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R&T Code 413d011---02

Technical Report No. 17

Refractive Index Measurements of the Beta" Aluminas

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Prepared for Publication

in

Optics Letters

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July 1, 1988

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Unclassified
SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS			
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public use and sale; its distribution is unlimited			
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE						
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 17			5. MONITORING ORGANIZATION REPORT NUMBER(S)			
6a. NAME OF PERFORMING ORGANIZATION Department of Materials Science and Engineering		6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research			
6c. ADDRESS (City, State, and ZIP Code) 6532 Boelter Hall University of California, Los Angeles Los Angeles, CA 90024-1595			7b. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217			
8a. NAME OF FUNDING/SPONSORING ORGANIZATION same as #7 above		8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-83-K-0498			
8c. ADDRESS (City, State, and ZIP Code)			10. SOURCE OF FUNDING NUMBERS			
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Refractive Index Measurements of the Beta" Aluminas						
12. PERSONAL AUTHOR(S) S. C. Adams, B. Dunn, and O. M. Stafsudd						
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM 8/87 TO 8/88		14. DATE OF REPORT (Year, Month, Day) 1988, July 1		15. PAGE COUNT
16. SUPPLEMENTARY NOTATION Submitted to Optics Letters						
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)			
FIELD	GROUP	SUB-GROUP	Beta" alumina, refractive index, birefringence, (JES) ←			
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The refractive indices of selected monovalent and divalent beta" alumina single crystals have been determined using prism refraction techniques. The birefringence was found to vary from uniaxial negative to uniaxial positive depending upon the electronic polarizability of the exchanged ion. Thus, beta" alumina represents a novel material in which the magnitude and polarity of the birefringence can be tuned simply by ion exchange. The refractive index data have been used to predict the iso-index point ($n_e = n_o$) for the mixed system Na/Ag - beta" alumina compositions.						
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified			
22a. NAME OF RESPONSIBLE INDIVIDUAL			22b. TELEPHONE (Include Area Code)		22c. OFFICE SYMBOL	

REFRACTIVE INDEX MEASUREMENTS OF THE BETA" ALUMINAS

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ABSTRACT

The refractive indices of selected monovalent and divalent beta"-alumina single crystals have been determined using prism refraction techniques. The birefringence was found to vary from uniaxial negative to uniaxial positive depending upon the electronic polarizability of the exchanged ion. Thus, beta" alumina represents a novel material in which the magnitude and polarity of the birefringence can be tuned simply by ion exchange. The refractive index data have been used to predict the iso-index point ($n_e = n_o$) for the mixed system Na^+/Ag^+ -beta" alumina compositions.

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Introduction

Na^+ -beta" alumina ($\text{Na}_{1+x}\text{Mg}_x\text{Al}_{11-x}\text{O}_{17}$) is a non-stoichiometric sodium aluminate that is well known for its high ionic conductivity for Na^+ ions. The structure and properties of sodium beta" alumina have been reviewed [1,2]. The crystal structure has a distinct two-dimensional character. It consists of spinel-like blocks of closely packed Al^{3+} and O^{2-} separated by relatively open planes containing Na^+ and O^{2-} . The Na^+ ions exhibit fast ion transport properties within these planes, i.e., in two dimensions.

Dunn and Farrington [3,4] have shown that beta" alumina possesses a rich ion exchange chemistry. The rapid ionic transport phenomenon enables Na^+ to be replaced by a number of monovalent, divalent or trivalent cations. The ion exchange process is a fairly refined process and as a result, it is possible to control the nature of the dopant ion, its concentration and valence state.

Recent investigations have explored the optical properties of transition metal and lanthanide beta" aluminas [5,6]. The work on Nd^{3+} exchanged beta" alumina has shown some rather significant results including degenerate four-wave mixing and both pulsed and cw laser action [6,7]. In addition, Cu^+ beta" alumina shows considerable promise as a tunable solid state laser for visible wavelengths [8].

