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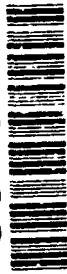
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13. ABSTRACT (Maximum 200 words) A new process has been developed for the synthesis of multi-component glasses. In this, a liquid aerosol of organo-metallic glass precursors is convectively transported into an oxygen rich region of high temperature. The liquid aerosol pyrolyzes, or combusts to yield solid, multi-component ultra-small oxide particles. These particles are then thermophoretically deposited on a surface and subsequently sintered to form a vitreous, pore-free layer. (Morse, 1990, 1991) The advantage of this process, is that elements whose precursors have a low vapor pressure may be dissolved in the organo-metallic precursor that acts as a natural solvent (typically, TEOS, tetra-ethyl ortho-siloxane). This process is being applied to the fabrication of large GRIN lenses, and to optical fibers with glasses that exhibit larger nonlinearities. It is also being used to synthesize glasses that exhibit larger photorefractive effects.					
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With Applications to Gradient Index Lenses, Photorefractive Effects

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1. Foreword

We have developed a new process for the synthesis of multi-component glasses. In this, a liquid aerosol of organo-metallic glass precursors is convectively transported into an oxygen rich region of high temperature. The liquid aerosol pyrolyzes, or combusts to yield solid, multi-component ultra-small oxide particles. These particles are then thermophoretically deposited on a surface and subsequently sintered to form a vitreous, pore-free layer. (Morse, 1990, 1991) The advantage of this process, is that elements whose precursors have a low vapor pressure may be dissolved in the organo-metallic precursor that acts as a natural solvent (typically, TEOS, tetra-ethyl ortho-siloxane). This process is being applied to the fabrication of large GRIN lenses, and to optical fibers with glasses that exhibit larger nonlinearities. We are also using this process to synthesize glasses that exhibit larger photorefractive effects.

2. Body of Report

A. Statement of the Problem Studied

This process described above is, in essence, a new method for the synthesis of both ceramic and amorphous oxides. Organo-metallic liquid solvents, that may even have solid organo-metallic compounds dissolved in them, are nebulized. The liquid organo-metallic aerosol is convectively transported into a region of high temperature and excess oxygen. These aerosol particles decompose at temperatures of the order of 500 centigrade yielding gaseous precursors for the high temperature reactions that occur. Typical organo-metallic precursors are TEOS (tetra-ethyl ortho-siloxane), aluminum-sec butoxide, rare earth alcoxides or acetyl-acetonates, and butoxides of a host of elements, among them tantalum, niobium, gallium, etc. Essentially the whole palette of the periodic table is available for the formation of single and multi-component oxides using this process of synthesis. (Morse, 1991)

The chemical reactions that occur are analogous to those found in typical sol-gel reactions in which organo-metallics react to form cross-bridging oxygens with the metal ions until a complete network is developed. The reaction products would be a hydrated silica, typically, with alcohols and water as by products. In a multi-component sol-gel system, one of the problems that occur is that the different sol-gel precursors have differing chemical reaction times, and it is often necessary to resort to various schemes to retard or speed up a particular reaction rate. This is a consequence of the customary sol-gel process occurring at or near room temperature. Indeed, the reaction times can be of the order of several hours, to several days, or even several weeks. In a process in which the sol-gel precursors are atomized and transported into a region of high temperature, these reactions occur on a millisecond time scale. For this reason, differences in reaction rates of the precursor materials seem to play no role in the formation of the final material, independent as to whether it is a ceramic or an amorphous oxide. Similar reactions from the gas phase have been studied previously. (Ulrich, 1982, 1984, Mazdiazny, 1982)

We have demonstrated that the above process may be used in the formation of optical fiber lasers in which the core has been doped with various rare earth elements. The precursor solutions have been TEOS (liquid), aluminum-sec-butoxide (liquid), and the solid alcoxides of the rare earth elements dissolved in the liquid solvents. This has been done using MCVD (Modified Chemical Vapor Deposition) (MacChesney, et al., 1974, Nagel, et al, 1982) which is a process in which the inside of a high purity silica substrate tube is doped with layers of glass of differing composition to structure the radial profile of the index of refraction. This can insure that the optical fiber drawn from the finished preform will have the proper light-guiding characteristics. In this process, we have used a 1.5 MHz transducer that is capable of transporting 1.5 gm-liquid/min. This limitation has led us to consider higher rate processes that will be described in detail below.

