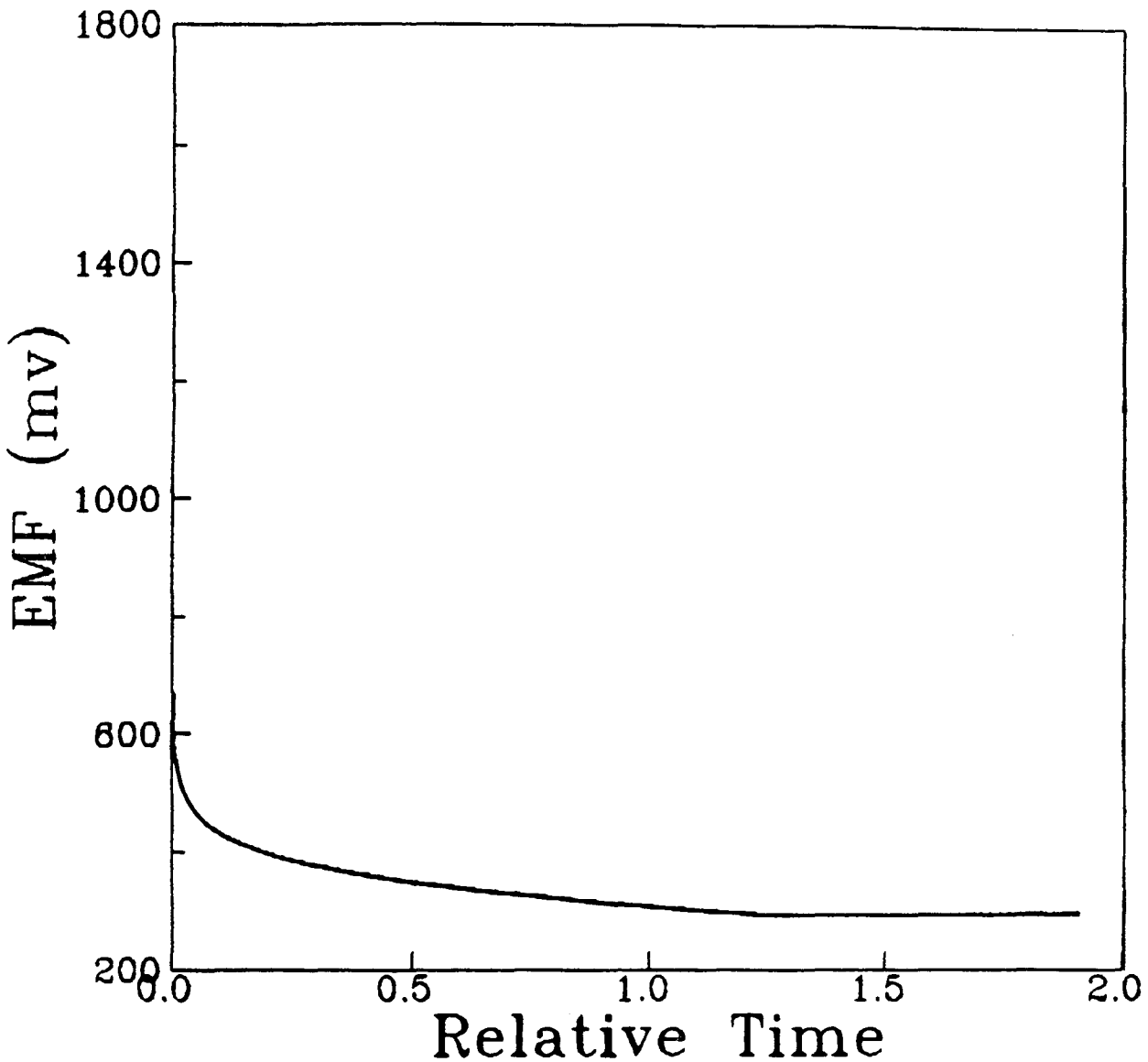

Figure 15: The relative time, t_{rel} versus time of LCB25 with CaO m/o 10.

