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ScienceDirect
Journal of Non-Crystalline Solids 353 (2007) 2919–2925
JOURNAL OF NON-CRYSTALLINE SOLIDS
www.elsevier.com/locate/jnoncrysol

IR absorption spectra of lithium and silver vanadium–tellurite based glasses

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Received 28 March 2007

Abstract

The aim of the present paper is to give structural information in order to set a correlation between the electrical conductivity behavior and structures of lithium and silver vanadium–tellurite based glasses. We report our structural studies and compare the effect of the nature of the metallic cation on glasses of the form $XM_2O \cdot (1-X)V_2O_5 \cdot 2TeO_2$ (where $0 \leqslant X < 1$ and M = Li or Ag). Fourier transform infra-red (FTIR) spectra were recorded for all compositions and complementary differential scanning calorimetry (DSC) measurements and X-ray diffraction (XRD) measurements were also carried out . This paper should be considered as complementary to a previous article reporting the conductive behavior of theses glasses. In the latter we reported the obtained results on electrical conductivity studies. The results confirm the existence of a transition from a typically electronic (polaronic) conductive regimen when the molar fraction (X) of M_2O is equal to 0, to an ionic conductive regimen when X tends to 1. The evidence for the independent migration path for both electrons and ions was put into evidence by studying the electrical conductivity behavior in a complementary system of the form $X M_2O \cdot (1-X)[0.5V_2O_5–0.5MoO_3] \cdot 2TeO_2$. In this system vanadium was partially replaced by molybdenum which acts as a 'diluting' agent of the active centers involved in the electronic transport.

PACS: 72.80.N; 61.43.F

Keywords: X-ray diffraction; Conductivity; FTIR measurements; Tellurites; Calorimetry

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1. Introduction

In recent papers we reported our studies on the effect of metallic oxides on the electronic (polaronic) conductivity on vanadium tellurite glasses of the form $XM_2O \cdot (1-X)$-$V_2O_5 \cdot 2TeO_2$ (X being either Li or Ag) [1,2]. For these glasses the existence of a deep minimum in the isotherms of conductivity was verified. The explanation for this minimum was given assuming the existence of two kinds of independent migrating paths: one kind of path consisting of an electronic transfer in the chain V(IV)–V(V) and the other kind of path made by the regular position of non-bridging oxygens along the network-former chains allowing ion displacement. In a complementary paper, extra data supporting the first explanation were presented [3,4]. In that paper we studied the effect of changing the magnitude of only one type of conductivity (electronic) on the whole conductive behavior of the system, based on previous results on vanadium tellurite glasses given by Lebrun et al. [5]. Then , the electrical studies on the system of the form $XAg_2O \cdot (1-X)[0.5V_2O_5–0.5MoO_3] \cdot 2TeO_2$ allowed us to conclude that the deliberate 'dilution' of *only* the electronic conducting centers, by the replacement of vanadium

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0022-3093/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2007.06.032

by molybdenum ions, directly causes the diminution of *only* the electronic conductivity with a concomitant constancy on the ionic conductivity. This experimental result confirms the idea of the existence of two kinds of independent migrating paths: when adding the network modifier to the electronic V_2O_5–$2TeO_2$ glasses the electronic paths are progressively blocked causing the electronic conductivity to diminish. Consequently, the whole shape of the curves for isothermal conductivity can be seen as the intersection of two curves corresponding to electronic and ionic conductivities and the relative minimum corresponding to a change in the mechanism of the electrical transport process.

The present paper can then be considered as complementary of these previous articles, its main purpose being to report our new results on the structural aspects of the systems and to correlate these data with the reported electrical behavior. The experimental data mainly includes our results on FTIR spectroscopy and also complementary results on DSC and X-ray diffraction analysis.

2. Experimental

The samples were prepared following the experimental procedure given in a previous work [1]. The amorphous character of the resulting solids was tested by X-ray diffraction analysis and confirmed by the differential scanning calorimetry (DSC). In fact, the DSC thermograms showed the characteristic endothermic peak, which is associated to the temperature of transition (Tg).

The IR spectra of tellurite glasses and pure oxides, previously grounded to fine powders were registered as Nujol mulls on a Nicolet Nexus FTIR instrument, in the 2000–400 cm^{-1} range using KBr windows at room temperature. Differential Scanning calorimetry studies were performed using a Perking Elmer Pyris 1 instrument at a heating rate of 10°/min in the interval ranging from 100 to 400 °C, and the data were analyzed using the software included in the instrument. The X-ray powder diffraction was performed with the help of a Rigaku instrument using the Cu Kα radiation at room temperature.

