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ELECTRICAL CONDUCTION AND CORROSION PROCESSES IN FAST LITHIUM ION CONDUCTING GLASSES

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### Author

Tuller, H.L.

### Publication Date

1988-09-01



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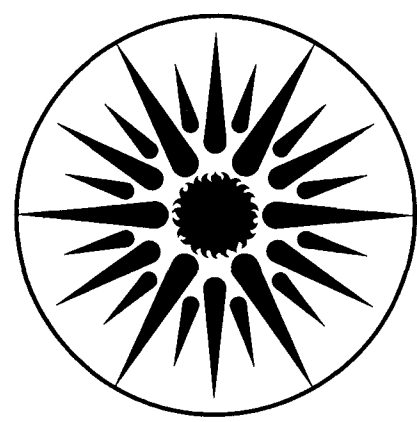
**Electrical Conduction and Corrosion Processes in  
Fast Lithium Ion Conducting Glasses**

**Final Report**

H.L. Tuller

September 1988

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**ELECTRICAL CONDUCTION AND  
CORROSION PROCESSES IN  
FAST LITHIUM ION CONDUCTING GLASSES**

Final Report

September 1988

by

**Harry L. Tuller**

Massachusetts Institute of Technology  
Department of Materials Science & Engineering  
Crystal Physics & Optical Electronics Laboratory  
Cambridge, Massachusetts 02139

for

Applied Science Division  
Lawrence Berkeley Laboratory  
1 Cyclotron Road  
Berkeley, California 94720

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Storage and Distribution, Energy Storage Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, Subcontract No. 4548010 with the Lawrence Berkeley Laboratory.

## RESEARCH SUMMARY

Two primary approaches have been pursued towards preparing fast lithium ion conducting glasses with improved stability towards lithium attack. In the first approach we have modified the bulk composition of lithium metaborate glasses by the addition of CaO which is, on its own, stable in molten lithium. Electrochemical studies of the composition  $(50-x)\text{Li}_2\text{O}\cdot x\text{CaO}\cdot 50\text{B}_2\text{O}_3$  with maximum  $x = 8$  mol% show it to be stable. Extensions to highly conductive, but less stable chloroborates are being pursued to test the stabilizing character of CaO more critically.

An alternative approach being pursued for finding highly conducting but stable glass systems is to "apply" a passivation layer to a highly conductive but less stable base glass. Lithium metaborate and lithium chloroborate glasses have been ion exchanged in  $\text{Ca}(\text{NO}_3)_2\text{-LiNO}_3$  molten salt baths to enrich their surfaces with CaO. Glasses exchanged in this manner remained transparent and exhibited no signs of devitrification. ESCA profiles on the metaborate confirm exchange to a depth of at least  $1\ \mu\text{m}$ . Preliminary tests in our double electrochemical cell indicate that glasses normally susceptible to Li attack can be stabilized by Ca ion exchange. Further experiments are being run to confirm these results and to establish optimum exchange conditions.

Several reviews on fast ion transport in glasses have been completed for publication. Compilation of recent data again confirms the importance of glass structure on

transport. This year, we completed our investigation of the  $R_2O-RCl-B_2O_3$  ( $R=Li,Na,K$ ) system. We conclude that ion transport is controlled primarily by the strain component of the migration energy. The most recent results on the potassium analog show that for the larger mobile cations an increasing shear modulus may compensate for increasing free volume as the composition is varied. For Li and Na glasses, the free volume factor appeared to dominate at all compositions. Optical absorption studies on Cr and Co doped alkali chloro-borate glasses appear to confirm on a local level the dilating characteristics of both the interstitial alkali and chlorine species.

## FINAL REPORT

### INTRODUCTION

To achieve high energy density storage capabilities in batteries, highly active reaction couples such as molten alkali metals and sulfur are required. Confinement of such reactants is greatly simplified by use of newly developed solid electrolyte "membranes" rather than liquid electrolytes. This program focuses its attention on the relative merits of highly conducting glasses as solid electrolytes. In particular, we focus on the transport, electrochemical, and corrosion resistance properties of alkali ion conducting glasses. Although other programs exist which are examining ion transport in glasses, none (as far as we are aware) are also studying the stability of such glasses in various corrosive media in a detailed and systematic way.

During this contract period we have focussed our efforts towards preparing lithium fast ion conducting glasses with improved stability towards lithium attack. Two primary approaches have been followed. The first concerns modification of the bulk composition of the glass by addition of oxides known to be stable in molten lithium. Here, one must concern oneself with the impact such additives may have on the ionic conductivity and thermal stability as well as chemical stability. In the second approach we attempt to stabilize a highly conductive, but perhaps less stable glass, by the formation of a "passivation layer" on the

surface of the bulk glass. Both types of glasses have been examined for stability in our electrochemical cells and preliminary results as described below are encouraging.