The present paper reports the first refractive index measurements for beta" alumina isomorphs. The crystal structure is rhombohedral and is thus uniaxial. Both the ordinary and extraordinary refractive indices were determined for a series of beta" alumina compositions which contained ions with widely differing electronic polarizabilities (Na^+ , Ca^{2+} , Ba^{2+} , Ag^+).

The composition effects are rather pronounced and depending upon the specific composition, crystals may be either uniaxial positive or negative. This behavior sug-

gests that the birefringence can be controlled by the ion exchange process and that crystals exhibiting an iso-index point can be obtained.

Experimental

The methods for producing single crystal of Na-beta alumina and its various isomorphs have been described [3,4]. Single crystals of Na-beta alumina were grown by a flux evaporation method and possessed the nominal composition $\text{Na}_{1.67}\text{Mg}_{0.67}\text{Al}_{10.33}\text{O}_{17}$. The conditions used for ion exchange are shown in table 1. The composition of the exchanged isomorphs was determined by X-ray absorption and gravimetric analysis.

After ion exchange, the various beta alumina crystals were mounted in boro-silicate glass and then ground and polished into prisms of approximately 45 degrees. The crystals were oriented in the prism such that the optic axis was normal to the plane of the triangle defining the prism. The apparatus used to measure the refractive indices consisted of a small divided-circle spectrometer which was modified to accommodate an Ar ion laser and various He-Ne lasers operating at wavelengths throughout the visible. The angle of the refracted beam was measured using the telescope and vernier of the spectrometer.

Measurements of the refracted beam angle were taken at the minimum deviation condition [9]. At this condition, the index of refraction, n , is given by

$$\frac{n}{n'} = \frac{\sin [(\psi + \beta)/2]}{\sin [\beta/2]}$$

where: n' = index of air

ψ = angle of refracted beam relative to the incident beam

β = angle of the prism

Results and Discussion

The measured refractive indices are summarized in table 2. Also tabulated here are values of the birefringence, $n_e - n_o$. Using a nonlinear least squares computer program, the refractive index data was fit to the Sellmeier equation of the form:

$$n(\lambda) = 1 + \frac{A}{1 - B/\lambda^2}$$

where A (no units) and B (nm^2) are the Sellmeier coefficients and λ the wavelength of interest. Values of A and B for the ordinary and extraordinary indices of each crystal are listed in table 3. Figure 1 illustrates the fitted Sellmeier curve for one of the isomorphs studied, namely Ca^{2+} -beta" alumina.

One noteworthy characteristic observed was the considerable variation of the birefringence with composition. Na^+ -beta" alumina exhibited the most negative value of -0.036 (uniaxial negative) while at the other extreme, Ag^+ -beta" alumina was uniaxial positive with a birefringence of +0.019. Both Ca^{2+} - and Ba^{2+} -beta" aluminas were less uniaxial negative with Ba^{2+} -beta" alumina being the closest to an isotropic material.

In an attempt to understand the variation of birefringence with composition, we have considered the role of the electronic polarizabilities of the ions substituted in beta" alumina. Table 4 lists values of the electronic polarizability for each ion and the birefringence of the corresponding beta" alumina crystal. The polarizabilities presented here are a result of the work of Tessman et. al. [10], and were obtained from an analysis of isotropic crystals. It is evident that the birefringence increases from

negative to positive values as ions of increasing electronic polarizability are exchanged into the crystal.

Figure 2 illustrates the influence of the electronic polarizability on both the ordinary and extraordinary refractive indices ($\lambda = 488 \text{ nm}$). The effect of having crystals change from uniaxial negative to uniaxial positive is to produce a cross-over point where the indices are equal. This point, which corresponds to an isotropic material, nearly occurs for Ba^{2+} beta" alumina.

