

Physical properties of some rare earth tellurite glasses

A. A. BAHGAT, E. E. SHAISHA, A. I. SABRY

Department of Physics, Faculty of Science, Al-Azhar University, Nasr-City, Cairo, Egypt

Mossbauer and IR spectra as well as the electrical conductivity have been measured to give an idea about the structure and the electrical properties of some rare earth tellurite glasses containing Fe_2O_3 . The glasses denoted $[1 - (2x + 0.05)] \text{TeO}_2 \cdot x\text{Fe}_2\text{O}_3 \cdot (x + 0.05) \text{Ln}_2\text{O}_3$, where $x = 0.0$ and 0.05 and Ln = lanthanum, neodymium, samarium, europium or gadolinium, were prepared by fusing a mixture of their respective reagent grade oxides in a platinum crucible at 800°C for one hour. The Mossbauer parameters such as isomer shift, quadruple splitting and line width were found to be a function of the polarizing power (charge/radius) of the rare earth cations. The Mossbauer parameters were not affected by the heat treatment of the glass samples. Both of the Te-O-Ln and Te-O-Fe stretching vibrations were obtained from the IR results which indicate that the rare earth oxides and iron oxide are partially covalent. The electrical resistivity was measured as a function of temperature from 293 to 520 K. Both the electrical resistivity and the activation energy were found to be a function of the atomic number (Z) of the rare earth cations. The results were interpreted on the basis of the electronic structure of the glass.

1. Introduction

There have been a considerable number of publications dealing with the properties and the Mossbauer effect parameters of silicate, borosilicate, borate and phosphate glasses containing iron. However, only a few studies have been published on the binary tellurite glasses, e.g. TeO_2 - Fe_2O_3 [1-3], Li_2O - TeO_2 [4], La_2O_3 - TeO_2 [5], B_2O_3 - TeO_2 [6] and P_2O_5 - TeO_2 [7].

Generally, tellurite glasses are a relatively new type of non-crystalline material, where the main glass former (TeO_2) under normal conditions does not have the ability to go into the glassy state without a modifier. This behaviour is extremely important for the vitreous transition of the tellurite melt. There has been a considerable interest in the semiconducting glasses in which tellurium oxide is a glass forming factor [2, 8]. The importance of the study of electrical conductivity of tellurite glasses is based on the fact that conductivity of Fe_2O_3 - TeO_2 is several orders of magnitude greater than that of the equivalent Fe_2O_3 - B_2O_3 glasses [2]. This behaviour is attributed to the unshared pair of electrons in the TeO_4 group.

Previous infra-red studies [1, 2, 9] of these glasses show that the main bands between 550 and 850 cm^{-1} are due to the distribution of the TeO_4 polyhedron. This forms the framework and the basic oscillations of the building units in the tellurite glasses.

No previous studies have been found concerning the ternary glasses of TeO_2 - Fe_2O_3 - Ln_2O_3 system (Ln stands for rare earth elements). On the other hand, because of the technological importance of glasses containing rare earth ions, it is worthwhile to exploit

any experimental technique which yields information about their properties and structure.

In the present study, glass samples of the composition $[1 - (2x + 0.05)] \text{TeO}_2 \cdot x\text{Fe}_2\text{O}_3 \cdot (x + 0.05)\text{Ln}_2\text{O}_3$, where $x = 0.0$ and 0.05 and Ln = lanthanum, neodymium, samarium, europium or gadolinium were investigated using Mossbauer effect, IR and electrical conductivity measurements to study the effect of rare earth cations on the structure and properties of these glasses.

2. Experimental procedure

Two types of rare earth tellurite glasses have been studied in the present work. A binary system free of iron with the compositions $0.95 \text{TeO}_2 + 0.05 \text{Ln}_2\text{O}_3$, where Ln = lanthanum, neodymium, samarium, europium or gadolinium, and a ternary system containing a fixed amount of iron, according to the formula $0.85 \text{TeO}_2 + 0.1 \text{Ln}_2\text{O}_3 + 0.05\text{Fe}_2\text{O}_3$. Glasses were prepared by fusing a mixture of their respective reagent grade oxides in a platinum crucible at 800°C for one hour in an electric muffle furnace. The resulting glass was brittle in nature and had a reddish-brown colour. The glass sample of the composition $0.85 \text{TeO}_2 + 0.1 \text{La}_2\text{O}_3 + 0.05 \text{Fe}_2\text{O}_3$ was heat-treated at 400°C for 24 h. The amorphous state of the heat-treated and untreated samples was checked by the X-ray diffraction technique which confirmed the glassy state of all the glasses. Mossbauer effect (ME) measurements were carried out at room temperature by a constant acceleration driving system. The source used was ^{57}Co in rhodium. All the Mossbauer spectra were fitted to two Lorentzian lines of