The examination of ion transport in the system  $R_2O-RC1-B_2O_3$  ( $R=Li,Na,K$ ) and its relation to structure have been completed. The most recent results, on the potassium analog, have, on the one hand, confirmed the importance of molar free volume on the strain component of ion migration but have also illustrated for the first time the corresponding importance of the shear modulus dependence on composition. Glasses in the above system were doped with Cr and Co and their absorption spectras examined as a means of monitoring composition induced structural variations in the glasses. The results summarized below are in concert with our earlier expectations.

## Review of Results

### Electrochemical and Stability Studies

#### 1. CaO doped $Li_2O-LiCl-B_2O_3$ glasses

Binary oxides known to have Gibbs free energies of formation more negative than  $Li_2O$  should be stable in molten lithium. These include  $CaO$ ,  $Y_2O_3$ ,  $La_2O_3$ , and  $MgO$ .<sup>(1)</sup> Divalent and trivalent additives can in general however be expected to lower ionic conductivities. Preliminary studies by us<sup>(2)</sup> on CaO additions up to 10 mol% demonstrate that (a)



conductivities do not drop dramatically as first feared and (b) thermal stability is improved via increase of the glass transition temperature.

During the present period we have examined a number of specimens of  $(50-x)\text{Li}_2\text{O}\cdot x\text{CaO}\cdot 50\text{B}_2\text{O}_3$  with  $x = 8$  mol% (designated as "C") in our electrochemical cells operating at  $345^\circ\text{C}$  with titration currents of 0.8mA (sample area  $\approx 1.0$   $\text{cm}^2$ ). These are summarized in Table 1.

In these experiments Li is titrated from the "source" electrode (See Fig. 1) into the initially pure Sn working electrode thereby increasing the lithium activity until a second phase is precipitated out resulting in a break in the Emf (measured across the sensor cell) versus titration time curve. Since the activity at which this arrest is known, one can readily calculate the titration time necessary to reach this point. This we call the "ideal" time, in contrast to those cases in which side reactions delay the attainment of this point. Assuming that the "delay" is due only to the glass reacting with the lithium, the delay time is a measure of the reaction kinetics.<sup>(3)</sup> Run 13 points to no reaction. The relatively short 1 hr delays in runs 12 and 14 are believed to be due to partial oxidation of some of the Li-Sn. We are now working on refining the atmosphere control in our glove box to minimize such errors.

Given the relative success with the above CaO doped glass we are presently preparing two series of glasses with the following formulations  $x\text{Li}_2\text{O}\cdot y\text{LiCl}\cdot z\text{CaO}\cdot (1-x-y-z)\text{B}_2\text{O}_3$

where  $(1-x-y-z) = 50 \text{ mol\%}$  and  $62.2 \text{ mol\%}$ . The former is the metaborate series generally noted for its high conductivity and relative chemical stability and the "boracite" noted for its high conductivity but relatively poor chemical stability in contact with Li. In these experiments, we plan to increase "z" substantially above the 8 mol% we have investigated so far. In doing this we will determine the maximum CaO that can be accommodated into the glass, the rate at which the Li ion conductivity is depressed with CaO addition and the influence it has in stabilizing the glass against Li attack particularly in the boracite case.

## 2. "Multi-layer" glasses.

An alternative to finding a homogeneous glass with both optimized ionic conductivity and chemical stability is to "apply" a chemically stable but perhaps less conductive thin glass layer on top of a more conductive but intrinsically less conductive host. The "passivation" layer, as long as it is ionic and sufficiently thin, will insure that the Nernst Emf. will be maintained under open-circuit conditions and that the ohmic drop will remain small under current drain conductions.

Thin glass layers with high concentrations of CaO have been formed in our laboratory by several techniques. These include:

- a) Evaporation of thin films. We have had preliminary success so far with binary  $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$  glasses;
- b) Ion exchange of our conductive glasses with, e.g. Ca ions; and,
- c) Ion implantation.

We have concentrated on the second option during this contract period since it represents a technology commonly used in the glass industry and one which we can readily replicate in our laboratory.

Lithium metaborate and most recently, lithium "boracite" glasses were ion exchanged in  $\text{Ca}(\text{NO}_3)_2-\text{LiNO}_3$  molten salt baths. The eutectic of this system occurs at  $237^\circ\text{C}$  with Ca at 16 mol%. The bath was operated at  $350-365^\circ\text{C}$  to allow for a higher calcium concentration (22 mol%) in the melt but low enough to limit crystallization of the glass. Glasses exchanged in this manner for 48-110 hrs remained transparent and exhibited no sign of devitrification under examination with x-rays. ESCA profiles performed earlier on the metaborate confirm Ca exchange at least to a depth of  $1\ \mu\text{m}$ . We plan to perform calibration runs on the ESCA equipment which will allow us to obtain a more quantitative measure of the exchange.

Complex impedance measurements were performed on the exchanged metaborate glass to determine how blocking the layer might be to Li transport across the enriched layer. After completing a series of measurements which gave results similar to the unexchanged glass, we now suspect that

exchanged layer may have been mechanically abraded during electroding. New specimens are now being studied where care has been taken to insure that the interface is not abraded.

Several exchanged boracite(B) specimens were tested for chemical stability in our double cell titration apparatus. The results are summarized in Table 2.

