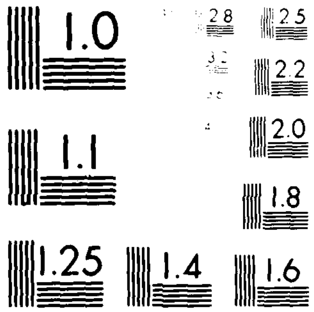
AD-A112 147   POLYTECHNIC INST OF BROOKLYN N Y   F/G 7/4
SYNTHESIS OF NEW SOLID ELECTROLYTES.(U)
MAR 82 E BANKS   DAAG29-80-C-0138
UNCLASSIFIED   ARO-15433.3-MS   NL

1 OF 1
AD A
112147

END
DATE
FILMED
04-82
DTIC


1.0
2.8
2.5
3.2
2.2
3.6
2.0
4.0
1.1
1.8
1.25
1.4
1.6

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

ADA112147

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER
15433.3-MS

2. GOVT ACCESSION NO.
AD-A112 147

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
Synthesis of New Solid Electrolytes

(12)

5. TYPE OF REPORT & PERIOD COVERED
Final:
1 Jul 78 - 31 Dec 81

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
E. Banks

8. CONTRACT OR GRANT NUMBER(s)
DAAG29 78 G 0150;
DAAG29 80 C 0138

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Polytechnic Institute of New York
Brooklyn, NY 11201

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
U. S. Army Research Office
Post Office Box 12211
Research Triangle Park, NC 27709

12. REPORT DATE
Mar 82

13. NUMBER OF PAGES
45

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

DTIC
ELECTE
MAR 18 1982
H

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

solid electrolytes	solid solutions
alkali metals	zirconium phosphates
cations	ternary systems
ionic conductivity	sodium oxides

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The project originated in a search for new solid electrolytes by preparing compounds containing alkali metal cations distributed in sites which are connected in three-dimensional fashion, in the hope that such an arrangement would provide conditions conducive to improved ionic conductivity. Two approaches were used. The first, which was successful in that an extensive composition range was achieved for investigation, was to substitute variable concentrations of the mobile ions in a structure containing a large concentration of interstitial cavities. This was

DTIC FILE COPY

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. ABSTRACT CONTINUED

achieved in the cubic ZrR_2O_7 solid solutions where alkali ions were introduced into large interstitial sites while the excess positive charge was compensated by tripositive ions in the Zr^{+4} sites. Conductivity and X-ray studies are reported herein for these phases. The second approach, the attempt to synthesize phases having the structure of the conducting region of a two-dimensional ionic conductor, β-alumina, was unsuccessful in the system investigated, Na_2O-Al_2O_3-TiO_2. Some results are reported on conductivity of the sodium titanium bronze-like phase found in that ternary system.

Polytechnic Institute of New York

FINAL REPORT
on
SYNTHESIS OF NEW SOLID ELECTROLYTES

Grant No. DAAG-29-78-G-0150
Project No. P-15433-ms

and

Contract No. DAAG-29-80-C-0138
Project No. P-15433-MS

Covering the Period
1 July 1978 to 31 December 1981

U.S. Army Research Office
Durham, North Carolina

FINAL REPORT

on

SYNTHESIS OF NEW SOLID ELECTROLYTES

Grant No. DAAG-29-78-G-0150
Project No. P-15433-ms

and

Contract No. DAAG-29-80-C-0138
Project No. P-15433-MS

Covering the Period
1 July 1978 to 31 December 1981

U.S. Army Research Office
Durham, North Carolina

POLYTECHNIC INSTITUTE OF NEW YORK
333 Jay Street
Brooklyn, New York 11201

FINAL REPORT
on

SYNTHESIS OF NEW SOLID ELECTROLYTES

Grant No. DAAG-29-78-G-0150
Project No. P-15433-ms

and

Contract No. DAAG-29-80-C-0138
Project No. P-15433-MS

Covering the Period
1 July 1978 to 31 December 1981

U.S. Army Research Office
Durham, North Carolina

APPROVED FOR PUBLICATION RELEASE DISTRIBUTION UNLIMITED

This Report Was Prepared by Professor E. Banks

Personnel Working on Project:

E. Banks
R. Sacks
J. Foise
G. Gashurov
W. Scharf
B. Post (Prof. of Physics)

Theses and Dissertations:

Ph.D. (Chemical Physics)

New Solid Electrolytes Having the Cubic ZrP_2O_7 Structure. R. Sacks, Polytechnic Institute of New York, June 1981, Thesis.

B.S. (Chemistry)

Synthesis of Doped Zirconium Pyrovanadate, Possible Solid Electrolytes. J. Foise, Polytechnic Institute of New York, June 1981, Thesis.

Papers Submitted for Publication: See Appendices

(Two additional Papers being written)

TABLE OF CONTENTS

I. INTRODUCTION

The project originated in a proposal to search for new solid electrolytes by preparing compounds containing alkali metal cations distributed in sites which are connected in three-dimensional fashion, in the hope that such an arrangement would provide conditions conducive to improved ionic conductivity. Two approaches were used.

The first, which was successful in that an extensive composition range was achieved for investigation, was to subsitute variable concentrations of the mobile ions in a structure containing a large concentration of interstitial cavities. This was achieved in the cubic ZrP_2O_7 solid solutions where alkali ions were introduced into large interstitial sites while the excess positive charge was compensated by tripositive ions in the Zr^{+4} sites. Conductivity and X-ray studies are reported herein for these phases.

The second approach, the attempt to synthesize phases having the structure of the conducting region of a two-dimensional ionic conductor, β-alumina, was unsuccessful in the system that we investigated, Na_2O-Al_2O_3-TiO_2. Some results are reported on conductivity of the sodium titanium bronze-like phase found in that ternary system. It is noted that a short repeat unit phase of the type sought, containing only the "conducting plane" portion of the β-Al_2O_3 structure, has been found by Sato, et. al. in the Na_2O-Fe_2O_3-TiO_2 system, at a composition near $NaFeTiO_4$. The same workers report ionic conductivity in that system. The absence of such a phase in the corresponding aluminum system poses some interesting crystal-chemical questions, and should be investigated by studing other related systems such as those involving Ga_2O_3, Cr_2O_3, etc. During the course of the present study, we were unable to follow up this direction, but plan to do so if further funding is available.

II. Solid Solutions in ZrP_2O_7-Type Phases

A. Preliminary Studies

The feasibility of forming ZrP_2O_7 solid solutions was first investigated here by Charles Bush[1] who prepared solid solutions of ZrP_2O_7 with Na and Li ions in the lattice, compensated by replacement of Zr^{4+} by Y^{3+}. The apparent limit of solubility was about 10% substitution, e.g. $Zr_{0.9}\ Li_{0.1}\ Y_{0.1}\ P_2\ O_7$. Higher limits were not explored because of the appearance of new peaks in the x-ray patterns. Subsequently, some of these new peaks were identified as the peaks belonging to the 3 x 3 cubic superstructure first described by Kierkegaard[2]. In the interest of obtaining higher alkali ion concentrations, we shifted our attention to samples in which In^{3+} was the charge-compensating species.

B. ZrP_2O_7 and Related Systems

1. Charge Compensation on Cationic Sites

Two systems for introducing alkali metal ions into the ZrP_2O_7 system were attempted, and success was obtained with both. The first method of charge compensation was, as indicated above, to compensate the excess positive charge of the interstitial univalent ion by substituting In^{3+}, and in some cases Y^{3+} and Eu^{3+} ions on the zirconium sites. Sodium, potassium and silver ions were introduced, with compensation by In^{3+}, but by far the largest concentration achieved were obtained in the case of the system $Zr_{1-x}\ In_x\ Li_x\ P_2\ O_7$, where the value of x was as high as 0.35. Ceramic discs were prepared by pressing powders in an evacuated die, with a naphthalene binder. After driving off the binder, the discs were fired at 1200° and air-quenched. The quenching was necessary because these solid solutions proved to be metastable, decomposing to multiphase systems when slowly cooled.

The discs were provided with electrodes by vacuum evaporation of thin layers of chromium, followed by a thick gold layer. These were mounted between platinum electrodes in a spring-loaded electrode assembly. Electrical measurements were made using a pulse technique across the sample in series with a known resistor, and the voltage pulse across the sample was compared to the voltage across the circuit on a dual-trace oscilloscope. The method was described by Johnson, et al[3]. It has several advantages over methods using non-blocking (reversible) electrodes. First, many samples may be screened without the precautions needed when alkali metal electrodes are used. It measures total conductivity (ionic plus electronic). Electronic conductivity, where present, is measured by substituting a battery for the pulse generator and measuring the D.C. conductivity, which is entirely due to electron flow when the electrodes are blocking.

The essential results of this investigation are summarized in the paper by Sacks, Avigal and Banks, which has been accepted for publication by the Journal of the Electrochemical society. The entire manuscript, as accepted, appears in ths report as Appendix 1.

The major conclusion in the paper is that the size of the "bottlenecks" connecting the interstitial sites in the ZrP_2O_7 structure is the limiting factor in the conductivity. In particular, the NMR data indicated that the Li^+ ions are highly mobile even below room temperature. To improve this situation, it is desirable to go to systems having a larger unit cell dimension. A number of experiments on the CeP_2O_7 (Li, In) system were attempted, but the tendency for Ce^{4+} to be reduced to Ce^{3+} under synthesis conditions showed that this system would not be useful because of the likelihood of electronic semiconduction. The only likely quadrivalent ion that forms the ZrP_2O_7 structure is Th^{4+}. Work in this system was not started during the contract period because we were not equipped to handle radioactive materials in quantity, even though the specific activity of thorium is quite low. We have plans to set this up in the near future.

2. Charge Compensation on Phosphorus Sites

The substitution of phosphorus by silicon was the second mode of charge compensation attempted with Li^+ and Na^+ ions in ZrP_2O_7, e.g. $ZrLi_xSi_xP_{2-x}O_7$. The solubility limit in this case was $x = 0.4$. Initially, great hope was placed on this series because the silicon substitution leads to lattice expansion, which promised to open up the "bottlenecks" and improve the mobility of the alkali ions. In addition, the silicon-substituted samples did not decompose when slowly cooled-the solid solutions were thermally stable rather than metastable under operating conditions. However, when attempts at electrical measurement were made, the initial relatively high conductivity decreased rapidly with time under measurement, indicating a possible electrochemical decomposition. Some evidence of lithium phosphates was found on powdery deposits near the electrode, but the problem was not investigated in depth.

3. Mixed Charge Compensation

Some attempts were made to extend the range of incorporation of Li into ZrP_2O_7 by combining the two modes of charge compensation in the same sample. The composition of these samples would be $Zr_{1-x/2} In_{x/2} Li_x P_{2-x/2} Si_{x/2} O_7$. Single phase powders were prepared for x values greater than 0.5. For the last composition, we have not quite succeeded in eliminating one peak which appears in samples fired at 1200° and hard-sintered or partially fused at that temperature. The incorporation of more Li than is the case with In alone is an encouraging note. These samples were not suitable for measurement because of their multiphasic character, and time did not permit further investigation during the remainder of the contract period.

4. Effect of Li, In Substitution on the phase Transition in ZrP_2O_7

During the course of this investigation, this laboratory was asked to test a new high temperature x-ray diffractometer unit, manufactured by the Paar Co. of Austria. Among the samples we chose for test were several of the ZrP_2O_7 solid solutions we had prepared.

