Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 147 (2015) 163–172

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Spectroscopic and ultrasonic investigations on structural characterization of borate glass specimen doped with transition metal ions

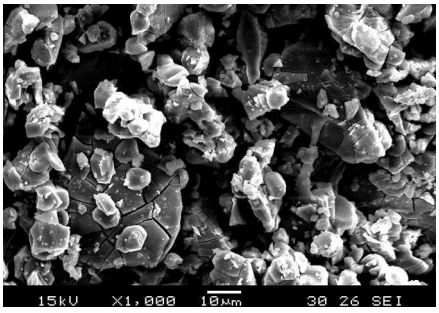
K. Sathish [a], S. Thirumaran [b,*]

[a] Department of Physics, Annai College of Arts & Science, Kovilacheri, Kumbakonam 612 503, India
[b] Department of Physics (DDE), Annamalai University, Annamalai Nagar 608 002, India

HIGHLIGHTS

- The doping of V_2O_5 with borate enhances the hardening of the glassy structure.
- The FTIR spectral analysis confirms the presence of functional groups in the glass specimen.
- The surface morphological studies of glass exhaustively surveyed using SEM analysis.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 May 2014
Received in revised form 13 January 2015
Accepted 8 February 2015
Available online 28 February 2015

Keywords:
Melt quenching
FTIR
SEM
Glassy structure infrared absorption
Diborate structure
Stretching vibration

ABSTRACT

The present work describes the glass samples of composition (x% V_2O_5–(80–x)% B_2O_3–20% Na_2CO_3) VBS glass system and (x% MnO_2–(80–x)% B_2O_3–20% Na_2CO_3) in MBS glass system with mol% ranging from x = 3, 6, 9, 12, 15 and 18 in steps of 3 mol% are prepared by melt quenching technique. For these prepared glass systems, sound velocity (longitudinal and shear velocities) and density have been measured. The sound velocity (longitudinal and shear) was measured by using pulse-echo technique at 5 MHz. The XRD study was carried to out to ascertain the amorphous nature of the glass specimen. Using these measured values, the elastic moduli, Poisson's ratio, Debye temperature, acoustic impedance and thermal expansion coefficient of the two glass systems were evaluated. The elastic and mechanical properties of the prepared glass systems are analyzed from ultrasonic study and the structural characterization from spectroscopic study. The effects due to the doping of transition metal ions with borate have been discussed. In the V_2O_5 doped glass system, (VBS glass system) the sound velocity, density and elastic moduli, steeply increases after 12 mol% comparatively with MnO_2 doped glass system (VBS glass system). The present study critically observes the doping of V_2O_5 with borate enhances the strengthening of network linkage and hardening of the glassy network structure than MnO_2. The IR spectral analysis reveals depolymerization of the borate network and conversion of BO_3 or BO_4 units with the formation of non-bridging oxygen. The FTIR spectral studies confirm the presence of various functional groups of the sample. FTIR spectrum of sample exhibits broad absorption bands indicating the wide distribution of borate structural units. The effect of Na_2CO_3, V_2O_5 and MnO_2 contents on the structures of borate glass is evaluated from the FTIR spectra. The topological aspects of the prepared glass samples are exhaustively reported from SEM micrographs.

* Corresponding author.
E-mail address: thirumaran64@gmail.com (S. Thirumaran).

http://dx.doi.org/10.1016/j.saa.2015.02.031
1386-1425/

Introduction

The propagation of ultrasonic wave in solids such as glass provides valuable information regarding the solid state motion in the material. Interest in glasses has rapidly increased in recent years because of diverse applications in electronic, nuclear, solar energy and acousto-optic devices. The acoustic wave propagation in bulk glasses has been of considerable interest to understand the mechanical properties [1]. The study of elastic properties of the glasses has inspired many researches [2,3] and significant information about the same has been obtained. The elastic properties are related to microscopic properties through the behavior of the network and the modifier. The elastic moduli of glasses are influenced by the by many physical parameters, which may in turn be studied by measuring the ultrasonic velocities. The dependence of ultrasonic velocity on the composition of glass indicates the various changes in the structural configuration between the network former and modifiers [4].

B_2O_3 is one of the best known glass formers and it is present in varieties of commercial glasses. The structure of amorphous B_2O_3 is made up of planar BO_3 triangles linked through B–O–B linkages. The addition of network modifier to pure B_2O_3 glass may result either in the conversion of triangular BO_3 structural units to BO_4 tetrahedral or the formation of non-bridging oxygen atoms (NBOs), or simply saying the main structural unit of borate glasses are BO_3 triangles, by the addition of modifiers, it can convert from BO_3 to BO_4 units. Borate glasses are very important optical materials because of their low melting point, high transparency, and high thermal stability [5]. They are generally used to make insulating and dielectric materials. But incorporation of transition metal ions makes these glasses semiconductor in nature.

