

AD-A159 408

PREPARATION AND PROPERTIES OF TRANSITION METAL BETA
ALUMINAS(U) CALIFORNIA UNIV LOS ANGELES DEPT OF
MATERIALS SCIENCE AND ENGINEERING J D BARRIE ET AL
SEP 85 TR-4 N00014-83-K-0498

1/1

UNCLASSIFIED

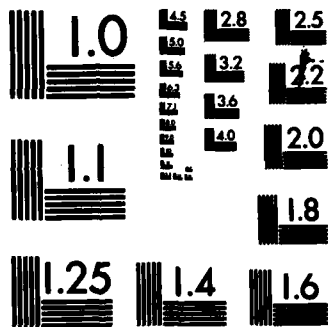
F/G 20/2

NL

END

11-81-0

01C



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

AD-A159 408

6

OFFICE OF NAVAL RESEARCH

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

TECHNICAL REPORT NO. 4

Preparation and Properties of Transition Metal Beta'' Aluminas

by

J. D. Barrie**, B. Dunn**, O. M. Stafsudd** and G. C. Farrington*

Prepared for Publication in
Solid State Ionics

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

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

September, 1985

Reproduction in whole or in part is permitted for any
purpose of the United States Government.
This document has been approved for public release and sale;
its distribution is unlimited.

DTIC FILE COPY

DTIC
ELECTE
SEP 24 1985
S E D

85 09 23 062

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 4	2. GOVT ACCESSION NO. A159408	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Preparation and Properties of Transition Metal Beta" Aluminas		5. TYPE OF REPORT & PERIOD COVERED Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) J. D. Barrie, B. Dunn, O. M. Stafsudd 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 5
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) Cr ³⁺ , Co ³⁺ , Ni ²⁺ , Mn ²⁺ in beta" alumina, absorption and emission spectra, fluorescent lifetime.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Ion exchange techniques were used to produce a family of 3d transition metal B"-alumina single crystals. Complete or nearly complete replacement was obtained for Cr ³⁺ , Mn ²⁺ , Co ²⁺ and Ni ²⁺ compositions. Optical properties of the crystals were studied and both broad absorption and broad fluorescence bands were observed. Environmental exposure produced detrimental effects over long time periods, suggesting hydration of the conduction planes.		

PREPARATION AND PROPERTIES OF TRANSITION METAL β'' ALUMINAS

J. D. BARRIE^{*}, B. DUNN^{*} and O. M. STAFSUDD^{**}

Department of Materials Science and Engineering^{*}
Electrical Engineering Department^{**}
University of California, Los Angeles, CA 90024

and

G. C. FARRINGTON

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

Ion exchange techniques were used to produce a family of 3d transition metal β'' -aluminas by substitution of the sodium ion content in Na^+ - β'' -alumina single crystals. Complete or nearly complete replacement was obtained for Cr^{3+} , Mn^{2+} , Co^{2+} , and Ni^{2+} compositions. Optical properties of the crystals were studied and both broad absorption and broad fluorescence bands were observed. Environmental exposure produced detrimental effects over long time periods, suggesting hydration of the conduction planes.

1. INTRODUCTION

Previous studies^{1,2} have found that the entire sodium ion content of β'' -alumina can readily be replaced by a variety of divalent and trivalent cations. In several cases, it has been found that the resultant materials have interesting optical properties in addition to fast ion transport. For example, Nd^{3+} exchanged β'' -alumina single crystals have been found to lase and to exhibit extremely high fluorescent gain coefficients in comparison with $\text{Nd}:\text{YAG}$ lasers.³

The research on lanthanide β'' -aluminas prompted our interest in the 3d-transition metals as candidates for exchange into β'' -alumina. Several ions within this series exhibit broadband, vibronic fluorescent transitions due to the interaction of their incomplete 3d electron shells with local crystal fields. This phenomenon allows for the development of tunable solid state lasers using various oxide and non-oxide host materials. Relatively little work has been done, however, with β'' -alumina systems

in which the exchanged ions were capable of multiple valence states. In addition to this problem, the exchange of transition metal ions generally involves the substitution of ions with very small radii, potentially inducing large stresses within the crystals. The preparation of these materials, and their interesting optical properties are reported in this paper.