Three crystallographic forms of ZrP_2O_7 have been reported. A low temperature form (I) has a cubic unit cell with a ~ 8.25 A. When heated, form I transforms irreversibly to form II which has a cubic unit cell of triple size (a ~ 24.75A). Form II transforms reversibly to form III which again has the simple cell with a ~ 8.27A. This transformation is reported by Harrison, et. al[4] to be reversible. The triple lattice of form II is characterized by very weak superstructure lines, which disappear on going above the transition temperature. Most of the pattern can be indexed on the basis of the smaller cell with one third the unit cell dimension. Figure 1 shows the temperature dependence of the "subcell" dimension and clearly shows a sharp transition at about 300°C in good agreement with Harrison, et. al.

Figure 2 shows the lattice expansion data for several solid solutions of ZrP_2O_7: Li, In and Na, In. The transition temperatures shown on the curves were estimated by the disappearance of the superstructure peaks. It appears that sodium is more effective than lithium in lowering the transition temperature. In the case of the solid solution of composition $Zr_{0.65}$ $Li_{0.35}$ $In_{0.35}$ P_2O_7, the volume change at the transition is completely suppressed, suggesting that the transition is second order.

There is no observed effect of this transition in the conductivity data for the samples containing the concentrations of Li, In or Na, In covered by the study of the phase transition. This is probably due to the fact that the triple unit cell is already transformed in the more concentrated samples at the temperatures where the conductivity is of significant value.

5. ZrV_2O_7 and its Solid Solutions

The compound ZrV_2O_7 has been reported by Burdese and Barlera[5] and Graig and Hummel[6], who prepared it by solid state reaction of Zr O_2 and V_2O_5. In all attempts to duplicate their results, ZrV_2O_7 was found, but unreated ZrO_2 was always present. Sealed tube reactions failed to give a single phase product, because the compound was found to decompose above 740°C. Products were made with large excess of V_2O_5, but attempts to wash free the V_2O_5 led to partial decomposition of ZrV_2O_7.

The most successful method was a combined aqueous-solid state preparation. Zirconyl nitrate, $ZrO(NO_3)_2 \cdot xH_2O$ was dissolved in concentrated nitric acid and V_2O_5 was added in suspension, followed by evaporation to dryness. The orange powder thus obtained was fired in a crucible at 500°C, followed by a second firing at 600°C, yielding a yellow-tan powder of ZrV_2O_7 showing only traces of ZrO_2 and V_2O_5 as determined by x-ray diffraction.

Two approaches to doping ZrV_2O_7 with alkali metals were tried, using the nitric acid suspension method described above. Earlier attempts to prepare such solutions by solid-state synthesis had led to multiphase samples, in which such extra phases as lithium and sodium vanadium bronzes (such as $Na_{0.33}$ V_2O_5) were detected in addition to the ZrV_2O_7 phase. When the appropriate oxides or carbonates were added to the nitric acid mixture, followed by drying and firing, as above, multiphase mixtures were also found, with alkali vanadium bronzes sometimes being found. Attempts to avoid reduction by increasing the oxygen partial pressure were ineffective.

Since the vanadium was being reduced, it was thought that a reduced valence vanadium could be used as charge compensator, with the additional possibility that if electronic and ionic conductivity were simultaneously present, the material might be a potential electrode material. Samples of the form $\mathrm{Zr\ M^{I}_{x}\ V^{IV}_{x}\ V^{V}_{2-x}\ O_7}$ ($\mathrm{M^I}$ = Ag, Na, Li) were attempted. Only the lithium samples formed single phases up to x = 0.30. The Na and Ag samples showed second phases of the sodium vanadium bronze type. In the lithium series, several samples were formed into pellets and provided with blocking electrodes by vacuum evaporation of chromium followed by gold. Conductivity measurements using pulsed and DC voltages indicated that these lithium-doped materials are indeed mixed electronic-ionic conductors, as prepared. When this phase of the investigation was concluded, there were a number of anomalies in the study. The most disturbing was an apparently non-monotonic dependence of conductivity on Li concentration. The pulse and DC conductivity data gave very good linear plots of log σT vs. reciprocal temperature, as expected:

$$\ln(\sigma T) = -(E_a/R)\ 1/T \quad \ln \sigma_o$$

where σ is conductivity, T temperature (K) E_a is activation energy and R the gas constant. The total conductivity values appeared to peak at x = 0.10, but the ionic conductivities seemed to be peaking between x = 0.20 and 0.30. The highest total conductivity ranged from 10^{-2} $(\text{ohm-cm})^{-1}$ at 650 K to 2×10^{-4} at 300 K for the sample with x = 0.10. When the ionic component of conductivity was estimated by subtracting the DC conductivty (electronic), these values were lower by an order of magnitude. Similar measurements on other samples showed no regular trends as between the two conductivity types in each sample or from sample to sample. The data for a series of samples are shown in Figures 3-5. The uncertainties reflect variations in sample preparation, electroding and probably the actual measurement technique. Some evidence of changes during measurement was noted in the appearance of color changes in the pellets after measurement, probably indicating the formation of high concentrations of reduced vanadium at the cathode and similar electrochemical effects. Some of these problems may be possible to eliminate, but they must be investigated in much greater detail. The only thing that appears to be definitely established is that lithium-doped ZrV_2O_7 is a mixed ionic-electronic conductor. The electronic part appears to be semiconduction because the semilogarithmic behavior of the conductivity is preserved in DC measurements, while metallic conductivity would be linear in its temperature dependence (of resistivity).

Some of the problems connected with DC measurements are probably attributable to space charge buildup, largely associated with the ionic component. These may be eliminated by low-frequency AC measurements. However, at the present time, the need is for improvements in sample preparation techniques.

In part because of the apparent electrochemical decomposition described above, an attempt was made to prepare solid solutions of ZrP_2O_7 - ZrV_2O_7, in the hope that a compromise between chemical stability and increased lattice parameter could be achieved in the materials. The result is that a complete range of solid solution exists, showing a cubic subcell of dimension 8.776 for ZrV_2O_7 to 8.25 for ZrP_2O_7 and following Vegard's rule of linearity for intermediate compositions. There was no time available for the preparation of alkali-doped samples, so no conductivity data are available. It is expected that solid solutions of ZrP_2O_7 in ZrV_2O_7 will tend to suppress the electronic semiconductivity found in ZrV_2O_7 because of the interruption of paths for the transfer of electrons from reduced to oxidized vanadium sites. This problem seems worthy of further study.

III Search for Three-Dimensional Analogs of β-Alumina

A. Introduction

In our original proposal, some ideas were advanced for chemical modifications of the β-alumina ($NaAl_{11}O_{17}$) structure in ways that would eliminate the spinel blocks which do not contribute to ionic conductivity. One such suggestion was due to Wells[7], based on linking the conducting planes of the β-alumina structure by ditetrahedral groups such as $Si_2O_7^{-6}$ or $P_2O_7^{4-}$. Some attempts to realize such structures were made, in particular toward $BaZrSi_2O_7$ as a potential parent compound. When we obtained only $BaZrO_3$ and barium silicates, that approach was abandoned. The second approach, that of synthesizing a structure that eliminated all but the block containing the conducting planes, is described in the next section.

B. Attempts at β-alumina Modification

This work was suggested by the successful elimination of the spinel blocks in the $BaFe_{12}O_{19}$ structure by Haberey and Velicescu[8], who prepared the phase $BaTi_2Fe_4O_{11}$ by substituting enough Ti^{4+} for the Fe^{3+} to produce electrically neutral layers having the structure of the so-called R-layers in the $BaFe_{12}O_{19}$ structure, eliminating the spinel blocks.

We attempted to synthesize compounds analogous to the conducting layers in $NaAl_{11}O_{17}$ (β-alumina). The same calculation as in the case of the R-layers leads to a formula of $NaTi_2Al_3O_9$ for the ideal double layer. Dozens of samples were prepared in the ternary system Na_2O-TiO_2-Al_2O_3. The only observed phases in the system, except for known compounds in the binary systems, were a β-alumina phase and a phase previously described by Kixel et. al, as having the structure of sodium titanium bronzes, with a composition ranging from 75-86 mol percent TiO_2 along the $NaAlO_2$-TiO_2 join. We prepared samples of some single phase materials and found that they became conductive on heating in the argon atmosphere used for measurement. This conductivity was found to be electronic and evidently of d-band type. Details have been published in a communication to Material Research Bulletin, which is included in this report as Appendix 2.

During the course of this investigation, a report appeared, indicating that a phase had been discovered in the Na_2O-TiO_2-Fe_2O_3 system which had crystallographic properties similar to those we were seeking, i.e., a structure similar to β-alumina, with a short repeat unit corresponding to the c-axis direction in $NaFe_{11}O_{17}$. The composition was reported to be close to $NaFeTiO_4$, which would be the 1:1 composition on the $NaFeO_2$-TiO_2 join. We attempted to prepare samples in the neighborhood of $NaAlTiO_4$, but the samples only showed a β-alumina phase and the phase with the titanium bronze structure, nominally $Na_2Al_2Ti_6O_{16}$. When the paper on $Na_{0.9}Ti_{1.1}Fe_{0.9}O_4$, by Sato, et al.[9], appeared, those workers reported that they had been unsuccessful in preparing analogous aluminum samples. The reason for the difference is as yet unexplained. It may be that sodium β-alumina is more stable thermodynamically than $NaFe_{11}O_{17}$, or that the titanium bronze-like phase is less stable with Fe^{3+} than the compound containing Al^{3+}. It would be of considerable interest to investigate this question in detail, initially by examining mixed samples with Fe and Al, then by using substituents such as Ga^{3+} and Cr^{3+}, whose well known tetrahedral and octahedral (respectively) site preferences would stabilize the new phase.

Sato, et. al. report that their new phase is an ionic conductor having a smaller activation energy than any β-alumina materials (0.11 eV), but the absolute value of conductivity is somewhat lower, probably because of the orthorhombic distortion they observed. It would be of some interest to determine if similar phases can be found in related ternary systems, where such distortions may be reduced.

REFERENCES

1. C. Bush, B.S. Thesis, Polytechnic Institute of New York, 1977.
2. L. Hagman and P. Kierkegaard, Acta Chem. Scand. 23, 327 (1969).
3. R.T. Johnson, Jr., R.M. Biefeld, M.L. Knotek and B. Morosin, J. Electrochem. Soc. 123, 680 (1976).
4. D.E. Harrison, H.A. McKinstry and F.A. Hummel, J. Am. Ceram. Soc. 37, 277 (1954).
5. A. Burdese and M.L. Borlera, Annali di Chim. 50, 1570 (1960).
6. D.F. Graig and F.A. Hummel, Jr. Am Ceram. Soc. 55, 532 (1972).
7. A.F. Wells, Report No. NGR-07-002-058 to NASA (Oct. 1973).
8. F. Haberey and M. Velicescu, Acta Cryst. B30, 1507 (1974).
9. H. Sato, H. Kuwamoto, Y. Hirotsu, N. Otsuka and G.L. Liedl, Revue Chim Minerale 17, 404 (1980).

