4

OFFICE OF NAVAL RESEARCH

Contract N00014-83-K-0498
R&T Code 413d011---02

Technical Report No. 21

Energy Transfer Effects in β'' Alumina

by

L.A. Momoda[1], J.D. Barrie[1], B. Dunn[1] and O.M. Stafsudd[2]

Prepared for Publication

in

Electrochemical Society Symposium on Luminescence

1. Department of Materials Science and Engineering

2. Department of Electrical Engineering
University of California, Los Angeles,
Los Angeles, California 90024

June 15, 1989

REPRODUCED AT GOVERNMENT EXPENSE

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

3. DISTRIBUTION / AVAILABILITY OF REPORT
Approved for Public use and sale; its distribution is unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
Technical Report No. 21

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 ofNaval Research

6c. ADDRESS *(City, State, and ZIP Code)*
6531 Boelter Hall
University of California, Los Angeles
Los Angeles, CA 90024-1595

7b. ADDRESS *(City, State, and ZIP Code)*
Chemistry Division
800 N. Quincy Street
Arlington, VA 22217

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
Office of Naval Research

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
N00014-83-K-0498

8c. ADDRESS *(City, State, and ZIP Code)*
Chemistry Division
800 N. Quincy Street
Arlington, VA 22217

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE *(Include Security Classification)*
Energy Transfer Effects in β" Alumina

12. PERSONAL AUTHOR(S)
L. A. Momoda, J. D. Barrie, B. Dunn, O. M. Stafsudd

13a. TYPE OF REPORT
Technical

13b. TIME COVERED
FROM 8/88 TO 7/89

14. DATE OF REPORT *(Year, Month, Day)*
1989, June, 15

15. PAGE COUNT
8

16. SUPPLEMENTARY NOTATION
Submitted to: Electrochemical Society Symposium on Luminescence

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
energy transfer, ion exchange, cerium, neodymium
Beta" Alumina

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

Cerium (+3) Neodymium (+3) Beta"

Energy transfer between Ce^{+3} and Nd^{+3} exchanged into β" alumina is observed. Synthesis of the crystals was achieved by ion exchange. Both radiative and nonradiative transfer mechanisms are evident. The nonradiative transfer is attributed to electrostatic dipole-quadrupole interactions where the highest measured transfer efficiency was 40%. (AW)

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL
Bruce Dunn

22b. TELEPHONE *(Include Area Code)*
(213) 825-1519

22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.

SECURITY CLASSIFICATION OF THIS PAGE

ENERGY TRANSFER EFFECTS IN β"-ALUMINA

L.A. Momoda, J.D. Barrie, B. Dunn and O.M. Stafsudd+
University of California, Los Angeles
Department of Materials Science and Engineering
+Department of Electrical Engineering
Los Angeles, CA 90024

Energy transfer between Ce^{+3} and Nd^{+3} exchanged into β"-alumina is observed. Synthesis of the crystals was achieved by ion exchange. Both radiative and nonradiative transfer mechanisms are evident. The nonradiative transfer is attributed to electrostatic dipole-quadrupole interactions where the highest measured transfer efficiency was 40%.

1. INTRODUCTION

The unique crystal chemistry of sodium β"-alumina, nominally $Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$, manifests itself in a wide range of interesting physical properties (1). The β"-alumina structure contains loose packed regions within its unit cell, called conduction planes (2). These conduction planes are sufficiently spacious that the Na^{+} ions within them can be replaced by a wide range of cationic species via low temperature ion exchange techniques. Many of the trivalent lanthanides and the transition metals ions can be readily diffused into the into the β"-alumina structure in this manner (3). The use of low temperatures and controlled atmospheres have provided a method by which stable, homogeneous crystals can be synthesized.