2. PREPARATION OF THE MATERIALS

Several transition metal β'' -aluminas were prepared using standard ion exchange techniques on single crystals of Na^+ - β'' -alumina (Table 1). Crystals were either immersed in molten halide salts of appropriate compositions or placed in the proximity of heated, but unmelted, salts for varying times. In this latter case the salt exhibited a sufficiently high vapor pressure such that ion exchange occurred from exposure to the vapor phase. For all samples, careful atmospheric control was required to prevent oxidation of the halide salts as well as to prevent

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



TABLE 1: Ion Exchange Conditions for Transition-Metal- β' -Aluminas

ION	EXCHANGE MEDIUM	TEMPERATURE(°C)	TIME(hr)	PERCENT EXCHANGED
Cr ³⁺	Liquid: 31CrCl ₃ /69NaCl	700	1	30
	Vapor: CrCl ₃		12	90
Mn ²⁺	Liquid: MnCl ₂	650	15	100
Co ²⁺	Liquid: CoCl ₂	750	2	100
Ni ²⁺	Liquid: 32NiCl ₂ /68NaCl	700	12.5	25
	Vapor: NiCl ₂		35	90

formation of multiple valence states of the cations.

Results indicate that substantial or complete exchange was attained for Cr³⁺, Mn²⁺, Co²⁺, and Ni²⁺ using both the liquid and vapor phase techniques. The crystals possess good mechanical integrity and x-ray diffraction indicates that the β' -alumina structure was retained without modification, despite the small size of the substitutional ions. The extent of the exchange reactions was monitored by both gravimetric means and Energy Dispersive X-ray (EDX) analysis, the latter also being used to identify impurities and inhomogeneities in the crystal.

The vapor phase exchanges, achieved by either burying the crystal in an excess of the halide powders or by suspending it above the powder source, required longer reaction times than corresponding melt exchanges. This method, however, enables one to obtain complete exchange at much lower temperatures than those required for the melt phase. In general, the resulting milder synthesis conditions prevent detrimental effects to the crystal. For example, complete exchange of Ni²⁺ ions from a melt of NiCl₂ would require melting the salt in excess of 1100°C, while the vapor phase exchange was possible at 700°C. This temperature reduction is critical, for it has been shown that several of the

exchanged β' -aluminas are prone to decomposition when heated to temperatures of above 900°C.⁴

3. OPTICAL PROPERTIES

Although most lasers operate at single wavelengths, the success of the room temperature operation of the Cr:BeAl₂O₄ (alexandrite) tunable laser, operational over the range for 7300 to 8000Å, has spurred much interest in the utilization of broad band vibronic transitions. Most radiative transitions within the 3d transition metal ions take place via such broad bands, and thus, there is the potential for a whole series of solid state lasers that are tunable over large wavelength regions. Numerous studies of transition metal ions in various crystal hosts have taken place. Although there is a wealth of spectroscopic information, there are relatively few effective laser hosts available. Our initial experiments were performed with the intent of determining the applicability of β' -alumina as a host for tunable solid state lasers, in that it has already demonstrated success as a laser host for Nd³⁺ ions.

Absorption and fluorescence spectra for several single crystals of ion exchanged β' -alumina with various Cr³⁺ concentrations (the balance being residual Na⁺ ions within the conduction plane) were performed. The absorption

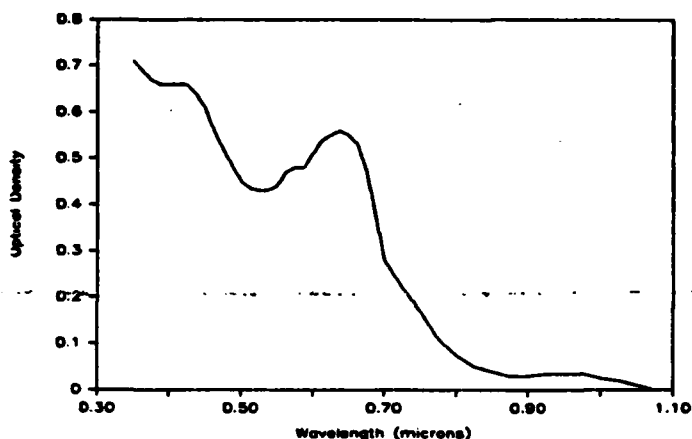


Figure 1. Absorption Spectrum of Cr^{3+} - β' -alumina.