It is interesting to consider in greater detail the relationship between composition of beta" alumina and the birefringence results. The ion exchange process affects only the conduction plane. This procedure appears to have two effects: (1) it introduces ions with different electronic polarizabilities and (2) the ions produce changes in the c-axis lattice parameter (also the optic axis of the crystal). From the few compositions studied, it appears that the electronic polarizability of the ion is a far more important contribution than any structural effect. Among the divalent beta" aluminas, the Ca^{2+} and Ba^{2+} isomorphs represent the minimum and maximum c_0 values (3.31 and 3.41 nm respectively). That is, the presence of Ba^{2+} extends the c-axis and makes the crystal structure slightly more anisotropic. The refractive index, however, does not reflect this behavior as Ba^{2+} beta" alumina is the least birefringent ($\Delta n = -0.003$) of the beta" aluminas studied to date, and much less birefringent than the Ca^{2+} isomorph ($\Delta n = -0.026$). It would appear, therefore, that the electronic polarizability is the more significant feature in determining birefringence. Similar behavior is observed for the monovalent compositions, Na^+ and Ag^+ beta" alumina. The c_0 lattice parameter for these two materials is quite comparable, yet their birefringence is enormously different. It is important to note that Na^+ and Ag^+ also exhibit the widest divergence in the electronic polarizabilities (table 4) for the ions studied in this work.

The results reported here were obtained with those crystals which were fully exchanged, i.e., the initial Na^+ content was completely replaced by the exchanging ion. It is possible to obtain partial exchange by either adjusting the melt composition or the ion exchange conditions (temperature and/or time). Such control of ion exchange conditions has, for example, enabled the optical properties of Nd^{3+} beta" alumina to be investigated as a function of Nd^{3+} concentration [6]. In the present case, the use of partial exchange provides an interesting opportunity; that of mixing an ion with a uniaxial negative behavior with one of uniaxial positive behavior. This effect has been calculated by following Vegards rule, i.e., using a weighted average of the refractive indices of the pure isomorphs. The result for a crystal of mixed Na^+/Ag^+ beta" alumina with 62% Ag^+ exchange is shown in figure 3. The significant feature is that there exists a wavelength (450 nm in figure 3) where the ordinary and extraordinary indices intersect and the crystal behaves as an isotropic material. Such behavior suggests that beta" alumina may be of interest as a Lyot iso-index filter material [11]. It should be noted that in recent years interest in underwater laser communications has spurred a renewed search for materials which exhibit an iso-index point in the blue/green (around $\lambda = 450$ nm) [12]. Moreover, calculations indicate that crystals with other Ag^+ concentrations will intersect at other wavelengths. Thus, there exists the possibility of utilizing controlled partial ion exchange to tune the iso-index point. That is, there should exist a continuous series of beta" alumina compositions which exhibit iso-index behavior throughout the visible and infrared regions. Experiments with such mixed systems are in progress.

Acknowledgments

This work was supported in part by the U.S. Office of Naval Research.

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Table 1: Cation Exchange with Beta" Alumina

Ion Exchanged For Na ⁺	Melt composition	Temp. (C)	Time
Ag ⁺	AgNO ₃	320	24 hrs
Ba ⁺⁺	Ba(NO ₃) ₂ :BaCl ₂ 62:38 mol%	550	2 days
Ca ⁺⁺	CaCl ₂	800	24 hrs

Table 2: Measured Refractive Indices and Birefringence of Beta⁺ Alumina Isomorphs

Crystal	Biref.		Wavelength (nm)					
			488	514.5	543.5	594.1	612	632.8
Ag ⁺ Beta ⁺	+0.02	n _o	1.771	1.768	1.766	1.760	1.760	1.758
		n _e	1.793	1.788	1.785	1.780	1.779	1.776
Ba ⁺⁺ Beta ⁺	-.003	n _o	1.694	1.692	1.690	1.687	1.686	1.685
		n _e	1.691	1.688	1.686	1.682	1.681	1.681
Ca ⁺⁺ Beta ⁺	-.026	n _o	1.689	1.687	1.685	1.681	1.680	1.679
		n _e	1.663	1.660	1.658	1.655	1.654	1.653
Na ⁺ Beta ⁺	-.036	n _o	1.681	1.679	1.676	1.673	1.673	1.671
		n _e	1.646	1.643	1.640	1.637	1.637	1.635

