# REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-00-

0577

| 1. REPORT DATE (DD-MM-YYYY) 10/13/00 | 2. REPORT TYPE Final Technical Report | 3. DATES COVERED (From - To) 01 MAR 95 - 30 APR 98 |
|---|---|---|

| 4. TITLE AND SUBTITLE Interface Chemical Modification for Property Control of Oxide Reinforced Ceramic Matrix Composites | 5a. CONTRACT NUMBER |
|---|---|
| | 5b. GRANT NUMBER F49620-95-1-0191 |
| | 5c. PROGRAM ELEMENT NUMBER |

| 6. AUTHOR(S) Bonnell, Dawn A. | 5d. PROJECT NUMBER |
|---|---|
| | 5e. TASK NUMBER 2306/BS |
| | 5f. WORK UNIT NUMBER |

| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Trustees of the University of Pennsylvania 133 S. 36th Street Philadelphia, PA 19104-3246 | 8. PERFORMING ORGANIZATION REPORT NUMBER 526289 |
|---|---|

| 9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NA 801 N. Randolph St., Room 732 Arlington, VA 22203-1977 | 10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR/NA |
|---|---|
| | 11. SPONSOR/MONITOR'S REPORT NUMBER(S) |

**12. DISTRIBUTION / AVAILABILITY STATEMENT**

## DISTRIBUTION STATEMENT A
### Approved for Public Release
### Distribution Unlimited

**13. SUPPLEMENTARY NOTES**

**14. ABSTRACT**
The Air Force requirements for high temperature structural materials include applications in aircraft afterburner and in propulsion systems. Ceramic matrix composites are candidate materials systems for several types of these applications. In the effort to develop composites for high temperature structural applications attention has turned towards oxide-oxide systems. The objective of this project is to systematically investigate the segregation behavior and high temperature stability of complex oxides. The project has an experimental and a theoretical component. The approach combines Auger electron spectroscopy (AES), Rutherford backscattering spectrometry (RBS) and scanning probe microscopies (STM, AFM), along with conventional transmission and scanning electron microscopies (TEM,SEM) to characterize surface and interface composition. The theoretical approach emphasizes a coherent model of segregation that connects statistical mechanics and first principles calculations. This work is in collaboration with the R. Kerans and the Ceramics Group at Wright Patterson Air Force Base.

**15. SUBJECT TERMS**
Oxide Reinforced Ceramic Matrix Composites

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON Dawn A. Bonnell |
|---|---|---|---|---|---|
| a. REPORT UU | b. ABSTRACT UU | c. THIS PAGE UU | UU | | 19b. TELEPHONE NUMBER (include area code) 215-898-6231 |

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

DTIC QUALITY INSPECTED 4

# INTERFACE CHEMICAL MODIFICATION FOR PROPERTY CONTROL OF OXIDE REINFORCED CERAMIC MATRIX COMPOSITES

by:

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# I. INTRODUCTION

The Air Force requirements for high temperature structural materials include applications in aircraft afterburner and in propulsion systems[1]. Ceramic matrix composites are candidate materials systems for several types of these applications. In the effort to develop composites for high temperature structural applications attention has turned towards oxide-oxide systems. The optimal composite will consist of phases that are thermodynamically stable (i.e. coexist without reaction) at high temperatures, that have small thermal expansion mismatch, and that can be formed in a fiber-matrix morphology. These conditions are not obtained for systems such as SiC/LAS, SiC/alumina, etc[2], but are for oxide-oxide systems such as $Y_3Al_5O_{12}$-alumina[3],[4]. The properties of fiber-matrix composites are dictated by the properties of grain boundaries in the matrix, of grain boundaries in the fiber, and of interfaces between the fiber and matrix. Since properties of most ceramic matrices are, for the most part, understood, much recent attention has focused on controlling properties of the interface between fiber and matrix. Two strategies are discussed for controlling interface properties: coating fibers with compounds that allow decohesion[5],[6],[7],[8] and altering interface chemistry *in situ* via segregation[9].

