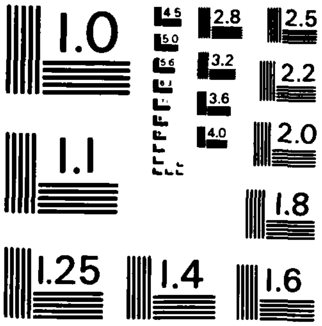
AD-A159 526 RECENT DEVELOPMENTS IN BETA ALUMINA(U) CALIFORNIA UNIV 1/1
LOS ANGELES DEPT OF MATERIALS SCIENCE AND ENGINEERING
B DUNN ET AL. SEP 85 TR-6 N00014-83-K-0498

UNCLASSIFIED F/G 7/4 NL

END
FILMED
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

(2)

OFFICE OF NAVAL RESEARCH

Contract N00014-83-K-0498
Task No. NR 627-842

TECHNICAL REPORT NO. 6

Recent Developments in Beta'' Alumina

by

B. Dunn* and G. C. Farrington**

Prepared for Publication in
Solid State Ionics

*Department of Materials Science and Engineering
University of California, Los Angeles
Los Angeles, CA 90024

**Department of Materials Science
University of Pennsylvania
Philadelphia, PA 19104

September, 1985

AD-A159 526

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER
6

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
Recent Developments in Beta" Alumina

5. TYPE OF REPORT & PERIOD COVERED
Technical Report

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
B. Dunn and G. C. Farrington

8. CONTRACT OR GRANT NUMBER(s)
N00014-83-K-0498

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Department of Materials Science and Engineering
University of California, Los Angeles
Los Angeles, CA 90024

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

11. CONTROLLING OFFICE NAME AND ADDRESS
Office of Naval Research
800 N. Quincy
Arlington, VA 22217

12. REPORT DATE
September 1985

13. NUMBER OF PAGES
9

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
Office of Naval Research Detachment
1030 East Green Street
Pasadena, CA 91106

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

This document has been approved for public release and sale; its distribution is unlimited.

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

18. SUPPLEMENTARY NOTES

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

Multivalent beta" aluminas, mixed ion and mixed valence effects, transport and optical properties.

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

The multivalent β'' aluminas are the first family of high conductivity solid electrolytes for divalent and trivalent cations. The rich ion exchange chemistry of these materials leads to a variety of chemical environments within the conduction plane which consequently influence their ion transport and optical properties. This paper reviews some of the pertinent structural aspects of the multivalent β''-aluminas and considers the properties of selected systems which contain either mixed ions or ions with two valence states within the conduction plane.

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

RECENT DEVELOPMENTS IN β'' ALUMINA

B. Dunn

Department of Materials Science and Engineering,
University of California, Los Angeles, CA 90024

and

G. C. Farrington

Department of Materials Science and Engineering,
University of Pennsylvania, Philadelphia, PA 19104

The multivalent β''-aluminas are the first family of high conductivity solid electrolytes for divalent and trivalent cations. The rich ion exchange chemistry of these materials leads to a variety of chemical environments within the conduction plane which consequently influence their ion transport and optical properties. This paper reviews some of the pertinent structural aspects of the multivalent β''-aluminas and considers the properties of selected systems which contain either mixed ions or ions with two valence states within the conduction plane. The results indicate that the multivalent exchanged β''-aluminas are excellent materials for studying the effects of ion/lattice and ion/ion interactions in 2-dimensional systems.

INTRODUCTION

The β''-aluminas are one of the most widely investigated solid electrolytes. One of the most interesting features to be observed within the past few years is the remarkable ion exchange characteristics of the β''-aluminas. We have found that both divalent and trivalent cations diffuse rapidly in the β''-alumina structure (but not in β-alumina) and we have utilized this effect to prepare a wide range of divalent and trivalent compositions.[1,2] The ion transport properties of these materials are unique. The divalent β''-aluminas represent the first family of high conductivity solid electrolytes for divalent cations. One composition, $Pb^{2+}\beta''$-alumina exhibits an anomalously high conductivity, nearly equal to that of $Na^{+}\beta''$-alumina, at room temperature and below.[1] Similarly, the lanthanide β''-aluminas are the first solid electrolytes for trivalent cations. Although $Gd^{3+}\beta''$-alumina is an insulator at room temperature ($\sigma < 10^{-12}$ ohm^{-1} cm^{-1}), the Gd^{3+} conductivity at 400°C is comparable to that of O^{2-} in calcia stabilized zirconia. From a more fundamental standpoint, these studies of the "multivalent" β''-aluminas demonstrate that the phenomenon of fast cation transport in solids is not restricted to monovalent cations.