Table 3: Sellmeier Coefficients

Crystal		A (no units)	B (nm ²)
Ag ⁺ Beta ⁿ	n _o	0.7384	1.018 x 10 ⁴
	n _e	0.7553	1.108 x 10 ⁴
Ba ⁺⁺ Beta ⁿ	n _o	0.6723	7.499 x 10 ³
	n _e	0.6656	8.716 x 10 ³
Ca ⁺⁺ Beta ⁿ	n _o	0.6646	8.579 x 10 ³
	n _e	0.6392	8.472 x 10 ³
Na ⁺ Beta ⁿ	n _o	0.6575	8.242 x 10 ³
	n _e	0.6204	9.322 x 10 ³

Table 4: Variation of Birefringence with Electronic Polarizability of Ionic Species, [10].

Ion	Electronic Polarizability (nm) ³	Birefringence
Na ⁺	2.1 x 10 ⁻⁴	-0.036
Ca ⁺⁺	5.1 x 10 ⁻⁴	-0.026
Ba ⁺⁺	1.6 x 10 ⁻³	-0.003
Ag ⁺	2.4 x 10 ⁻³	+0.02

CAPTIONS TO FIGURES

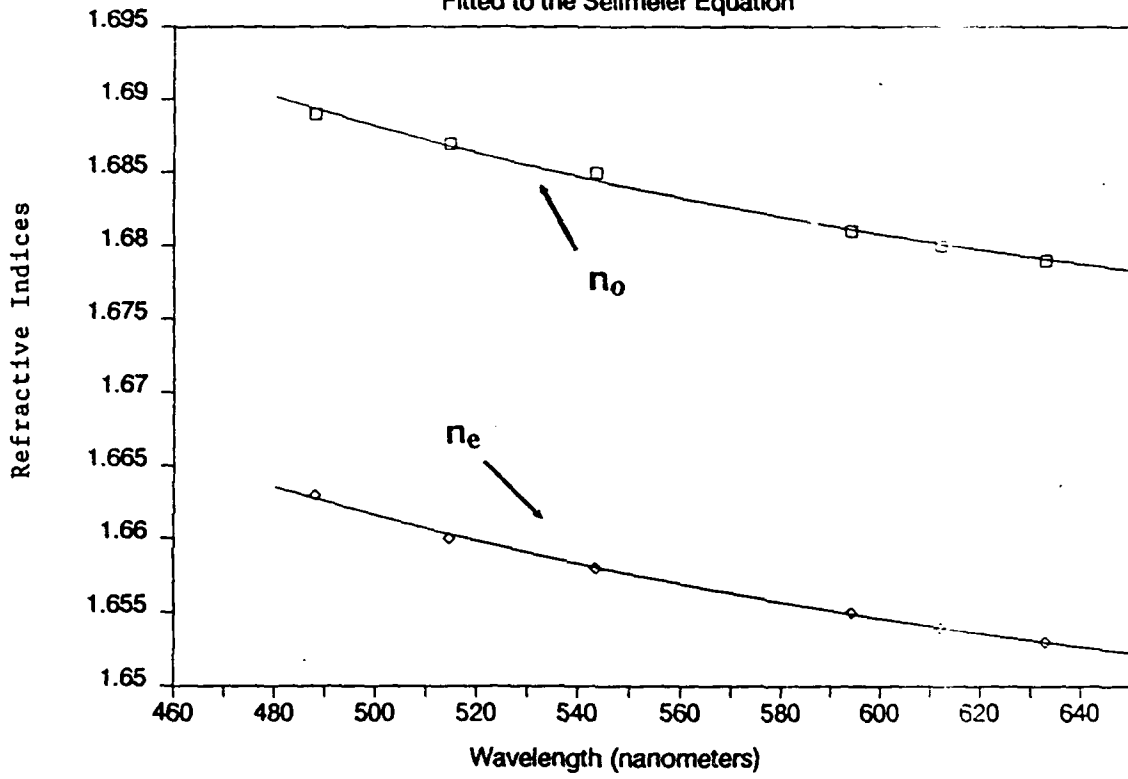
Figure 1: Measurements of the ordinary (n_o) and extraordinary (n_e) refractive indices of Ca^{2+} beta" alumina fitted to the Sellmeier equation.