The results of run 21 look very promising, i.e. they seem to suggest that a glass normally susceptible to Li attack can be stabilized by Ca ion exchange. To substantiate this result we will be repeating these experiments after completing our glove box overhaul. We suspect the delay in run 20 may have resulted from an unwanted side reaction.

### Transport Studies

We have recently completed several reviews<sup>(4,5)</sup> under this program in which we have compiled and analyzed transport data for several hundred glasses with high Ag, Li, Na, K, Pb, and F ion conductivities.

Based on these data, we concluded that FIC in glasses is a rather general phenomenon and is likely to be found in many glass forming systems. On the other hand, understanding of transport phenomena in glasses has been greatly hampered by poor knowledge of glass structure and the manner in which carrier density and mobility contribute

to overall ionic conductivity. Our efforts of the past years has, in part, been directed towards answering these questions.<sup>(6-12)</sup>

This year, we completed our investigation of the  $R_2O-RC1-B_2O_3$  ( $R=Li,Na,K$ ) system which we have found to be particularly instructive regarding the role of structure on transport. We recently completed a re-examination of this system<sup>(12)</sup> given the recent completion of experiments on the potassium analog. The key conclusions are summarized in the following.

While there are large differences in ion size ( $R_{Li} = 0.6\text{\AA}$ ,  $R_{Na} = 0.95\text{\AA}$ , and  $r_x = 1.33\text{\AA}$ ), the 0.88 eV activation energy for K ion motion is only marginally different from that of Na (0.77 eV) and Li (0.74 eV), (see Fig. 2). We have demonstrated with supplementary density measurements that the larger Na and K ions induce larger molar free volumes in the glasses--thereby, in large part, compensating for their larger size. A major conclusion of this part of the study is that conduction in these glasses is dominated by the influence of strain on ion mobility rather than dissociation of carrier complexes. In Figure (3), we show how the three diborate glasses are influenced by the addition of alkali chloride dopant salts. The respective salts are added in such a manner so as to maintain the total alkali ion concentration fixed. For the smaller alkali ions, the chlorine substitution is observed to have a strong enhancing effect resulting in a near linear increase in log

σ. Figure (4) shows this to be due to a corresponding decrease in the activation energy E. When we combine this information with excess free volume data obtained from density measurements, as in Figure (5), we find a linear correlation between E and the excess free volume. This strongly suggests that the dilation of the glass network induced by the chlorine results in a reduction of the strain energy due to a reduction in the  $r-r_D$  term in the strain energy given by

$$E_s = 4\pi G r_D (r-r_D)^2$$

where G is the shear modulus, r is the ionic radius, and  $r_D$  the doorway size connecting two near equivalent ion sites.

In the lithium and sodium glasses, the effect of chlorine on ion transport is further enhanced by the dopant induced decrease in the glass transition temperature  $T_g$  and correspondingly in the modulus G. For the potassium glasses, in certain composition ranges,  $T_g$  actually increases with chlorine addition and consequently apparently compensates in large part for the dilation in the structure resulting in only a weak dependence of potassium ion conduction on dopant.

In an attempt to examine structural changes induced by composition variations on a more microscopic level than by density measurements, we have prepared a series of Cr and Co doped glasses of the type  $R_2O \cdot 2B_2O_3$  (R=Li,Na,K) and  $(33-x)Li_2O \cdot x(LiCl)_2 \cdot 67B_2O_3$  where the dopant contents were 0.07

and 0.02 mol% for  $\text{Cr}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$  respectively. A shift, for example, in the crystal field split intraband transition between the d-levels to longer optical wavelengths implies a decrease in field strength. Thus, leaving all other factors constant, implies a dilation in the structure on a local level.

Figures 6 and 7 illustrate the peak shift for cobalt absorption to longer wavelengths with increasing cation size and chlorine substitution respectively. This confirms similar trends in density observed earlier. These results are now being analyzed to provide further detail on local site symmetries.

Table 1

<u>run #</u>	<u>Glass</u>	<u>Temp.</u>	<u>I(mA)</u>	<u>t(expt)</u>	<u>t(delay)</u>
12	C	344°C	0.8	18,972sec	1.01hr
13	C	345°C	0.8	9,612	ideal
14	C	344°C	0.8	14,244	0.97hr

Table 2

<u>run #</u>	<u>Glass</u>	<u>Temp.</u>	<u>I(mA)</u>	<u>t(delay)</u>
19	B w/o exch	339°C	0.5	3.93hr
20	B w/exch	339°C	0.8	2.11hr
21	B w/exch	352°C	1.0	ideal