The rich ion exchange chemistry of the β''-aluminas is able to produce a variety of interesting properties in addition to those of fast ion transport. As the chemical environment within the conduction plane is changed, the resulting ion transport and/or optical properties are affected. The present paper reviews recent experimental and theoretical work in which mixtures of ions or ions with mixed valences are present in the conduction plane. The results indicate that multivalent ion exchanged β''-aluminas offer an excellent opportunity in which to observe the effects of ion/lattice and ion/ion interactions in 2-dimensional systems.

TABLE 1: Lattice Parameter and Ion Distributions in Divalent β''-Aluminas (4,6)

Ion	Ionic Radius (A)	a(A)	c(A)	Mid-Oxygen Occupation (%)
Ba^{2+}	1.35	5.169	34.084	-
Pb^{2+}	1.19	5.610	33.967	10
Sr^{2+}	1.18	5.610	33.720	61
Ca^{2+}	0.98	5.613	33.270	47
Cd^{2+}	0.95	5.620	33.146	53
Mn^{2+}	0.83	5.618	33.141	60
Zn^{2+}	0.74	5.623	33.517	27

STRUCTURE AND ORDERING

Structural studies provide substantial insight regarding the chemical environment within the β''-alumina conduction plane as well as whether ordering effects are present. Thomas and co-workers have performed single crystal X-ray diffraction studies on many of the multivalent β''-alumina compounds.[3,4] In the case of divalent compositions, considerable variation in the average M^{2+} arrangement is observed and no two distributions are quantitatively alike. The distributions range from having M^{2+} primarily in the 6c (Beevers-Ross type) sites with minor amounts in the 9d (mid-oxygen) sites, to having the majority of M^{2+} in the 9d site (see Table 1). In addition, the 6c site occupations are generally unequal. Displacements in the column oxygen O(5) from the 3b site and towards the 6c or 9d sites are also evident. The O(5) shows varying degrees of disorder, ranging from the undisplaced case (Ba^{2+}) to 0.59A displacement in Mn^{2+}β''-aluminas. The latter composition also exhibits the minimum c-axis lattice parameter for the M^{2+}β''-aluminas, and the relationship between ion size, O(5) distortion and interaction between M^{2+} ions and the rest of the spinel block is beginning to emerge.

In contrast to the divalent β''-aluminas, the lanthanide isomorphs exhibit structural similarities. The structure of Gd^{3+}β''-alumi was reported previously[5] and the behavior of Nd^{3+} and Eu^{3+}β''-aluminas appear to be comparable. The lanthanide ion exhibits strong preference for the 9d site, with only minor occupation of the 6c site. This feature is clearly shown in the Fourier synthesis for th Gd^{3+} distribution (Fig. 1). As in the case c most divalent β''-aluminas, the O(5) is disordered and displaced from the 3b site, towards the lanthanide ion.

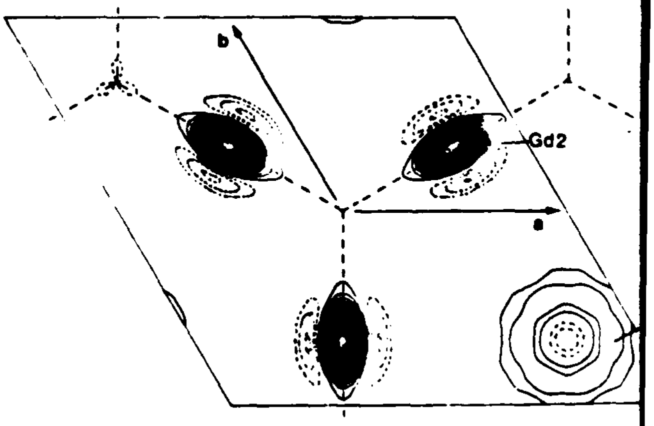


Figure 1 Fourier synthesis for Gd^{3+} in Gd^{3+} alumina (z = $\frac{1}{6}$ plane) (after Ref 5).