The structural characteristics of the crystal aid in its behavior as an optical host. The ion arrangement within the conduction planes allows the structure to readily expand or contract to accommodate ions with a wide range of size and charge. Consequently, the formation of luminescence quenching lattice defects are prevented. Ions in the plane can also undergo structural relaxations which have contributed to the anomalous absorption strength of Nd^{+3} within the material (4).

The intent of this paper is to consider the synthesis and optical properties of the β"-alumina host when it is 'double-doped'. Ion exchange techniques are used to simultaneously introduce two different optically active species into the lattice. Evidence of short range interaction between the two species is studied by the crystal's ability to transfer optical energy. In particular, the nature of the interaction between Ce^{+3} and Nd^{+3} ions in the structure is examined.

2. EXPERIMENTAL METHODS

Single crystals of sodium ß"-alumina were grown by a flux evaporation technique (5). Transparent platelets retrieved from the flux are cut and are subsequently stored under vacuum. The typical sizes of these platelets are 3 x 3 x 0.2 mm^3.

The simultaneous exchange of two different optically active species (i.e. sensitizer and activator) was achieved by variation of the technique used for the exchange of a single ionic specie (3). A mixture of the chlorides for the sensitizing and activating ions was used to produce the molten exchange bath. To insure a low melting temperature, eutectic mixtures of each of the chlorides with NaCl were made. The amount of each eutectic was determined by the desired sensitizer to activator ratios (6). The salt mixture was slowly dried under a chlorine/nitrogen atmosphere to achieve the complete removal of all waters of hydration. An exchange temperature of 650°C was used to provide sufficient thermal activation for ionic diffusion.

The composition of the exchanged crystal was determined by a combination of methods. The total exchange of sodium for lanthanide ions was determined gravimetrically (3). All crystals discussed in this study had 55% of the sodium ions replaced with lanthanides. The concentrations of the sensitizing and activating were then separately determined by quantitative optical absorption techniques (7) or by energy dispersive x-ray analysis (EDX).

Optical excitation and emission spectra were recorded by a SPEX Fluorolog F112 spectrofluorometer pumped by a 150W Xe arc lamp. The pump source for the fluorescence decay measurements was a Lambda Physik EMG 201 MSC XeCl excimer laser (emission wavelength of 308 nm). The fluorescence detection of Ce^{+3} was achieved by a reverse biased Hamamatsu S1722-01 Silicon PIN photodiode (35 V bias and 50 ohm load) coupled to a Tektronix 2430A digital oscilloscope. The temporal response of this system was 7 nm. The detection of Nd^{+3} luminescence was achieved by a Hamamatsu 7102 photomultiplier tube (S1 response) biased with 800 V and a load of 1 Kohm.

3. RESULTS AND DISCUSSION

3.1 Ce^{+3}-ß"-Alumina

The excitation and emission spectra of Ce^{+3}-ß"-alumina containing approximately 1 x 10^{21} Ce^{+3} ions/cm^3 are shown in Figure 1. The broad excitation band of Ce^{+3} effectively covers the emission regime of mercury flashlamps. The emission of Ce^{+3} peaks at 395 nm with a shoulder at 370 nm. The two peaks result from the radiative decay from the 5d band to the $^2F_{7/2}$ and $^2F_{5/2}$ (4f) states respectively. The suppressed emission of the shorter wavelength transition is consistent with the reabsorption of this radiation by Ce^{+3} itself. The condition of overlap necessary for this transfer is evident by the small Stokes shift between the excitation and emission bands.

The spectral overlap in Ce^{+3}-ß"-alumina prompted the investigation of possible Ce^{+3} concentration quenching effects. The possibility of energy transfer between Ce^{+3} ions via nonradiative processes was studied by luminescent decay measurements performed as a function of Ce^{+3} concentration (Figure 2). Although a very slight decrease in the measured lifetime of Ce^{+3} was detected as a function of Ce^{+3} concentration, this effect was not pronounced. A small linear decrease in lifetime from 42 nsec to 31 nsec was measured over the concentration range of 3.0×10^{20} Ce^{+3} ions/cm^3 to 1.3×10^{21} Ce^{+3} ions/cm^3. This decrease, however evident, is not consistent with the strong concentration dependence predicted by energy migration models (8). Considering the smaller range of Ce^{+3} concentrations present in the double-doped crystals, this quenching effect is even less evident and falls within the uncertainty of our measurement technique. The effect of concentration quenching via nonradiative transfer in Ce^{+3}-ß"-alumina is therefore considered to be negligible.