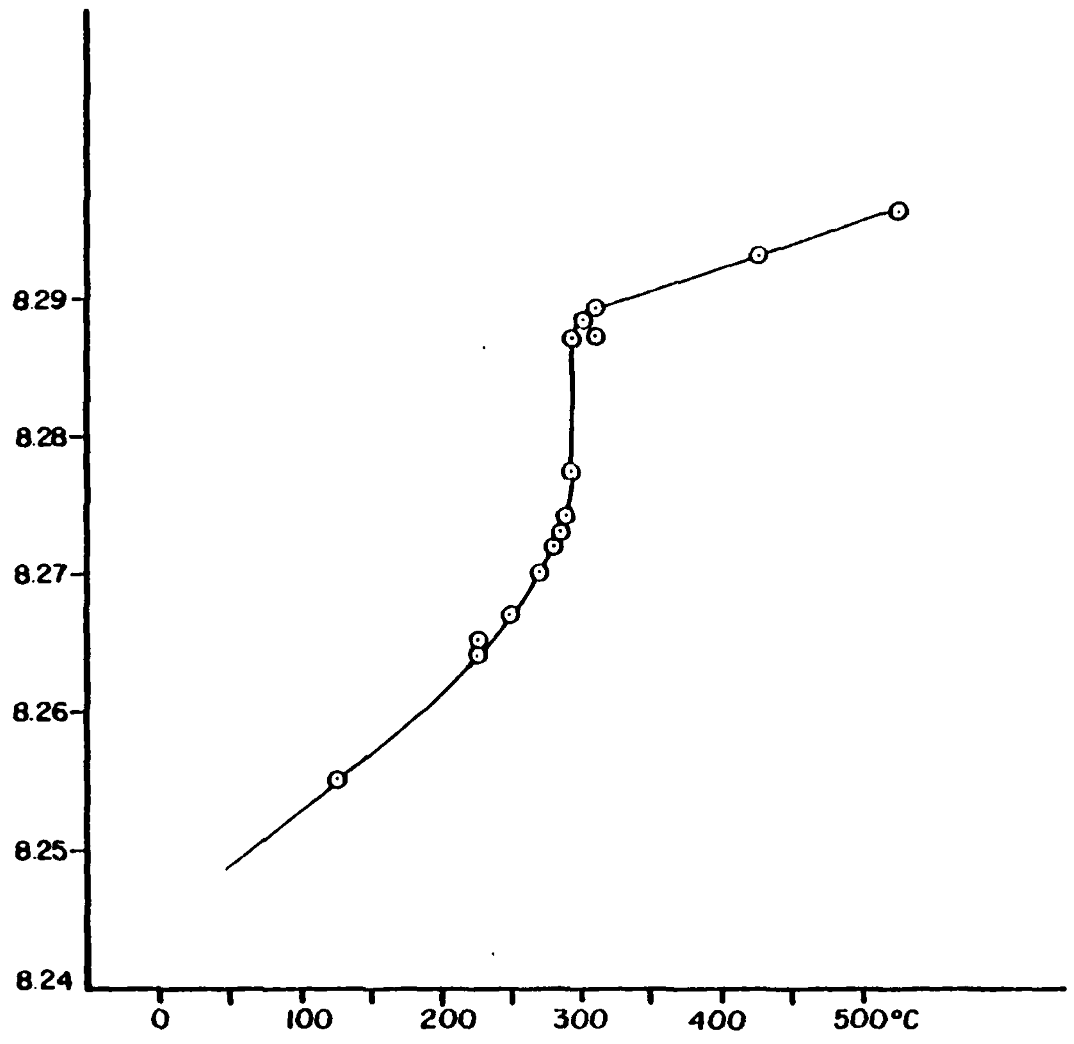


Fig.1 Thermal Expansion of ZrP_2O_7

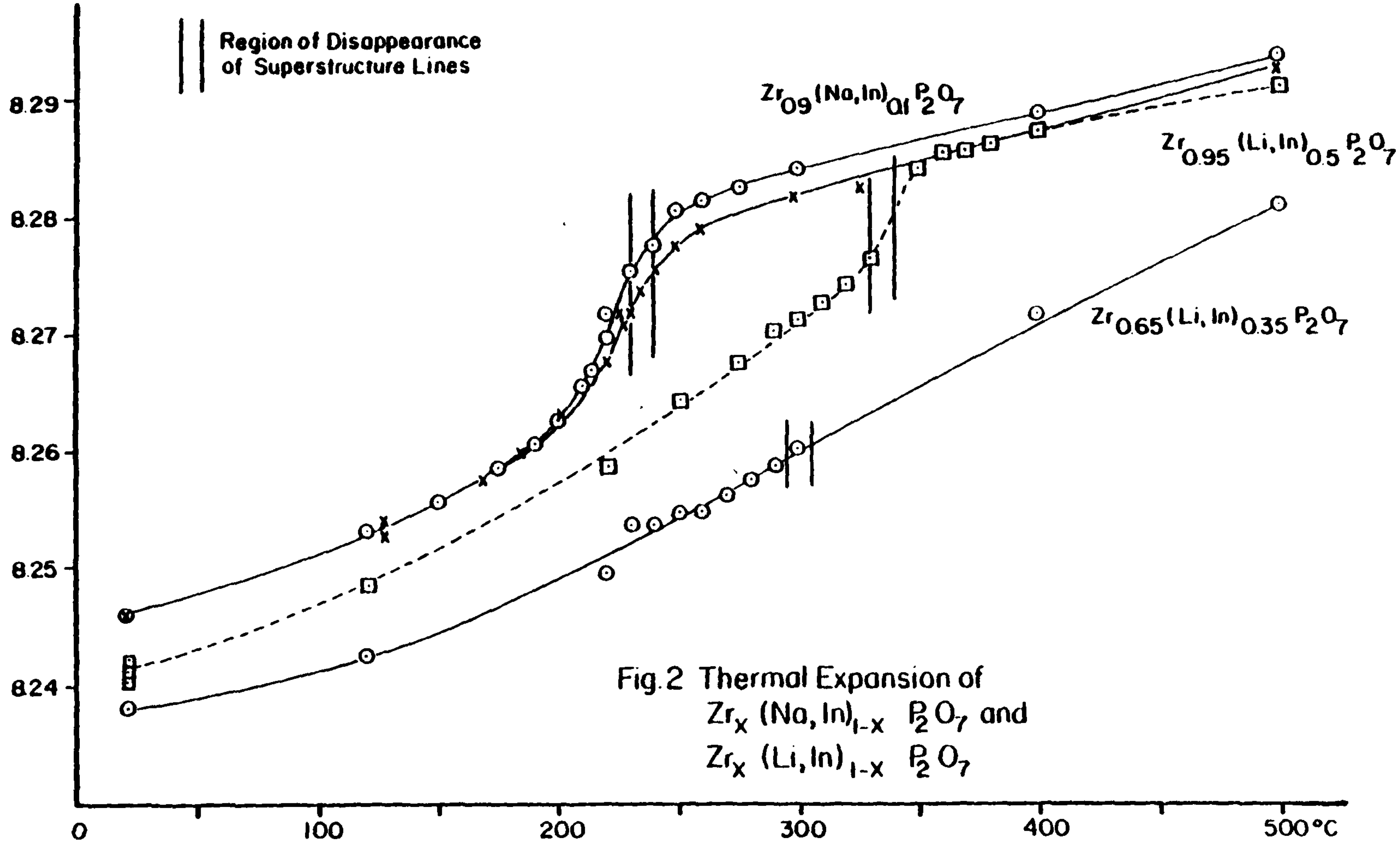


Fig.2 Thermal Expansion of
$Zr_X\ (Na,In)_{1-X}\ P_2O_7$ and
$Zr_X\ (Li,In)_{1-X}\ P_2O_7$