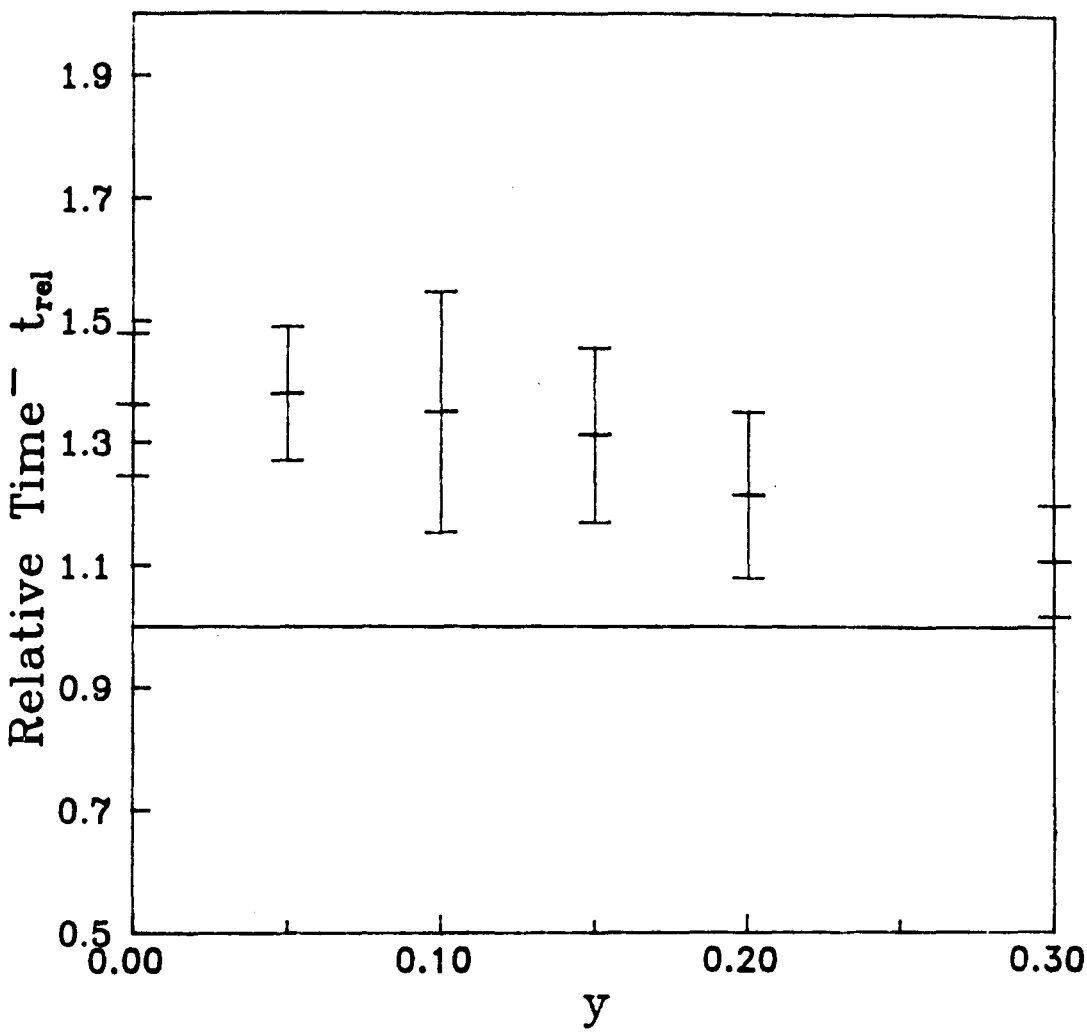

Figure 16: The relative time, t_{rel} versus CaO substitution