3.2 Ce^{+3}/Nd^{+3}-ß"-Alumina

The occurrence of energy transfer between Ce^{+3} and Nd^{+3} ions in ß"-alumina was first verified by the excitation spectrum of the 890 nm emission of Nd^{+3} (Figure 3). The appearance of an additional, broad band in the ultraviolet region of the spectrum compares favorably with that of Ce^{+3} in ß"-alumina and indicates that energy absorbed by Ce^{+3} subsequently produces luminescence from Nd^{+3}.

Radiative energy transfer is also evident in Ce^{+3}/Nd^{+3}-ß"-alumina. The appearance of three minima at 354 nm, 381 nm and 430 nm in the emission band of Ce^{+3} correspond to excitation peaks measured in Nd^{+3}-ß"-alumina. These minima indicate that photons emitted by Ce^{+3} at these wavelengths are reabsorbed by Nd^{+3}.

The occurrence of Nd^{+3} to Ce^{+3} back transfer was also investigated. In these measurements, the luminescent lifetime of Nd^{+3} emission at 1.06 µm was determined for crystals with and without Ce^{+3}. The measured lifetimes were on the order of 400 µsecs and they were independent of Ce^{+3} content indicating that nonradiative back transfer processes do not occur. The measured lifetimes were also independent of Nd^{+3} concentration indicating that Nd^{+3} cross relaxation processes also do not occur in ß"-alumina.

An additional indication of Ce^{+3} to Nd^{+3} energy transfer was made evident by the shortening of the Ce^{+3} luminescent lifetime with the introduction of the Nd^{+3} activator. Transfer of nonradiative energy to Nd^{+3} provides a faster route for the de-excitation of excited state energy of Ce^{+3} and should decrease the sensitizer's luminescence decay time. Quantitatively, this decrease can used to determine the nonradiative transfer efficiency, η_T, by the expression (8):

$$\eta_T = 1 - (\tau/\tau_0) \qquad (1)$$

where τ and τ_0 are the Ce^{+3} luminescent decay times with and without the presence of Nd^{+3} respectively. The values of transfer efficiencies measured by this expression are listed in Table 1.

Table 1
Measured Nonradiative Transfer Parameters
in Ce^{+3}/Nd^{+3}-ß"-Alumina

Ce^{+3}:Nd^{+3} Conc. Ratio	Measured Ce^{+3} Lifetime, nsec	Transfer Efficiency	Transfer Rate, sec^{-1}
1:10	26 ± 5	0.41	2×10^7
1:4	32 ± 5	0.27	8×10^6
1:2	36 ± 4	0.15	4×10^6
3:5	35 ± 5	0.14	4×10^6
1:1	37 ± 6	0.12	2×10^6

Table 1 clearly shows a dependence of the measured efficiency values on the Ce^{+3} to Nd^{+3} ion concentration ratio. Physically, the ion concentration ratio is an indication of the Ce^{+3}/Nd^{+3} interaction distance since all the crystals examined in this study contain the same total amount of lanthanide ions (approximately 1×10^{21} ions/cm^3). A variation in the amount of Ce^{+3} relative to the amount of Nd^{+3} therefore leads to a change in the average interaction distance. Assuming a random distribution of ions within the plane, a crystal containing one Ce^{+3} for every ten Nd^{+3} ions should have most of its Ce^{+3} ions surrounded by Nd^{+3} ions. In ß"-alumina, electronic spin resonance (9) and x-ray diffraction studies (10) both show that Ce^{+3} and Nd^{+3} ions favor occupation of the mid-oxygen (mO) site within the conduction plane. The closest site to site distance for the mO site is 5.6Å. One can assume, therefore, that the Ce^{+3}/Nd^{+3} interaction distance in a 1:10 Ce^{+3}:Nd^{+3} ß"-alumina crystals is on the order of 6Å. Furthermore, as the Ce^{+3} content of the crystal is increased, the average interaction distance also increases. A crystal containing 1 Ce^{+3} ion for every Nd^{+3} ion, for example, should have an average interaction distance on the order of 9Å.