It is clear that in either case the effects of dopant segregation must be understood. This can be illustrated by considering the $Y_3Al_5O_{12}$ (YAG) system. Since the technology for producing YAG fibers is under development, the potential of segregating dopant to YAG surfaces and interfaces was studied. If dopants segregate they might be exploited to reduce the adhesion of fiber matrix interfaces; however, they might also degrade fiber strength by reducing YAG grain boundary cohesion within the fiber. If dopants do not segregate, the then potential for fiber strength reduction due to diffusion of elements in the coatings is less likely. Regardless of the source of the impurities, segregation behavior in the relevant materials must be understood.

The three most promising oxide fibers are Saphikon™ fibers, YAG fibers, and mullite fibers. While segregation in alumina has been a (sometimes controversial) topic of study for over 40 years, similar information about YAG was only recently developed and is nonexistent for mullite. The objective of this project is to systematically investigate the segregation behavior and high temperature stability of complex oxides. The project has an experimental and a theoretical component. The approach combines Auger electron spectroscopy (AES), Rutherford backscattering spectrometry (RBS), and scanning probe microscopies (STM and AFM), along with conventional transmission and scanning electron microscopies (TEM,SEM) to characterize surface and interface composition. The theoretical approach emphasizes a coherent model of segregation that connects statistical mechanics and first principles calculations. This work is in collaboration with the R. Kerans and the Ceramics Group at Wright Patterson Air Force Base.

# II.    SUMMARY OF RESULTS

The following objectives were met in this project:

Analytical solutions for charged induced segregation in YAG were derived and limiting values of defect formation energies determined by comparison with measurements.

Since YAG is an insulator, many of the electron beam based spectroscopic measurements are problematic. Protocols for measuring surface composition by Auger electron spectroscopy in insulators were developed and the standards for YAG evaluated.

Surface segregation in single crystal YAG were measured including self segregation and that for isovalent and aliovalent dopants.

Segregation was distinguished from precipitation with morphological analysis with AFM and high resolution SEM.

Polycrystals were synthesized and spectroscopic analysis performed on fracture surfaces to compare grain boundary and volume compositions.

TEM was performed on selected polycrystals and the protocols for grain boundary composition measurement determined.

The previous reports documented the calculations and surface segregation of dopants to single crystal YAG surfaces. The results are reviewed in the papers appending this report. This report will focus on interface chemistry in polycrystalline YAG and YAG composites.

## Summary of Segregation in YAG

Garnets are cubic minerals with the formula $AB(SiO_4)_3$, where $A = Ca^{2+}$, $Mg^{2+}$, $Fe^{2+}$, $Mn^{2+}$, etc. and $B = Al^{3+}$, $Fe^{3+}$, $Cr^{3+}$, etc[10]. The compositions of naturally occurring garnets range widely between the ternary end members. Since the mid 1960's synthetic yttrium aluminum garnet (YAG) has been doped with Nd to make high power lasers. Most recently the mechanical properties of YAG single crystals and polycrystals have been exploited in ceramic matrix composites for high temperature structural applications. In all cases impurity atoms are critical to properties; therefore, solubility limits and atomic substitution mechanisms have been extensively studied for many garnets. Equally important to the stability of properties is the tendency of dopant atoms to remain distributed throughout the crystal or to segregate to internal or external interfaces. The mobility, or lack thereof, of dopant atoms had not been studied and was the focus of the previous AFOSR project. We determined the effect of site occupancy, charge, and size on segregation in YAG single crystals and developed the solutions to ionic space charge models that allow calculations of segregation in YAG.