For the sake of simplicity, in the future we will identify the different systems in a compact manner as follows:

Ag*X*: $X\mathrm{Ag_2O}(1-X)\mathrm{V_2O_5}\cdot 2\mathrm{TeO_2}$,

AgMo*X*: $X\mathrm{Ag_2O}(1-X)[0.5V_2\mathrm{O_5}\text{–}0.5\mathrm{MoO_3}]\cdot 2\mathrm{TeO_2}$,

Li*X*: $X\mathrm{Li_2O}(1-X)\mathrm{V_2O_5}\cdot 2\mathrm{TeO_2}$,

LiMo*X*: $X\mathrm{Li_2O}(1-X)[0.5\mathrm{V_2O_5}\text{–}0.5\mathrm{MoO_3}]\cdot 2\mathrm{TeO_2}$,

AgMo*Y*: $0.7\mathrm{Ag_2O}0.3[(1-Y)\mathrm{V_2O_5}\cdot Y\mathrm{MoO_3}].2\mathrm{TeO_2}$,

where Ag or Li indicates the presence of Ag_2O or Li_2O as a modifier oxide, respectively. When molybdenum is present 'Mo' is added to the denomination. The '*X*' indicates that the *varying* amounts are those corresponding to the modifier metallic oxide. The '*Y*' indicates that the *varying* amount corresponds to molybdenum oxide.

3. Results

3.1. IR spectra

For several decades the structures and properties of crystalline forms of TeO_2 and binary and ternary tellurite glasses have been investigated using the IR and Raman spectroscopic techniques as central or complementary tools (see [6,7]-and references cited therein). For these glasses, the complex spectra are dominated by the strong bands produced by vibrations of the TeO_4 or TeO_3 basic structural units and by the polyhedra of several modifiers like MoO_3 and V_2O_5 [6,8,9]. In Figs. 1–4, we present a selected portion of our FTIR spectra for the complete series of

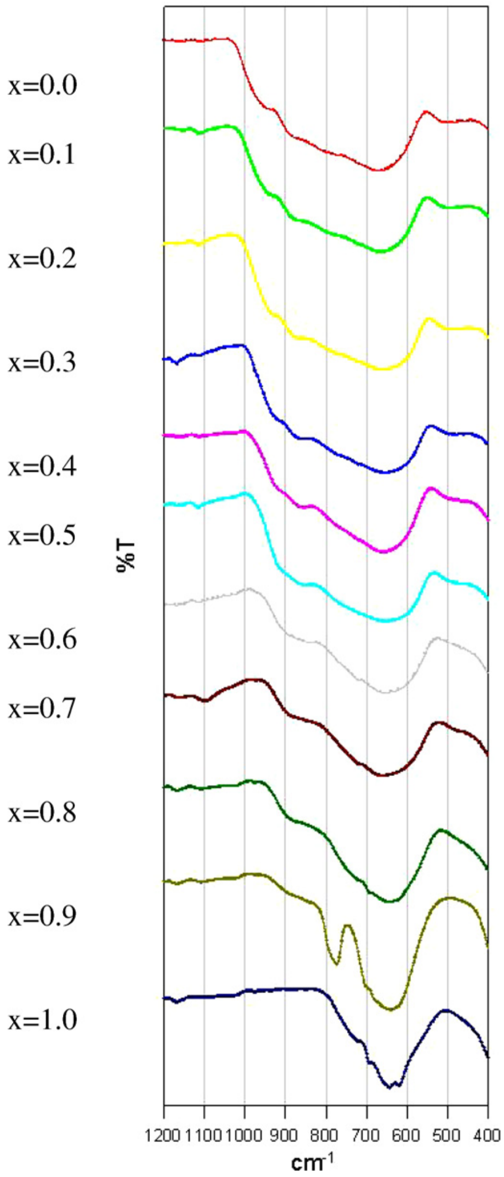

Fig. 1. IR spectra for $X\mathrm{Ag_2O}\cdot(1-X)[0.5\mathrm{V_2O_5}\text{–}0.5\mathrm{MoO_3}]\cdot 2\mathrm{TeO_2}$ systems.