The change in interaction distance is consistent with the trends we observe in the transfer efficiency values. As the the Ce^{+3} to Nd^{+3} interaction distance is increased, the probability of transfer between the ions is reduced. Energy transfer processes consequently become less efficient. The highest values for the transfer efficiency were measured at the lowest Ce^{+3} : Nd^{+3} concentration ratios, with the peak efficiency measured at approximately 40% for ß"-crystals containing 1 Ce^{+3} for every 10 Nd^{+3} ions.

The decrease in Ce^{+3} lifetimes with the presence Nd^{+3} activation was also used to quantify the transfer kinetics. The energy transfer rate, k, is defined by the expression (8):

$$k = 1/\tau - 1/\tau_o \qquad (2)$$

The transfer rate, or the probability that Ce^{+3} will transfer energy to Nd^{+3}, was also examined as a function of relative Ce^{+3} and Nd^{+3} concentrations. As was seen for the transfer efficiency, the highest transfer rates were measured for the Ce^{+3} : Nd^{+3} ratios where the shorter interaction distances made transfer more probable. The highest transfer rate measured was on the order of 2×10^7 sec^{-1} for crystals containing 1 Ce^{+3} ion for every 10 Nd^{+3} ions.

The transfer rates were used to determine the most likely mechanism of nonradiative transfer between Ce^{+3} and Nd^{+3} in ß"-alumina. The most common mechanisms for nonradiative transfer are the Coulombic multipolar interactions and the exchange interaction. The latter requires overlap of the electron clouds of the sensitizer and the activator and is consequently a short range interaction (<4 Å) (11). As was mentioned previously, the closest site to site distance in ß"-alumina for mid-oxygen site occupation is 5.6Å. Consequently, the exchange mechanism for nonradiative transfer seems highly unlikely in ß"-alumina.

The superexchange mechanism, where the column oxygen within the conduction plane would act as an intermediate in the exchange interaction between the Ce^{+3} and Nd^{+3} ions, is also deemed to be unlikely because the overlap between the 2p orbitals of oxygen and the 4f orbitals of the lanthanides is not appreciable (11).

The remaining and most feasible nonradiative transfer mechanism are the longer range electrostatic multipolar interactions. The probability of transfer via the coupling of two electric dipoles, P_{sa}^{dd}, can be described by the equation (12):

$$P_{sa}^{dd} = \frac{3h^4c^4Q_a}{4\pi n^2\tau_s r^6} \int f_a f_s \frac{dE}{E^4} \qquad (3)$$

where h is Planck's constant, c is the speed of light, n is the index of refraction, Q_a is the absorption cross section of the activator, τ_s is the lifetime of the sensitizer and r is the interaction distance. The integral represents the spectral overlap of the sensitizer (s) and activator (a) in units of energy, E. This equation was expressed in more measurable parameters by Blasse (11):

