CHALCOGENIDE GLASSES FOR INFRARED OPTICS

A. Ray Hilton, Sr.

Chalcogenide Glasses for Infrared Optics

Dr. A. Ray Hilton, Sr.
Chairman of the Board and Technical Director
Amorphous Materials, Inc.
Garland, Texas

New York Chicago San Francisco
Lisbon London Madrid Mexico City
Milan New Delhi San Juan
Seoul Singapore Sydney Toronto

The McGraw-Hill Companies

Cataloging-in-Publication Data is on file with the Library of Congress

1 2 3 4 5 6 7 8 9 0 DOC/DOC 0 1 5 4 3 2 1 0 9

ISBN 978-0-07-159697-8
MHID 0-07-159697-6

Sponsoring Editor
Taisuke Soda

Editing Supervisor
Stephen M. Smith

Production Supervisor
Richard C. Ruzycka

Acquisitions Coordinator
Michael Mulcahy

Project Manager
Gita Raman,
Glyph International

Copy Editor
Patti Scott

Proofreader
Shivani Arora,
Glyph International

Indexer
Edwin Durbin

Art Director, Cover
Jeff Weeks

Composition
Glyph International

Printed and bound by RR Donnelley.

McGraw-Hill books are available at special quantity discounts to use as premiums and sales promotions, or for use in corporate training programs. To contact a representative, please e-mail us at bulksales@mcgraw-hill.com.

This book is printed on acid-free paper.

About the Author

Dr. A. Ray Hilton, Sr., is known worldwide through publications describing his efforts in chalcogenide glasses. He serves as Chairman of the Board and Technical Director of Amorphous Materials, Inc. (AMI). Under Dr. Hilton's direction and guidance, a process was developed to compound and cast high-purity homogeneous plates of chalcogenide glasses carried out under high vacuum in high-purity quartz containers. Thousands of glass blanks required for government FLIR systems produced in the 1980s for the Army were supplied by AMI. AMI is currently developing new glass compositions for lenses for use in inexpensive infrared cameras.

Acknowledgments

When you read this book describing my 50 years' experience, you will find the applied research process is not flawless. Bad choices and false starts I made are identified. But when it came to choosing with whom I was going to share my life, I was dead on. My wife, Madora Pauline Bull Hilton, of 58 years has been in my corner, on my side every step of the way, through the years in college, followed by service in the Air Force, and graduate school while raising three children on the G.I. Bill. A few people influenced me as I pursued this path in life. We had help from John Beckham, the business manager of the chemistry department, and I taught freshman labs under Dr. Tom Burkhalter and finally received a research fellowship via Dr. Albert Jache, my senior adviser, who also taught me the love of research. We finally finished in 1959, there was one more oil company job in Houston, and then it was off to a good-paying job at Texas Instruments in Dallas in 1960.

Texas Instruments was a great place to work. The colleagues who helped me most were Charlie Jones, Harold Hafner, and Dr. George Cronin. Technicians were Jimmie Parker and Joyce Jones. In 1974, after 14 years in the TI CRL, 5 years as a senior scientist, I left to manage the infrared glass production in the EO Division. The production of the glasses had become very important. I soon realized there was a need for a second source of the glass, a unique opportunity for me. Like many, I had always wanted to run my own company. In 1977 when I told Madora what I wanted to do, she said go ahead, since it has always been your dream. I will join the company, she said, but I will still need time to be with my children and grandchildren.

So I left TI in March 1977, borrowed some money from a bank, using land we owned as collateral, and accepted stockholders. We started in a small rented building. Our first employee was Glen Whaley, a master glass blower from TI. His son, Greg Whaley, and our oldest son, Ray Hilton, Jr., worked part-time while still going to school. Glen's friend Mitchell Jones was our first technician. Our oldest daughter, Gail Hanna, soon joined us as a technician followed by James McCord from TI. AMI has been in operation 32 years, and our son is now president. Greg Whaley is vice president and director

for sales and contracts. Our daughter, Gail Hanna, is our antireflection coating specialist. Madora is retired and spends time with her 12 grandchildren, all of whom live here.

