HALIDE GLASSES

I

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HALIDE GLASSES I

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PREFACE

Until 1974, only a few halide glass forming systems – primarily $ZnCl_2$ and those based on BeF_2 – were known. These were mainly of academic interest. In March, 1974 Michel Poulain, then a research technician at the Université de Rennes, produced quite by accident the first known heavy metal fluoride glass while attempting to synthesize a fluorozirconate single crystal. An extensive research effort in these materials was started at the Université de Rennes, partly because of the practical implications of their broad range of I.R. transparency and partly because of their novelty. A large number of published papers on heavy metal fluoride glasses, starting in 1975, resulted from this work. However, it was not until about 1978 that the French work began to be noticed and similar research efforts were commenced in laboratories in the United States and Japan. In 1979, it was realized that heavy metal fluoride glasses had real potential as materials for fiber optic waveguides which might exhibit losses 100 times less than those of silica based fibers.

In 1980, the two editors of these volumes met with Martin Drexhage in the Boston area to discuss mutual research interests. During this meeting, the opinion was jointly ventured that there was now sufficient activity in halide glasses to warrant a small informal conference. At that time, we thought such a meeting might attract perhaps twenty five participants. It was nearly two years later, in March, 1982 that this meeting actually occurred, ably implemented in a more formal fashion by John Gannon, held at Cambridge University in the U.K., and entitled the "First International Symposium on Halide and Other Non-Oxide Glasses". The major portion of this conference was devoted to halide glasses, and by that time interest in the field had perked up to the point that 39 papers were presented on halide glasses and 96 conferees took part in the meeting.

This first Symposium was so successful that it was immediately decided to hold a second meeting, restricted now to halide glasses only. The "Second International Symposium on Halide Glasses", organized by one of us (C. T. Moynihan) took place in August, 1983 at Rennselaer Polytechnic Institute in the U.S.A. This time, 60 papers were presented and 135 persons participated.

In the present two volumes are collected the papers given at the "Third International Symposium on Halide Glasses", organized by the other of us (J. Lucas) at the Université de Rennes in France in June, 1985. The accelerating research activity in this area is evidenced by the fact that 109 papers were presented and some 220 scientists and engineers were in attendance. As will be evident to the reader, the field of halide glasses is beginning to show some maturation and distinct progress has been made in addressing fundamental questions, e.g., with regard to the structure of fluorozirconate glasses and to the intrinsic optical properties of halide glasses in general. On the other hand, many fundamental questions remain unanswered. Much work remains to be done on understanding devitrification in these materials, and to date no complete phase diagrams have been determined for the important fluorozir-

conate systems, nor has a complete viscosity temperature curve been measured for even one heavy metal fluoride glass composition. On the more practical side, high optical quality bulk fluorozirconate glasses with highly reproducible properties can now be prepared routinely, and several laboratories have reported preparation of fluoride glass fibers with minimum losses of a few dB/km in the mid-I.R. At the same time, it has become evident at this Symposium that truly novel and stringent materials preparation and fabrication procedures will be required if fiber optic losses are to be reduced much below this level. We hope that answers to some of these questions and problems will be presented at the "Fourth International Symposium on Halide Glasses", tentatively planned for the end of 1986 or the beginning of 1987. In the meantime, we hope that these two volumes will serve to give the reader a complete state-of-the-art picture of halide glass science and engineering.

Organization of this Symposium would not have been possible without the help of many, many of our colleagues and coworkers. To them, we extend our heartfelt thanks. Likewise, with regard to the always important financial side, implementation of the Symposium could not have been accomplished without support from government agencies and private companies in both France and the United States. Our sincerest thanks to them also.

Jacques LUCAS & Cornelius T. MOYNIHAN
Rennes, France, June, 1985.