$$P_{sa}^{dd} = 3.0 \times 10^{12} \frac{f_a P_r I}{r^6 E^4} \qquad (4)$$

where P_r is the probability of radiative decay of the sensitizer, I is the energy overlap in eV^{-1} and E is the energy of the transition. Taking the measured value for the oscillator strength of the ^4D_J, $^2I_{11/2}$, $^2L_{15/2}$ transition in Nd^{+3}-β''-alumina to be 13 x 10^{-6} (4), the radiative decay probability of Ce^{+3} to be $1/\tau_0 = 2 \times 10^7$ sec^{-1}, the energy of the transition to be 3.5 eV and the energy overlap to be approximately 10^{-3} eV^{-1}, the interaction distance, r, to be in the range of 6-10 Å, the approximate probability of transfer via the dipole-dipole mechanism in Ce^{+3}/Nd^{+3}-β''-alumina is in the range of 5 x10^3 to 1 x 10^5 sec^{-1}. This range is substantially lower than that of the measured transfer rates of 2 x 10^6 to 2 x 10^7 sec^{-1} for a 1:10 Ce:Nd crystal. Thus, it seems unlikely that a dipole-dipole mechanism occurs in Ce^{+3}/Nd^{+3}-β''-alumina. Physically we can rationalize the unlikelihood of a dipole-dipole mechanism since the 4f-4f transition of Nd^{+3} is dipole forbidden.

Instead let us consider the probability of dipole-quadrupole interaction, P_{sa}^{dq} (11):

$$P_{sa}^{dq} = 3\,(\lambda/r)^2 (f_q/f_d) P_{sa}^{dd} \qquad (5)$$

where λ is the wavelength of the transition (4000 Å) and f_q and f_d are the oscillator strengths of the quadrupole and dipole transitions respectively. Here the calculated value is in the range of 5 x 10^6 to 1 x 10^8 sec^{-1}. These approximate values compare much more favorably with that of the measured transfer rate.

While the dipole-quadrupole nonradiative transfer mechanism seems to operate in Ce^{+3}/Nd^{+3}-β''-alumina, it is important not to de-emphasize the importance of radiative transfer mechanisms. The measured excitation and emission spectra tell us that both Ce^{+3} to Ce^{+3} and Ce^{+3} to Nd^{+3} reabsorption processes occur. It is also worthwhile to note that the probability of radiative decay of Ce^{+3}, P_r is approximately 2 x 10^7 sec^{-1}. The value is about equal to the measured transfer rate suggesting the radiative and nonradiative processes are competitive. This might serve to explain the discrepancies in the transfer efficiency values we reported previously based on measured decreases in the emission intensity of Ce^{+3} in Ce^{+3}/Nd^{+3}-β''-alumina (6).

3.3 Other systems

The double exchange process has also been used to produce other energy transfer couples (6). Energy transfer has been observed in β''-alumina crystals containing Ce^{+3} and Tb^{+3}. While the system has not been studied as much as Ce^{+3}/Nd^{+3}-β''-alumina, we have determined that a six fold increase in the luminescent intensity of the 540 nm emission of Tb^{+3} can be achieved when 1 Ce^{+3} ion is added for every 10 Tb^{+3} ions in the crystal and pumped in the UV. Also, the up-conversion of near infrared light at 970 nm to green and red luminescence has been observed in Yb^{+3}/Er^{+3}-ß"-alumina. Research is currently being done to characterize both of these systems.

4. CONCLUSIONS

The ion exchange process has been successfully used to produce crystals containing controlled amounts of sensitizing and activating ions. Interactions between these ions are evident from the occurrence of energy transfer of Ce^{+3} to Nd^{+3}. Evidence of Nd^{+3} to Ce^{+3} back transfer was not seen. In Ce^{+3}/Nd^{+3}- ß"-alumina both radiative and nonradiative transfer processes are observed, the latter most likely occurring via the electrostatic interactions between Ce^{+3} dipolar transitions and Nd^{+3} quadrupolar transitions.

ACKNOWLEDEMENTS

The work was supported by the U.S. Office of Naval Research.