Yttrium aluminum garnet has the formula $Y_3Al_5O_{12}$ and consists of a network of aluminum atoms that are octahedrally and tetrahedrally coordinated, figure 1 (a). The polyhedra are slightly distorted and are corner shared such that every octahedron is connected to six tetrahedra, and each tetrahedron is connected to four octahedra. The yttrium atoms reside in the dodecahedral interstices formed by this network. The lattice is cubic with the space group Ia3d and a unit cell dimension of 12.01 Å. To examine the effect of charge and size on segregation, various cations were substituted onto the yttrium and aluminum sites. It is known from optical studies that Nd, as well as most other rare earth elements, substitute on the dodecahedral sites of Y[11,12,13,14,15,16,17,18]. Occupancy of Fe and Ga in the tetrahedral and octahedral sites of Al is inferred from the stability of YIG (yttrium iron garnet) and YGG (yttrium gallium garnet). Similarly, Gd is inferred to substitute for Y from the existence of GGG (gadolinium gallium garnet). The transition metal cations, such as V, Cr, Mn, Mo, and Ni have been found to occupy both tetrahedral and octahedral sites, adopting a 4+ valence in the former and a 3+ valence in the latter.[19,20,21,22,23,24]. For aliovalent substitution the charge imbalance is compensated by oxygen vacancies[25] and/or co-dopants[26], such as Mg and Ca. The formation of vacancies rather than interstitial point defects suggests a Schottky defect structure for YAG, which is conducive to substitutions of impurity elements over incorporation of dopants in interstitial sites.
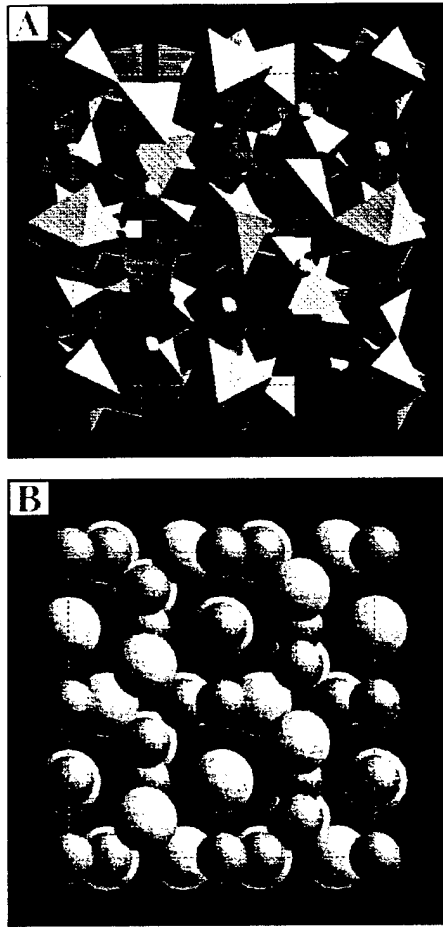
**Figure 2:** Structure of yttrium aluminum garnet from the cube face (001) direction in (a) polyhedral representation and (b) without O. Y is yellow, Al is blue, and O is red. some description here pointed to dodecahedral tetrahedral and octahedral sites.

Single crystal boules of Ca:YAG, Ca:Sr:YAG[27], Ca:Nd:YAG, and Ca:Cr:YAG[28] grown by the Czchrolski growth method were oriented in the [111] direction. Compositions of the samples listed in Table I were determined using inductively coupled plasma spectroscopy[29]. Surfaces were polished to a finish of 1 μm. Samples were annealed in ambient atmosphere with a heating rate of 5 °C/min and a cooling rate estimated at 50 - 100 °C/sec. After annealing the surface composition was determined by Auger electron spectroscopy (AES) in UHV (~1 x $10^{-9}$ torr). Since sample charging represents an experimental difficulty the primary beam voltage was restricted to 3 kV, precluding detection of Auger electrons with energies above 1000 eV; consequently, detection of Y and Al depended on the distinction of peaks within the complex peak structure below 150 eV. Standards[30] were compared to determine the structure of the low energy peaks associated with Y and Al in YAG. No difference was detected in the peak shapes of Y and Al in YAG as opposed to those in binary oxides of Y and Al.
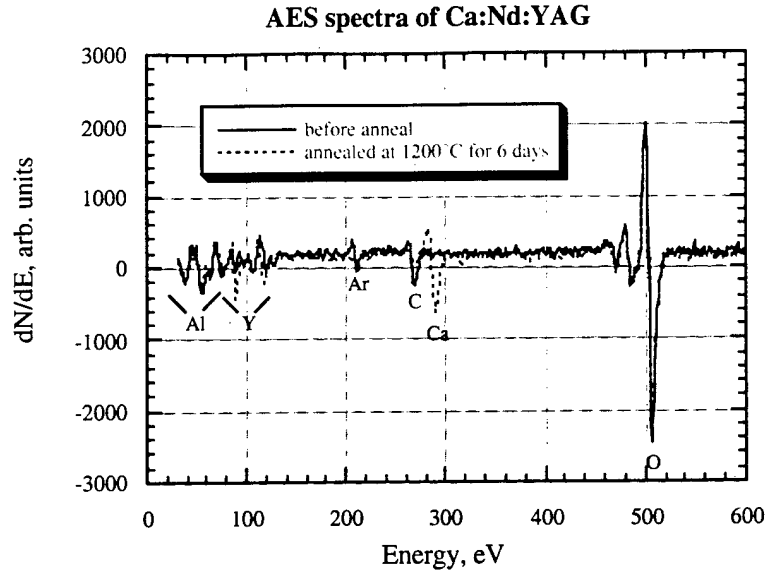
## AES spectra of Ca:Nd:YAG



**Figure 3:** AES spectra of YAG single crystal before and after annealing at 1000°C for 4 days showing the presence of the Ca peak at ~291 eV.