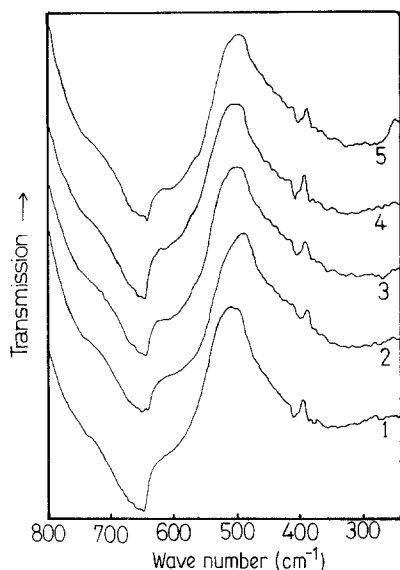


Figure 1 IR spectra of glasses of composition $0.95 \text{TeO}_2 \cdot 0.05 \text{Ln}_2\text{O}_3$, where Ln stands for 1, lanthanum; 2, neodymium; 3, samarium; 4, europium and 5, gadolinium.

different positions, width and amplitudes by computer calculations.

Infra-red measurements were carried out by a fully automatic IR-spectrophotometer (4250 Beckman). The d.c. conductivity measurements were made in the temperature range from room temperature up to 520 K, where the I-V characteristics were linear.

3. Results and discussion

The effect of the presence of some rare earth oxides in the tellurite glasses and their role on their properties and structure, will be classified into the following subheadings:

3.1. IR measurements

The IR spectra of $\text{Ln}_2\text{O}_3\text{-TeO}_2$ glasses are shown in Fig. 1, where all have the same characteristic bands. The shoulder at 765 cm^{-1} and the broad bands at 655 and 330 cm^{-1} are due to the distribution of the TeO_4

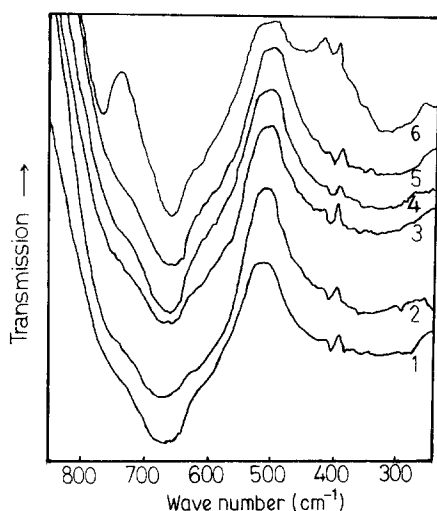


Figure 2 IR spectra of glasses of composition $0.85 \text{TeO}_2 \cdot 0.05 \text{Fe}_2\text{O}_3 \cdot 0.1 \text{Ln}_2\text{O}_3$, where Ln stands for 1, lanthanum; 2, neodymium; 3, samarium; 4, europium, 5, gadolinium and 6, $0.95 \text{TeO}_2 \cdot 0.05 \text{Fe}_2\text{O}_3$.