Another significant result related to the structure is the observation that superstructures exist for some of the multivalent β''-alumina compositions. Boilot et al.[6] used X-ray diffuse scattering techniques to detect 2D short range order in $Sr^{2+}\beta''$-alumina. A local superstructure of 2a x 2a (coherence length ~80A) was observed, and the results are consistent with the indirect evidence for short range order in Ca^{2+} and $Ba^{2+}\beta''$-aluminas as obtained from the X-ray diffraction studies of Thomas.[4] In 2-dimensional order it is generally assumed that there is no interaction between the conducting ions and the host lattice. In contrast, 3D order indicates the existence of interplanar correlations. Boilot et al.[6] reported 3D long range order in $Cd^{2+}\beta''$-alumina (superstructure of 2a x 2a x 2c; coherence length >100A within the plane and ~50A along the c-axis). It is interesting to note that this material was characterized by the presence of excess CdO in the conduction plane. This stoichiometry fluctuation is apparently affected by synthesis conditions. $Pb^{2+}\beta''$-alumina is different than the Cd^{2+} isomorph. There are no stoichiometry fluctuations and 3D order is still observed. In this case, synthesis conditions determine whether long range order or short range order is observed. Ordering effects in lanthanide β''-aluminas have also been reported. Davies et al.[7] used high resolution TEM to observe 3D superstructures of Nd^{3+}, Gd^{3+}, and $Eu^{3+}\beta''$-aluminas. In $Nd^{3+}\beta''$-alumina, the authors found that approximately 50% of the material exhibited an ordered phase with a superstructure 3a x 3a x 3c.

The structural studies indicate that a variety of different chemical environments exist for the multivalent β''-aluminas. As will be shown later, site symmetry and small displacements from these sites exert a large influence on optical properties. Site occupations, which appear to have little effect on the transport properties of most divalent β''-aluminas, are quite significant for the transport properties of mixed ion compositions. Finally, the fact that ordering phenomena are observed in the multivalent β''-aluminas indicates that substantial interaction occurs between conduction planes as well as within planes. The origin of such superstructures and their influence on properties are not fully established and remain an intriguing area for future investigations.

TRANSPORT IN MIXED ION SYSTEMS

The ability of β''-alumina to incorporate such a large variety of ions has enabled researchers to consider ion transport in situations where more than one cation is located within the conduction plane. When multivalent ions substitute for Na^{+}, several interesting factors arise. The presence of a higher valence cation (M^{2+} or R^{3+}) should lead to enchanced coulombic interactions as well as stronger lattice polarization.[8] In addition, charge neutrality requires that more vacant sites be created as Na^{+} is replaced by M^{2+} or R^{3+}. To date, the transport properties of two mixed systems, Na^{+}/Ba^{2+} and $Na^{+}/Nd^{3+}\beta''$-aluminas, have been examined. It is evident that ion exchanged β''-alumina offers a model system for theoretical and experimental studies. Both studies carry out Monte Carlo calculations using a procedure similar to that of Murch and Thorn[9] to understand the mechanisms and magnitude of ion transport.

The approach presented by Pechenik et al. is based on a lattice gas hopping model with nearest-neighbor repulsion.[8] The Na^{+}/Ba^{2+} system was selected because the ions reside only in Beevers-Ross positions. As Ba^{2+} replaces Na^{+} in the conduction plane, the presence of the additional vacancy leads to an increase in

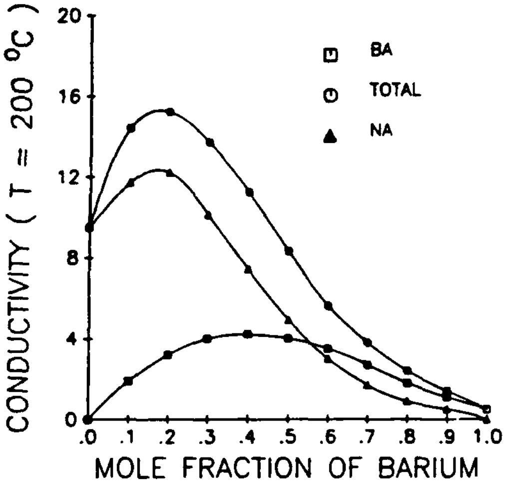


Figure 2 Calculated ionic conductivity for Na^+/Ba^{2+} β''-alumina as a function of Na^+ content 200°C (after Ref. 8).