The samples listed in Table I allow comparison of the mobilities of isovalent and aliovalent substitution on the dodecahedral site (Nd and Ca respectively), isovalent substitution on the octahedral site (Cr), aliovalent substitution on the tetrahedral site (Si) and size differences from 9-33%. Regardless of the temperature or length of anneal, no surface enrichment of Nd or Cr was observed. The possible segregation of Si and Sr was more difficult to confirm due to the overlap of low energy peaks with those of Y and Al.[31] Therefore small amounts of Si or Sr enrichment are not ruled out by these measurements, but it can be stated that significant segregation did not occur. Calcium was found to segregate in all samples, regardless of bulk concentration. An example of surface enrichment is illustrated in the AES spectra of figure 3. The average enrichment of Ca to the surfaces of all four single crystals annealed at 1000 °C is shown in figure 4. It is apparent that the enrichment rate begins to diminish after 1 day and reaches saturation after 4 days at Ca/O rations ranging from 0.2 - 0.25. The saturation enrichment appeared to be greatest for the sample with the highest Ca concentration, as expected.
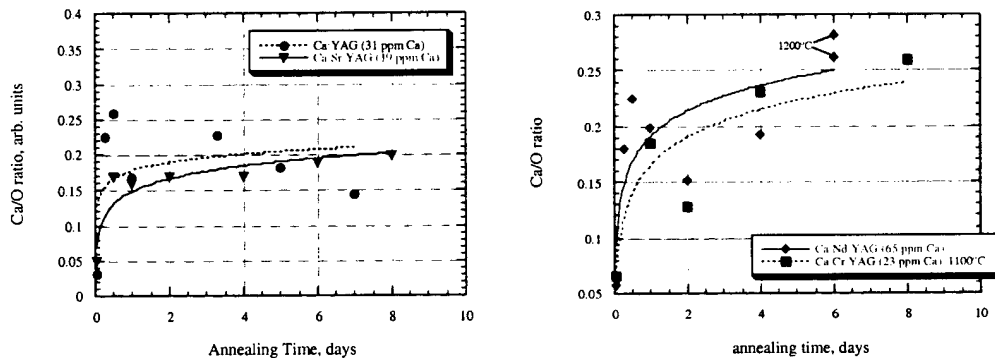


**Figure 4.** Calcium surface enrichment on YAG (111) in single doped and co-doped crystals

An Arrhenius analysis of the Ca:Nd:YAG annealed at temperatures ranging from 900 - 1300 °C for 4 days was done to determine the segregation enthalpy. The enthalpy was calculated according to the following equation:

$$\left(\frac{Ca}{O}\right)_{surface} = \left(\frac{Ca}{O}\right)_{bulk} \exp\left(\frac{-\Delta H_{seg}}{RT}\right) \qquad \text{from which} \qquad \Delta H_{seg} = -32.33 \ \frac{kJ}{mol}.$$