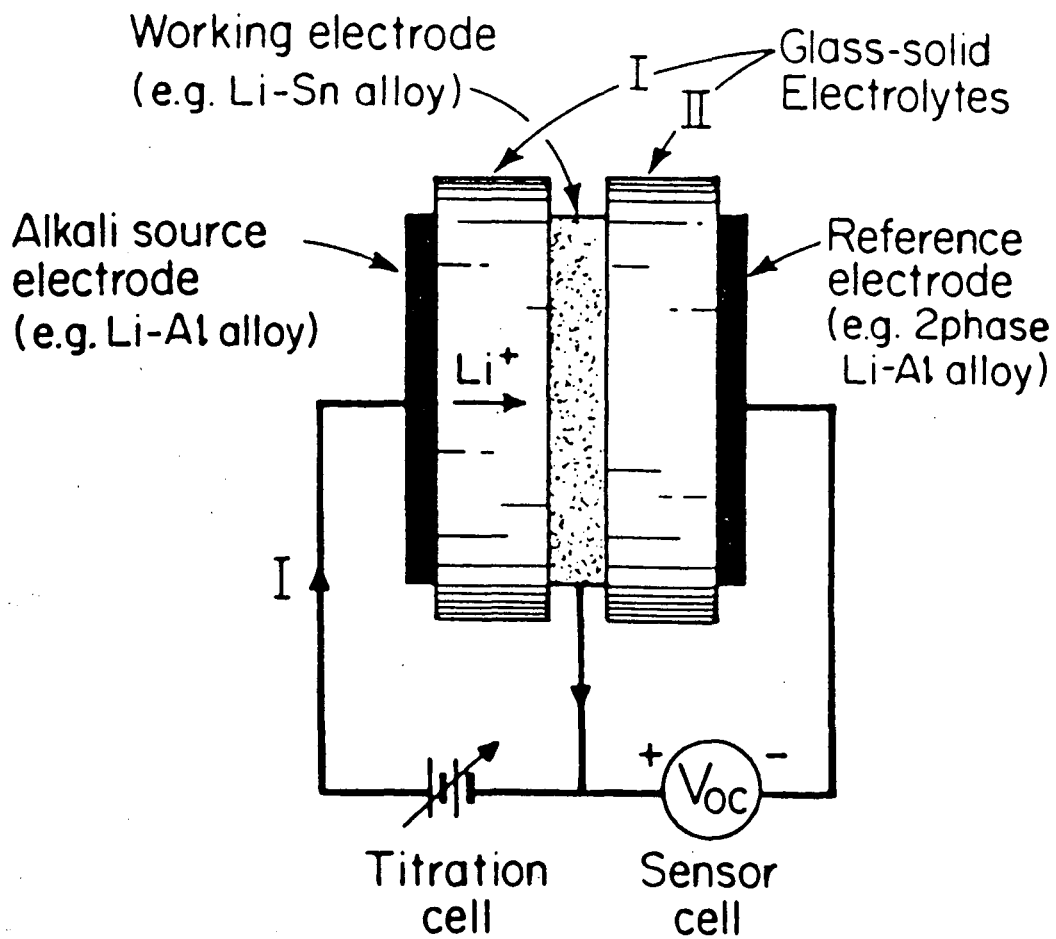


Fig. 1: Schematic of symmetrical electrochemical cell. A constant current is passed through electrolyte I while the Emf is monitored across electrolyte II.

