

بسم الله الرحمن الرحيم



HOSSAM MAGHRABY



شبكة المعلومات الجامعية التوثيق الالكتروني والميكروفيلم



HOSSAM MAGHRABY

جامعة عين شمس

التوثيق الإلكتروني والميكروفيلم

قسم

نقسم بالله العظيم أن المادة التي تم توثيقها وتسجيلها
على هذه الأقراص المدمجة قد أعدت دون أية تغيرات



يجب أن

تحفظ هذه الأقراص المدمجة بعيدا عن الغبار



HOSSAM MAGHRABY



بعض الوثائق الأصلية تالفة



HOSSAM MAGHRABY



بالرسالة صفحات

لم ترد بالأصل



HOSSAM MAGHRABY

B16559

STRUCTURAL INVESTIGATIONS OF FLUORIDE GLASSES

A THESIS

Submitted for the Degree of Doctor of Philosophy
in Solid State Physics to Physics Department,
Faculty of Science, Menoufia University, Egypt

By

IBRAHIM ZAKY EL-SAYED HAGER

M. Sc. (Solid State Physics)

SUPERVISED BY

- 1 - *Prof. Dr. Marcel Poulain*,
Director of Lab. Mater. Photoniques,
University of Rennes 1, France.
- 2 - *Prof. Dr. M. A. Ewaida*,
Physics Department, Faculty of Science,
Menoufia University, Egypt.
- 3 - *Prof. Dr. R. A. El-Mallawany*,
Physics Department, Faculty of Science,
Menoufia University, Egypt.
- 4 - *Dr. A. H. Khafagy*,
Assist. Prof. Physics Department, Faculty
of Science, Menoufia University, Egypt.

M. A. Ewaida

R. A. El-Mallawany

A. H. Khafagy

1996

ACKNOWLEDGMENTS

The author is deeply indebted to Prof. Dr. Marcel Poulain, director of Lab. Mater. Photoniques, University of Rennes 1, France, for his kind supervision, suggesting the problem and kind help during carrying out the research work, stimulating discussion and encouragement. He Sincerely expresses his deep gratitude to Prof. Dr. R. El-Mallawany, Physics Department, Faculty of Science, Menoufia University, Egypt, for his supervision, suggesting the problem and kind help during carrying out the research work, stimulating discussion and encouragement.

The author also expresses his deep thanks to prof. Dr. M. A. Ewaida Physics Department, Faculty of Science, Menoufia University for his supervision, valuable suggestions and kind help during carrying out the research work, stimulating discussion and encouragement. He wishes to offer his gratitude to Dr. A. H. Khafagy, Assist. Prof., Physics Department, Faculty of Science, Menoufia University, Egypt for his supervision, valuable suggestions and kind help during carrying out the research work, stimulating discussion and encouragement. He also wishes to offer his gratitude to Dr. Michel Poulain, Labo. Mater. Photoniques, Univ. of Rennes 1, France for kind help and facilities during carrying out the glass preparation of this work, also for Dr. Marc Matecki, Labo. of Ceram. and Glasses, Univ. of Rennes 1, France for kind help and facilities during carrying out the specific heat measurements of the present glasses.

Many thanks are due to Lab. Physics (Spectra Lab.), Univ. of Rennes 1, France for kind help and facilities during carrying out the measurements of Raman and Brillouin Scattering. The auther, wishes to offer his thanks to all the members of the Labo. of Mater. Photoniques, Univ. of Rennes 1, France and all the staff members of physics Department, Faculty of Science, Menoufia Univ., Egypt for their kind cooperation.

To

MY Dear Parent,

My Love Wife Hala

and

My Daughters, Hadil and Iman

CONTENTS

Acknowledgments

Abstract	1
----------------	---

CHAPTER 1 Introduction	3
------------------------------	---

1.1 Glass Formation Behaviour of Halides	3
1.2 Glass Forming Systems	4
1.2.1 Fluoroberyllates	5
1.2.2 Fluorozirconates	5
1.2.3 Transition Metal Fluoride Glasses	7
1.2.4 Miscellaneous Fluoride Glasses	8
1.2.5 Fluorophosphate and Oxyfluoride Glasses	8
1.3 The Coordination number and Neutralization of Electric Valence	9
1.4 General Rules for Glass Formation	10
1.5 Structure of Fluoride Glasses.....	14
1.6 Physical Properties of The Fluoride Glasses	16
1.6.1 Thermal Properties	16
1.6.1.1 Glass Transition Temperature	16
1.6.1.2 Thermal Expansion Coefficient	18
1.6.1.3 Specific Heat	21
1.6.2 Density and Molar Volume	23
1.6.3 Optical Properties	26
1.6.3.1 Refractive Index	26
1.6.3.2 Infrared Spectra	27
1.6.3.3 Ultraviolet Absorption	28
1.6.4 Raman Scattering	31
1.6.5 Brillouin Scattering	37
1.7 Aim of the present work	42