Establishing the large OVD (Outside Vapor Deposition) (Morrow, et al., 1985) laboratory donated by AT&T, we have modified a commercial nebulizer to produce an aerosol of organo-metallic liquids that pyrolyzes and deposits oxide particles on a rotating mandrell. This has been done for amorphous oxides, and for nano-phase ceramic particles as well. The chemical reactions that occur are completely analogous to sol-gel reactions that occur near or at room temperature. These reactions can be quite slow; however, at elevated temperatures of the order of several thousand degrees centigrade, the reactions occur on a millisecond time scale. Consequently, differing reaction rates among the various precursors play no role in the formation of the multi-component oxides.

The establishment of this OVD laboratory has been possible because of an equipment donation to the Laboratory for Lightwave Technology by AT&T Bell Laboratory. We have just brought the equipment on-line. This laboratory will play a major role in the use of the OVD process to synthesize large GRIN lenses from lower melting point glasses, and our experiments have demonstrated that "soot" for such lenses can be made with organo-metallic precursors. Our consolidation furnace is still being set up, so we have not yet consolidated any of the small preforms formed using our aerosol process. It is anticipated that this will occur over the next few months.

The other aspect of our research supported by the Army Research Office, was concerned with photo-refractive effects in amorphous materials. In particular, we have continued to examine the role that UV laser radiation can play in the establishment of photo-refractive gratings in fibers synthesized in our laboratory. In particular, we have examined further the detailed spectroscopy of a Europium fiber that has exhibited a remarkable rate of the initiation of photo-refractivity. In an analysis of this glass, we have published an article on the spectroscopy of a Eu^{2+} fiber made with the aerosol deposition process. This is included.

There is great interest in the enhancement of the photo-refractive effect for the role that internally written fiber gratings may play in passive devices such as mirrors, filter gratings, wavelength division multiplexers, etc. The fundamental mechanism for the creation of these gratings is still a subject of active discussion; however, it has been speculated that the uv light may be responsible for the breaking of oxygen bonds in the material and that this results in a densification of the structure. This may well be a plausible mechanism for the photo-refractivity, which, for a typical grating, is of the order of 10^{-3} to 10^{-4} . The index of refraction is, to first order, proportional to density. The mechanism is straight-forward. As the molecules move closer together, their optical density also increases. Local strain or compression can have an influence on the index of refraction, and this has been demonstrated by some experiments in which a depressed cladding fiber with a pure silica core was pulled under different drawing conditions. As the fiber was pulled, the central core of silica was the first to become solid while the boron down-doped outer cladding was still less viscous. It solidified with the inner core still in tension, and when the fiber reached a homogeneous lower temperature, the tension in the silica core was "frozen" into the fiber. For this reason, fibers with a higher melting point silica core will exhibit a lower refractive index in the core if they are pulled at a higher tension, and the fiber design is such that the tension remains "frozen" in a lower temperatures. We have demonstrated this effect in several optical fibers synthesized in our

laboratory, and we believe that this can play a role in the enhancement of photo-refractive gratings.

B. Summary of the Most Important Results

1. The establishment of our OVD laboratory for the fabrication of GRIN lenses as well as "soft" glass fiber preforms using organo-metallic precursors has been one of the main thrusts of our effort. This laboratory, we believe, is the only such facility at a university in the U.S. The equipment for this laboratory was donated by AT&T Bell Laboratory, Engineering Research Center, Princeton, NJ.

2. Using the above facility, we have performed our first experiments on the use of OVD in forming boules of multi-component glass oxides. Our first boule consisted of a glass with the following composition in the precursors: 13 wt% Na₂O, 12 wt % Al₂O₃, 12 wt % CAO, 13 wt % Ba₂O₃, and 50 wt % SiO₂.

in the precursors. For the first time we have used nitrates rather than organo-metallics as precursors and we are presently awaiting an analysis of the synthesized glass. We believe that this method of synthesis may also have important implications for planar waveguides.

3. We have spectroscopically analyzed samples from our Eu²⁺ preforms and fibers in an attempt to gain a further understanding of the photo-refractivity of this glass. This work has appeared in the Journal of Non-Crystalline Solids.

