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STUDY OF NON-OXIDE MATERIALS WITH DEFECT STRUCTURES

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Task No. .... Proj NR 015 - 501; ARPA order

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Contractor .... Bausch & Lomb Inc[redacted]
Rochester, [redacted] N.Y.

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Project Scientist .... [redacted] D. A. Buckner

LOcust, 2-3000
Ext. 493

REPORT FOR [redacted] PERIOD ENDING 1 APR [redacted] 64

[redacted] by: D. A. Buckner and N. J. Kreidl

I. **Background and Objectives**

The purpose of this study is the exploration of ~~the~~ properties of non-oxide materials designed to have controllable gross defects. The exploration of ~~the~~ properties is aimed at the correlation of the amount and nature of ~~the~~ defects with the properties; and, next, at the potential development of properties based on the understanding of controllable defects.

Examples of a desirable class of materials that might be developed are polycrystalline infrared transmitting or special dielectric materials. Polycrystalline compacts prepared from selected raw materials by sintering under pressure are to be studied for their mechanical, optical and electrical properties.

A prototype illustrating the idea of controlled gross defects would be a system containing the fluoride of a divalent cation and the fluoride of a trivalent cation, the latter being held completely in solid solution by the host structure of the former. The result might be a vacancy of cation sites normally filled by the divalent cation, since the presence of the higher valent cation would cause a local surplus of positive atomic charge. The study is not restricted to any particular engineering property or compositional field. The study of single crystals may be included in certain cases.

II. **Assignment of Responsibility**

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III. Project Activity

The study program has now entirely entered its second phase: the preparation of fairly large amounts of the defect compositions suggested by the earlier survey work. The purpose of this step is to secure enough well defined starting material to proceed with measurements of physical properties. Preparation of large specimens is contemplated as part of the physical property determination program. The following systems have been concentrated upon:

A. CaF_2 - $NaLaF_4$

B. CaF_2 - YF_3

C. CaF_2 - $NaYF_4$

D. MgF_2 - NiF_2

E. MgF_2 - $KNiF_3$

F. NiF_2 - $KMgF_3$

Selected compositions were reacted in various atmospheres e.g. N_2, NH_4F and vacuum. The reaction products were studied by microscopy and x-ray diffraction methods to determine the degree of solid state reaction. Evaluations of results point the way to experimental changes in methods of mixing ingredients, and in firing conditions. The results have shown steady improvement. Two main problems are chronic. The first, oxydation of the products yields a very non-uniform two-phase system. The main cause of the oxydation is thought to be thermal hydrolysis (promoted by the presence of water, either free in the general system or bound to one or the other fluoride end members). Steps to eliminate both water and oxygen from the systems have been taken. The second major problem is that of incomplete mixed-crystal reaction products. The non-homogeneity could be caused by several factors: poor mixing of ingredients, too short time of reaction, improper firing conditions, or unmixing during cooling. The first three reflect inadequate preparation practices which are not expected to be difficult to correct. The last seems to be the most likely, however, and is the hardest to prove and to combat.

Hot pressing of some compositions in the CaF_2 - YF_3 system has not been encouraging. It seems conclusive that the solid state reaction cannot be effected during the hot-pressing schedule by merely pressing the mixed ingredients. Hot-pressing the reacted end members has probably been discouraging because of the aforementioned problems in preparing homogeneous starting materials.

Cold pressing of starting materials to pressures of the order of 30-40 kilobars is generally sufficient to produce transparent, essentially 100% dense, specimen wafers. These are useful in studying material character, but probably are of limited value in determining physical properties. An increased activity using this tool is contemplated especially to examine microstructure of some of the materials.

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