spectra were obtained using a Cary Model 14 spectrophotometer. Cr^{3+} - β' -alumina was found to have strong absorption peaks centered at 4200Å and 6400Å (Fig. 1), giving the crystals a deep green color. Fluorescent emission (induced by pumping with a Spectra-Physics argon ion laser at 4880Å) was observed from 6900Å to 9000Å. These values are quite typical of Cr^{3+} optical spectra in a variety of other hosts, representing interaction between the 4T_1 (at 4200Å) and 4T_2 (at 6400Å) states with the vibronically broadened ground state 4A_2 . No evidence of the parity and spin forbidden ${}^2E \leftrightarrow {}^4A_2$ transition is observed, probably due to overlap of the 2E state with the 4T_2 . The placement of these transitions suggests that the local crystal field environment of the Cr^{3+} ions within the β' -alumina conduction plane is octahedral, which would place them within the mid-oxygen (mO) cation of the crystal.

The absence of the 2E line suggests that the magnitude of the crystal field environment in Cr^{3+} - β' -alumina is similar to that of Cr^{3+} in SGG [$\text{Gd}_3(\text{Sc,Ga})_2\text{Ga}_3\text{O}_{12}$], which has an octahedrally symmetric Cr^{3+} site with a crystal field of $Dq = 1450 \text{ cm}^{-1}$ and a Racah parameter $B = 658 \text{ cm}^{-1}$ ($Dq/B = 2.20$).⁵ This produces

a direct overlap of the 2E and 4T_2 levels.

However, the observed room temperature fluorescent lifetimes of the β' -alumina crystals is much greater than that observed in SGG (650 versus 115 microseconds). This trend usually suggests that there is a greater separation between the 2E level, which typically has lifetimes of several milliseconds, and the 4T_2 level, whose lifetime is measured in the tens of microseconds. Given that we observe a lifetime greater even than that of alexandrite (262 microseconds at room temperature)⁶, it would suggest a larger crystal field than concluded above, more on the order of $Dq/B = 2.5$.⁷

The temperature dependent behavior of the fluorescent lifetime of Cr^{3+} - β' -alumina fails to provide any explanation for these contradictory observations. The lifetimes are found to decrease exponentially with increasing temperature, inferring the presence of some competing non-radiative process. A plot of the non-radiative decay rate versus inverse temperature (Fig. 2) indicates that the process has an activation energy of 0.16 eV, which is of the same order of that for sodium ion motion in this temperature range.⁸ While it is tempting to associate the non-radiative processes with Na^+

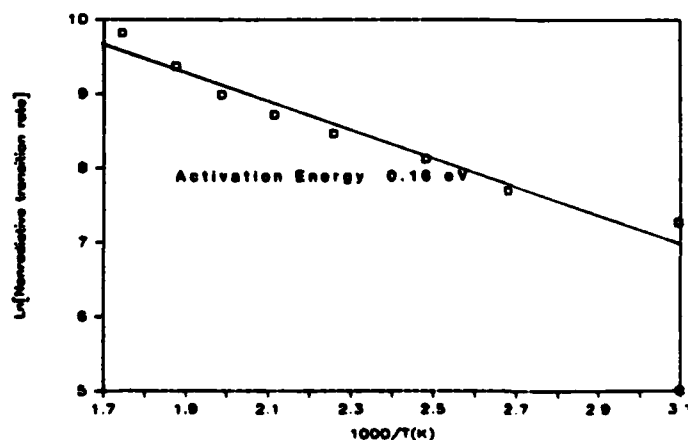


Figure 2. Non-radiative decay rate in Cr^{3+} - β' -alumina versus temperature.

3

ion motion, there may be other competing non-radiative processes, such as multi-phonon decay, and partitioning via Boltzmann distributions between the closely lying 2E and 4T_2 levels.⁶ More detailed optical and ion transport studies are necessary in order to understand the non-radiative mechanisms occurring in this solid electrolyte.