4. Finally, with regard to the development of techniques that may change the index of refraction of materials, we have examined the effects of draw tension on the refractive index of optical fibers.

This was done with an eye to enhancing the photorefractive effect which has relevance to several types of passive fiber devices. This work was presented at the SPIE Conference on Optical Fibers in Boston, MA this past September. With a simple theory for the "freezing" of stress levels in the core of an optical fiber during the drawing process, we have indicated how "frozen in" strain may result in an increase in the refractive index of the material.

C. List of All Publications and Technical Reports

1. Kyungwhan Oh, T.F. Morse, et al, "Spectroscopic analysis of a Eu-doped aluminosilicate optical fiber preform", J. Non-Crystalline Solids, to be published

2. Q. Zhang, T. F. Morse, et al, "Temperature Dependence of Effective Cutoff Wavelength in Depressed Clad Single Mode Fibers", SPIE Conference on Optics and Fibers, to be published

3. T.F. Morse, "Novel Aerosol Techniques for Glass and Ceramic Formation", published in the 38th Sagamore Army Materials Research Conference *Proceedings, Electromagnetic, Electro-Optical and Electronic Materials*, edited by Thomas V. Hynes, 1991.

D. List of all Participating Scientific Personnel Showing any Advanced Degrees Earned by Them While Employed on the Project

none

3. Report of Inventions.

none

4. References

R. Clasen, "Preparation of Glass and Ceramics by Sintering Colloidal Particles Deposited from the Gas Phase", *Glastech. Berichte*, 61, 119-126, 1987.

D.J. DiGiovanni, T.F. Morse and J.W. Cipolla, Jr., "The Effects of Sintering on Dopant Incorporation in Modified Chemical Vapor Deposition," *J. Lightwave Tech.*, vol. 7, p. 1967-1972, December 1989.

D.J. DiGiovanni, T.F. Morse, and J.W. Cipolla, Jr., "Theoretical Modelling of the Incorporation of Phosphorus in the MCVD Process", *J. Amer. Ceram. Soc.*, 71, no. 11, 914-923, 1988.

T. Kodas, "Generation of Complex Metal Oxides by Aerosol Processing: Superconducting Ceramic particles and Films", *Advanced Materials*, 1990.

K.S. Mazdiasni, "Powder Synthesis from Metal-Organic Precursors", *Ceramics International*, vol. 8, pp. 42-56, 1982.

A.J. Morrow, A. Sarkar, and P. Schultz, "Outside Vapor Deposition" pp. 65-95, in *Optical Fiber Communications*, vol. 1, Fiber Fabrication, ed. by Ting-Yi Li, Academic Press, New York, 1985.

T.F. Morse, L. Reinhart, Kilian, W. Risen, Jr., and J.W. Cipolla, Jr. ``Aerosol Doping Technique for MCVD and OVD'', SPIE Proceedings, Fiber Laser Sources and Amplifiers, vol. 1171, pp. 1-7, 1989.

T.F. Morse, L. Reinhart, A. Kilian, W. Risen, Jr., and J.W. Cipolla, Jr., ``Aerosol Deposition in Modified Chemical Vapor Deposition'', J. Aerosol Sciences, accepted for publication in special issue on aerosol processing, 1991.

T.F. Morse, L. Reinhart, A. Kilian, W. Risen, Jr., and J.W. Cipolla, Jr. ``Aerosol Techniques for Glass Formation'', J. Non-Crystalline Solids, to be published 1991.

G.D. Ulrich, and J.W. Riehl, (1982), ``Aggregation and Growth of Submicron Particle in Flames'', J. Colloid and Interface Science 87, 257.

Ulrich, (1984), ``Flame Synthesis of Fine Particles'', Chemical and Engineering News, 6 August p. 23.

Wen Wen Xu, et al., ``Preparation and Characterization of TiO_2 Films by a Novel Spray Pyrolysis Method'', Mat. Res. Bull., vol 25, pp. 2385-1392, 1990.

M.R. Zachariah, D. Chin, H.G. Semerjian, and J.L. Katz, (1989) Silica Particle Synthesis in a Counterflow Diffusion Flame Reactor" Combustion and Flame 78, 287.