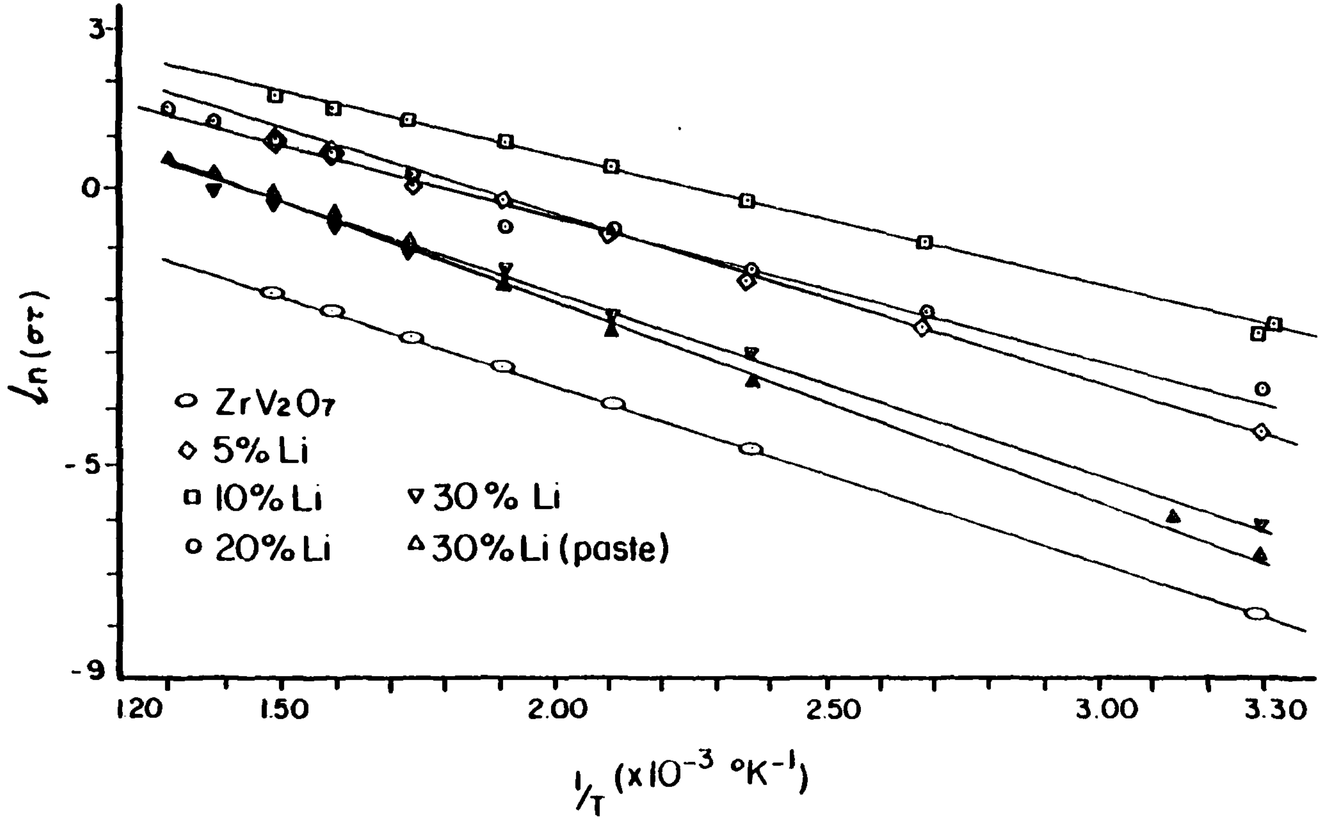


Fig. 3 Conductivities - Pulse Mode in (σ T) versus 1/T

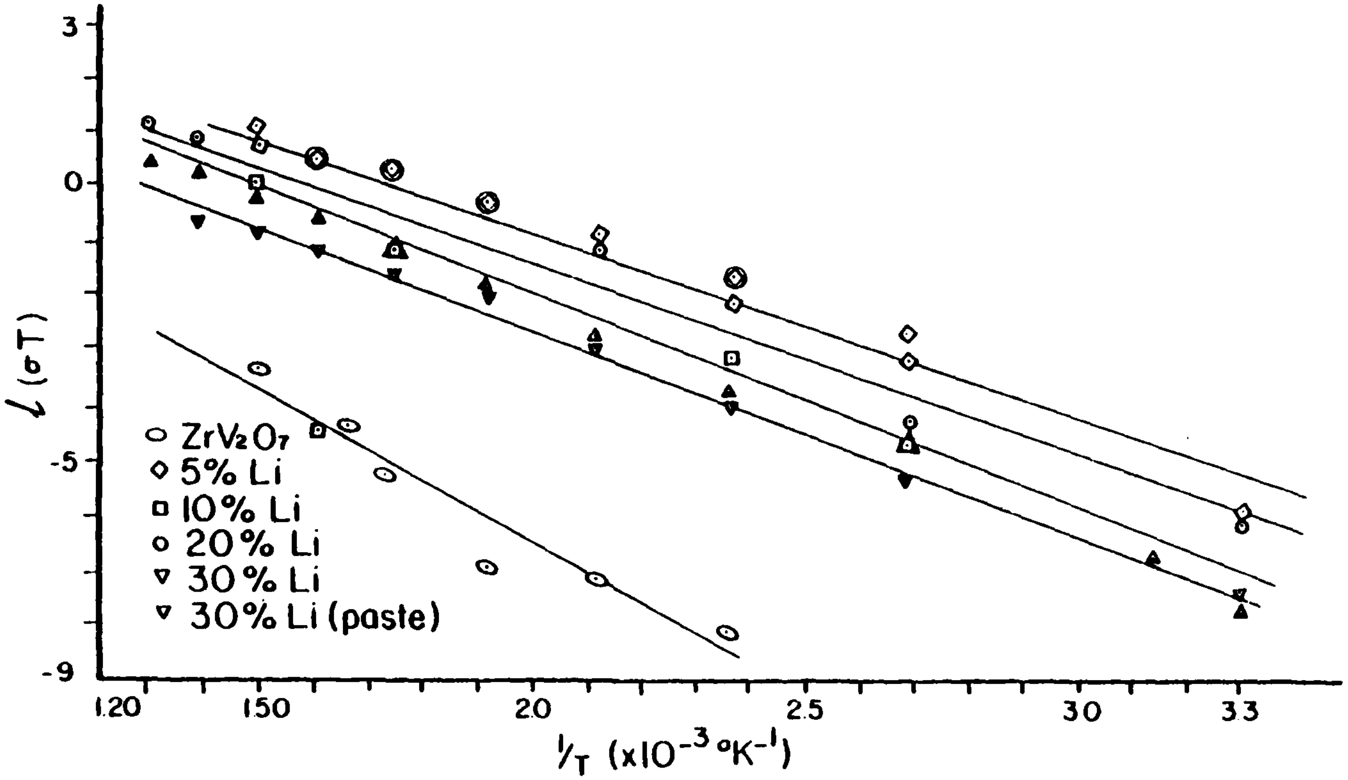


Fig. 5 Ionic Conductivities in (σT) versus $^1/_T$

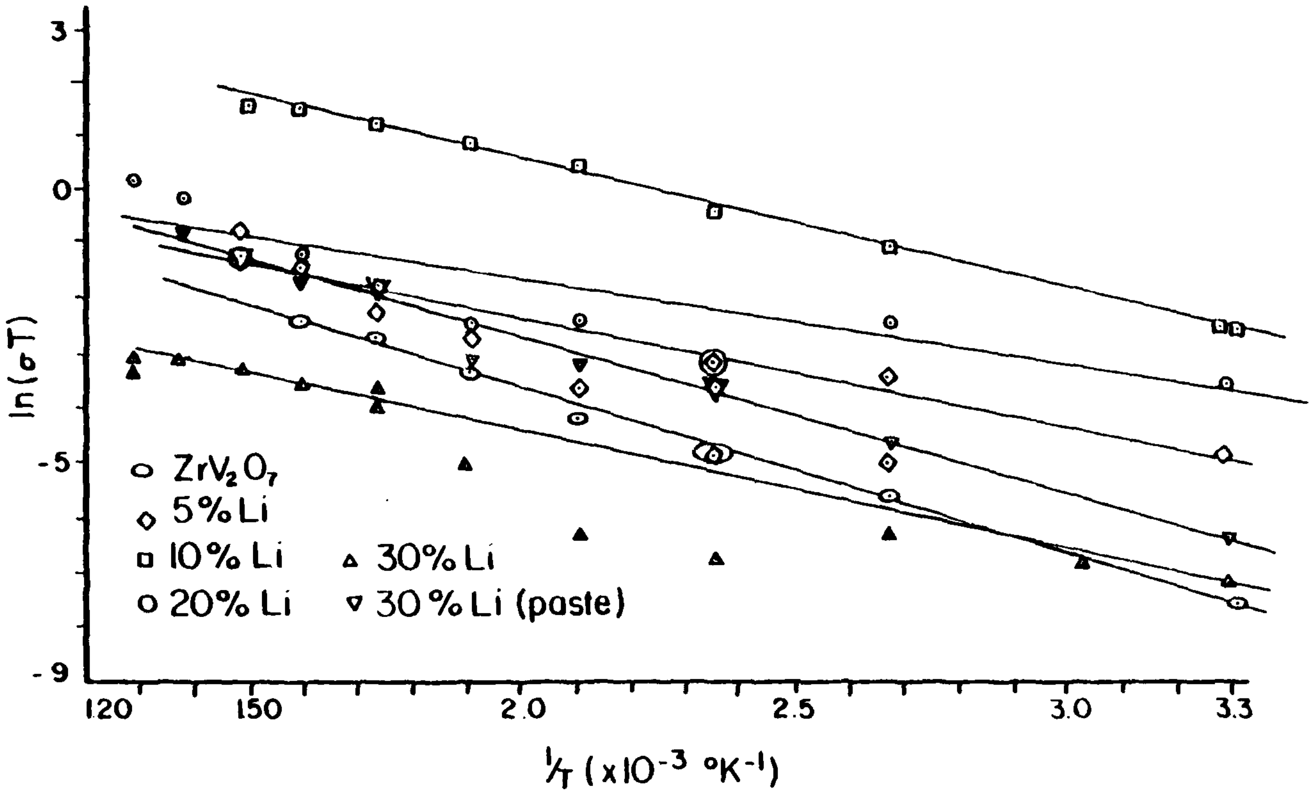


Fig. 4 Conductivities - DC Mode in(σT) versus $^1/_T$

APPENDIX 1

New Solid Electrolytes Based on Cubic ZrP_2O_7

by

R. Sacks[1], Y. Avigal[2] and E. Banks*
Department of Chemistry
Polytechnic Institute of New York
Brooklyn, New York 11201

ABSTRACT

New solid electrolytes have been formed by inserting univalent cations, Li^+, Na^+, K^+ and Ag^+, into the large, three-dimensionally connected interstitial spaces of ZrP_2O_7. Charge compensation was accomplished by substitution of M^{3+} ions (In,Y,Eu) for Zr^{4+} or by replacement of P atoms in the P_2O_7 groups with Si. The best conductivity observed was in a sample of composition $Zr_{0.65}(Li,In)_{0.35}P_2O_7$ with $\sigma=1.52 \times 10^{-4}$ $(ohm\text{-}cm)^{-1}$ at 300° . The low values are believed to be due to the small size of the "bottleneck" regions connecting the interstitial cation sites.

* Electrochemical Society Active Member

1. Present address: Eaton Corp., AIL Div., Walt Whitman Rd.,
   Melville, N. Y. 11747

2. Present address: Intel Corp., Juliette Lane, Santa Clara,
   California 95051

Key Words: Solid Electrolyte, Solid Solution, ZrP_2O_7

INTRODUCTION

Solid electrolyte materials for use in high energy batteries have attained great prominence in recent years because of their potential application for energy storage in electric vehicles and utility load-leveling. The material which has had the most attention is sodium β-alumina, $NaAl_{11}O_{17}$, which has one of the highest-known sodium ion conductivities ($\sigma_{300°C} \sim 0.2$ (ohm-cm)$^{-1}$). This material is a two-dimensional conductor, the Na^+ ions migrating in conducting planes separated by about 11Å. Other things being equal, a structure where the sites of the mobile ions have three-dimensional connectivity should be a better conductor, especially in polycrystalline ceramics. Indeed, this concept was the basis for the development by Hong and co-workers (12) of another excellent sodium ion conductor, the "Nasicon" family of sodium-zirconium phosphate-silicates. The same concept was the starting point for this investigation.

While Hong synthesized entirely new materials, our approach was to modify an already known structure. Zirconium pyrophosphate, ZrP_2O_7, and its many isomorphs have a cubic structure, shown in Figure 1, which can be thought of as a NaCl type arrangement of Zr^{4+} and $P_2O_7{}^{4-}$ ions, the chlorine position being occupied by the central oxygen of the pyrophosphate ion, while the other six oxygens are distributed in such a way as to form large, three-dimensionally connected interstitial spaces. The Zr^{4+} ions are octahedrally coordinated and the P atoms are tetrahedrally coordinated (3,4,5). Using the published lattice parameter, a rough calculation of the size of the interstitial space indicated it to be about large enough for a potassium ion, and thus easily able to accommodate Li^+ or Na^+. To compensate for the excess positive charge of the alkali ions, the charge at the Zr sites could be decreased by substitution of tervalent ions or the charge of the P sites could be decreased by substitution of a group IV element with tetrahedral site preference, such as silicon replacing phosphorus. Both types of substitution have been accomplished in this work.

The effects of such substitution on the lattice parameters can be complicated by the fact that coupled substitution in two sites is being done, and the extent of solid solution might be difficult to follow from lattice parameter measurements. Early work in this laboratory by Bush (6) on the system $Zr_{1-x}Li_xY_xP_2O_7$ had indicated that solubility was at least 10 m/o, but the system could not be followed much further because of the small lattice shifts. The use of In^{3+} as charge-compensator was then pursued, because any lattice shifts would be almost entirely due to the effect of the univalent ion, as the ionic radii of Zr^{4+} and In^{3+} are almost identical (e.g. Pauling radius for Zr^{4+} = 0.80Å; for In^{3+}, r = 0.81Å).

EXPERIMENTAL

A. Synthesis

Samples were prepared by standard solid-state techniques. Starting materials were reagent grade Li_2CO_3, $NaHCO_3$, $AgNO_3$, KH_2PO_4, In_2O_3, Y_2O_3, Eu_2O_3, SiO_2, $NH_4H_2PO_4$ and either ZrP_2O_7 previously prepared, or a hydrated zirconyl phosphate used as a precursor, by modification of a procedure described by Willard and Hahn (7) for zirconium analysis. This involved precipitation of $Zr(HPO_4)_2 \cdot H_2O$ (8) from zirconyl salt solutions with a trialkyl phosphate. This hydrated zirconium hydrogen phosphate precursor is then fired overnight in a covered platinum crucible at 1100°C forming well crystallized, homogeneous ZrP_2O_7. Whether ZrP_2O_7 or the zirconium hydrogen phosphate is used as a starting material makes no difference in the final product, but using the precursor requires finding a gravimetric factor for its conversion to ZrP_2O_7 for each batch. In addition, the precursor, when dried, is a very fine, light powder which scatters, forming airborne dust, making it difficult to handle. Thus, the preferred starting material was ZrP_2O_7, which could be prepared in large quantities.

Starting materials were combined in the desired proportions with about 10% excess $NH_4H_2PO_4$, ground in an agate mortar and fired overnight at 1100°C in covered platinum crucibles. The product was reground with 7-20% additional $NH_4H_2PO_4$.

A larger excess was required for higher substituent concentrations, and more was required for Na samples than for Li samples. Refiring was done at 1200°C for about 20 minutes followed by air quenching.