REFERENCES

(1) B. Dunn and G.C. Farrington, Solid State Ionics, 18&19 (1986) 31.
(2) M. Bettman and C.R. Peters, J. Phys. Chem., 73 (1969) 1774.
(3) B. Dunn and G.C. Farrington, Solid State Ionics, 9&10 (1983) 223.
(4) A.J. Alfrey, J. Chem. Phys., O.M. Stafsudd, B. Dunn, D.L. Yang and L. Salmon, J. Chem, Phys., 88 (1988) 707.
(5) J.L. Briant and G.C. Farrington, J. Solid State Chem., 33 (1980) 385.
(6) L.A. Momoda, J.D. Barrie, B. Dunn and O.M. Stafsudd, Proceedings of the International School on Excited States of Transition Elements, ed. W. Strek, in press.
(7) J.D. Barrie, B.Dunn and O.M. Stafsudd, J. Lumin., 37 (1987) 303.
(8) R.C. Powell and G. Blasse, Structure and Bonding, 42 (1980) 43.
(9) J.D. Barrie. L.A. Momoda, B. Dunn, D. Gourier, G. Aka and D. Vivien, to be submitted for publication.
(10) J.O. Thomas, W. Cabrillo-Cabrera and G.C. Farrington, Solid State Ionics, in press.
(11) G. Blasse, Philips Res. Reps., 24 (1969) 131.
(12) D.L. Dexter, J. Chem. Phys., 21 (1953) 836.

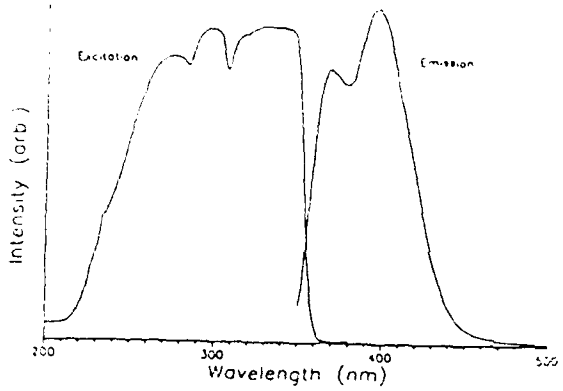

Figure 1. Excitation and emission spectra of Ce^{+3}-ß"-alumina.

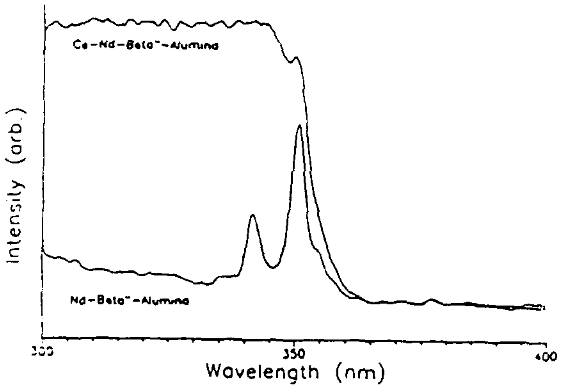

Figure 2. Excitation spectra of the 890 nm emission from Ce^{+3}/Nd^{+3}-ß"-alumina and Nd^{+3}-ß"-alumina.

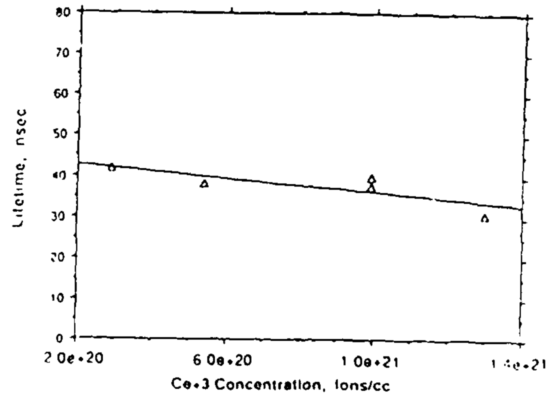

Figure 3. Luminescent lifetime of the 395 nm emission from Ce^{+3}-ß"-alumina as a function of Ce^{+3} concentration.