conductivity (Fig. 2). In the case of low temperatures (200°C), a maximum conductivity is observed with increasing Ba^{2+} content. The calculations by Pechnik et al. indicate that ordering effects are responsible for the decrease in conductivity at the higher Ba^{2+} concentrations, and that Na^+ and Ba^{2+} exhibit correlated motion through the lattice. These correlation effects, which become larger with increasing Ba^{2+} content, lead to non-Arrhenius behavior in the conductivity-temperature relation. It is interesting to note that the ordered superlattice suggested by the authors is consistent with the results of the structural studies.

The work on Na^+/Nd^{3+} β''-alumina involves both experimental measurements and theoretical calculations.[10] The results are quite different from the Na^+/Ba^{2+} case. Na^+ diffusivity was determined at 335°C as a function of Na^+ content. The diffusivity was found to decrease sharply when approximately 60% Na^+ was replaced (Fig. 3). This behavior is nicely approximated by the computer simulation for Na^+ diffusion developed by Rohrer et al.[10] The model makes the assumption that the presence of (immobile) Nd^{3+} in a mid-oxygen site effectively blocks Na^+ motion through the two adjacent Beevers-Ross positions. The authors also demonstrate that the decrease in Na^+ diffusivity above 60% Na^+ replacement is consistent with the effect of ion percolation through a 2D honeycomb lattice.

The research effort on mixed ion systems is clearly at its inception. The models provide substantial evidence that transport properties will be affected by both ion/ion and ion/vacancy interactions in such systems. Relatively little experimental work is available (especially in regard to divalent and trivalent ions) and, therefore, detailed transport measurements and corresponding structural studies will be very significant future contributions. A related topic of interest is the "picture frame" effect, where ion exchange provides a sharp concentration gradient.[8] The phenomenon has been noted previously but was neither characterized nor explained.

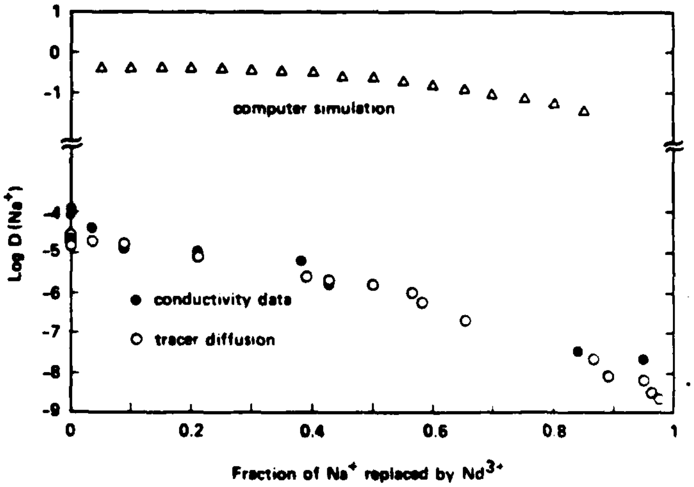


Figure 3 Comparison of measured and calculated diffusion coefficients for Na^+ in Na^+/Nd^{3+} β''-alumina as a function of Na^+ content. Temperature = 335°C (after Ref. 10).

MIXED VALENCE EFFECTS

We previously reported that Cu^{2+} exchange led to the presence of both Cu^{+} and Cu^{2+} in β''-alumina.[1] Another system exhibiting mixed valences, $Eu^{2+}/Eu^{3+}\beta''$-alumina, has the added advantage of being amenable to study by optical techniques. Ghosal et al.[11] synthesized both the pure compounds as well as compositions containing a mixture of valences. Emission spectra were found to be a very sensitive means for distinguishing between the two valences. Recently, Saltzberg and Farrington[12] demonstrated that the valence state of Eu could be controlled by heat treatment. These valences changes are readily apparent by considering the optical spectra in Figs. 4 and 5.