The excess phosphate was needed because P_2O_5 is lost at higher temperatures (9). The quenching was found necessary because the solid solutions of the form $Zr_{1-x}(M^{I}M^{III})_x P_2O_7$ showed evidence of exsolution when slowly cooled. It was subsequently found that solid solutions of the form $Zr(M^{I}Si)_x P_{2-x}O_7$ are thermally stable. Initially, sample preparation was considered successful if the only crystalline phase present had the x-ray pattern corresponding to the ZrP_2O_7 structure.

B. Conductivity Measurements

The samples obtained by the above procedure were fine powders, and it was necessary to prepare ceramic pellets for the measurements. About 0.6g of powder was mixed with about 0.03 of napththalene (lubricant and binder). The dried powder was pressed in an evacuated die (Perkin-Elmer) usually used for preparation of KBr pellets for infrared spectroscopy. The pellets were pressed under 3500 lb/in^2 while being pumped, for about 10 minutes. The "green" pellets were 1.30 cm in diameter and 0.18-0.20 cm thick. They were then heated at 250°C for 1 hour to drive off the binder, followed by sintering at 1200°C for 3-20 minutes and air-quenching. Samples with higher concentrations of additive seemed to lose P_2O_5 more readily requiring the shorter firing times. X-ray patterns taken of the pellets were identical with those of the powders when the firing times were adjusted to avoid loss of P_2O_5. No difficulties involving shattering of pellets from thermal shock were encountered.

The pellets ranged from 1.20 to 1.25 cm in diameter and 0.16-0.20 cm in thickness. Relative densities were 75-90%. After sintering, electrodes were evaporated on opposite faces, consisting of a thin layer of Cr followed by thicker gold contacts. These are blocking electrodes, being irreversible to alkali metal deposition.

A pulse technique (10) was the primary measuring technique used, as it obviated the need for reversible electrodes and, in combination with D. C. measurements, permitted separation of ionic and electronic components of the conductivity. The sample, clamped between spring-loaded Pt discs, was placed in series with a known resistor. Square pulses from 50-100 μsec in duration, and separated by 30 msec, were applied across the series circuit. Pulse heights varied from 5-15 volt. The total voltage drop ($V_t = V_{known} + V_{sample}$) and the voltage drop across the sample (V_s) were measured using a dual-trace oscilloscope. A 9 volt battery was wired into the circuit so that it could be switched in place of the pulse-generator for D.C. measurements, using oscilloscope deflection to measure the voltage drops.

Measurements at 10^5 Hz were made on a number of samples, using a Hewlett-Packard Digital Multi-frequency LCR Meter (4274 A). The highest frequency available, 10^5Hz, was not high enough to eliminate grain boundary resistance. Measurements at 10^5Hz agreed within 20% or less with pulse measurements. The high frequency values plotted in Figure 4 for ZrP_2O_7

were used because they behaved more regularly than the pulse measurements on that sample, whose resistance is much higher than that of the "doped" samples.

The resistance of the sample was calculated using the formula:

$$R_s = (V_t/V_k - 1)R_k \qquad \text{(Eq.1)}$$

Even though V_s is measured, V_k is easily obtained from $V_t = V_k + V_s$. The resistivity is calculated from the R_s value using the electrode geometry and the conductivity; σ is the reciprocal of the resistivity.

A spring-loaded sample holder was constructed, using a fused silica tube 30 cm long and 2 cm in diameter, with the lower end collapsed to form a support for a brass cylinder which supports a thin platinum disc as the bottom electrode. A second brass cylinder is pressed onto the upper Pt disc electrode by a hollow ceramic tube, and pressure is applied to the whole assembly by means of three tension springs pulling the lower electrode up against the upper electrode, and an alumel wire was fused to the contact point, permitting temperature measurement close to, but not within the sample. Using this assembly, it was found that an adequate range of sample temperatures could be attained using the gradient established by the furnace when its controller was set to the maximum desired temperature. Only about ten minutes were required to establish thermal equilibrium after the sample position was changed.

C. Lattice Parameters

X-ray powder data were obtained using a Norelco powder diffractometer. All samples were mixed with silicon powder as an internal standard. After correcting Si peak positions, sample peaks were corrected by interpolation of Si corrections. The number of peaks used (in the range of $60^{\circ} \leq 2\theta \leq 135^{\circ}$) varied from twelve to seventeen, with the solid solutions of lower "x" having a larger number of usable peaks due to their better crystallinity.

Lattice parameters calculated were extrapolated to $\theta=90^{\circ}$ on a plot of the "a" values against $\cos^2\theta$. Error estimates are maximum values obtained by calculating maximum deviations in "a" at each peak and extrapolating to 90° for positive and negative deviations.

RESULTS AND DISCUSSION

In the system $Zr_{1-x}(Li,In)_xP_2O_7$, cubic "ZrP_2O_7" patterns appeared with no peaks of other crystalline phases up to X=0.5. However, at X=0.45 a "halo" appeared in the low angle region, indicative of a glassy phase. The pattern of this amorphous phase was found to intensify when a sample having X=0.75 was prepared. When the cubic lattice parameters were plotted against composition (Figure 2) the values can be seen to decrease until X=0.35, followed by a constant value of a_o. When a mixture of Li_2CO_3, In_2O_3 and $(NH_4)H_2PO_4$ in molar ratio 1:1:2 was heated to 1200°C and quenched the product was a glass. The conductivities of the Li, In series also level off at about X=0.35. All of these observations indicate that X=0.35 represents the solubility limit. Similar results were obtained for $Zr_{1-x}(Na,In)_xP_2O_7$. Here the decrease in lattice constant is much more gradual, the limiting value of a_o being 8.241A for $Zr_{0.65}(Na,In)_{0.35}P_2O_7$. The solubility limits in the cases of silver and potassium are less clear. No measurable shift in lattice parameters was found, and the conductivity data were inconclusive on this point.

Other series synthesized were $Zr_{1-x}(M^IM^{III})_xP_2O_7$, and $Zr(M^ISi)_xP_{2-x}O_7$, where M^I=Li or Na and M^{III}=Y or Eu. Attempts at $Zr(Na,Ge)_xP_{2-x}O_7$ failed. Table I shows estimated solubility limits deduced from x-ray and conductivity data.

TABLE I

Estimated Solubility Limits

	M^I-Li	Na	Ag	K
M^{III} - In	0.35	0.35	~0.35	~0.35
Y	< 0.30	< 0.30		
Eu	< 0.20	< 0.20		
M^{IV} - Si	> 0.50	> 0.50		

It should be noted that Y, Eu and Si all had the expected expanding influence on the lattice. The largest lattice parameter was found for $Zr_{0.8}(Na,Y)_{0.2}P_2O_7$ where $a_o = 8.282A$.

Table II lists representative conductivities. The highest conductivity was found in $Zr_{0.65}(Li,In)_{0.35}P_2O_7$, for which $\sigma_{300^\circ C} = 1.52 \times 10^{-4}$(ohm-cm)$^{-1}$. This sample had a relative density of 0.89 or a fractional porosity of 0.11. Using a formula derived by Juretschke, Landauer and Swanson (11) for conductivity of sintered powders, we derived a corrected value of 1.78×10^{-4}(ohm-cm)$^{-1}$ for this sample, an increase of about 18%. Other factors such as incomplete electrode contacts, might add a few percent, but two orders of magnitude improvement would be needed to make these materials candidates for practical use. It should be noted that all samples were checked for D.C.

conductivity as described above. The D.C. component of conductivity was less than 3% of the total and it was concluded that there is no electronic conductivity in the range investigated.

TABLE II

Conductivity $(\text{ohm-cm})^{-1} \times 10^6$ for $Zr_{1-x}(M^I,M^{III})_xP_2O_7$ at 300°C

(Uncorrected for Porosity)

		M^I			
	X = 0.2	Li	Na	Ag	K
	In	107	4.18	1.01	0.053
M^{III}	Y	198	1.11		
	Eu	27.8	0.71		
	X = 0.3				
M^{III}	In	139	5.74	2.92	0.162
	Y		2.27		
	Eu	16			

Figure 3 is a plot of ^7Li NMR linewidths (full width at half-height) in a sample of composition $Zr_{0.55}(Li,In)_{0.45}P_2O_7$. This measurement was performed in the laboratory of Professor Bruce McGarvey at the University of Windsor, Ontario, Canada. The substantial narrowing between 300-400 K indicates the onset of lithium ion mobility. The ^{31}P resonance was also monitored and showed no significant changes in the same temperature range. A sample containing sodium was also measured, but the large quadrupole splitting in ^{23}Na made the detection of such line-narrowing too difficult to permit conclusions about the Na^+ mobility. The line-narrowing of the ^7Li spectrum, however, strongly indicates that Li^+ is indeed the mobile species in the Li-containing samples.

Figure 4 shows Arrhenius plots (-ln T vs 1/T) for several samples. Activation energies for these samples were: ZrP_2O_7 - 13.0; $Zr_{0.9}(li,In)_{0.1}P_2O_7$ - 19.0; $Zr_{0.8}(Li,In)_{0.2}P_2O_7$ - 16.7; and $Zr_{0.7}(Li,In)_{0.3}P_2O_7$ - 16.9 Kcal/mole. The activation energies for Na-containing samples were about 18 Kcal/mole. The finding of a measurable conductivity for ZrP_2O_7 itself may possibly be attributed to oxygen ion mobility. The low activation energy does not seem to support such an interpretation. The possibility that the conductivity of "undoped" ZrP_2O_7 is due to alkali metal impurities was also ruled out because of the low activation energy, compared to that of deliberately alkali-doped samples. However, it is possible that the observed very low conductivity is due to small concentrations of alkali metal impurities migrating along surface sites. Such surface conductivity would have lower activation energy than bulk material and would not be detected in the doped samples. All other samples studied showed activation energies in the same range (14-20 kcal/mole).

Attempts to measure the conductivitities of $Zr(M^ISi)_xP_{2-x}O_7$ were unsuccessful, owing to apparent electrolytic breakdown of these materials in the applied field, High conductivities were observed initially, but they decreased rapidly with time. In the case of $Zr(Li,Si)_{0.35}P_{1.65}O_7$, a white powder was observed to form at the interface with the electrode. X-ray diffraction gave a pattern which was similar to that of LiH_2PO_4. If this product is actually present, it must be a result of a reaction of Li or Li_2O with traces of moisture, and attack on the sample material itself, or of formation of a separate lithium phosphate phase followed by hydration.

The low conductivities observed for these materials are understandable in terms of the size of the "bottlenecks" (pathways between interstitial sites). In unsubstituted ZrP_2O_7 the bottleneck is a puckered pentagon of oxide ions. Two sides of the pentagon are edges of ZrO_6 octahedra and the remaining three sides are edges of PO_4 tetrahedra, two being from the same P_2O_7 group and the third formed by two outer oxygens of another pyrophosphate ion. To estimate the size of this bottleneck, we approximate it by a planar pentagon (Figure 5). Using Chaunac's values (4) for the various interatomic distances, one obtains the sides of the pentagon. By averaging the distances, a regular pentagon is obtained, yielding an average distance from oxygen to the center of the pentagon of 2.20A. Using an ionic radius of 1.40A for O^{2-}, one obtains a "radius of passage" of about 0.80A. This is too small for Na^+(r_{Na^+}~1.02A) but should be just large enough for Li^+(r_{Li^+}~0.76A). However, this calculation was for pure ZrP_2O_7. The observed lattice contraction in $Zr_{1-x}(Li,In)_xP_2O_7$ would be expected to decrease the interatomic distances in the neighborhood of lithium ions, especially since the indium ions would be expected to induce a local expansion ($r_{In^{3+}} \sim 0.80$A; $r_{Zr^{4+}} \sim 0.72$A). All radii used in this discussion are taken from Shannon (12). The larger conductivity found for the $(Li,Y)_{0.2}$ sample as compared with $(Li,In)_{0.2}$ (Table II) supports this concept. The lattice parameter of the Li,Y sample was 8.270A, compared to 8.236A for the Li,In sample. If higher concentrations could have been achieved in the Li,Y series, it is likely that quite good conductivities would have resulted. Current work in this direction is aimed at achieving high interstitial ion concentrations combined with expansion of the lattice.

