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**OAK RIDGE
NATIONAL
LABORATORY**

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**CRADA Final Report
for
CRADA Number ORNL93-0227**

**FORMATION OF NOVEL OPTICAL MATERIALS BY ION
IMPLANTATION**

**Oak Ridge National Laboratory
Corning Incorporated**

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**MANAGED BY
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CRADA FINAL REPORT

CRADA NO.: ORNL93-0227

COMPANY: CORNING INCORPORATED

TITLE: Formation of Novel Optical Materials by Ion Implantation

1. **Abstract:** Ion implantation into glasses shows considerable promise as a technique for producing novel materials having unique optical properties. There is also significant commercial interest in the marketing of optical waveguides, high-performance polarizing glasses, and birefringent glasses. In this work, special glass compositions, including both two-phase and anisotropic materials, were prepared by bulk processing techniques and then implanted with Ag, Au, and Cu ions at different temperatures, energies, and doses. The composite materials produced showed strong resonant absorption at the surface plasmon resonance frequency. The plasmon frequency was consistent with the formation of spherical colloids of the implanted metals having diameters on the order of 10 nm. No anisotropic behavior of the implanted materials was observed. Possible applications for these materials, had such anisotropy been developed, would have included optical isolators, Faraday rotators, optical waveguides, and switching devices for use in optical communication and computing.
2. **Objective:** The primary objective of this work was to determine if useful light polarizing glasses could be produced by ion implantation of colloidal metal particles into elongated, phase-separated glasses. The hope was that the implanted colloidal metals would be concentrated in one glassy phase, or perhaps decorate the glass-glass interface in a manner to lead to enhanced optical anisotropy.
3. **Meeting Objectives:** The objectives of this CRADA were met, even though the final results were negative. A number of different glasses were prepared by Corning Inc. and subsequently implanted at ORNL with a variety of ions using different temperatures, energies, and doses. The optical properties of these materials were then measured both before and after subsequent thermal annealing, and their potential for use as birefringent and polarizing materials was determined.
4. **DOE Mission:** This CRADA supported the DOE mission in several ways. First it significantly strengthened work already in progress at ORNL on the optical properties of ion implanted glasses. Second, it allowed ORNL to share the expertise of the industrial partner in bulk-glass processing, optical spectrometry, and commercially viable applications. Third, it provided materials for study in the form of specialty glasses, some prepared by proprietary techniques, that would not otherwise be available. Finally, this work strongly supported long-standing collaborative research projects with Vanderbilt University, Belmont College, and Fisk University on the modification of the optical and magnetic properties of glasses by ion implantation.
5. **Technical Discussion:** Two basic types of glasses were prepared by the industrial partner, Corning Inc., for implantation and optical testing. Glasses of the first type were alkali alumino-borosilicates containing small volume fractions ($<0.1\%$) of aligned, elongated silver halide or copper halide particles. These glasses are typical of the type used in Corning's Polarcor TM brand polarizing glasses. The second type of glass was a phase-separated alkali-alkaline earth borosilicate opal glass. Both types of glasses contained elongated second-phase particles and microstructures. Numerous examples of each of these glasses were then implanted

with metallic ions at different energies, temperatures, and doses in the Surface Modification and Characterization facility at ORNL. The ions used were Ag, Au, and Cu and doses were from 1×10^{16} to 2×10^{17} ions/cm². Implantation temperatures were either 0° or 400°C and ion energies ranged from 160 keV to 1.1 MeV. For all implanted samples, Rutherford ion backscattering using 2.3 MeV ⁴He⁺⁺ was used to measure the retained amounts and depth distributions of the implanted ions. Optical transmittance and reflectance measurements were made on the implanted samples in the visible and near infrared. In some cases, the transmittance measurements were run using polarized light. Transmission electron microscopy and atomic force microscopy were performed on selected samples. Some of the glasses were further heat treated in either an oxidizing atmosphere or hydrogen gas to enhance the precipitation of the metal colloids.

Transmittance and reflectance measurements indicated strong absorption bands at wavelengths characteristic of the respective colloidal metal electron plasma resonances. No light polarization was observed, other than the slight degree of polarization already present in the unimplanted glasses. The heat treatments changed the absorption somewhat, but no enhanced light polarizing effects resulted. Transmission electron microscopy of the type-two phase-separated glass showed that the implanted colloidal particles were concentrated within the matrix glass phase. Relatively few of the second-phase glassy particles extended into the implanted surface layer, and where they did, there was no evidence of the metal colloids forming preferentially within them or at their surfaces. The surface plasmon resonance frequency was consistent with the formation of spherical metallic colloids of the implanted element having diameters on the order of 10 nm.

6. **Inventions:** No inventions were made or reported.
7. **Assessment of Commercial Possibilities:** We believed going into this CRADA that to achieve the desired polarization effects would be a "long shot." It appears that we were correct. However, the potential commercial value of the sought after effects more than justified the effort put forth in conducting this CRADA.
8. **Plans for Future Collaboration:** There are obviously further experiments which could be performed with glasses of different elongated microstructures, but such glasses are not now readily available to us.
9. **Conclusions:** In the silver halide and copper halide containing glasses, we believe the very low-volume fraction and relatively large size (approx. 1 micron length) of the second-phase particles results in too few of these particles being present in the ion-implanted area to be effective in developing anisotropy. The second type of glass suffers from similar problems. While in this case the volume fraction of the elongated second-phase glassy "particles" is considerably greater, their size is much larger compared with the depth of the implantation. If in future investigations two-phase glasses were to be prepared with much smaller second-phase dimensions, we anticipate that it would be significantly more difficult to elongate the second phase, thereby partially negating the anticipated advantage of the ion-implantation approach.

Colloidal metal particles were successively precipitated in borosilicate glasses by ion implantation, thus extending the range of glass compositions over which this phenomenon has been demonstrated. Unfortunately, the goal of finding a new approach to making polarizing glasses was not realized.