In addition to the above effects there also seem to be other processes which contribute to the observed values of fluorescent lifetimes in these crystals. Concentration quenching has been observed, as increasing amounts of Cr^{3+} ions within the conduction plane have been found to reduce the lifetime by more than an order of magnitude (Fig. 3). Another quenching effect on the fluorescent lifetime occurs from the exposure of the crystals to ambient environments over long periods of time. For example, a crystal whose lifetime immediately after exchange was as high as 2 msec was found to degrade to 300 microseconds after prolonged ambient exposure (i.e., months). The process was found to be at least somewhat reversible. Heating the crystal to 350°C for 48 hours raised the lifetime to 650 microseconds.

Elevated heating was also found to affect

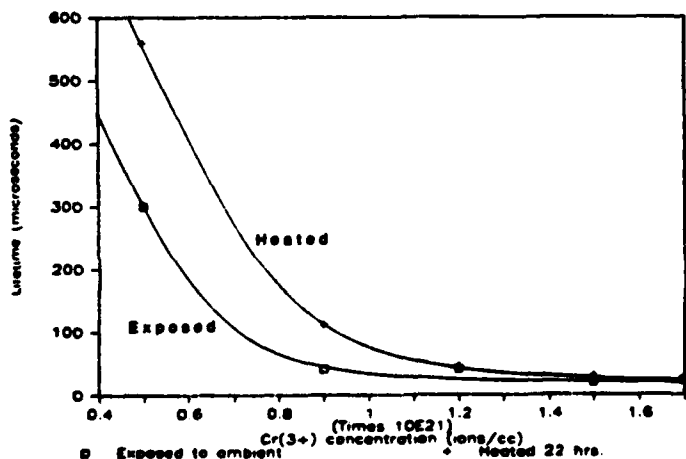


Figure 3. Fluorescent lifetime of $Cr-\beta'$ -alumina versus Cr concentration in hydrated and dried states.

the size of the c-axis lattice parameter of the crystals. In the unheated (short lifetime) state, a c-axis value of 33.666Å was measured, whereas after 48 hours of heating, the value was 33.547Å. The ability of water molecules to diffuse into β' -alumina and alter their lattice parameters is well established.⁹ In addition, water is well known for its ability to quench fluorescence over a wide variety of energies due to its many vibrational and bending modes. The present results indicate that certain optical properties may be sensitive to moisture. A more controlled study of this behavior is necessary to identify and characterize these effects.

The absorption spectra for Co^{2+} ion exchanged β' -alumina was also measured (Fig. 4), revealing strong peaks at 5500, 5825, and 6200Å, and lesser, but still strong, absorptions at 12,500, 13,625 and 15,250Å. The position of these peaks is in excellent agreement with the results reported for Co^{2+} in various oxide hosts containing tetrahedral sites.¹⁰ This indicates that the primary location of the Co^{2+} ions is the tetrahedral Beavers-Ross type site (6c), despite the fact that most divalent ions in β' -alumina exhibit significant population of both the BR and mid-oxygen sites.¹¹

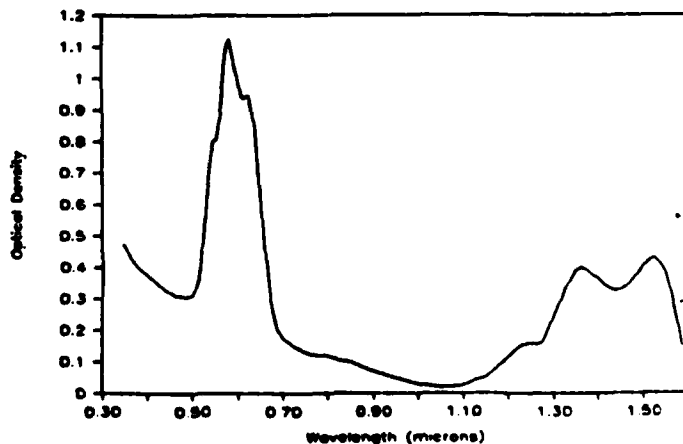


Figure 4. Absorption Spectrum of $Co^{2+}-\beta'$ -alumina.