Finally, it is somewhat puzzling that the ^{7}Li NMR data indicate the onset of high lithium ion mobility at 300 K, while the conductivity data at much higher temperatures indicate low mobility. We believe that the narrowing of the NMR line is caused by mobility of the Li^+ ions within the cages (the cage in ZrP_2O_7 can accommodate ions up to 1.2A in radius). The line broadening below 200 K would then be attributed to asymmetric binding of lithium ions to oxygen ions at one side of the cage, with a distribution over several types of binding site. The transition of the lithium ion mobility is not connected to the well-known transition in ZrP_2O_7 at about 300°C (9). We have investigated the effect of the coupled substitutions described above on that transition, an although the transition temperature is lowered, it never seems to fall below about 200°C.

ACKNOWLEDGEMENTS

The authors thank Mary Eschwei of the Physics Department, Polytechnic Institute of New York for the preparation of electrodes on the samples, and Professor Bruce McGarvey of the University of Windsor, Ontario, Canada for NMR measurements. This research was supported by Grant DAAG29-78-G0150 and Contract DAAG29-80-C-0138 from the Army Research Office, Durham, North Carolina. This paper is part of a dissertation submitted by Robert Sacks to the Polytechnic Institute of New York in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemical Physics).

REFERENCES

1. H. Y.-P. Hong, Mat. Res. Bull. 11, 173 (1976).
2. J. B. Goodenough, H. Y.-P. Hong and J.A. Kafalas, Mat. Res. Buel. 11, 203 (1976).
3. R.W.G. Wyckoff, "Crystal Structures", 2nd edition, Vol. 3, p.429, Wiley-Interscience, New York (1965).
4. M. Chaunac, Bull. Soc. Chim. France, 1971, 424 (1971).
5. C. H. Huang, O. Knop, D.A. Othen, F. W. D. Woodhams, and R. A. Howie, Can. J. Chem. 53, 79 (1975).
6. C. Bush, B.S. Thesis, Polytechnic Institute of New York (1977).
7. H. H. Willard and R. B. Hahn, Anal. Chem 21, 2 (1949).
8. A. Clearfield and J. A. Stynes, J. Inorg. and Nucl. Chem. 26, 117 (1964).
9. D. E. Harrison, H. A. McKinstry and F. A. Hummell, J. Am. Ceram. Soc. 37, 277 (1954).
10. R. T. Johnson, Jr., R.M. Biefeld, M. L. Knotek and B. Morosin, J. Electrochem. Soc. 123, 680 (1976).
11. H. J. Juretschke, R. Landauer and J.A. Swanson, J. Appl. Phys. 27, 838 (1956).
12. R. D. Shannon, Acta Cryst. A32 , 751 (1976) .

FIGURE CAPTIONS

Figure 1 - Structure of ZrP_2O_7. Large spheres are oxygens, smaller spheres are Zr. The P atoms are hidden.

Figure 2 - Lattice parameters of $Zr_{1-x}Li_xIn_xP_2O_7$. Versus x.

Figure 3 - ^{7}Li NMR linewidth for $Zr_{0.55}Li_{0.45}In_{0.45}P_2O_7$.

Figure 4 - Arrhenius plots of conductivity vs 1/t for ZrP_2O_7 and solid solutions.

Figure 5 - "Bottleneck" in ZrP_2O_7.

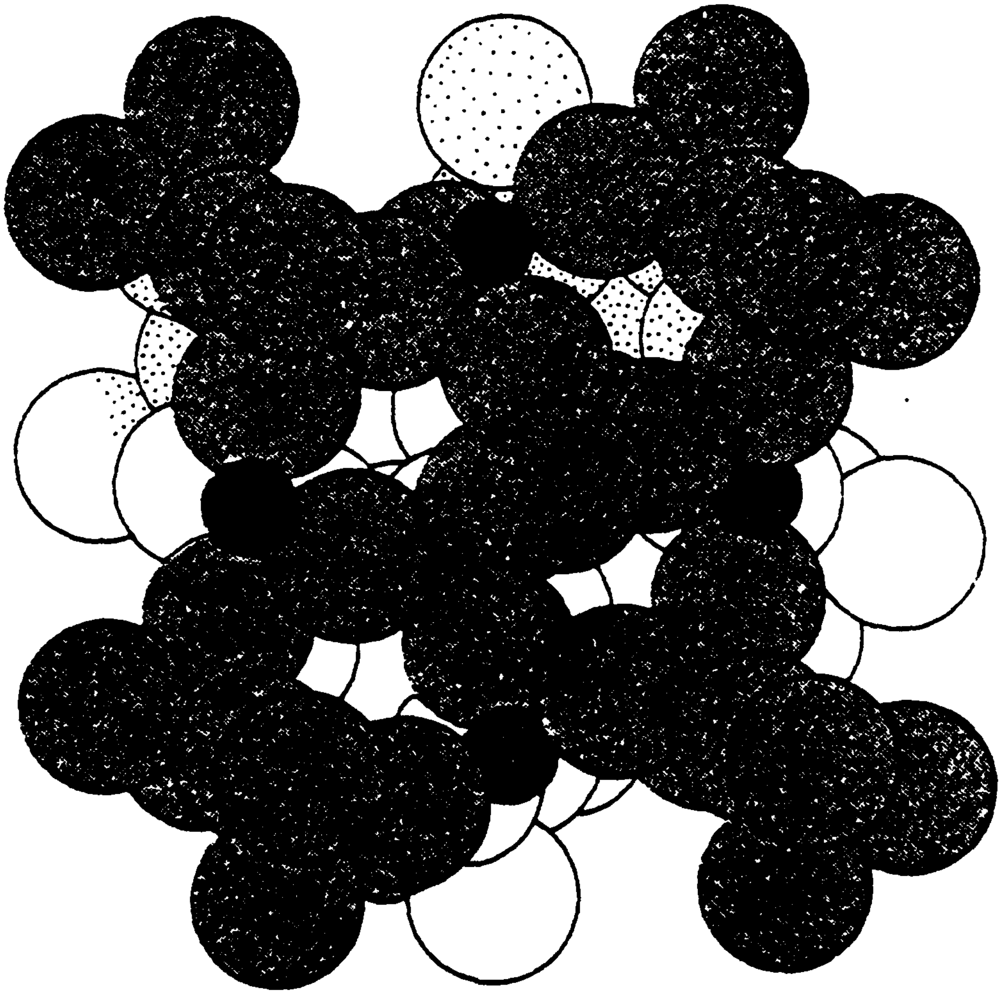


Figure I.

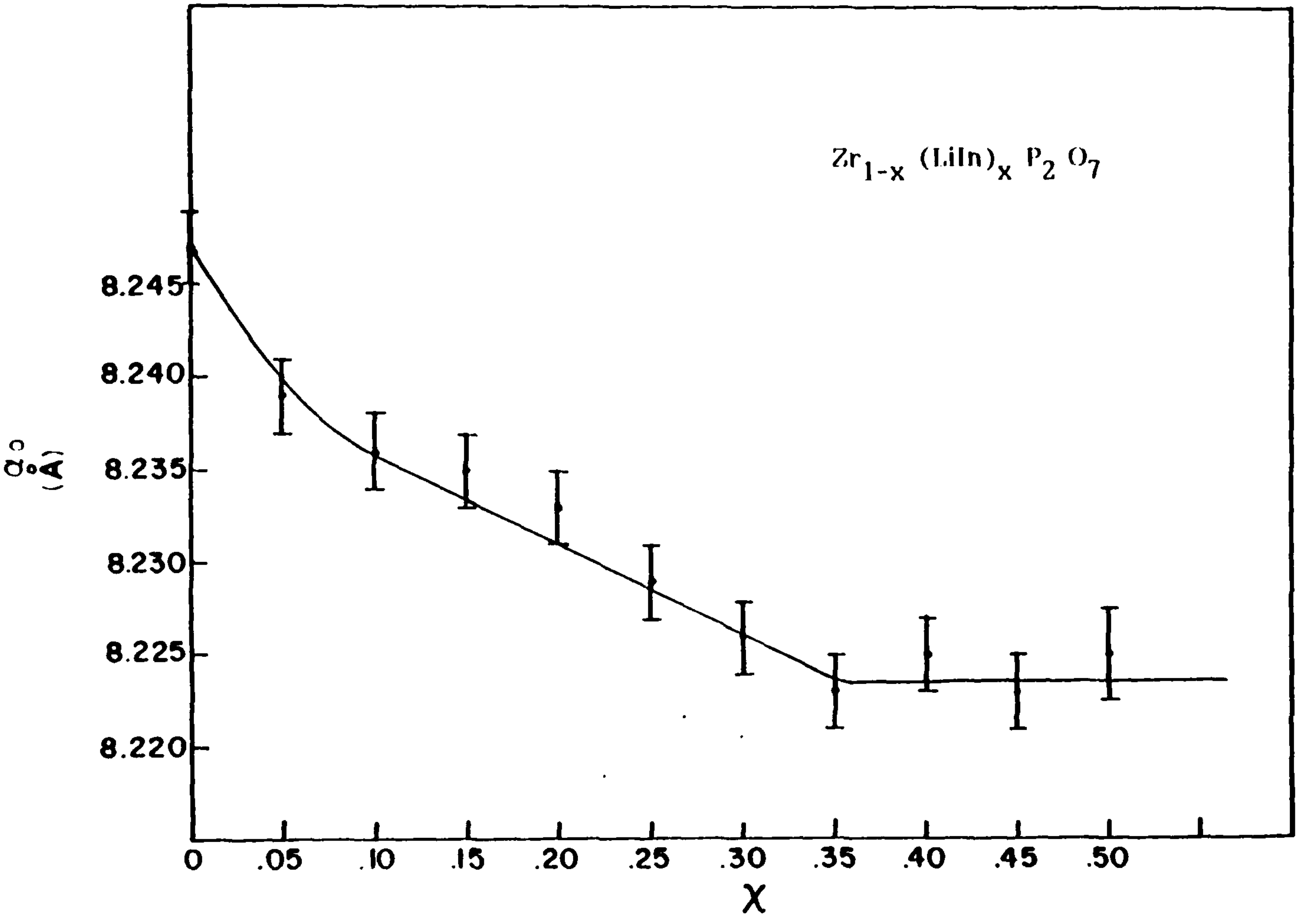

$Zr_{1-x}\ (LiIn)_x\ P_2\ O_7$
a_o (Å)
8.245
8.240
8.235
8.230
8.225
8.220
0
.05
.10
.15
.20
.25
.30
.35
.40
.45
.50
X

Figure II.