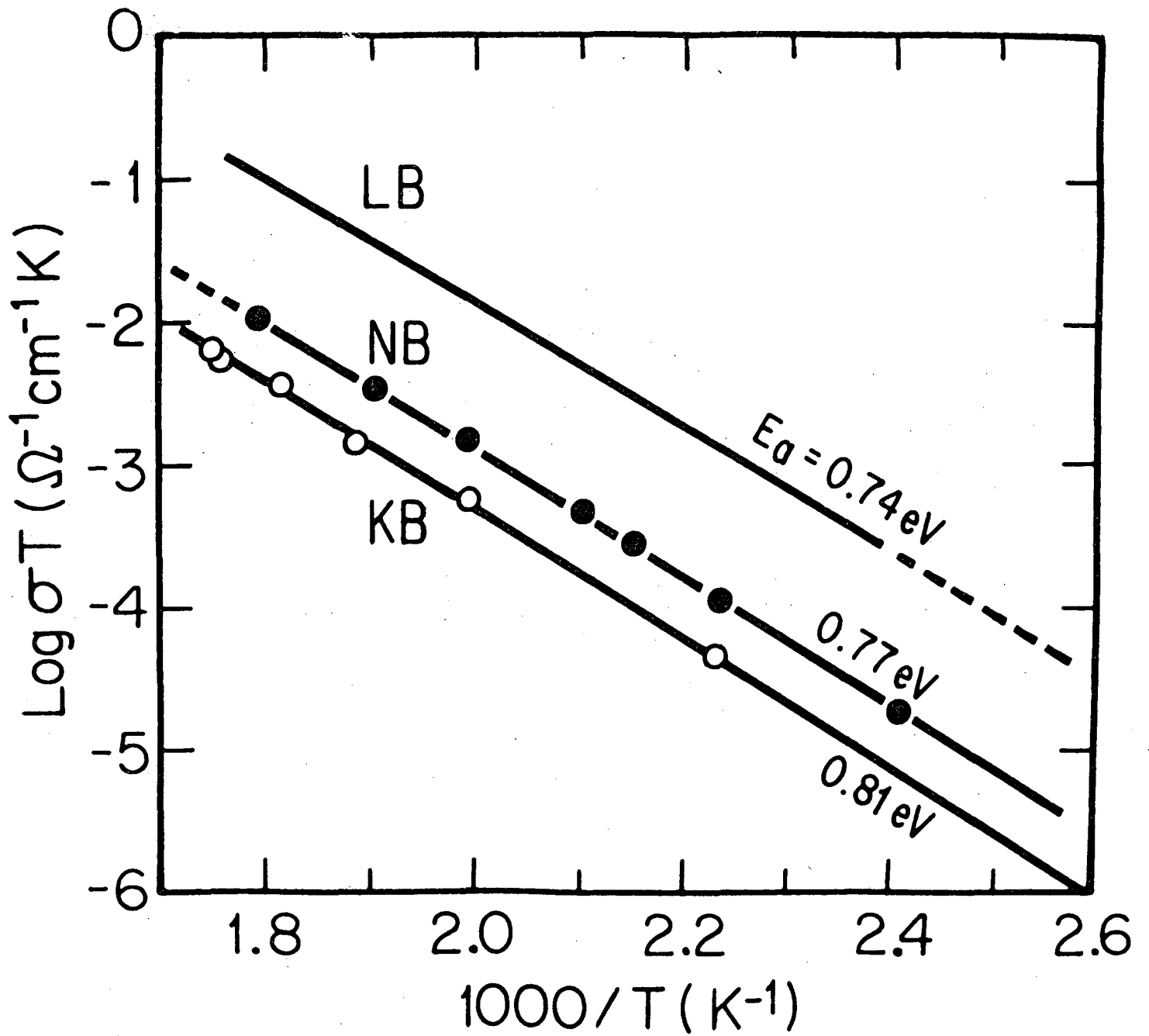


Fig. 2: Arrhenius plot of conductivity for lithium, sodium and potassium diborate glasses.