The excellent agreement with the theoretical line positions, as well as the absence of any unidentified lines helps to verify that all the cobalt ions present in the crystal are in the 2+ state, and that no Co^{3+} ions were formed during the exchange process.

Absorption spectra for Ni^{2+} - β -alumina (Fig. 5) produces peaks at 3760, 6000, 6375, 7200 and 11,500Å. This latter absorption is positioned similarly to the absorption due to the first excited state of Ni^{2+} in MgO .¹² However, the complexity of the spectra and the sensitivity of the Ni^{2+} ion to crystal fields prevents the identification of the other lines in the spectrum. Low temperature measurements will be necessary to resolve some of the overlapping and determine crystal field strength and site symmetry.

4. CONCLUSION

The preparation of a new family of ~~alpha~~ ^{Beta} aluminas by the substitution of 3d transition metal ions for Na^{+} ions has enabled us to begin investigating a new series of materials with potential as solid state tunable lasers. The optical properties of these materials compare favorably with those of materials previously

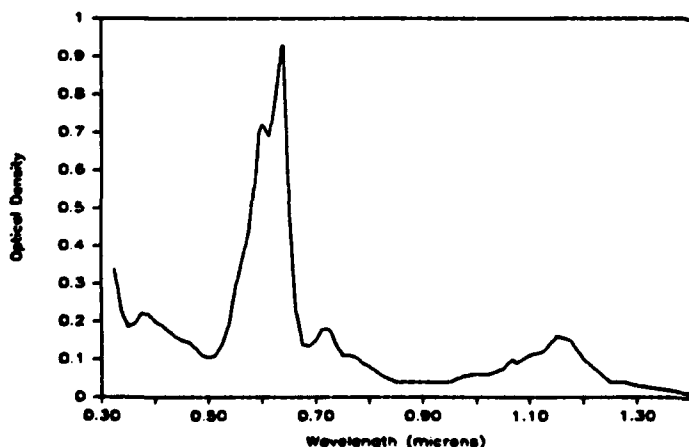


Figure 5. Absorption Spectrum of Ni^{2+} - β -alumina.

studied, and the vast benefits of ion exchange as a preparation technique permit the synthesis of many samples covering a wide variety of active ion concentrations. Initial results with Cr^{3+} exchanged ^{Beta} alumina indicate that hydration effects may influence the optical properties of this material.

ACKNOWLEDGEMENTS

The research was supported in part by the U.S. Office of Naval Research. We appreciate the experimental assistance of D. L. Yang, T. Alfrey, H. Dai, and P. Nelson. Thanks also go to L. Salmon and B. Schwarz for their work in preparing the Na^{+} - β -alumina crystals.

REFERENCES

1. G. C. Farrington, B. Dunn and J. O. Thomas, *Apl. Phys. A.* 32, (1983) 159.
2. G. C. Farrington and B. Dunn, *Solid State Ionics* 7, (1982) 267.
3. A. J. Alfrey, O. M. Stafsudd, B. Dunn, D. L. Yang and L. Salmon, submitted for publication.
4. D. L. Yang, unpublished results.
5. G. Huber and K. Petermann, in *Solid State Tunable Lasers*, (Springer-Verlag) 1985.
6. J. C. Walling, et al., *IEEE Journal of Quantum Electronics*, QE-16, (1980) 1902.
7. G. G. Imbusch in *Spectroscopy of Solid-State Laser-Type Materials*, B. DiBartolo, ed., in press.
8. J. B. Bates, et al., *Solid State Ionics* 5 (1981) 159.
9. J. B. Bates, et al., *Solid State Ionics*, 9/10, (1983) 237.
10. P. Cossee and A. E. VanArkel, *J. Phys. Chem. Solids* 15 (1960) 1-6.
11. J. O. Thomas, et al., *Solid State Ionics* 9/10 (1983) 301.
12. W. Low, *Phys. Rev.* 109 (1958) 247.

TECHNICAL REPORT DISTRIBUTION LIST, GEN

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

END

FILMED

10-85

DTIC