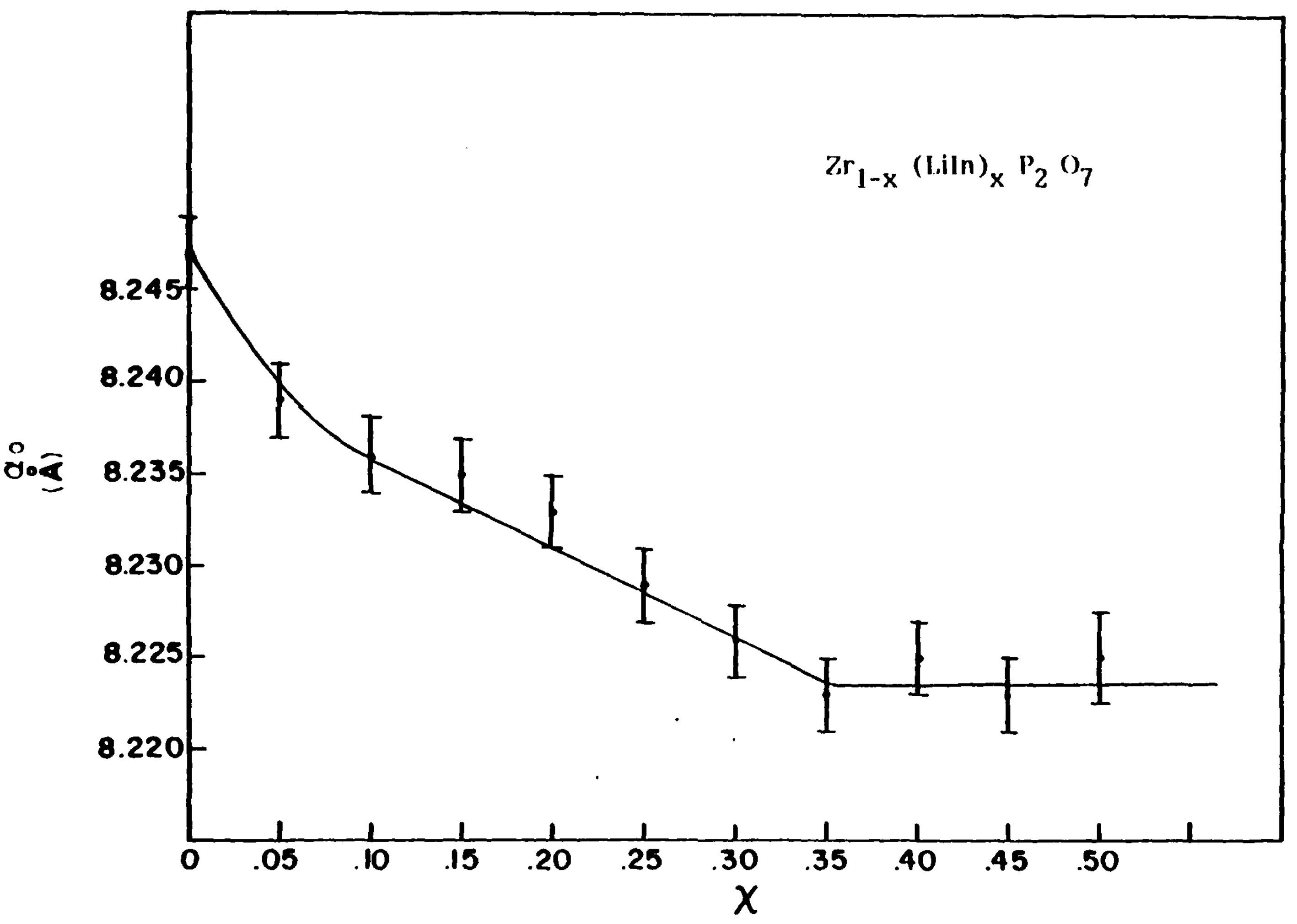

$Zr_{1-x}(LiIn)_x P_2 O_7$
a_o (Å)
8.245
8.240
8.235
8.230
8.225
8.220
0
.05
.10
.15
.20
.25
.30
.35
.40
.45
.50
X

Figure II.

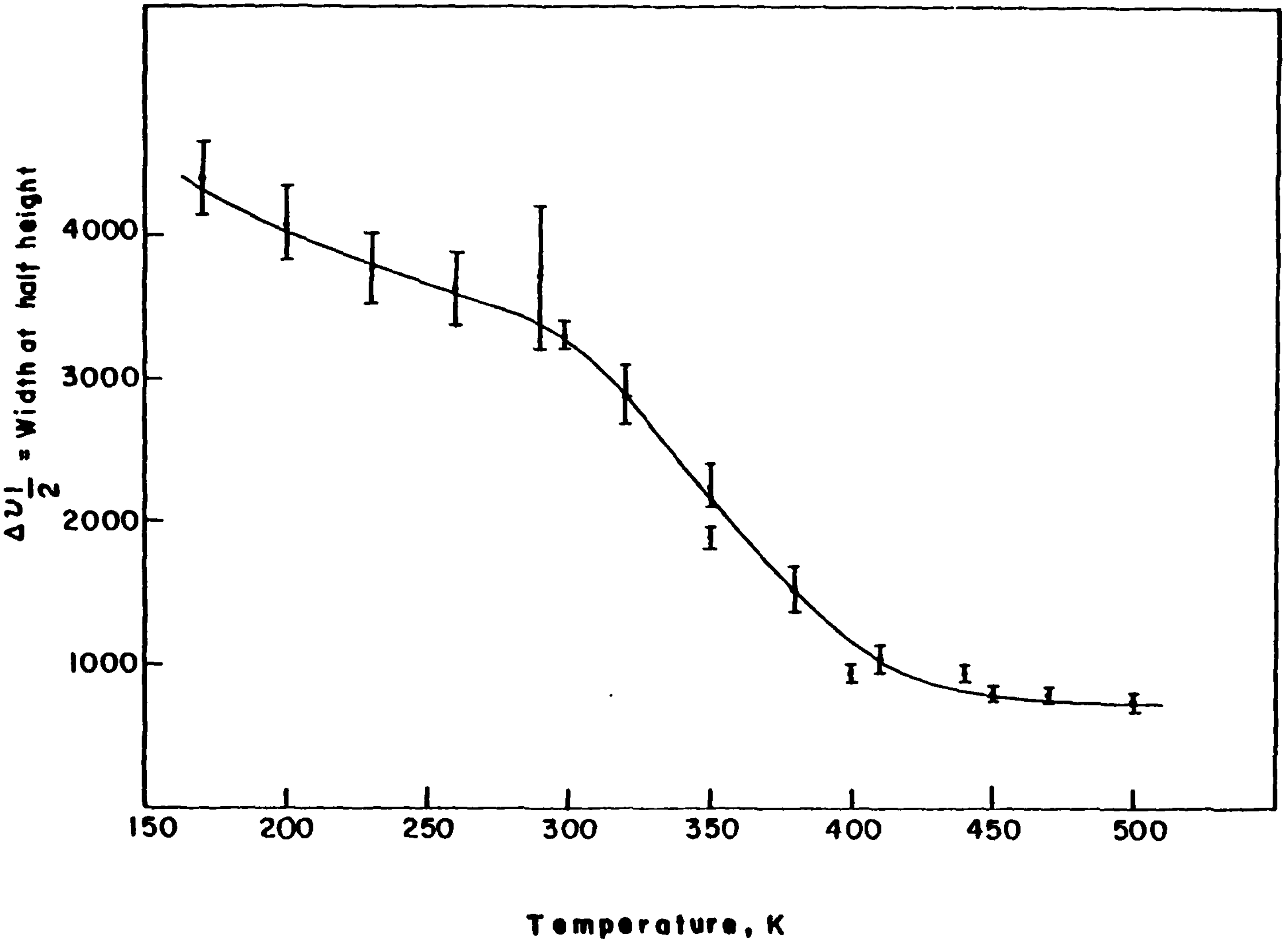

$\Delta\nu_{\frac{1}{2}}$ = Width at half height
4000
3000
2000
1000
150
200
250
300
350
400
450
500
Temperature, K

Figure III.

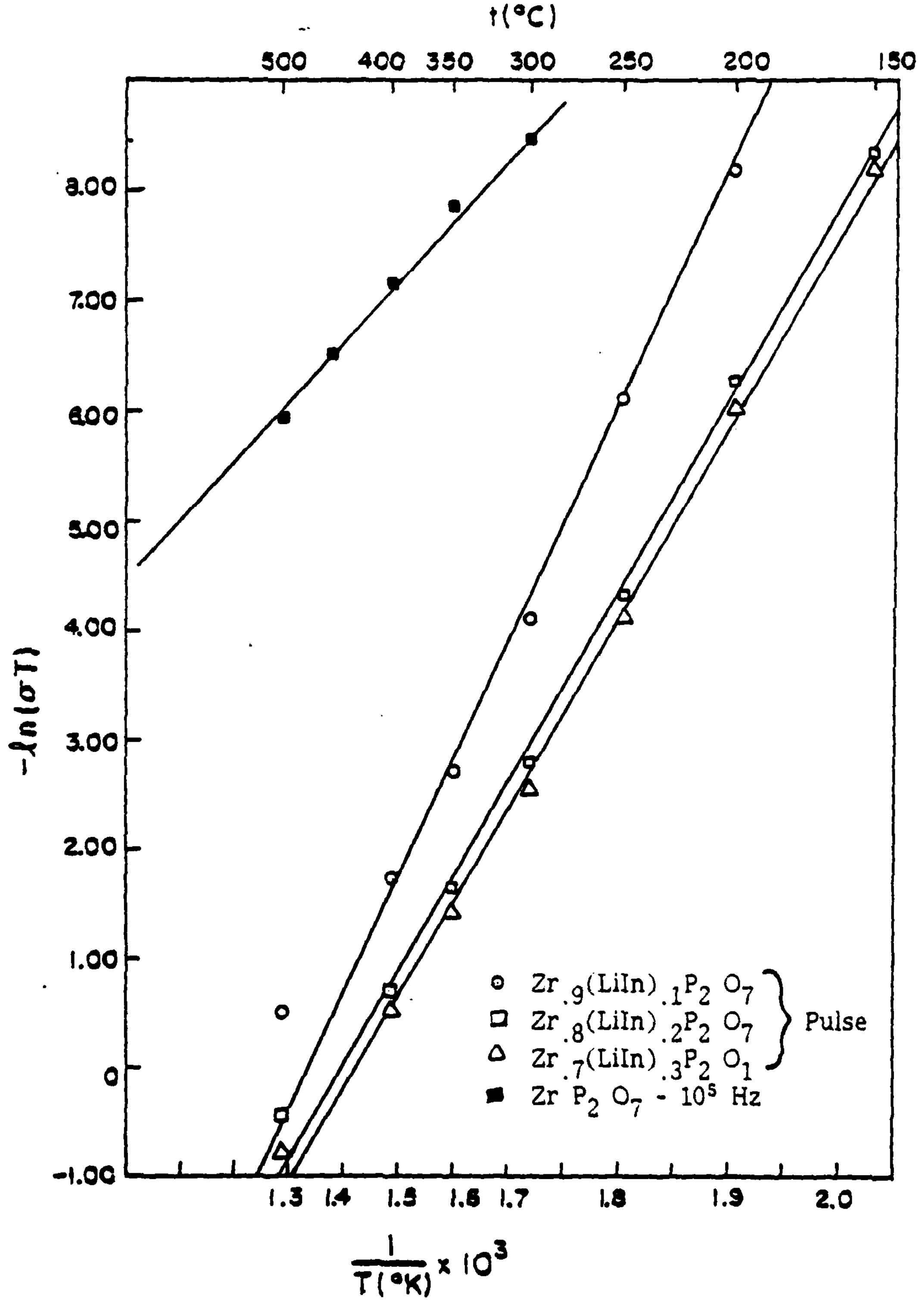

t(°C)
500
400
350
300
250
200
150
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0
-1.00
$-\ln(\sigma T)$
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
$\frac{1}{T(°K)} \times 10^3$
○ $Zr_{.9}(LiIn)_{.1}P_2O_7$
□ $Zr_{.8}(LiIn)_{.2}P_2O_7$
△ $Zr_{.7}(LiIn)_{.3}P_2O_1$
Pulse
■ ZrP_2O_7 - 10^5 Hz

Figure IV.