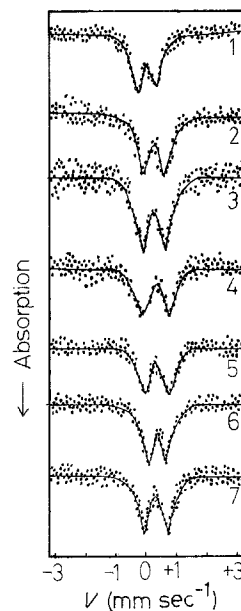


Figure 3 Mossbauer effect spectra for samples: 1, $0.95 \text{TeO}_2 \cdot 0.05 \text{Fe}_2\text{O}_3$; 2, $0.85 \text{TeO}_2 \cdot 0.1 \text{La}_2\text{O}_3 \cdot 0.05 \text{Fe}_2\text{O}_3$; 3, $0.85 \text{TeO}_2 \cdot 0.1 \text{La}_2\text{O}_3 \cdot 0.05 \text{Fe}_2\text{O}_3$ treated at 400°C for 24 h; 4, $0.85 \text{TeO}_2 \cdot 0.1 \text{Nd}_2\text{O}_3 \cdot 0.05 \text{Fe}_2\text{O}_3$; 5, $0.85 \text{TeO}_2 \cdot 0.1 \text{Sm}_2\text{O}_3 \cdot 0.05 \text{Fe}_2\text{O}_3$; 6, $0.85 \text{TeO}_2 \cdot 0.1 \text{Eu}_2\text{O}_3 \cdot 0.05 \text{Fe}_2\text{O}_3$, and 7, $0.85 \text{TeO}_2 \cdot 0.1 \text{Gd}_2\text{O}_3 \cdot 0.05 \text{Fe}_2\text{O}_3$.

tetrahedra [1, 10]. Another shoulder appeared around 575 cm^{-1} and is attributed to O-Ln stretching vibrations [10]; this means that a fraction of the rare earth was incorporated in the network of these glasses and acts as a network intermediate. The IR spectra of the $0.85 \text{TeO}_2 + 0.1 \text{Ln}_2\text{O}_3 + 0.05 \text{Fe}_2\text{O}_3$ are shown in Fig. 2, and are similar and show the same shoulder and broad bands at 765 , 655 and 330 cm^{-1} . Moreover, a shoulder appeared at 470 cm^{-1} and could be attributed to the formation of O-Fe stretching vibration, [1, 3, 9] i.e. there is a fraction of iron ions which is incorporated in the network of these glasses. Therefore, Fe_2O_3 and Ln_2O_3 are partially incorporated covalently and act as glass intermediate. Comparing the IR spectra shown in Figs 1 and 2, one can observe that the introduction of Fe_2O_3 to the $\text{TeO}_2\text{-Ln}_2\text{O}_3$ glasses has greatly increased the broadening of the absorption bands: this is due to the simultaneous existence of Ln_2O_3 and Fe_2O_3 which greatly increases the distribution of different polyhedra in the glass network.

3.2. Mossbauer effect measurements

The Mossbauer effect spectra of the $0.85 \text{TeO}_2 \cdot 0.1 \text{Ln}_2\text{O}_3 \cdot 0.05 \text{Fe}_2\text{O}_3$ glasses are shown in Fig. 3, including the spectrum of the heat treated glass sample with Ln = Lanthanum. The Mossbauer spectra consist of simple paramagnetic doublets caused by Fe^{3+} ions mostly of tetrahedral symmetry [11]. Mossbauer parameters such as isomer shift (IS), quadruple splitting (QS) and line width (LW) are plotted as a function of the polarizing power (charge/atomic radius) of rare earth cations and are shown in Fig. 4. The results are given in Table I. The solid straight lines in Fig. 4 are least squares fits to the data.

The IS is found to increase with increasing polarizing power. This is because the rare earth ions on the