### Table I. Compositions of Single Crystal Samples

| Sample | Dopant | Conc. (ppm) | Site Occupancy | Size (Å) | %size difference with site |
|--------|--------|-------------|----------------|----------|----------------------------|
| Ca:YAG | $Ca^{2+}$ | 31 | doc(Y) | 1.12 | 9.91 |
| | $Nd^{3+}$ | <6 | doc (Y) | 1.11 | 8.83 |
| | $Si^{4+}$ | 100 | tet (Al) | 0.26 | -33.33 |
| | $Sr^{2+}$ | <6 | doc (Y) | 1.26 | 23.65 |
| Ca:Sr:YAG | $Ca^{2+}$ | 19 | doc (Y) | 1.12 | 9.91 |
| | $Nd^{3+}$ | <6 | doc (Y) | 1.11 | 8.83 |
| | $Si^{4+}$ | 66 | tet (Al) | 0.26 | -33.33 |
| | $Sr^{2+}$ | 67 | doc (Y) | 1.26 | 23.65 |
| Ca:Nd:YAG | $Ca^{2+}$ | 65 | doc (Y) | 1.12 | 9.91 |
| | $Nd^{3+}$ | 7280 | doc (Y) | 1.11 | 8.83 |
| | $Si^{4+}$ | 350 | tet (Al) | 0.26 | -33.33 |
| | $Sr^{2+}$ | <6 | doc (Y) | 1.26 | 23.65 |
| Ca:Cr:YAG | $Ca^{2+}$ | est. ~23 | doc (Y) | 1.12 | 9.91 |
| | $Cr^{3+}$ | est. 1234 | oct (Al) | 0.615 | 14.95 |
| | $Cr^{4+}$ | est. 23 | (tet - Al) | (0.41) | (5.13) |

We make here a first order approximation of the relative Ca coverage. The range in saturation Ca/O peak intensity ratio is 0.2 - 0.25 for all samples. Using published sensitivity factors of Ca and O, this corresponds to a range in atomic ratios of 0.23 - 0.26. Since Ca occupies dodecahedral sites we compare the atomic ratio of Ca/O to the ratio of Y/O sites at the (111) surface. If the (111) surface terminates at O atoms the Y:O ratio is 3:9. If instead it terminates at Y or Al atoms, the ratio is 3:9 or 6:19, respectively. Taking 0.33 as the number of dodecahedral sites at the surface, the maximum Ca coverage is 61-76% of a monolayer. If the enriched surface region occupies one unit cell, the ratio of Y/O sites is 0.25 as determined from the stoichiometry, and the all sites are substituted with Ca.

It is notable that Ca segregates in samples which have concentrations as low as 20 ppm while Nd, similar in terms of site substitution and size difference, does not exhibit detectable segregation even though the concentration of Nd is two orders of magnitude greater than that of Ca. The primary difference between the two cations is the valence, the former being aliovalent requiring associated O vacancies and the latter being isovalent requiring no compensating defects. Similarly, in spite of large bulk concentration (1230 ppm) and a 15% size difference from that of the host ion (Al in the octahedral site), Cr did not segregate. Again, Cr is an isovalent substituent. From these results, it appears that segregation in garnet is electrostatically driven and can be considered in the context of ionic space charge models, which is presented in reference x.[32]. Questions remain regarding Si and Sr which are aliovalent dopants. Neither appear to segregate. The absence of Si segregation could be the result of the bonding characteristics. Since Si is tetragonally coordinated it is expected to be tightly bound, an

effect evident in the relatively high solubility of Si in YAG. Based on the behavior of Ca, Sr is expected to segregate. It is likely, however, that the size difference imposes such a low initial solubility that subsequent enrichment is not detectable.

A mechanistic question as to whether the segregation is a precursor to the precipitation of a new phase on the surface does arise. In previous studies of segregation in $TiO_2$ and $SrTiO_3$[33,34], diffusion of both anions and cations was found to form nanometer sized clusters that were detected with scanning probe microscopies (SPM) but were not detected by other compositional or structural probes. Evidence that this does not occur in garnet is shown below which is an atomic force microscopy image of the surface after extended annealing. While annealing results in an interesting array of pits exposing local (100) surfaces, no precipitation is observed. (It is likely that the pits evolve at dislocations or surface polishing damage and the symmetry suggests that the (100) surface of garnet is low with respect to that of the (111)).
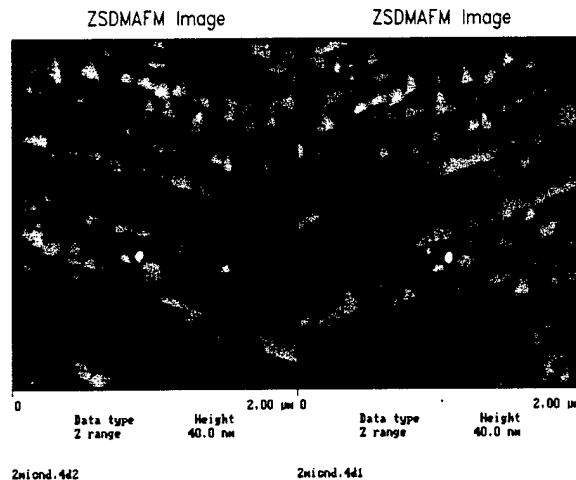


**Figure 5.** Atomic Force Microscopy Images of YAG single crystal oriented in (111) direction after annealing for 4 days at 1100 C.