In present days, transition metals are extensively used in glass field due to their existence in two or more valence states which affects the structural and optical parameters [6–8]. Transition metal doped borate glasses are also used as gamma ray shielding materials, UV filters and luminescent material [9,10]. The addition of transition metals such as V_2O_5, Fe_2O_3,WO_3, ZnO etc., make these glasses semi-conducting nature. These glasses have been studied due to their potential application as optical and electrical memory switching, cathode material for making solid state devices and optical fiber. The transition metal doped borate glasses have been extensively studied by several authors. Many authors have studied the effect of multiple transition metal on structural and optical properties of borate glasses with the help of ultrasonic, spectroscopic (FTIR), UV and dc conductivity studies [11,12].

Among transition metals, V_2O_5 is an important semiconductor whose electrical conductivity is due to the electron hopping between V^{5+} and V^{4-} ions [13]. The semiconducting nature of V_2O_5 is due to the valence states of V^{5+} and V^{4-} of vanadium [14]. This oxide is classified as a glass former and can enter as same network either as a network former or a network modifier depending upon its consideration. The other transition metal ion, manganese (Mn) ion is particularly interesting because it exists in different valence states in different glass matrices [15]. With the composition of the glass, the local environment of the transition metal (TM) ion incorporated into the glass network can be changed, leading to the local ligand field in homogeneities. Most Mn^{2+} complexes are octahedral and have a high spin arrangement with five unpaired electrons [16]. In recent years, an interest in inorganic glasses containing transition metal ions has grown because these glasses have properties of technological importance in electronic, tunable solid state lasers and fiber optic communication system [17].

Much work has been made on borate glasses containing MnO_2 [18] but the work on borate glasses containing V_2O_5 and MnO_2 together is found very few. In the present work, efforts are made to study the effect of physical (elastic and mechanical properties) and structural properties of the glasses in the presence of multiple transition metals with the help of ultrasonic, spectroscopic, X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) studies.

The present investigation is represented with the preparation of two glass systems, namely (i) V_2O_5–B_2O_3–Na_2CO_3 (VBS glass system) and (ii) MnO_2–B_2O_3–Na_2CO_3 (MBS glass system). In the former glass system, V_2O_5 has been doped with B_2O_3 in increasing mole percentage from 3, 6, 9 . . ...18 in steps of 3 mol% and in the latter glass system, MnO_2 have been doped with B_2O_3 in the same increasing mole percentage as former glass system. The mole percentage of alkaline metal Na_2 CO_3 is kept constant at 20 mol%. There is nothing significant in fixing at this mole percentage. For these prepared glass systems, sound velocity (longitudinal and shear velocities) and density have been measured. The sound velocity has been measured using pulse-echo technique at 5 MHz. From these measured values, the elastic moduli, Poisson's ratio, Debye temperature, acoustic impedance and thermal expansion coefficient of the two glass systems have been meticulously calculated. The results of the ultrasonic study have been discussed in terms of elastic mechanical and physical properties of prepared glass specimen. Apart from the ultrasonic study, the authors have extended their investigation by carrying out spectroscopic study (FTIR treatment) to explore about the structural characterization elucidation of borate glasses due to the doping of transition metal ions., XRD study (to confirm the amorphous nature) and Scanning Electron Microscopy (SEM) study to survey the surface morphological aspects of the glass specimen.

Experimental procedure

Sample preparation

The chemicals used in the present research work were Analytical Reagent (AR) and Spectroscopic Reagent (SR) grade with

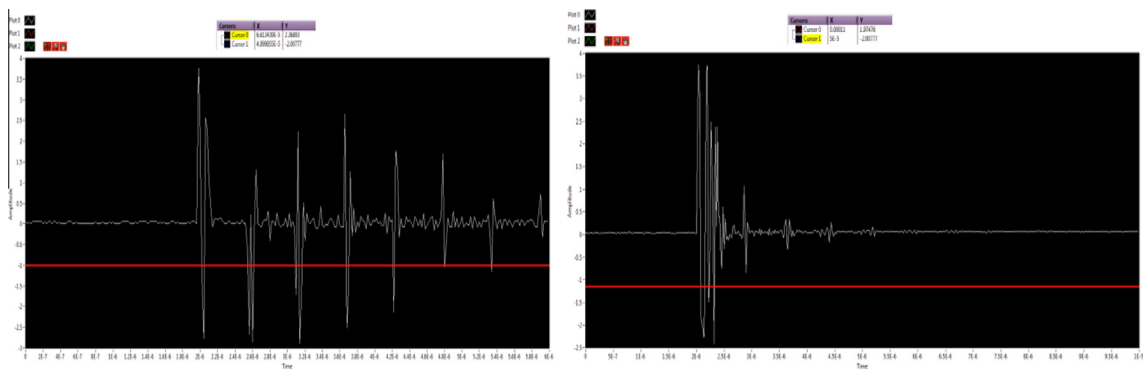


Fig. 1a. Longitudinal velocity U_L and shear velocity U_S for VBS glass system.