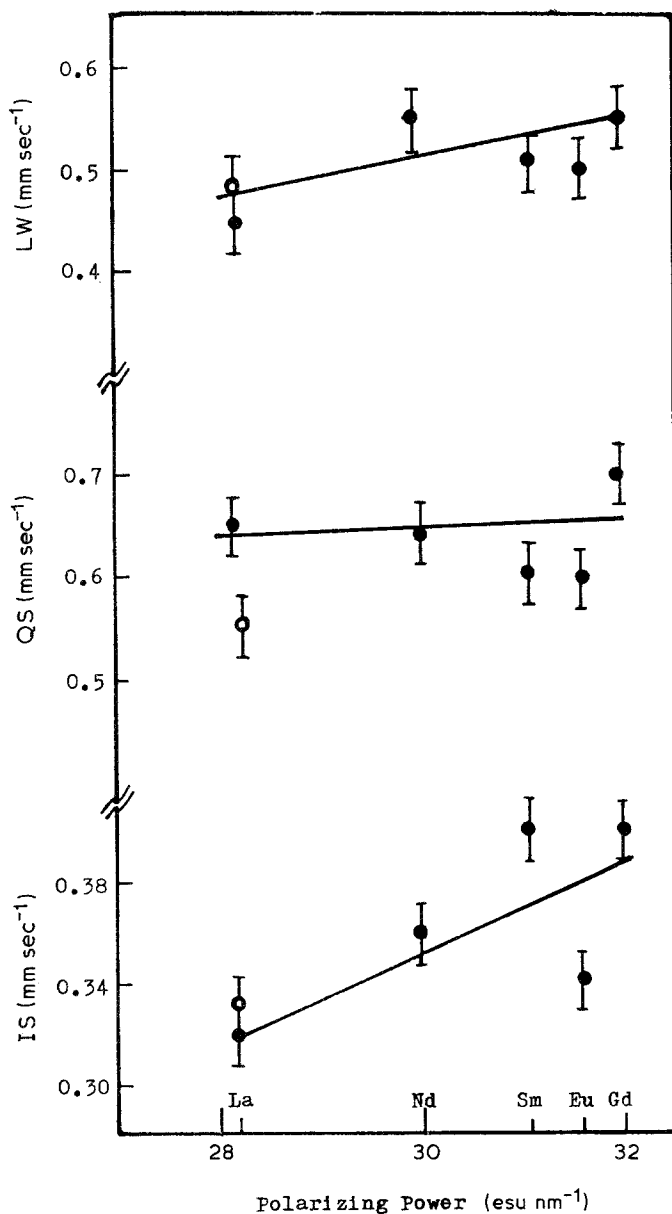


Figure 4 Mossbauer effect parameters of the quadruple doublet of Fe^{3+} ions against polarizing power of the cations of the rare earth oxides in the glasses. ●, Untreated; ○, treated at 400°C for 24 h.

average polarize the valence electrons in the hybrid orbit of the Fe^{3+} cations. This leads to a decrease in the effective 4s-electronic charge density at the iron nuclei. Moreover, this indicates also that the density of the 4s-electrons at the ^{57}Fe nucleus in Gd-Te glasses is smaller than that in the other glasses of this group. Such a decrease in the 4s-electron charge density leads to a decrease in the covalency of the Fe-bond on going from lanthanum to gadolinium as nearest neighbours.

On the other hand, the QS is found to be almost

constant with increasing the polarizing power of the rare earth cations. This is because these cations polarize the valence electrons in the non-symmetrical orbits such as the 3d and 4p, which affect the electronic part of the electric field gradient (EFG) tensor by an equal amount. On the other hand, the lattice contribution to the EFG should have an insignificant effect, because all the rare earth cations have almost the same atomic weight and volume.

However, an increase in the values of LW is also detected. This is attributed to the increase of the

TABLE I Room temperature Mossbauer effect parameters in the glass system $\text{TeO}_2 \cdot \text{Fe}_2\text{O}_3 \cdot \text{Ln}_2\text{O}_3$

Composition (mol %)	Polarizing power (esu nm ⁻¹)	IS (mm sec ⁻¹)	QS (mm sec ⁻¹)	LW (mm sec ⁻¹)
95 TeO ₂ 5Fe ₂ O ₃	—	0.39	0.60	0.51
85 TeO ₂ 10 La ₂ O ₃ 5Fe ₂ O ₃	28.2	0.32	0.65	0.45
85 TeO ₂ 10 La ₂ O ₃ 5Fe ₂ O ₃ treated at 400°C for 24 h	—	0.33	0.55	0.48
85 TeO ₂ 10 Nd ₂ O ₃ 5Fe ₂ O ₃	30.15	0.36	0.64	0.57
85 TeO ₂ 10 Sm ₂ O ₃ 5Fe ₂ O ₃	31.1	0.40	0.60	0.51
85 TeO ₂ 10 Eu ₂ O ₃ 5Fe ₂ O ₃	31.58	0.34	0.60	0.45
85 TeO ₂ 10 Gd ₂ O ₃ 5Fe ₂ O ₃	31.98	0.40 ± 0.03	0.70 ± 0.03	0.55 ± 0.03