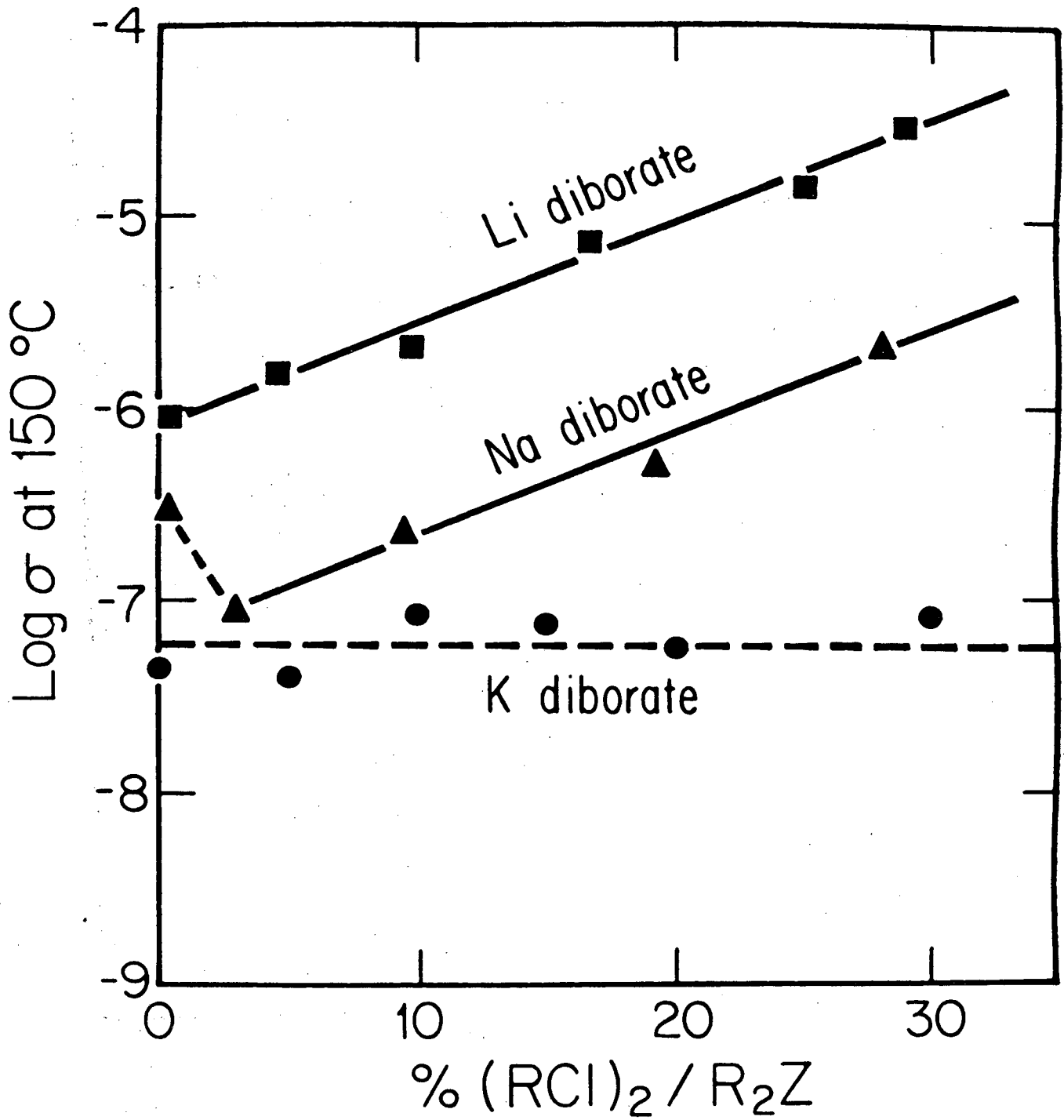


Fig. 3: Log  $\sigma$  versus chloride substitution for Li, Na and K diborate glasses.

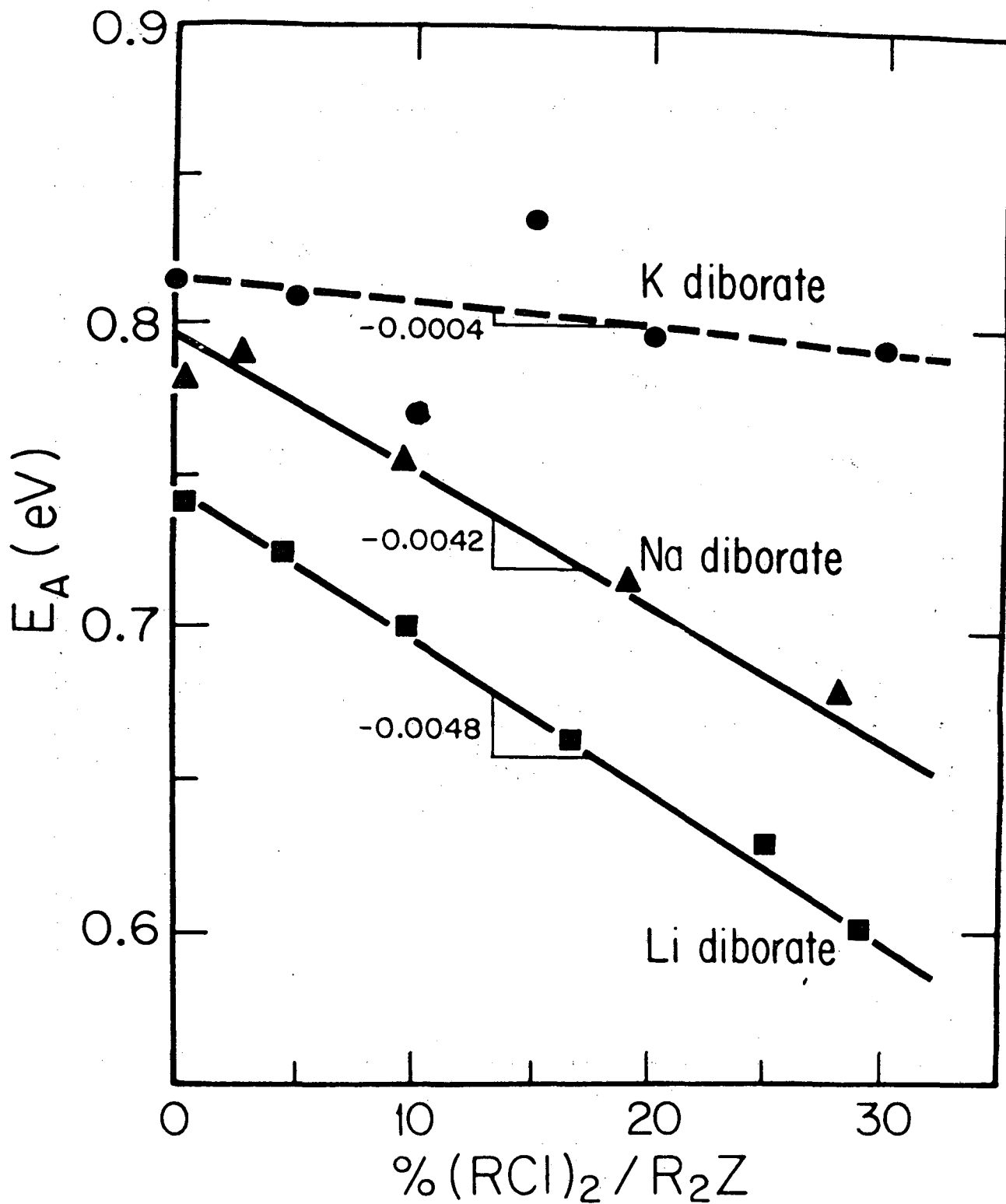


Fig. 4: Activation energy as a function of chloride substitution in a series of alkali diborate glasses.