I would also like to acknowledge the following individuals who contributed to the work reported in the designated chapter(s):

	Chapters
Cam Allen, System Design, TI	10
Max Amon, Optical Design, LMCO	6
Dr. R. J. Archer, Ellipsometry, Hewlett-Packard	10
Dr. Werner Beyen, laboratory director, TI	10
Dr. Steve Boldish, AMI consultant	9
Maurice Brau, SC Materials, TI	2, 6
Max Bryant, Mass Spectrometry, TI	2
Dr. Tom Burkhalter, laboratory director, TI	10
Ed Carr, coatings consultant, AMI	5, 6, 8
Ron Child, glass blower, TI	10
Igeno Lombardo Codman, Johnson & Johnson	7
Dr. George Cronin, SC Materials, TI/AMI	7, 9
Gene Daniels, computer programmer, TI	10
Jim Davidson, Thermalscan	8
Dr. Robert Dobrot, X-ray Structure, TI	2
Gerald Ferguson, AMI Navy Representative	7
Dr. Jacob Fraden, Thermoscan	7
Carl Fritz, grandson, IR Refractometer, AMI	7
Dr. Tommy George, Mass Spectrometry, TI	2
Amy Graham, IR&D, LMCO	6
Harold Hafner, Glass Science, TI	3, 9
Dr. John Hall, Optical Design, NVL	9
Gail Hanna, daughter, coating technician, AMI	5, 6, 8
Bob Harp, senior technician, TI	9
Dr. Jim Harrington, professor, Rutgers University	7
Dr. Don Hayes, president, Micro Fab	3
Ray Hilton, Jr., president, AMI	3, 5–9
Bob Icovazzi, Optics Production, LMCO	9
Dr. Pete Johnson, Ceramics, TI	10

Charlie Jones, Materials, TI	2, 3, 9, 10
Dr. Eric Jones, Computer Science, TI	10
Mitchell Jones, senior technician, AMI	3, 9
Edward Knerr, IRAD program, LMCO	6
Dr. Heinz Krebs, professor, Stuttgart University	2
John Lawson, Optics Design, CBC America Optics	6
Rich LeBlanc, IR&D, LMCO, AMI director	6
Tom Loretz, Glass Science, AMI consultant	7, 8
Al Lyon, Optical Design, LMCO	9
James McCord, senior technician, AMI	3, 6–9
Dr. Peter Melling, president, Remspec	8
Paul Modlin, Advantek Engineering	8
Robert Patterson, TI 1173 Glass Composition	4
Charles Ratliff, Computer Science, TI	10
Dr. Mike Rechtin, Materials Science, TI	3
Dr. Allen Rineberg, Physics, TI	10
Dr. Grady Roberts, Materials Science, TI	2
Nate Rosebrooks, Sancliff Equipment	7
Dr. Laird Shearer, Physics, Lasers, TI	10
Doug Sinclair, senior technician, TI	10
Horace Spain, production engineer, Exxon	10
Dr. Larry Swink, X-ray Structure, TI/AMI	3
Jan Terlouw, vice president, CBC America Optics	6
William Thompson, consultant for optics, AMI	4, 6, 8
Ronald Timm, senior technician, AMI	6
Dale Welt, senior technician, AMI	9
Dub Westfall, senior technician, TI	10
Glen Whaley, vice president, AMI	3, 7–10
Dr. Donald Wierauch, TI 20 Glass Composition	2
Gary Wiese, Optical Design, LMCO	8
Dan Woody, IR&D, LMCO	6

Introduction

The purpose of this book is to describe the technology developed over 50 years to utilize chalcogenide glasses as infrared optical materials. Chalcogenide glasses are based on the chalcogen elements sulfur, selenium, and tellurium excluding oxygen, the first member of the family. The name is a misnomer since chalcogen is from the Greek meaning chalk former and oxygen is the only member of the family that forms chalk. All its compounds are called oxides. Methods used to identify qualitatively chalcogenide glass compositions with promise to become useful infrared optical materials are discussed. Once identified, the optical and related physical properties must be measured quantitatively. The method best suited for the production of homogeneous glass in high purity and quantity must then be developed. Thus, a great deal of effort is required before a glass composition is considered by optical designers ready for use in an infrared system. For this reason, only a few glass compositions have been fully developed and used in quantity over the years.