Figure 2: The variation of beta" alumina crystal refractive index at $\lambda = 488$ nm as a function of the electronic polarizability of the ion resident in the conduction plane.

Figure 3: The calculated refractive indices of the mixed system Na:Ag-beta" alumina at 61.9 % Ag.

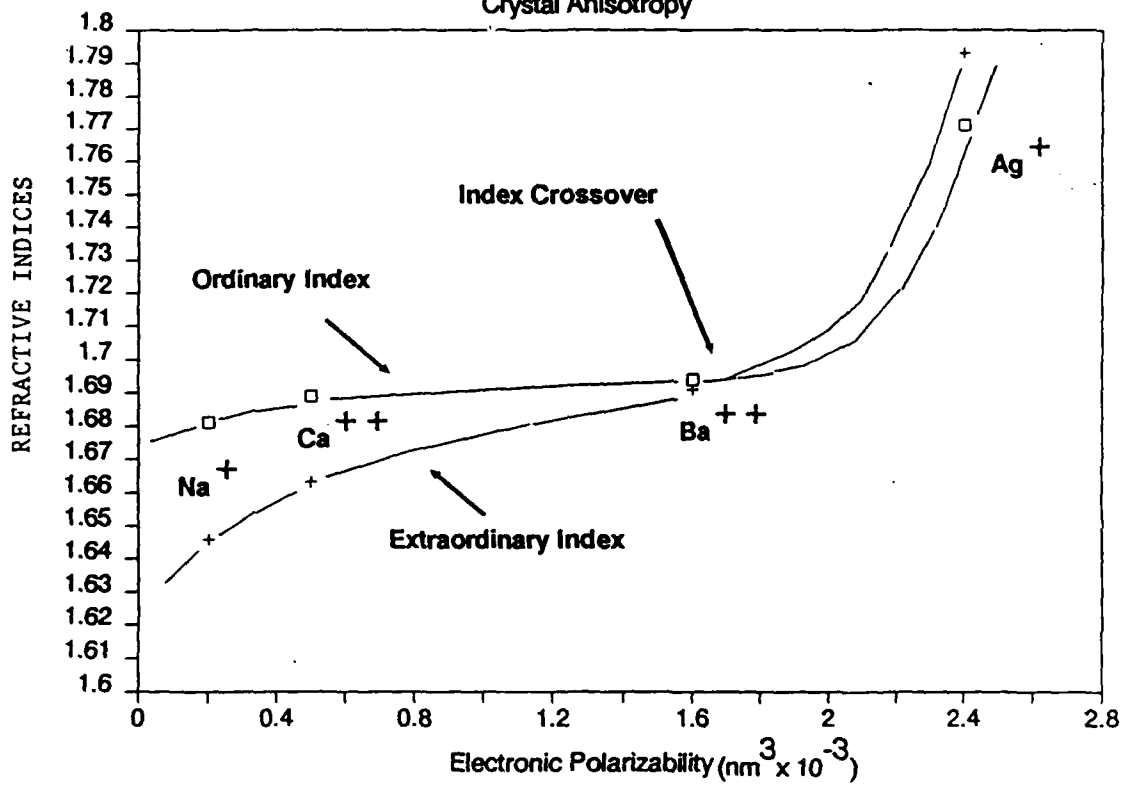
Ca-B⁺ Alumina Index of Refraction Data

Fitted to the Sellmeier Equation



Effect of Electronic Polarizability on

Crystal Anisotropy



Na/Ag Beta" Alumina

Refractive Index @ 61.9% Ag