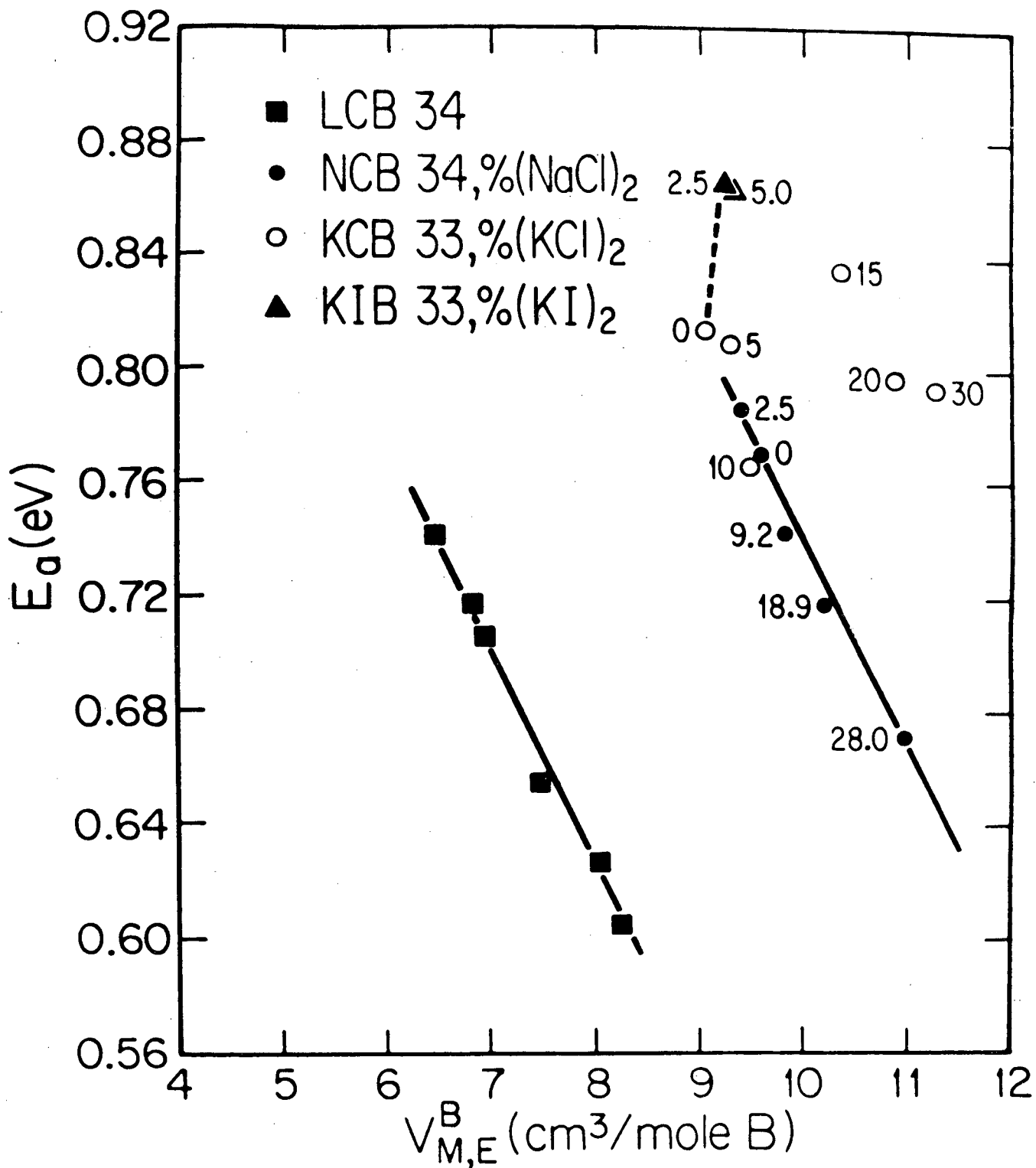


Fig. 5: Dependence of  $E_a$  on excess volume for alkali haloborate glasses.