Infrared light by definition is light with a wavelength greater than the sensitivity region of the human eye, 4000 to 8000 Å. For infrared discussions, the more commonly used terms are 0.4 to 0.8 μm with μm being the abbreviation for micrometers. Of special importance are materials useful for infrared imaging systems designed to respond to infrared energy transmitted through the atmosphere. Figure I.1 illustrates infrared light absorption in the air at sea level due to water vapor, carbon dioxide gas, and ozone. The bottom illustration is the resultant total for the three gas molecules. Notice there are two windows indicated where energy is transmitted well, from 3 to 5 μm (hot window) and about 7 to 14 μm (thermal window). The window is called thermal since the peak of emitted radiation from a body at room temperature, about 300 K, occurs in this window. Thermal imaging of a living subject is based on emitted radiation, which is transmitted in this atmospheric window. The hot window refers to the fact that heated objects emit at the shorter wavelengths in this range. Examples might be the tailpipe of a jetplane or a missile exhaust.

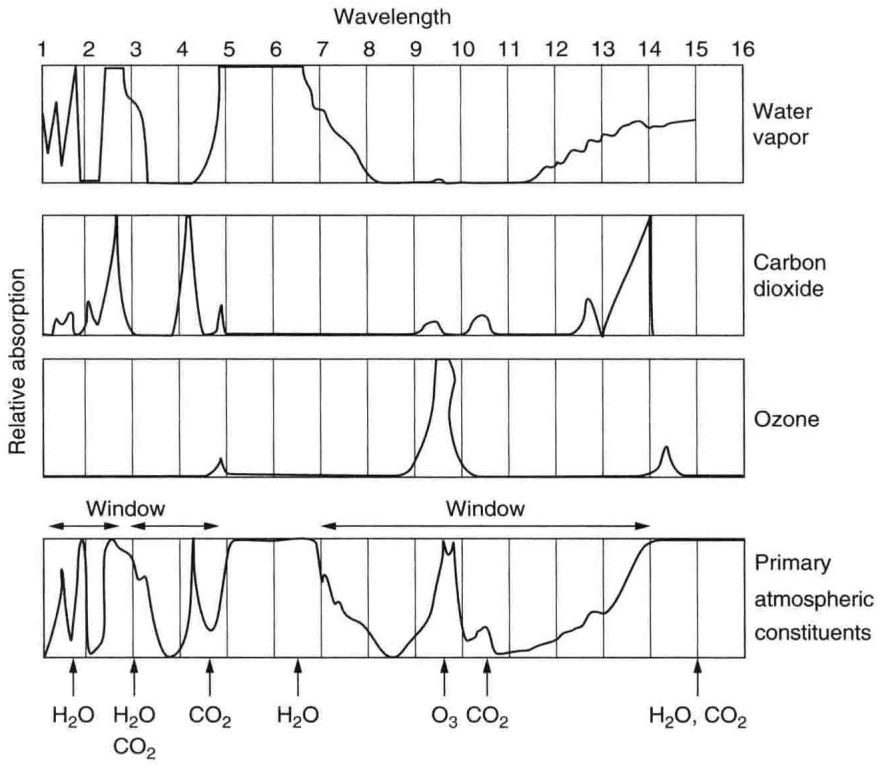

Figure I.1 Infrared absorption bands of primary atmospheric constituents for average conditions at sea level.

Over the years, materials used in infrared systems have included alkali halides, alkaline earth halides, melt formed semiconductors, vapor grown fine-grain polycrystalline semiconductors, and chalcogenide glasses. Each of the crystal materials has some advantages and some disadvantages that will be discussed toward the end of this book. However, this book will concentrate chiefly on chalcogenide glasses. After 17 years at Texas Instruments (TI), the author left in 1977 to found Amorphous Materials (AMI), a small company dedicated to producing infrared transmitting glasses for use in infrared optical systems. The company is still active in developing new glass compositions for new applications.

Some crystalline materials were produced at AMI. The production of vacuum float zoned silicon, gallium arsenide, and cadmium telluride, all useful in infrared technology, will be described. Most of the early glass work reported here was carried out at TI in government-sponsored programs as indicated in the references. Discussions of glasses developed at AMI and their applications will be given. Some results of infrared techniques applied to semiconductors at TI will be

described. Glasses have a major advantage over crystalline materials in that they can be easily cast, molded, extruded, and drawn into fiber. Such processes generally cannot be applied to crystalline materials but were applied to chalcogenide glasses. Also, the composition of a glass can be changed within limits to enhance properties important to an application. Very little such latitude exists with crystals. The ratios among constituent atoms of most crystalline materials are fixed. Examples of how the composition of some glasses was changed at AMI to enhance a property will be discussed.