The implications of these results are that isovalent dopants, used for example to alter optical properties, will be stable with respect to redistribution on heating. Divalent dopants will segregate regardless of size difference or concentration up to temperatures of 1200 C. Therefore any properties dependent on the homogeneous distribution of divalent cations may vary with heating. It may be possible to exploit the latter in the design of fiber reinforced composite materials.[35]

**Calculations of Electrostatically Driven Diffusion in YAG**

The details of the solutions of the ionic space charge model for YAG are shown in the appendix. The figure below compares the vacancy concentrations and the charge densities below the surface of pure YAG for the case where the oxygen vacancy formation energy is higher and lower than those of the cations. The difference illustrates the important role of defect formation energies and the necessity of linking to calculations that can provide them.
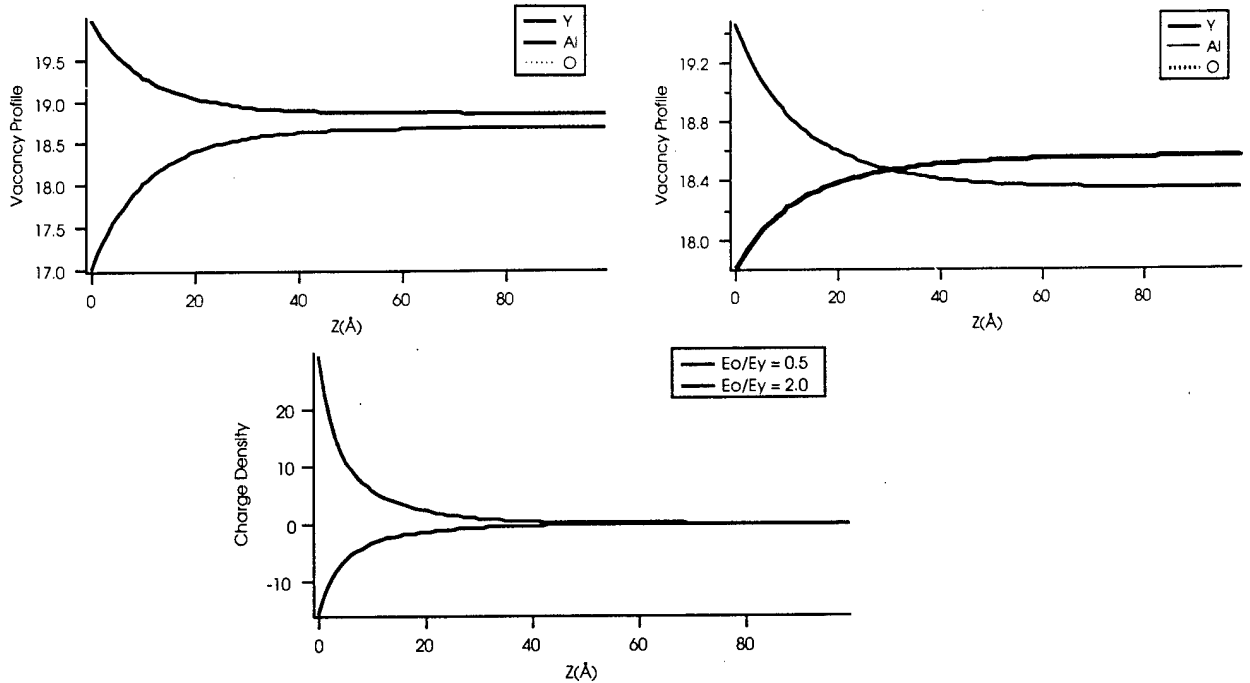
**Figure 6.** The vacancy concentration profiles predicted when the formation energy for oxygen are larger and smaller than those of yttrium and aluminum are shown above and the associated charge density profiles are compared below.

