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**OPTICAL STUDIES OF DYNAMICAL PROCESSES
IN DISORDERED MATERIALS**

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PROGRESS REPORT

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PART I. Summary of Activities and Continuing Programs:

A. Introduction

In this section, we present a brief outline of the research we have accomplished during the current year and a discussion of the experiments which are underway at the moment. We also discuss, albeit briefly, our plans for the third period of this Grant.

Our research continues to focus on the study of the structure and the dynamic behavior of insulating solids which can be activated optically. We have been particularly interested in the physical processes which produce relaxation and energy transfer in the optical excited states. Our studies have been based principally on optical laser spectroscopic techniques which reveal a more detailed view of the materials of interest and which will ultimately lead to the development of more efficient optoelectronic materials.

The report contains an abbreviated description of the work we have concluded during the present grant period. In addition, we describe the research we are presently engaged in and discuss various initiatives we propose to undertake during the continuation of the Grant. We note that the following narrative is brief and seeks to convey only the thrust rather than the detailed substance of our interests and of our efforts. A compendium of publications appearing under the sponsorship of this Grant is given in Part II and gives a detailed view of our activities.

B. Progress Achieved During the Current Grant Period

i). **Transparent Ceramics:** We have concluded a comprehensive study of the properties of Cr^{3+} activated mullite ceramics [1] during this period and a number of publications and a doctoral thesis have resulted from this work [2,3]. We had reported earlier on the identification of two distinct Cr^{3+} ion sites in the ceramic. One of the sites is connected with the ordered phase and results in emission which is characteristic of high crystalline field Cr sites, i.e., originating from the ${}^2\text{E}$ R like states; these ions are surrounded by a minority of chromiums in the disordered mullite phase which lead to a spectra which is

broad and arises from the 4T_1 instead of the 2E states. One of the complications in interpreting the optical spectra of mullites is that the two types of ions are tightly coupled to each other through a radiative transfer mechanism and the luminescence signals are difficult to deconvolute using normal spectroscopic techniques. We had noted in our previous Progress Report that a new experimental technique, termed Saturation Resolved Fluorescence Spectroscopy (SRF) has been developed by us to allow decoupling of complex coupled spectra; a complete analysis of this technique has been completed during this period [4] and its usefulness has been fully demonstrated by decoupling the high and low field Cr spectra in mullites [2].

From these results, we have been able to enumerate the ratio of Cr ions in the two phases of the ceramic, with the ions in the ordered phase predominating. We believe that the low field or disordered sites surround the ordered phase and constitute a transitional region between the two principal constituents of the ceramic. We showed more recently [5] that the disordered sites could be reduced but not eliminated by proper heat treatment of the samples. The reduction of the latter resulted in a concomitant increase in the net quantum efficiency of the transparent ceramics and this, of course, points the way to the engineering and the design of more efficient materials.

ii). Localization of a single ion in a glass fiber: There continues to be considerable interest in the properties of a single atomic or ionic entity. The majority of the work being conducted centers on the properties of isolated atoms confined to a laser or magnetic trap. Our work expands on these ideas and will likely produce results which are of wider applicability. We, as others [6,7,8], seek to conduct single ion spectroscopy as a probe of the local structure of disordered solids. For this purpose we have developed what we term Dilution Narrowed Spectroscopy (DNS) on very lightly rare earth doped glass fibers. In these experiments, we exploit not only the diluteness of the dopant and the small fiber volume, but also the large frequency spread of the optical transitions induced by the

inhomogeneities of the amorphous materials of interest to this grant. We have reported in a preliminary presentation [9] the observation of the phenomenon of DFNS in a Nd^{3+} doped quartz fiber; we had estimated that we had localized about ten individual Nd ions at specific laser frequencies within our field of view. We also had noted at that time that since our techniques essentially randomly samples the inhomogeneous glass distribution of sites, small variations in the position of the sample and in the laser excitation area lead to totally different DNS spectra. It is thus that during the present grant period we have concentrated our efforts in stabilizing the experimental setup so as to prevent all external vibrations which have a bearing on the sample and the laser positions. This has proved to be a non-negligible task as stabilities of microscopic dimensions are required. We feel that we have developed a system which will fit these requirements and are now poised to continue our experiments.

Through an external collaboration with the Institute of Radioengineering of the USSR Academy of Sciences, we have in the meantime been able to obtain single mode glass fibers with exceptionally low rare earth doping levels. These fibers required special runs and have been doped with ppb levels of trivalent Nd or Eu. We are convinced that this reduction in doping concentration from the fibers with which we conducted our demonstration experiments will lead to the isolation of a single ion spatially and in the frequency domain.

iii). Laser heated pedestal growth (LHPG) synthesis of mixed crystalline fibers: With assistance from various sources, we have successfully established a LHPG fiber pulling facility in the past year and have been able to grow and to synthesize a great variety of unique crystalline materials which have been difficult to grow using conventional means. This is because the LHPG method allows, for example, the growth of materials with very high melting points and the synthesis of crystalline mixtures which are incongruent. The latter is of specific importance to the mission of this grant as it has provided us with a

variety of samples which are compositionally disordered and thus possess large spectral inhomogeneities [10].