Comments to the readers who are students: The author considers himself a physical chemist. Chemistry is an applied science and mostly empirical. Tools used while conducting a research project have changed immensely since 1948 when this author started out, from slide rules and burets to computers, infrared FTIR spectrophotometers, Raman instruments, electron microscopes, and differential thermal analysis (DTA) for glasses. Lasers were not even invented until 1959. There was no material sciences school, only chemistry and physics. Chemical structural theories have changed greatly based on results from the new instruments and techniques. The language of science is constantly changing, reflecting people's increased understanding, which improves their descriptions. Not nature! Nature never changes. Avoid having a preconceived solution to a problem before you start. Let nature guide you through the results of your experiments. Always remember, it is the investigation that is important, not the investigator. It is not important to be right at the start—only at the finish.

Chalcogenide Glasses for Infrared Optics

Contents

CHAPTER 1

Transmission of Light by Solids

1.1 Solids

In nature, material exists as gas, liquid, or solid. Gas atoms or molecules are free to move within the confines of their container. Liquids move to fill the shape of their container while solids are rigid in shape. There is about a 1000-fold increase in density in going from gas to the condensed state of liquid or solid. The atoms or molecules come much closer together as a liquid and closer still as a solid. The dense solid may have a precise three-dimensional spatial arrangement for the atoms making up the solid that covers thousands of neighbors in all three directions. When the long-range order is perfect, the solid may be referred to as single-crystal. Or the order may be maintained over limited atomic distances and be referred to as polycrystalline. The atoms or molecules of liquids are free to move within their arrangements continuously in any direction and are said to have no long-range three-dimensional order. Order found is that of nearest neighbors or second nearest neighbors or even more, but not long range in the structural sense. Depending on elemental composition, when the atoms or molecules of a solid come close together, they begin to share their electronic bonding states, which results in formation of an energy structure for the solid. When excited, bonding valence electrons are elevated into a higher conduction band state and are free to travel through the solid as charge if an electric field is applied. The energy difference between the valence state and the free conduction state is called the bandgap of the solid. The vacancies left in the valence band are called holes and can constitute charge flow moving in the opposite direction to the field. The band structure is well developed and precise in crystalline solids with good crystalline perfection. Liquids and amorphous solid glasses are condensed states but without long-range three-dimensional orders. A glass is referred to as a disordered solid. The energy band structure may exist, but the

energy level states in the band structure are not nearly as precise as in a crystalline solid.

1.2 Beginning of Transmission of Light—An Electronic Transition

Generally speaking, infrared optical materials are insulators or semiconductors as judged by their bandgaps and resistivity. Photons of light corresponding to energy greater than the bandgap of the solid are strongly absorbed at the surface. As the wavelength is increased and the photon energy decreased below the bandgap, light is transmitted through the solid. The beginning of light transmission of a solid occurs at the wavelength that corresponds to the bandgap energy. The absorption of the photon is a very strong, quantized electronic transition. One may think of this energy as representing the average ionization energy for the primary chemical bonds formed between the atoms that make up the solid. If the required ionization energy is large enough, transmission begins in the ultraviolet region of the spectrum, as in the case for alkali halides or alkaline earth halides. Then the solid appears water-clear or colorless. If it occurs in the visible region, the solid appears colored. If the absorption edge occurs in the infrared region, the solid appears metallic because all visible light is strongly absorbed and reflected.

The use of infrared spectroscopy as an analytical tool to identify and measure concentrations of organic compounds began in the late 1940s. Instruments, crude by today's standards, used salt prisms to disperse the light, salt windows for the instrument, and cells to contain the samples being analyzed. Petroleum refineries used the infrared-based technology for quality control in their laboratories. The bandgaps for both the alkali halides and the alkaline earth halides occur in the ultraviolet region and were not a factor in their infrared use. Most of these ionic solids are soft, weak, and hygroscopic, making them unsuitable for use outside of the laboratory.

The semiconductor revolution began in the early 1950s at Bell Telephone Laboratories when Gordon Teal et al.[1] developed the ability to grow high-purity germanium in single-crystal form. The result was the germanium transistor. Later in the 1950s, Gordon Teal joined Texas Instruments and under his direction accomplished the same feat for silicon, resulting in the silicon transistor. Both germanium and silicon found use as infrared optical materials and as infrared light detectors. Germanium windows and lenses became the optical material standard for the industry due to their wide transmission, 2 to 20 μm, with very little change in refractive index (low dispersion) and good physical properties. Silicon found use as a missile dome material due to its superior physical properties such as strength and hardness. The transmission range was 2 to 14 μm again with little