## Effect of Excess Ca in Properties of Polycrystalline YAG

Excess Ca was found to have a dramatic effect of fracture behavior in polycrystalline YAG. The SEM micrographs below show that the relative amounts of intergranular and transgranular fracture changes with Ca content. Pure YAG differs because the grain size is much larger. Ca at the boundaries inhibited grain growth so that the fracture behavior of the samples doped with 0.1% and 1% can be compared. The difference in the amount of transgranular implies that the grain boundary strengths differ. this is quantified be calculating the fracture toughness from four point indentation bend tests. The table below shows that Ca appeared to increase the toughness. These results are based on a series of 5 bend bars for each measurement; further measurements are required to confirm this trend and relate it directly to composition at the grain boundary.
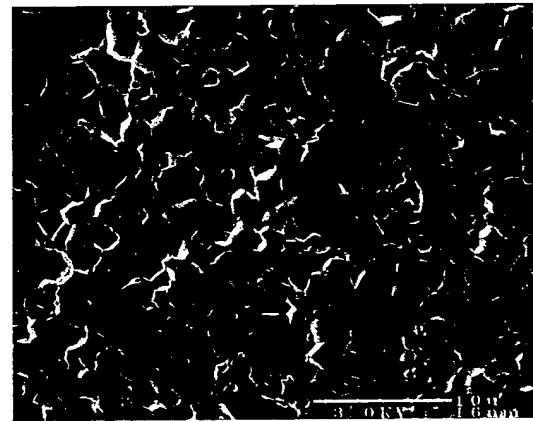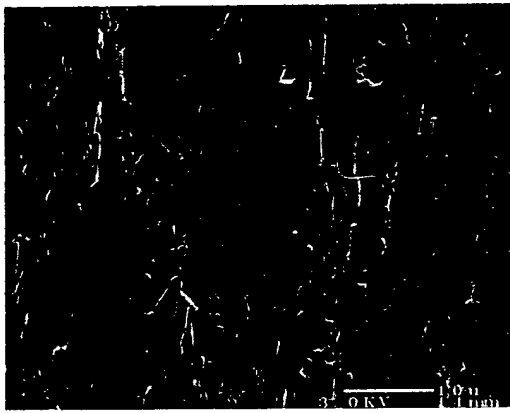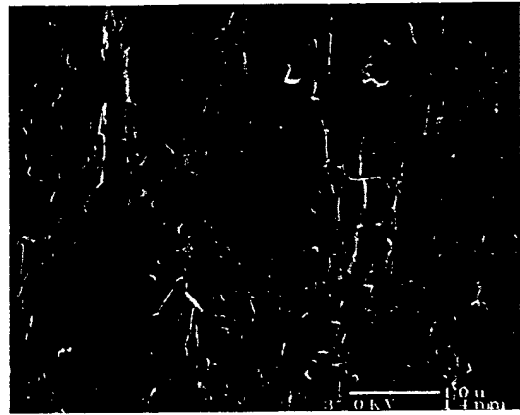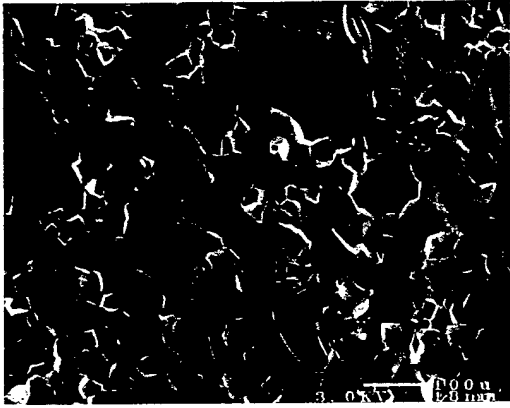
**Productivity Summary**

In addition to the PI, the following personnel contributed to the AFOSR project.

| | | |
|---|---|---|
| Rollin Lakis | staff *TEM of YAG-Alumina Interfaces* (July 1995) | |
| Filip Kral | post doc *TEM of YAG grain boundaries and Interfaces* (Oct 1997) | |

Kelly Brown      PhD in Materials Science (1998)
Effect of Segregation on Properties of Complex Oxides: YAG/Alumina

Jack Smith      PhD in Materials Science expected 2000 (50% one year)
Sintering YAG-alumina composites

Thomas Yeh      MS in Materials Science 1995
Effect of Sulfur Segregation to Interfaces on Properties in Composites

<u>Publication have or will emanate from this project</u>
Segregation in YAG I: Experimental Study of Single Crystal Surfaces
K. Brown, D. Bonnell *Journal of the American Ceramic Society.* **82** (1999) 2423-2430.