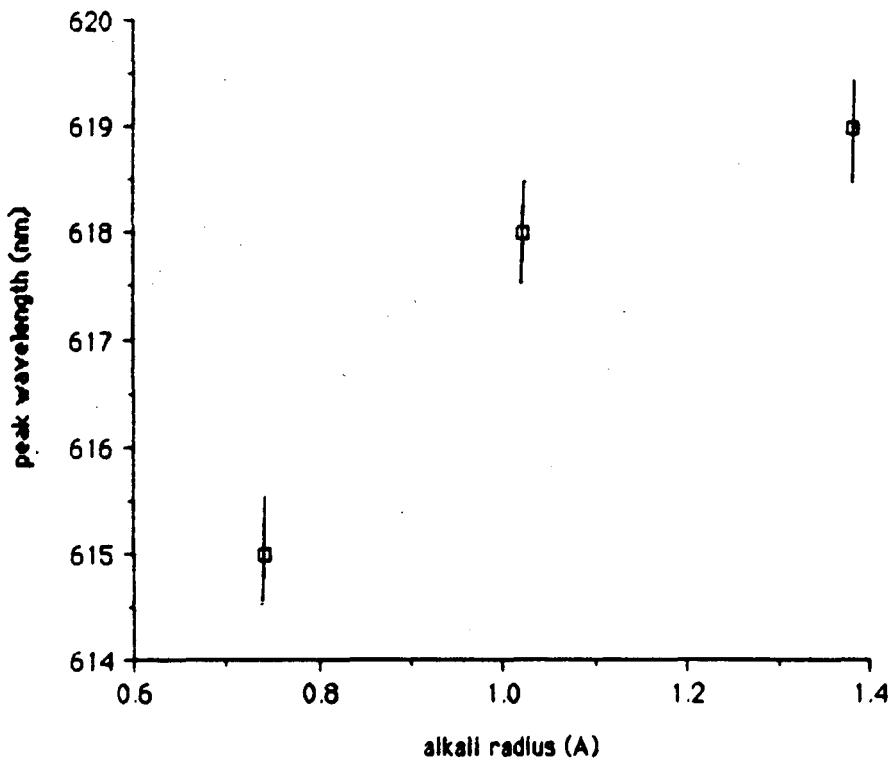


Fig. 6: Peak wavelength as a function of alkali radius for Li, Na, and K diborate glasses doped with chromium.

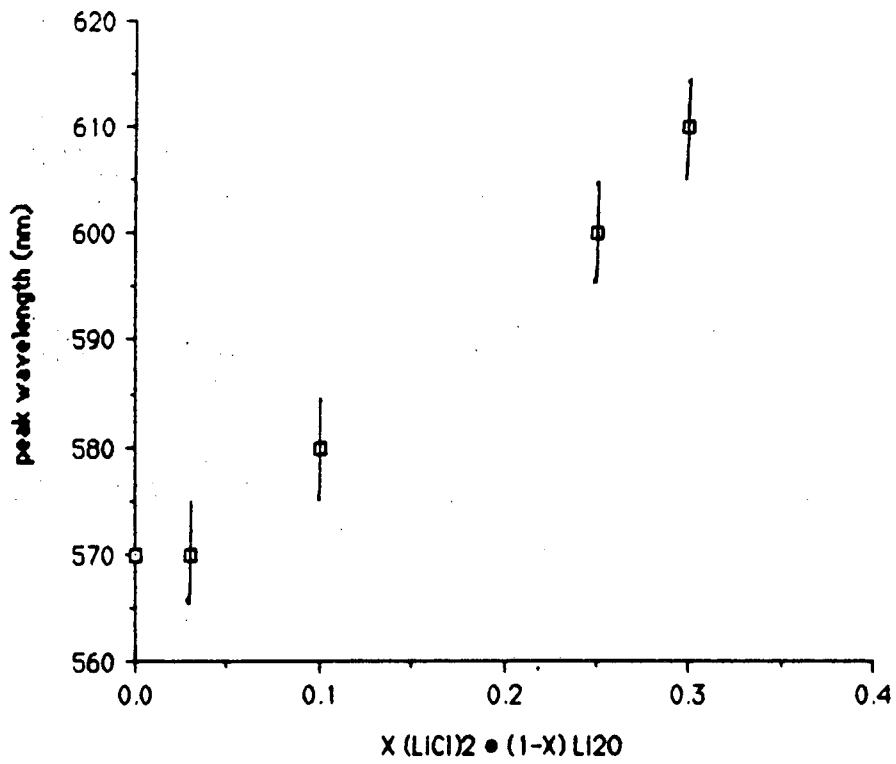


Fig. 7: Peak wavelength as a function of chloride substitution in lithium diborate glasses doped with cobalt.

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PUBLICATIONS RESULTING FROM THIS PROGRAM

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.

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PAPERS PRESENTED AS A RESULT OF THIS PROGRAM 1987-1988  
(\* Invited Lectures)

- 6/24/87 \* "Fast Ion Conducting Glasses," Solid State Chemistry Symposium, Mohammed V University, Rabat, Morocco
- 7/1-15/87 \* "Amorphous Fast Ion Conductors," NATO Advanced Study Institute on the Science & Technology of Fast Ion Conduction, Erice, Italy
- 12/7-9/87 \* "Fast Ion Conductors-Future Trends," ONR Symposium on Solid State Materials for Advanced Technology-Unresolved Issues, Carnegie Mellon University, Pittsburgh, PA
- 7/1-15/87 NATO Advanced Study Institute on the Science & Technology of Fast Ion Conduction  
"Effects of Halide Substitutions in Potassium Haloborate Glasses," (Co-Authored with F.A. Fusco)
- 10/18-23/87 Symposium on Electro-Ceramics and Solid State Ionics in Conjunction with the 172nd Meeting of the Electrochemical Society, Honolulu, Hawaii  
"Lithium, Sodium and Potassium Transport in Fast Ion Conducting Glasses: Trends and Models (Co-Authored with F.A. Fusco)

LAWRENCE BERKELEY LABORATORY  
TECHNICAL INFORMATION DEPARTMENT  
1 CYCLOTRON ROAD  
BERKELEY, CALIFORNIA 94720