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PREPARATION AND PROPERTIES OF HIGH OPTICAL QUALITY BULK FLUORIDE GLASSES

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INTRODUCTION

Heavy metal fluoride glasses (HMFG) have long presented a dilemma to those involved in their preparation and study: a considerable potential as bulk and fiber multispectral optical materials is mitigated by difficulties in routinely preparing large specimens of good quality. This is due in part to the comparatively poor glass-forming ability of the fluorides (in contrast to, e.g., silicates) which manifests itself as a low viscosity at elevated temperatures and an often-times high recrystallization rate upon cooling. Some investigators have compounded these "intrinsic" difficulties through experimental techniques which utilize, for example, poor quality raw materials or inadequate atmospheric control during the melting/fabrication process. The purpose of this paper is to review and assess techniques developed at this and other laboratories which appear to yield bulk fluoride glass specimens of reasonable size that exhibit reproducible physical and optical properties. In addition to developing reliable preparative methodologies applicable to a variety of HMFG compositions, our efforts have been motivated by a need for uniform bulk samples with which to conduct fundamental studies of light scattering, thermal properties, crystallization behavior, viscosity, infrared transmission and impurity related absorption. To some extent, the approaches offered here reflect both the experience and the bias of the author and co-workers; the reader should bear in mind that many alternatives exist and that a considerable amount of applied glass technology will be necessary to translate laboratory scale methods into commercial practice.

Glass Compositions

Perhaps the most frequently debated question among those involved with HMFG research concerns the nature of the "best" glass forming composition. Judging by the literature, a majority

of laboratories have focused on multicomponent fluorozirconate glasses as the materials of choice for fundamental and applied studies. Among these, two specific compositions (and their variants) have gained general acceptance for their apparent stability and have been utilized extensively in our own work: ZBLA (mol % 57ZrF4-36BaF2-3LaF3-4AlF3) and ZBLAN (55.8ZrF4-14.4BaF2-5.8LaF3-3.8AlF3-20.2NaF). These materials originated in the detailed searches for stabilizing additives (particularly AlF3) to ternary glasses carried out by workers at the Universite Rennes (1,2). The ZBLAN compositions were further refined by Japanese investigators, who have used them to draw fibers (3,4,5).

Representative differential scanning calorimeter (DSC) traces for these two compositions are shown in Fig. 1, utilizing fragments from large ingots prepared by techniques described later in this work. The glass samples were encapsulated in hermetically sealed gold DSC pans and scanned at 10 K/min between 450 and 925 K (177 to 625 centigrade, denoted "SCAN" in Fig. 1). The samples were then cooled in the DSC at approximately 100K/min and rescanned up to 925 K at 10 K/min (1st RESCAN). This was repeated a second time (2nd RESCAN) after which the samples were removed from the DSC and inspected.

The sequence of events on the DSC scans showed that the samples crystallized above Tg (appx. 585 K for ZBLA and 540 K for ZBLAN) and subsequently melted. The onset of crystallization occurs appx. 65 K and appx. 100 K above Tg for ZBLA and ZBLAN respectively. The agreement of Tg and specific heat change at Tg on rescanning with the initial scan indicated that the samples were quenched to glasses on cooling on the DSC, i.e., they had completely melted by 925 K. The samples were found to be glassy even after the second rescan, although a thin coat of black material (probably reduced ZrF4) was noted on their surface. Although the main melting endotherm ends at about 810 K for ZBLA and 730 K for ZBLAN, there are subsequent smaller endotherms, indicating that melting is not complete until about 875 K (appx. 600 centigrade) for ZBLA and 900 K (appx. 625 centigrade) for ZBLAN.

The ZBLA and ZBLAN compositions have provided the basis for closely related glasses of (apparently) equivalent stability. Among these are materials in which GdF3 has been substituted for LaF3 (6) and glasses containing LiF and/or small amounts of PbF2 in place of NaF (7). We have also been successful in routinely preparing ingots in which ZrF4 is replaced entirely with HfF4, i.e., HBLA glasses. An additive worthy of further exploration is InF3. In small quantities (0.1 to 1.0 mol %) it has been shown to considerably decrease the light scattering in bulk ZBLA/ZBLAN glasses (8) and to increase the difference between Tx and Tg in other HMFG (9).