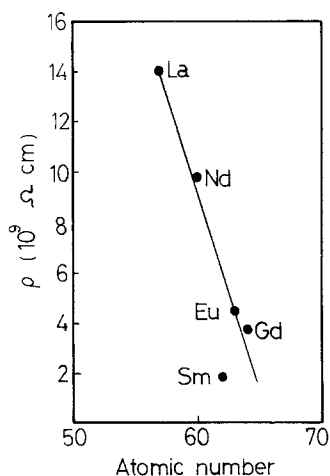


Figure 5 Room temperature resistivity against the atomic number of the rare earth atoms in the glasses.

distribution of IS and QS on going from lanthanum to gadolinium.

The Mossbauer effect parameters of the heat treated glass sample of the composition $0.85 \text{TeO}_2 \cdot 0.1 \text{La}_2\text{O}_3 \cdot 0.05 \text{Fe}_2\text{O}_3$ are marked on Fig. 4. The results show an insignificant change in the values of IS and LW, contrary to the reported results for the glasses of the system $\text{Fe}_2\text{O}_3\text{--TeO}_2$ [3], which show a susceptibility to crystallization. Consequently, one may say that the rare earth ions act as “crystallization inhibitors” in the studied glasses. On the other hand, a detectable decrease on the value of QS after heat treatment was found. This indicates the formation of a more closed glass structure with higher degree of symmetry. Such an observation may refer also to the formation of more octahedral sites of iron after heat treatment has taken place [12].

3.3. Electrical conductivity measurements

The electrical resistivity ρ of the glasses $0.5 \text{Fe}_2\text{O}_3 \cdot 0.95 \text{TeO}_2$ and $0.85 \text{TeO}_2 \cdot 0.1 \text{Ln}_2\text{O}_3 \cdot 0.05 \text{Fe}_2\text{O}_3$ were measured as a function of temperature from 293 up to 523 K. The results show an increase in the electrical conduction of the glasses with an increase in temperature, and on introducing rare earth oxides to the glass, a large decrease in resistivity is detected (see Table II). The resistivity at room temperature of the glass system ($0.85 \text{TeO}_2 \cdot 0.1 \text{Ln}_2\text{O}_3 \cdot 0.05 \text{Fe}_2\text{O}_3$) is plotted as a function of the atomic number of the rare earth cations (see Fig. 5), indicating that the resistivity increases with increasing the atomic number of the rare earth cations.

On the other hand, the activation energies of the

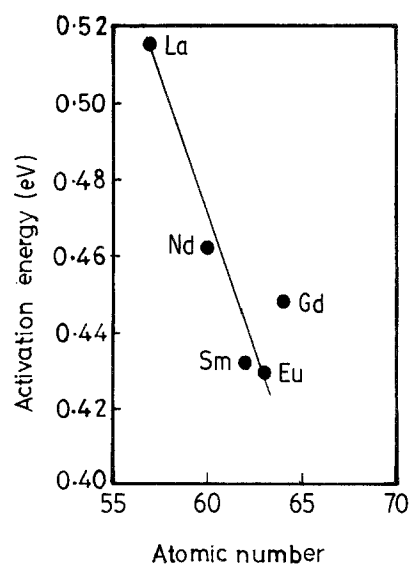


Figure 6 The relation between the activation energy and the atomic number of the rare earth atoms in the glasses.

rare earth tellurite glasses were calculated and plotted against the atomic number of the rare earth cations as shown in Fig. 6. The results show that the activation energy decreases with an increase in the atomic number and falls in the range from 0.4 to 0.6 eV. Accordingly, we may say that the electrical conduction process is carried out by electrons in these new tellurite glasses, where with an increase in the number of conduction electrons, the activation energy decreases and the conductivity increases.

On the other hand, the results of previous investigations [13, 14] concerning the electrical conductivity of oxide glasses containing transition metal ions (iron) revealed that bulk electrical conduction occurs predominantly by electrons and holes, if movable ions are absent or their mobility is suppressed by strongly bound ions of higher charge. The carriers are localized at the transition metal ions, i.e. the latter have to exist in more than one valence state. Conduction can take place by the transfer of electrons from low to high valence states, so the electrical conductivity depends on the concentration of ions in the lower valence state, as well as on the total content of transition metal ions. However, in the present case the obtained spectra of the glasses enable us to reconsider the mechanism of conductivity in these tellurite glasses, where the small or zero concentration of Fe^{2+} ions seems to exclude the possibility of conductivity resulting from electron hopping between Fe^{2+} and Fe^{3+} ions.

