D. C. RESISTIVITY AND STRUCTURAL INVESTIGATIONS OF BARIUM-BORO-VANADATE GLASSES CONTAINING IRON

By
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CERTIFICATE

It is to certify that the thesis "D.C. Resistivity and Structural Investigations of Barium-Boro-Vanadate Glasses Containing Iron" submitted for the award of the degree of Doctor of Philosophy to Indian Institute of Technology, Delhi, is a bonafide work carried out by Mr. Tarsem K. Bansal under my supervision and no part of this thesis has been submitted for any other degree.

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PREFACE

Glasses, or more generally amorphous solids, are of growing interest to chemists, physicists and material scientists. These materials are of great technical importance due to their applications. Presently, the glasses with any strength between that of metals and honey, of any conductivity between that of metals and insulators and of any magnetic properties between that of air and ferrites can be prepared by selecting suitable compositions and preparation technique. Glasses can be broadly divided into the following groups: inorganic oxides, metallic chalcogenides and glassy polymers. Among all these, inorganic oxide glasses are the oldest known amorphous materials and have been extensively studied in the past. This catagory of glass includes borates phosphates, silicates and germinates. These glasses find tremendous application in industry and in daily life.

The present thesis deals with the electrical and structural investigations of BaO-V_2O_5 - B_2O_3 - Fe_2O_3 glass systems. The importance of these glasses lies in the fact that the presence of V_2O_5 makes them semiconducting in nature and find applications in switching devices. The small polaronic hopping between V^{4+} and V^{5+} ions makes them electronically conducting. On the other hand borate glasses possess high resistivity and are used as electrical insulators and as optical glasses. It is well known that B_2O_3 is a good glass former whereas pure V_2O_5 is difficult to obtain in glassy state at normal cooling rates. The aim of the present work is to utilize together different properties of vanadate and borate glasses by developing a glassy structure which contains both B_2O_3 and V_2O_5, thereby offering materials with more versatile applications. An attempt has been made to understand electrical and structural behaviour of these glasses in presence of an alkaline earth oxide (BaO). A fixed amount of 10% Fe_2O_3 has been added as Mossbauer and EPR probes.

In the present work a systematic study of the following series is made using Mössbauer spectroscopic, infra-red (IR), electron paramagnetic resonance (EPR), d.c. resistivity, differential thermal analysis (DTA) and density techniques in order to get complete picture of the structure of these glasses.

(1) Z BaO, (0.9-Z) V_2O_5, 0.1 Fe_2O_3 ; $0.15 \leq Z \leq 0.45$,

(2) 0.3 BaO, 0.6 ((1-X) V_2O_5 , X B_2O_3), 0.1 Fe_2O_3 ; $0.0 \leq X \leq 1.0$,

(3) 3 Y BaO , (0.3 - Y) (V_2O_5 . 2 B_2O_3), 0.1 Fe_2O_3 ; $0.045 \leq Y \leq 0.165$.

Beside these, pure V_2O_5 and some other glass samples with composition $(0.9-X_1)\ V_2O_5 \cdot X_1B_2O_3 \cdot 0.1\ Fe_2O_3$; $0 \leq X_1 < 0.4$ which could not be prepared by normal cooling were prepared by using melt spinning technique yielding violet amorphous ribbons.

From the obtained spectroscopic and d.c. resistivity data the following structural informations with the change in composition are drawn.

1. Changes in bond angles.
2. Changes in bond lengths.
3. New bonds formed.
4. Glass forming ability.
5. Solubility limit of various components in each other.
6. Site occupancy of iron.
7. Changes in coordination number of boron, vanadium and iron.
8. Changes in density.
9. Changes in glass transition, melting and crystallization temperatures.
10. Changes in d.c. resistivity with temperature.
11. Changes in resistivity and activation energy.
12. Changes in the relative interaction of Ba^{2+} ions with boron, vanadium and iron. Conclusions and recomendations for further work are mentioned towards the end of the thesis.

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