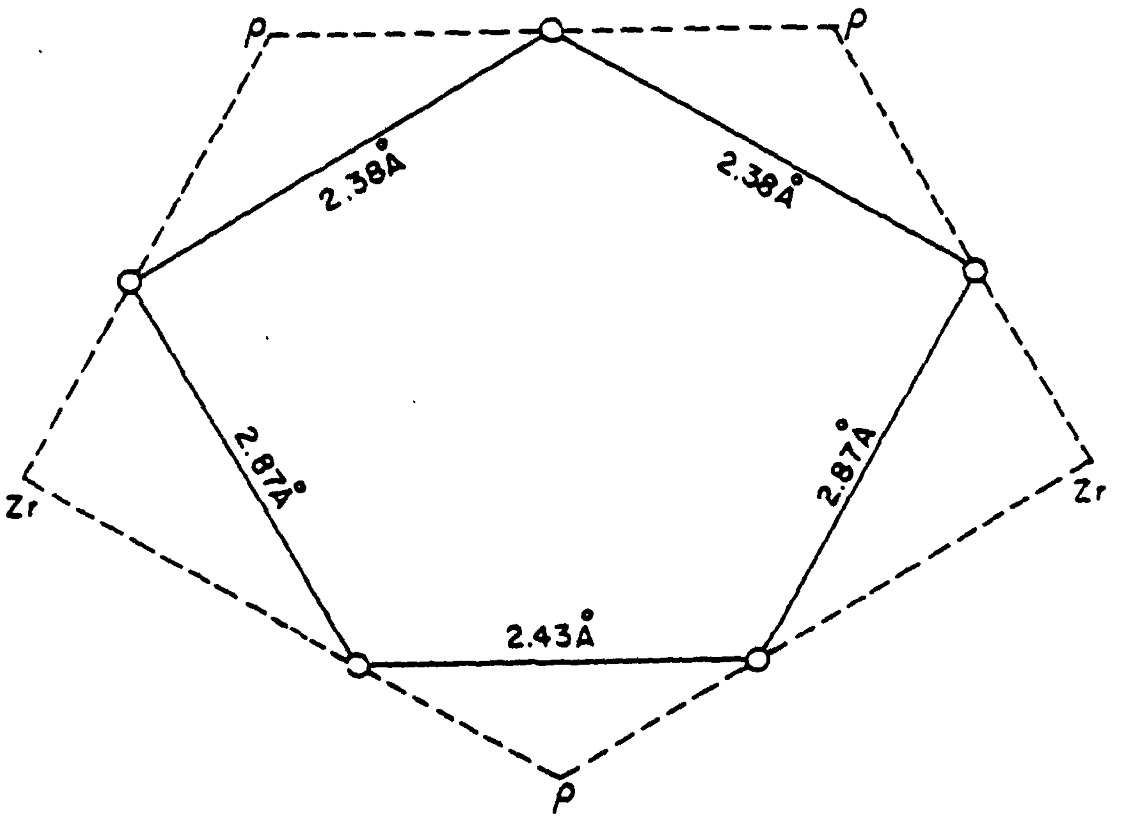


Figure V.

Mat. Res. Bull., Vol. 15, pp. 1381-1383, 1980. Printed in the USA.
0025-5408/80/101381-03$02.00/0

APPENDIX II

CONDUCTIVITY OF REDUCED SOLID SOLUTIONS IN THE SYSTEM $Na_2O-Al_2O_3-TiO_2$*

Y. Avigal** and E. Banks
Department of Chemistry
Polytechnic Institute of New York
Brooklyn, NY 11201

(Received June 25, 1980: Communicated by R. Roy)

ABSTRACT

Solid solutions of the "titanium bronze" phase found in the system $Na_2O-Al_2O_3-TiO_2$ were made conductive either by H_2 reduction or the use of metallic Ti. Conductivity measurements by pulse and D.C. methods (blocking electrodes) show semiconducting behavior with activation energies decreasing with the extent of reduction, from 101 kJ/mole in "unreduced" samples to 39.8 kJ/mole in samples reduced with Ti metal. At about 600°C, all samples have conductivities about 7×10^{-3} $ohm^{-1}cm^{-1}$, indicating that reduction occurs by oxygen loss in the Ar atmosphere. The occurrence of semiconductivity rather than metallic conductivity is explained by the blocking of conduction paths by the Al ions. Absorption spectra show no discrete spectrum for Ti^{3+}, but a broad absorption band indicates the presence of delocalized electrons.

Experimental

A solid solution with the structure of sodium-titanium bronze (1), Na_xTiO_2 has been shown to exist along the $BaAlO_2-TiO_2$ join in the ternary system $Na_2O-TiO_2-Al_2O_3$, with a homogeneity range between 75-86 mole percent TiO_2 (2).

We have found that this phase can be made electrically conductive by using either hydrogen gas or metallic titanium as a reducing agent. When hydrogen was used, samples were prepared by mixing and grinding analytical grade Na_2CO_3, Al_2O_3 and TiO_2 in appropriate proportions (10% excess Na_2CO_3 was added to compensate for firing losses), followed by 10 hour preheating at 700°C and final firing at 1200°C for 10 hours. These samples were then reduced in flowing hydrogen at 1000°C. After this treatment, the color of the samples changed from white through yellow to dark blue. The other method of preparation was

---

* Supported by the Department of the Army, Grant No. DAAG-29-78-G-0150.

** Present address: Intel Corporation, Santa Clara, California.

done as closely as possible to the method used by Andersson and Wadsley (1) for preparation of the Na_xTiO_2 phase. The starting materials were $Na_2Ti_3O_7$, Al_2O_3, TiO_2 and metallic Ti. These products were dark blue in color, and x-ray diffractometer patterns were identical for samples prepared by both methods, and also agreed with the patterns reported for the sodium-titanium aluminum oxide phase with the rbonze structure, within the precision of measurement of diffractometer peaks. Small differences in lattice parameters may exist.

For conductivity measurements, pressed pellets were aintered at 1000°C in argon or nitrogen. Electrodes were applied to the discs either by evaporating in a thin layer of chromium followed by gold, or by applying platinum paste and baking.

Measurements were made by applying spring-loaded platinum contacts in a sample holder enclosed in a fused silica tube fitted for a flowing argon protective atmosphere. This assembly was heated in a vertical tube furnace. The measuring circuit consisted of the sample assembly in series with a standard resistor, the power source and detector. For D.C. measurements, the power source was a battery and the detector a digital multimeter which measured the voltage drop across the known resistor to determine the current and across the sample to determine the voltage, from which the D.C. resistance could be determined. For pulse measurements, a square pulse generator was used, and the voltage pulse across the know resistor was displayed on a dual trace oscilloscope along with the pulse across the total circuit. This measured the total (electronic and ionic) conductivity of the sample (3), while the D.C. measurement (blocking electrodes) only determines the electronic conductivity.

Discussion and Conclusions

For a series of measurements on samples of a given initial composition, prepared without reduction, by hydrogen reduction and by reduction with Ti metal, no significant difference was found in resistivity between the D.C. and pulse methods, indicating that the conductivity in this temperature range is mainly electronic, the ionic contribution probably being less than 5%, the estimated error in the measurements. The "unreduced" sample is believed to have acquired its electronic conductivity during the process of sintering the pellets in argon atmosphere, where some loss of oxygen must have occurred.

Table 1 shows the resistivities at several temperatures for three samples having the same nominal starting composition of $Na_2Al_2Ti_6O_{16}$. As seen in the table, the substantial differences among the samples at room temperature are sharply reduced at higher temperatures. This shows clearly in Figure 1, a plot of lot σT against reciprocal temperature.

TABLE 1

Treatment:	Resistivity, kΩ-cm, at:				Ea, kJ/mole:
	30°C	200°C	300°C	425°C	
Non-reduced	----	1000	12	4	101.3
H_2 reduced	1200	11	5.5	----	49.7
Ti reduced	67	2	1	0.6	39.8

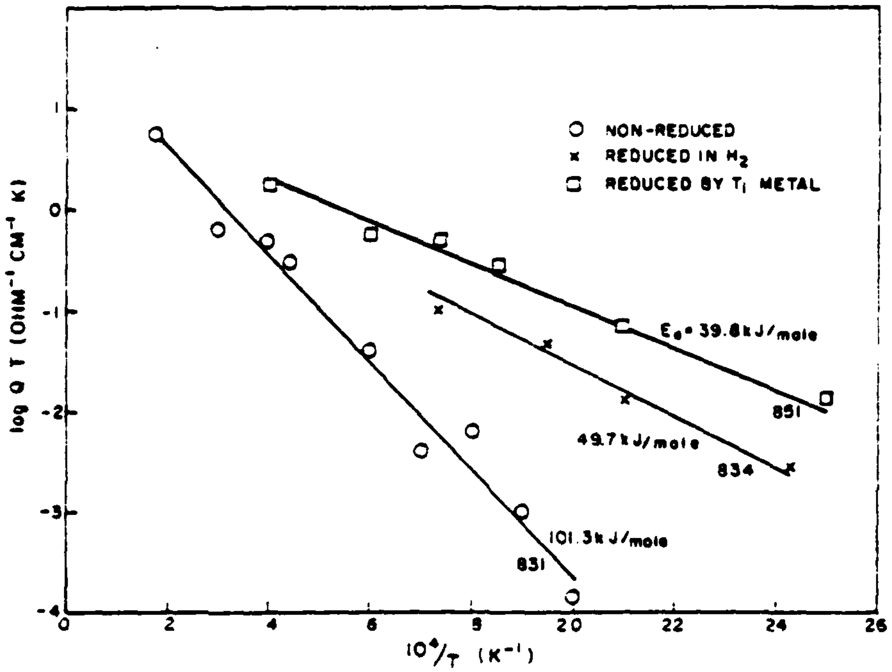


FIG. 1

Arrhenius plot (log σTvs. for 1/T for partially reduced $Na_2Al_2Ti_6O_{16}$.

Such exponential behavior is characteristic both of semiconductors and solid electrolytes. The observed equality of D.C. and A.C. conductivity eliminates any appreciable ionic component. The similarity in structure and appearance to the titanium bronzes suggest a bronze-like conductivity should be present. The semiconducting behavior observed here could originate from hopping among localized sites, or by conduction electrons of low mobility in a narrow band. In the former case, the localized donors should be detectable by the characteristic absorption band of Ti^{3+} in the vicinity of 20,000 cm^{-1}. Accordingly, we measured the absorption spectrum of a dispersion of the powdered sample in KBr. No characteristic band was observed, in agreement with observations of Reid and Sienko (4) on the titanium bronze $Na_2Ti_9O_{16}$. A broad absorption over the range 29,000 - 3000 cm^{-1} was found, just as in the case of the pure titanium bronze. This too is interpreted as due to the presence of delocalized conduction electrons. The observed semiconductive behavior is attributed to the effect of the aluminum ions which cannot participate in electron delocalization, thus interrupting electron transport across the sample

References

1. S. Andersson and A. D. Wadsley, Acta Cryst 15, 201 (1962).

2. N. G. Kixel and G. A. Shishlovskaya, Inorg. Materials (transl. of Izv. Akad. Nauk SSSR (Neorg. Mater.) 13(2), 1970 (1977).

3. R. T. Johnson, Jr., J. Electrochem. Soc. 1 3, 680 (1976).

4. A. F. Reid and M. J. Sienko, Inorg. Chem. 6, 321 (1967).

ATE

LMED

-8