TABLE II Room temperature resistivity (ohm cm) and activation energy for the glasses in the system $\text{TeO}_2 \cdot \text{Fe}_2\text{O}_3 \cdot \text{Ln}_2\text{O}_3$ (see [2])

Composition (mol %)	Resistivity (ohm cm)	Activation energy (eV)
95 TeO_2	56×10^9	0.70
85 TeO_2 10 La_2O_3	14.1×10^9	0.51
85 TeO_2 10 Nd_2O_3	9.7×10^9	0.46
85 TeO_2 10 Sm_2O_3	1.7×10^9	0.43
85 TeO_2 10 Eu_2O_3	4.8×10^9	0.42
85 TeO_2 10 Gd_2O_3	3.6×10^9	0.45
85 TeO_2 10 Eu_2O_3 treated at 400°C for 18 h	1.9×10^{11}	0.59

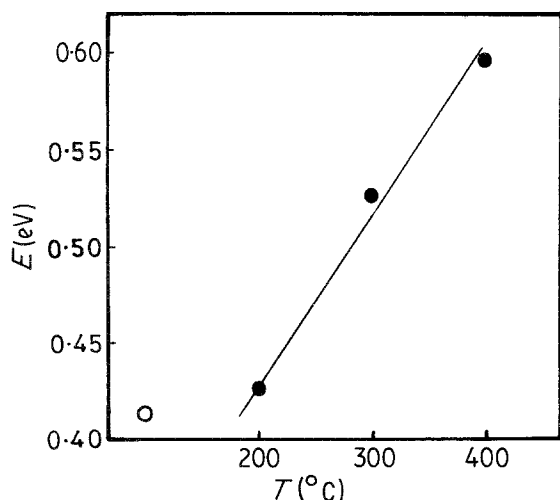


Figure 7 The effect of heat treatment temperature for a constant period of 18 h on the activation energy of the glass $0.85\text{TeO}_2 \cdot 0.1\text{Eu}_2\text{O}_3 \cdot 0.05\text{Fe}_2\text{O}_3$. ○, Untreated; ●, treated.

However, the absence of Fe^{2+} in these glasses does not exclude the possibility of $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ electron hopping. If it does exist, the ME measurements could not detect it, only line width broadening may result. This may be due to the electron hopping relaxation time being much shorter than the life time of the excited state of ^{57}Fe (10^{-8} sec).

Therefore the tellurium network must play the decisive role in electrical conductivity, due to the free electron pair of the tellurium atom. Moreover, the existence of Fe–O and Ln–O in the network of TeO_4 -polyhedra has led to the formation of new bonds, and new unshared electrons pairs are created [1].

The effect of heat treatment at 200, 300 and 400°C for 18 h on the resistivity of the glass sample, $0.85\text{TeO}_2 \cdot 0.1\text{Eu}_2\text{O}_3 \cdot 0.05\text{Fe}_2\text{O}_3$, was also studied. The observed increase in the activation energy on increasing the treatment temperature could be attributed to the formation of a more ordered glass phase with a more closed structure, as predicted from the Mossbauer effect data of QS. The movement of the conduction electrons through the network is resisted, and consequently the activation energy value increased with increasing the temperature of the treatment, as shown in Fig. 7.

4. Conclusion

On the basis of the results obtained above, it can be concluded that both of the Ln_2O_3 and Fe_2O_3 are partially covalent and act as a glass intermediate. The values of the Mossbauer parameters do not change after heat treatment of the glass samples which indicate that the rare earth oxides act in this glass system as “crystallization inhibitors”. The Mossbauer parameters increase as the polarizing power of the rare earth cations increases. Moreover, the introduction of the rare earth cations enhances the glassy state in the tellurite glass system. On the other hand, the electrical conduction process is carried out by electrons in these new tellurite glasses, where with an increase in the number of conduction electrons, the activation energy decreases and the conductivity increases.

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