Segregation in YAG II: Theoretical Predictions Based on Ionic Space Charge Models
K. Brown, D. Bonnell *Journal of the American Ceramic Society.* **82** (1999) 2431-2441

Scanning Tunneling Microscopy and Spectroscopy of Oxide Surfaces
D. A. Bonnell *Progress in Surface Science* **57** (1998) 187-252.

Local Structure and Properties of Oxide Surfaces: Scanning Probe Analyses of Ceramics
D. A. Bonnell *J. Am. Ceramic Soc.* "feature article" **81** (1998) 3049-70.

Segregation of Ca to $Y_3Al_5O_{12}$ (111) Surfaces
K. Brown, D. A. Bonnell *Surf. Sci.* **414** (1998) 341-352.

Atomic Force Microscopy of Mechanically Rubbed and Optically Buffed Films
K. R. Brown, D. A. Bonnell, S-T. Sun *Liquid Crystal* **25** (1998) 597-601.

Evidence for S Segregation to Intact Ni-Alumina Interfaces
J. Kiely, T. Yeh, D. A. Bonnell, *Surface Science* **393** (1997) L126-30.

<u>Presentations</u>
(Aspects of this work were discussed in presentations at the following meetings)

Wright Laboratory, Materials Directorate (July (1997)
Swiss Federal Technical University, Physics Department (July 1997)
Oxford University, Materials Science Department (Feb. 1997)
Queens University, Materials Theory Department (Feb. 1997)
Swiss Federal Technical University, Materials Science Department (Oct. 1996)
Wright Laboratory, Materials Directorate (Oct 1996)

Fudan University, Physics Department (Sept. 1996)
<u>Annual Meeting -American Ceramic Society</u> "Electronic Structure of Ceramics" (April 1996)
<u>Annual Meeting -American Ceramic Society</u> "Electronic Probes of Atomic Structure" (April 1996)
Rutger University Ceramics Department (March 1996)
Max Planck Institute for Materials Science Stuttgart, Germany (July 1996)
Materials Research Society, Boston, MA (Dec. 1996)
AFOSR Contractors Meeting, Hueston Woods OH (1996)
Gordon Conference, NH (1995)
AFOSR Contractors Meeting, Hueston Woods OH (1995)

The following publications resulted from the previous AFOSR contract.

Nanometer Scale Structures Resulting From Oxidation of Graphite
M. Nowakowski, D. Bonnell
<u>Proceedings of the Materials Research Society Meeting</u>       (1994).

Synthesis, Processing and Phase Evolution of TiN/TiB2 Nanocomposties from Polymeric Precursors
M. Nowakowski, V. Szabo, K. Su, M. Ruhle, L. Sneddon, D. Bonnell
<u>Proceedings of the Materials Research Society Meeting</u>  **286** (1993) 425-430.

Morphological Development in TiN/TiB2 using Energy Filtered TEM
V. Szabo, M. Nowakowski, K. Su, M. Ruhle, L. Sneddon, D. Bonnell
<u>Proceedings of the Materials Research Society Meeting</u>  **286** (1993).

Initial Stages of Silicate Growth on Graphite via TEOS Decomposition
D. Bonnell, D. Jiron, T. Flinn  *J. Materials Research*  **10** (1998)

Bonding and Initial Stages of Deposition of SiOx on Carbon
M. Hoveland, J. Danner, J. Vohs, D. Bonnell **9** *J. Mat. Res.* (1994).

Effect of Sputtering and Plasma Etching on the Reactivity of Carbon
M. Nowakowski, D. A. Bonnell  *J. Am. Ceram. Soc.* **76** (1993) 279-283.

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## III. APPENDICES

Segregation in YAG I: Experimental Study of Single Crystal Surfaces
K. Brown, D. Bonnell *Journal of the American Ceramic Society.* **82** (1999) 2423-2430.

Segregation in YAG II: Theoretical Predictions Based on Ionic Space Charge Models
K. Brown, D. Bonnell *Journal of the American Ceramic Society.* **82** (1999) 2431-2441

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