The materials Y_2O_3 and Sc_2O_3 illustrates some of the advantages cited above. Both of these compounds have melting points near 2500C and have only been grown in the few crystal facilities capable of scull melting. We have been able to pull single crystal fibers of both these compounds and the mixed phase $Y_{2-x}Sc_xO_3$ activated with the majority of the trivalent rare earths. Through spectroscopic measurements, we have been able to show that the fibers are of very good quality from the strain and the contamination points of view; we have also been able to show that by changing the Y to Sc ratios, we can control the width and the position of optical transitions of the dopant ions. This fact makes these materials very attractive for electro-optical applications where laser diodes are used as a pumping source; in addition, we have demonstrated that efficient frequency upconversion is observed in some of the singly as well as codoped materials [11] and that they are very promising candidates for solid state lasers.

More recently, we have been able to control the valence of the dopant ions through adjustment of the atmospheric growth conditions in the pulling chamber [12], or by providing proper charge compensation through codoping, thus also introducing yet another type of disorder. In this period, we have successfully controlled the Cr^{4+} content of fosterite, an NIR tunable laser material [13], and have been able to dope YAG with substantial amounts of Cr^{4+} when codoped with Ca^{2+} , a unique system. The spectroscopic evaluation of the latter is almost complete [13] and we believe it will prove to be a material superior to those currently being used in tunable laser devices.

C. Continuing Programs

We propose to continue the activities described in (B) to a satisfactory conclusion; in addition, during this period we wish to place emphasis or to initiate work in several supplementary areas:

i). Stimulation of optical energy transfer: We have noted in a previous progress report that the SRF illustrates that dynamical processes in solids can be driven nonlinearly under the proper excitation conditions, meaning that optical energy transfer can be stimulated. Stimulation can be accomplished in a number of ways; we have obtained preliminary results by tuning a FIR laser to the energy mismatch between donor and acceptor ions and observing the changes in the decay patterns of the donor excited state. In these cases, it is known that phonon mediation plays a role in the transfer process; the FIR radiation can increase transfer rates by creating phonons or by stimulating cooperative transitions. It is too early to determine the source of the change we have observed; i.e., whether they entail true stimulation or whether they are merely thermally induced effects. We have conducted our experiments in doubly doped crystalline systems where the energy mismatch is well defined; we propose to extend these experiments to amorphous and compositionally disordered systems during the third grant period.

ii) We also wish to concentrate our efforts in isolating a single optically active center in glass in order to bring these experiments to a successful conclusion. There is currently considerable interest in obtaining the spectra of individual isolated species. A whole session, for example, of a SPIE meeting [14] is being devoted to this topic; we will be presenting an invited contribution at that time. In conjunction with recent advances in the interpretation of site selective glass spectra by Kushida and his coworkers, the single ion studies will be extremely important in allowing the mapping of random structures on an atomic scale. To our knowledge, there is no other experimental method which permits such detailed analysis of disordered structures.

iii). Finally, our ability to synthesize compositionally disordered materials have opened a whole host of experimental possibilities in our efforts to understand the dynamics of the optically excited states of activated systems. We intend to continue studies in this area

with emphasis on the additional advantages one gains in employing the fiber configuration of our samples and the large interaction lengths that ensue from this geometry.

D. Summary

We have presented a brief narrative of the progress we have attained during the past two grant periods and the work which is currently being carried out. In addition, to concluding various projects in progress, we wish to concentrate our efforts in three areas during the last period of this grant. We will attempt to stimulate transfer processes in glasses; we will pursue single ion spectroscopy with an aim towards mapping random structures; and we will exploit our materials synthesis facilities towards better understanding of dynamical processes with a view towards their applicability to optoelectronic problems.

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PART II. Technical Publications Appearing Under Present Sponsorship:

1. H. Liu, R. Knutson and W.M. Yen, Saturation Resolved Fluorescence Spectroscopy of Cr^{3+} : Mullite Glass Ceramic, Phys. Rev. B41, 8-14 (1990); also J. Lumin. 45, 17 (1990).
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5. W. Jia, L. Lu, B.M. Tissue and W.M. Yen: Valence and Site Occupation of Chromium Ions in Single-Crystal Forsterite Fibers, J. Crystal Growth (in press); also Phys. Rev., to be published 1991.
6. B.M. Tissue, N.J. Cockroft, L. Lu, D.C. Nguyen and W.M. Yen: Comparison of the Spectra and Dynamics of Er^{3+} : $\text{Y}_{2-x}\text{Sc}_x\text{O}_3$, J. Lumin. (in press).
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Proceedings:

1. Proceedings of the Dynamical Processes in Excited States of Solids, VIIth
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Vol. 45, (1990); R.S. Meltzer, J.E. Rives and W.M. Yen, editors.

*We have also participated, as invited speakers or as contributors, at the APS–March, ECS–Annual, ICL'90 and SPIE (Jan. 1991).

PART III: Present Support and Facilities

The PI of this proposal also holds a grant from the National Science Foundation entitled, "Spectroscopic Studies of Ordered Materials," which is funded at the \$108K level this current fiscal. He is a co-investigator in a DARPA grant for the development of IR Solid State Laser Materials funded at the \$160K level. PI involvement is rated at 10% and 5% time, respectively, in the above grants and it has been established that there is no overlap or conflict between the NSF and DARPA projects and the work to be continued here.

We possess an up-to-date laboratory with complete capabilities to conduct all phases of the work proposed here. We are asking for a modest amount of capital equipment to refurbish a laser tube and to obtain additional NIR laser capabilities through diode lasers.

All additional facilities for mechanical, electronic and computing support are available to us at the University. The administration of the University of Georgia has also traditionally encouraged collaborations and interactions with all those who share our interest.

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