Figure 4 illustrates how $Eu^{2+}\beta''$-alumina is oxidized by heat treatment in air at 600°C. The characteristic absorptions of Eu^{2+} at the 25,000 cm^{-1} range are eliminated and the charge transfer band of Eu^{3+} at 40,000 cm^{-1} is produced. The opposite of this behavior is shown in Fig. 5. In this case emission spectra are used to demonstrate how single crystal $Eu^{3+}\beta''$-alumina changes under vacuum annealing at 650°C. The characteristic emission lines for Eu^{3+} at 16,000-17500 cm^{-1} are greatly diminished upon heating in vacuum and the broad band emission of Eu^{2+} appears. The fact that some of the Eu^{3+} lines still remain indicates that not all Eu^{3+} has been reduced. This result also illustrates the ability of optical spectra to sensitively detect mixed valences.

The results shown in Figs. 4 and 5 bring forward a number of issues which have never been fully explored in the β''-aluminas. The optical responses suggest that oxygen migration effects must somehow be involved, despite the fact that β''-alumina is not known for its anion transport properties. The precise means by which oxidation/reduction occurs and whether it is reversible is not fully known. What is apparent is that this multivalent β''-alumina has the

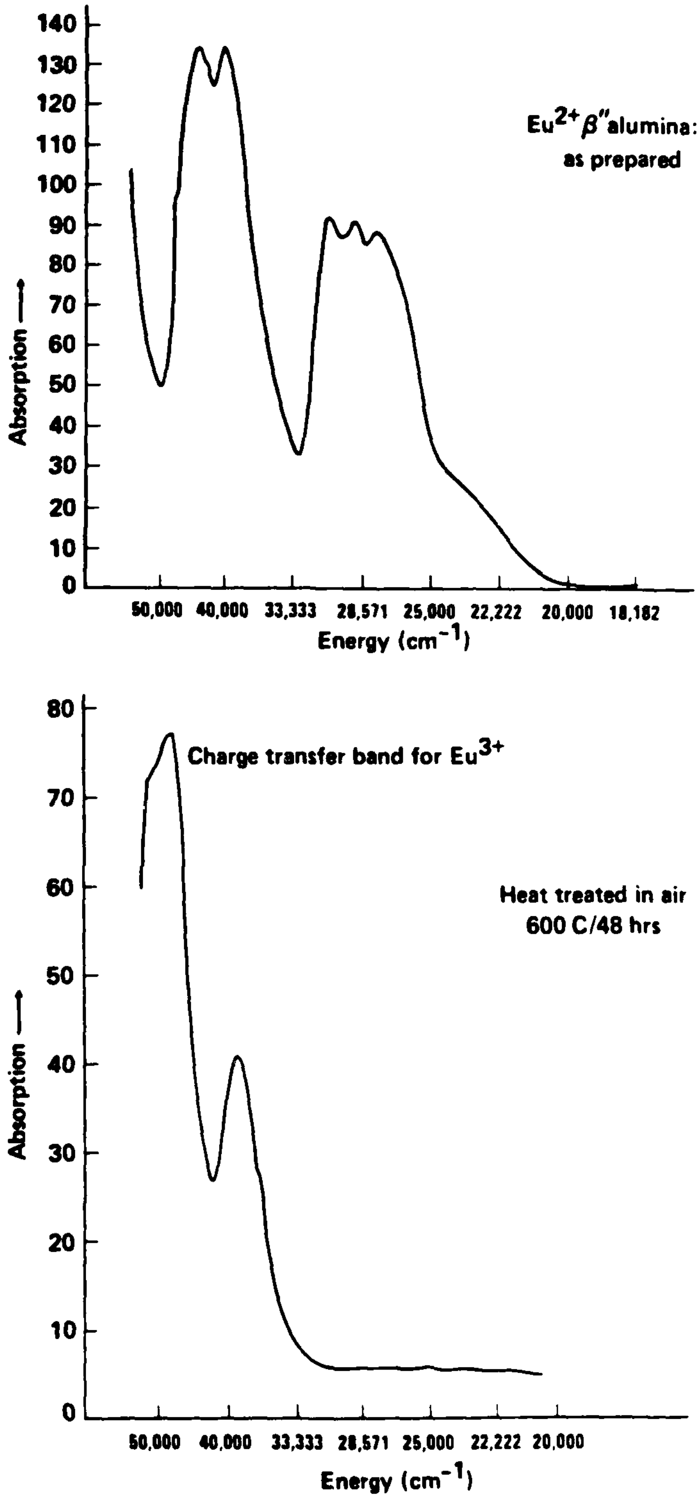


Figure 4 Absorption spectrum for $Eu^{2+}\beta''$-alumina: as prepared (upper) and heat treated in air at 600°C for 48 hours (lower) (after Ref. 12).

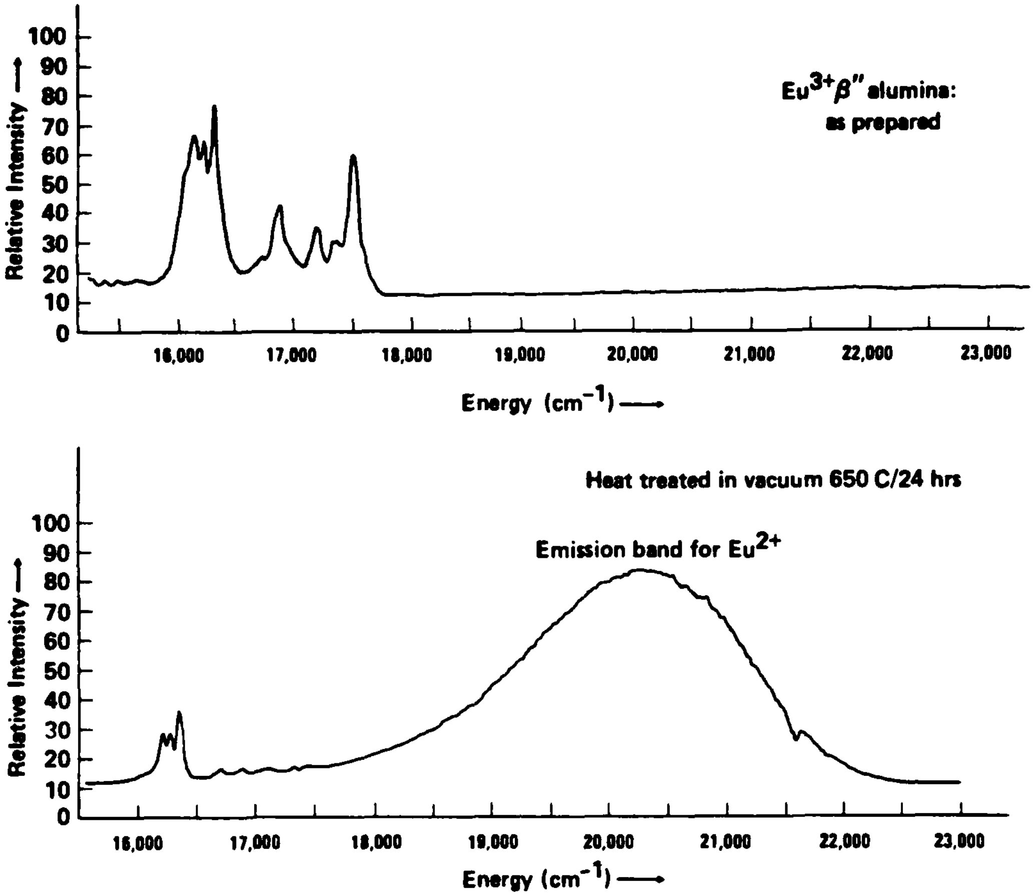


Figure 5 Emission spectrum for Eu$^{3+}\beta''$-alumina: as prepared (upper) and heat treated in vacuum at 650°C for 24 hours (lower) (after Ref. 12).

ability to change the local chemical environment within the conduction plane by relatively simple heat treatments. This is novel behavior for a β''-alumina because these solid electrolytes are generally not considered to be capable of altering their defect structure. On the other hand, the stoichiometry fluctuations observed for Nd$^{2+}\beta''$-alumina[6] do suggest that significant compositional changes within the conduction plane are possible in the multivalent compounds. In he case of Eu^{2+}/Eu$^{3+}\beta''$-alumina, there are alence changes involved rather than the incororation of neutral species. Thus, there are everal interesting questions to be considered oncerning processes occurring within the conuction plane; the source of the valence change, he means by which Eu ions interact and whether interplanar and/or spinel block defects are produced from the heat treatments.