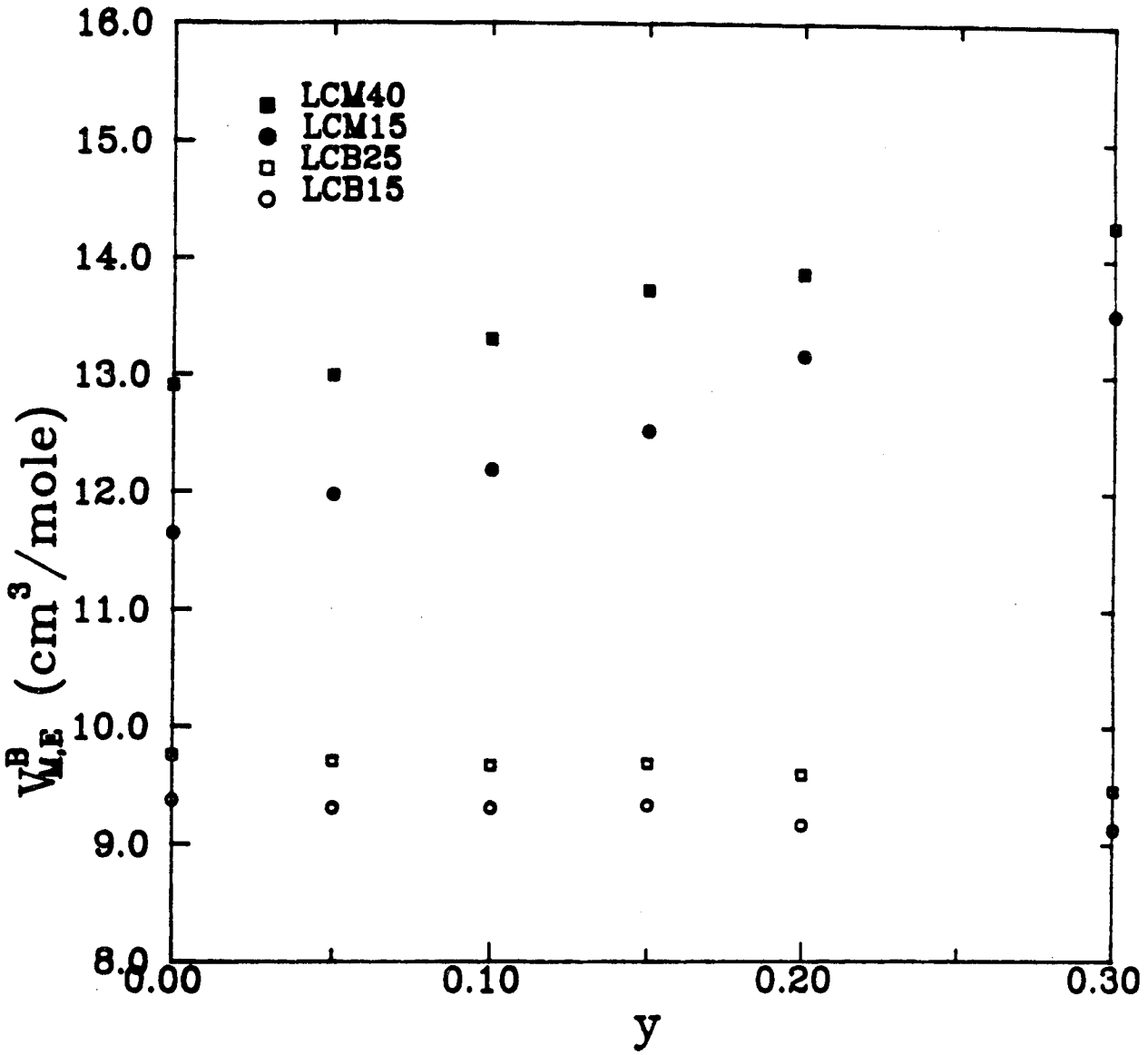

Fig. 17: Excess volume per boron vs. CaO fraction, y..