CHAPTER 2 Experimental Technique of Measurements	44
--	----

2.1 Glass Preparation	44
-----------------------------	----

2.2	Measurements	45
2.2.1	DSC measurements	45
2.2.2	Thermal Expansion Coefficient	47
2.2.3	Specific Heat	47
2.2.4	Density	48
2.2.5	Refractive Index	49
2.2.6	UV_Measurements	50
2.2.7	Infrared Measurements	50
2.3	Light Scattering Spectroscopy	51
2.3.1	Raman Spectroscopy	52
2.3.2	Brillouin Spectroscopy	54
CHAPTER 3 Results and Discussions		58
3.1	Glass Formation Area	58
3.2	Density and Molar Volume	63
3.3	Thermal Properties	67
3.3.1	Glass Transition Temperature T_g	67
3.3.2	Stability and Activation Energy	74
3.3.3	Thermal Expansion Coefficient	78
3.3.4	Specific Heat	82
3.4	Optical Properties	87
3.4.1	Refractive Index and Molar Refractivity	87
3.4.2	UV-Spectra	93
3.5	Optical Spectroscopy	99
3.5.1	Infrared Absorption	99
3.5.2	Raman Spectra	104
3.6	Elastic Properties By Brillouin Scattering	109
APPLICATIONS		114
CONCLUSION		116
REFERENCES		122
GLOSSARY		
Arabic Conclusion		

ABSTRACT

ABSTRACT

New fluoride glasses have been synthesized in ternary and quaternary systems based on NbO_2F - BaF_2 -RF where RF are the alkali fluoride, LiF, NaF, KF and mixed fluoride NaF-LiF. These glasses were prepared by the usual melt-quench technique. The effect of RF instead of NbO_2F on the glass forming range, physical properties and structure investigations of the produced fluoride glasses have been studied.

Glass densities were determined by the use of Archmedes' method and so the corresponding molar volume were calculated.

The physical properties of these glasses such as thermal properties have been carried out by applying the DSC technique. This has been done in order to find endothermic peak due to the glass transition temperature T_g , exothermic peak due to the glass crystallization T_c and endothermic peak due to the melting temperature T_m . From these results the glass stability factor S and the activation energy of crystallization E_a have been calculated. Also, thermal expansion coefficient α and specific heat C_p were determined.

The optical properties of the present new glasses such as the refractive index n_D has been measured and so the molar refractivity R_m has been calculated. From the dielectric theory, the relationship between the refractive index and number of ions /unit volume (N/V) with polarizability α' has been discussed. UV-spectra have been measured in order to calculate the optical energy

gap E_{opt} and the width of the tails of the localized states in the band gap E_{tail} of the present glasses.

The structural investigations of the present glasses have been implemented by using IR spectrophotometer in the range 400-1200 cm^{-1} of wavenumber and Raman scattering in the range of 200-1150 cm^{-1} of wavenumber. The observed absorption bands were assigned to their vibrational modes.

Finally the Brillouin scattering was used in order to determine the longitudinal wave velocity and elastic modulus for the tested glasses.

All the thermal, optical and mechanical properties of these fluoride glasses have been found to be very sensitive to the composition, i.e. depend on the presence of alkali fluoride, LiF, NaF and mixed NaF-LiF.

CHAPTER 1
INTRODUCTION

CHAPTER 1

INTRODUCTION

1-1 The Glass Formation Behaviour of Halides

An increasing interest is devoted in general, to halide glasses because of their potential use for making infrared optical components and ultra-low-loss optical fibres for laser applications and specific properties such as ionic conductivity.

The history and actual situation of glass chemistry are largely dominated by oxide systems. The glass-forming ability which requires the creation of a strong tridimensional 3D covalent bond is characteristic of small highly charged cations as found in oxides such as B_2O_3 , SiO_2 , P_2O_5 The lowering of energy due to the intrinsic disorder arising from the periodicity of the glass lattice is balanced by the very strong metal-oxygen bond originating from the overlapping of the atomic orbitals of M and O in the 3D directions.

The situation is different with halides $X = F, Cl, Br$ and I , especially with fluorine which is the most electronegative elements. When associated with a metal, they generally have a great tendency to monopolize the bonding electrons and to give a pure ionic bond, which consequently enhances the crystalline state whose stability is governed by Coulombic forces. The difficulty in stabilizing halide glasses is demonstrated by their recent discovery and their absence as a natural materials.