OPTICAL PROPERTIES

The optical properties of Nd^{3+} exchanged β''-alumina have been investigated in some detail and rather significant effects have been reported. Small single crystals of Na^{+}/Nd$^{3+}\beta''$-alumina exhibited laser action despite a short optical path (~5mm) and poor optical quality.[13] Jansen et al. also observed an anomalously strong absorption line at 5800A and a long fluorescence lifetime (>350μsec) at high Nd^{3+} concentration, both of which are instrumental in achieving lasing action. Recent work by Alfrey et al.[14] examined these optical properties and,

TABLE 2. Optical Properties for Nd^{3+} in Oxide Hosts

	HOST MATERIAL		
	YAG ($Y_3Al_5O_{12}$)	β''-Alumina	Glass (silicate)
Nd^{3+} concentration (cm^{-3})	1.4×10^{20}	5.7×10^{20}	3×10^{20}
Effective linewidth at 1.06μ(cm^{-1})	68	256	343
Fluorescence lifetime (μsec)	230	420	300
Stimulated Emission cross section (cm^2)	33×10^{-20}	2.1×10^{-20}	2.8×10^{-20}

once again, the local chemical environment within the β''-alumina conduction plane is of central importance.

The strong absorption at 5800A is believed to arise from subtle displacements of Nd^{3+} and O^{2-} within the conduction plane. In a mid-oxygen site, Nd^{3+} would occupy a site of inversion symmetry, which is inconsistent with the spectroscopy data. Thus, there must be certain factors which cause the loss of inversion symmetry. Alfrey et al.[14] performed a Judd-Ofelt analysis on the absorption spectrum and were able to identify the nearest neighbor environment responsible for the observed oscillator strengths. They calculated that a slight displacement of Nd^{3+} from the 9d site coupled with a small shift of the O(5) towards the Nd^{3+} were capable of producing the observed oscillator strength. The subtle distortions in the conduction plane are shown in Fig. 6. It is important to note that the displacements involved here are well within the variation in ion position as determined by X-ray diffraction (Fig. 1 represents the fully exchanged case). Furthermore, the asymmetric distribution of Na^+ and Nd^{3+} around the column oxygen is completely consistent with the Na^+/Nd^{3+} diffusion model.[10]

The positions shown in Fig. 6 represent an average of many specific displacement configurations. As a result of this variation, two interesting effects are observed; (1) the oscillator strength at 5800A is a function of Nd^{3+} concentration and exhibits a maximum value, and (2) the emission spectrum is inhomogeneously broadened.[14] The latter behavior is commonly observed in glasses where it arises from the large number of physically inequivalent sites

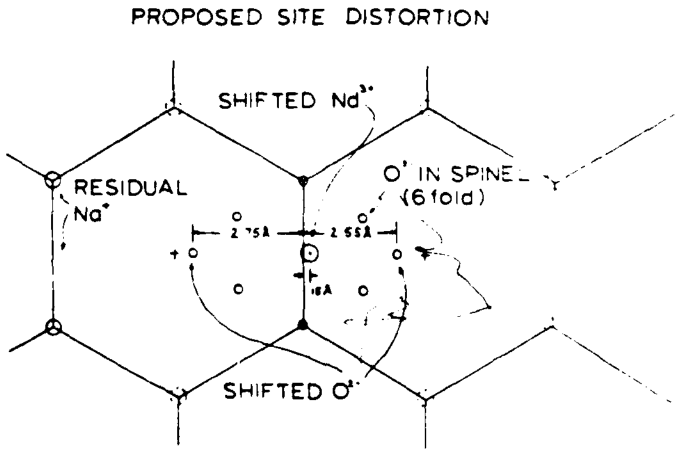


Figure 6 Proposed site distortions and occupations for Na^+/Nd^{3+} β''-alumina (after Ref. 14).

for Nd^{3+}. In the present case of Na^+/Nd^{3+} β''-alumina, where the Nd^{3+} occupies essentially one site, the existence of inhomogeneous broadening is consistent with the interpretation that Nd^{3+} is located in a variety of differently displaced positions within the conduction plane. Another property compatible with this explanation is the stimulated emission cross section, which also exhibits values comparable to that of glass hosts (Table 2).