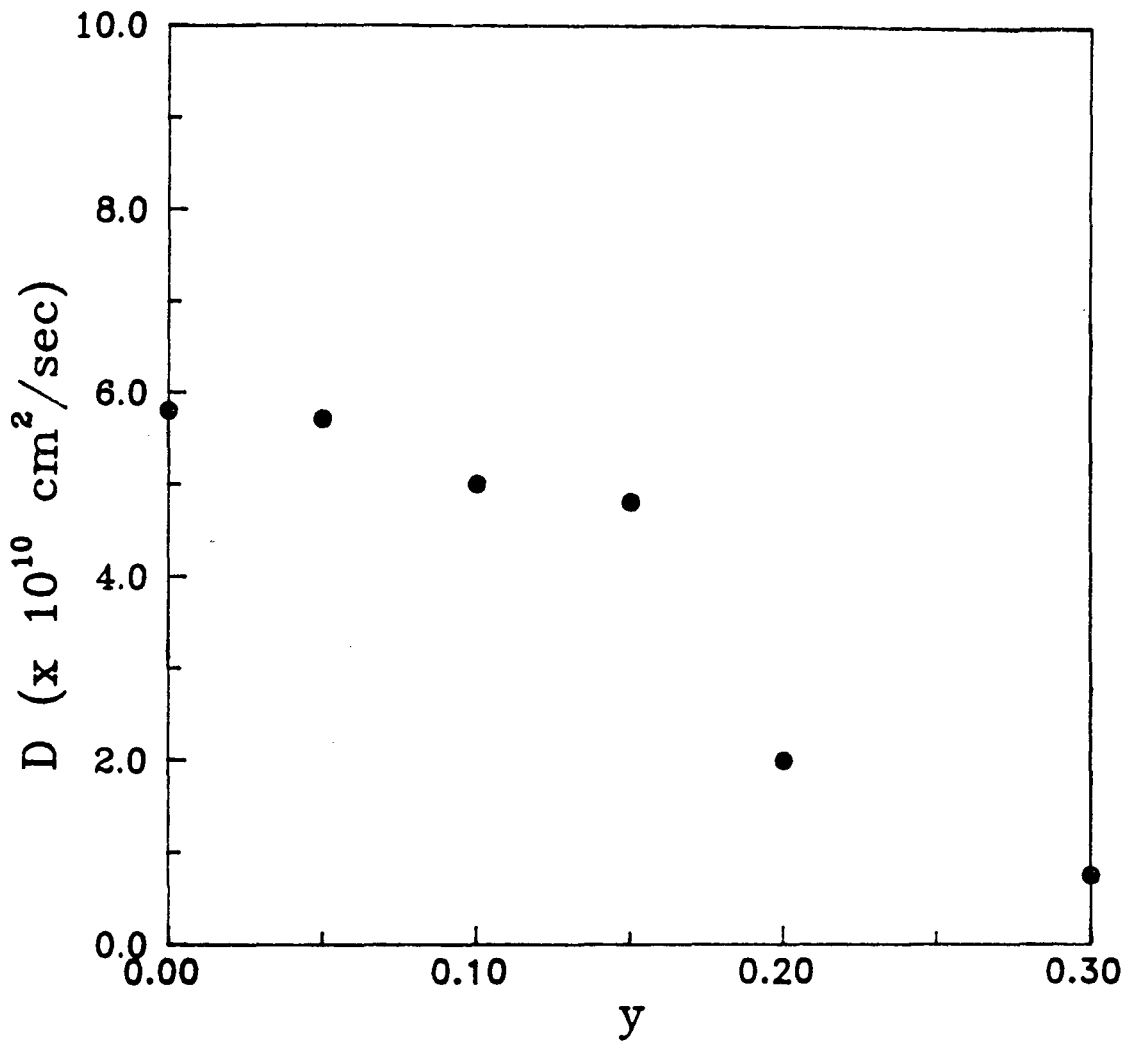

Figure 18: The average chemical diffusion coefficient, D, as a function of CaO substitution

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