One final topic of interest is the issue of how Na^+ motion influences the actual properties of Nd^{3+} exchanged β''-alumina. There is some evidence that mobile Na^+ ions may be involved in non-radiative processes. Fluorescence lifetime measurements made at elevated temperature indicate that the non-radiative recombination rate increases exponentially with temperature. The activation energy for this process, ~0.5eV, is in excellent agreement with the activation energy for Na^+ motion as obtained from dielectric relaxation measurements of similar compositions.[15] Although these results suggest that Na^+ motion in the conduction plane leads to non-radiative processes, it is important to note that the precise coupling mechanism is unknown and that other processes may also contribute to non-radiative recombination.

CONCLUSION

Ex+a

This paper has attempted to illustrate that the rich ion exchange chemistry of β''-alumina is able to produce a number of interesting properties beyond fast ion transport phenomena. The experimental and theoretical work reviewed herein indicate that a wide variety of chemical environments exist in the multivalent β''-aluminas and that these environments influence properties. Ion transport processes in mixed ion systems were found to be influenced by correlated ion motion and ordering effects, while optical properties of lanthanide

Ex+a

exchanged β''-aluminas were quite sensitive to local configurations. The precise means by which properties are affected by chemical environments is an area worthy of continued interest, and the multivalent β''-aluminas offer an excellent vehicle in which to study these effects in 2-dimensional environments.

ACKNOWLEDGEMENTS

The authors appreciate the helpful discussions with J. O. Thomas and O. M. Stafsudd. The work was supported in part by the U.S. Office of Naval Research.

REFERENCES

1. G. C. Farrington and B. Dunn, Solid State Ionics 7 (1982) 267.
2. G. C. Farrington, B. Dunn and J. O. Thomas, Appl. Phys. A 32 (1983) 151.
3. J. O. Thomas, M. Alden and G. C. Farrington, Solid State Ionics 9/10 (1983) 301.
4. M. Alden, J. O. Thomas and G. C. Farrington, Acta. Cryst. C40 (1984) 1763 and B40 (1984) 208.
5. W. Carrillo-Cabrera, J. O. Thomas and G. C. Farrington, Solid State Ionics 9/10 (1983) 245.
6. J. P. Boilot, Ph. Colomban, M. R. Lee, G. Collin and R. Comes, Solid State Ionics 9/10 (1983) 315.
7. P. K. Davies, A. Petford and M. O'Keefe, this volume.
8. A. Pechenik, D. H. Whitmore and M. A. Ratner, J. Solid State Chem. 58 (1985) 103.
9. G. E. Murch and R. J. Thorn, Philos. Mag. 35 (1977) 493 and 36 (1977) 529.
10. G. Rohrer, P. Sutter, S. Sattar and G. C. Farrington, submitted for publication.
11. B. Ghosal, E. A. Mangle, M. R. Topp, B. Dunn and G. C. Farrington, Solid State Ionics 9/10 (1983) 273.

2. M. Saltzberg and G. C. Farrington, submitted for publication.

3. M. Jansen, A. J. Alfrey, O. M. Stafsudd, D. L. Yang, B. Dunn and G. C. Farrington, Opt. Letts. 9 (1984) 119.

4. A. J. Alfrey, O. M. Stafsudd, B. Dunn, D. L. Yang and L. Salmon, submitted for publication.

5. J. J. Fontanella, M. C. Wintergill, D. L. Yang, B. Dunn and C. G. Andeen, Phys. Rev., in press.

DL/413/83/01
GEN/413-2

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 413 800 N. Quincy Street Arlington, Virginia 22217	2
Dr. Bernard Douda Naval Weapons Support Center Code 5042 Crane, Indiana 47522	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Washington, D.C. 20360	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12
DTNSRDC Attn: Dr. G. Bosmajian Applied Chemistry Division Annapolis, Maryland 21401	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1
Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1

END

FILMED

11-85

DTIC