EFFECTS OF TEMPERATURE AND FREQUENCY CHANGES ON THE DIELECTRIC PROPERTIES OF MODIFIED CHALCOGENIDES

M.M. ABOU SEKKINA *

Chemistry Department, Faculty of Science, Tanta University, Tanta (Egypt)

(Received 24 March 1987)

ABSTRACT

Antimony oxide (Sb_2O_3), antimony sulphide (Sb_2S_3) and antimony selenide (Sb_2Se_3) were prepared from high purity materials. Mixes of (I) Sb_2O_3 (25%) + Sb_2S_3 (75%) and (II) Sb_2S_3 (25%) + Sb_2Se_3 (75%) were prepared by mechanical mixing of the two components. Cylindrical blocks of the compressed powder were formed at a saturated pressure of 200 kg/cm^{-2}.

The dielectric constant, ϵ', a.c. electrical resistance, R_x, and dielectric loss, ϵ'', were determined in the frequency range 0.2–10 MHz and in the temperature range 30–100 °C.

The frequency dependence of the dielectric loss of each sample demonstrates the ohmic nature of the loss. Further discussion is put forward on the basis of the interaction of the dielectric dipoles of the two components of the mix and the partial ionic nature of the bond for the materials investigated.

INTRODUCTION

Theoretical efforts have been expended in connection with the dielectric constant of a mixture of two materials, for instance particles of one material suspended in the matrix of the other.

Kocharli and Imanov [1] studied the temperature and frequency dependence of the dielectric constant and the tangent of the angle of the dielectric loss for various mixes of antimony trisulphide and antimony triselenide only. The dielectric properties of antimony trioxide, antimony trisulphide and antimony triselenide have been studied individually by various authors [2–4].

The aim of the present investigation is to obtain a highly dielectric semiconducting material and to monitor the temperature and frequency dependence of its dielectric constant and loss. The materials involved were freshly prepared at a high purity.

---

* Present Address: Chemistry Department, Faculty of Science, The United Arab Emirates University, Al-Ain, P.O. Box 15551, U.A.E.

EXPERIMENTAL

Material preparation

Antimony trioxide, antimony trisulphide and antimony triselenide were prepared as polycrystals. The wet method was used for the preparation of antimony trioxide. This involves the hydrolysis of antimony trichloride with hot water followed by treatment of the precipitate with sodium carbonate. The orthorhombic form obtained was purified from traces of the cubic form by heat treatment for twelve hours at $590\,^{\circ}$ C [5]. This was followed with a careful course of X-ray diffraction measurements using a Berthold-type diffractometer to ensure the correct preparation and the existence of only one crystalline phase, the orthorhombic.

Antimony trisulphide was prepared after Fricke and Donges [6] with little modification.

Antimony triselenide was prepared by the dry method which is very similar to that given by previous authors [7,8] followed by a master alloying technique (neutralization of the excess component) to attain an exact and correct stoichiometric compound as proved by measurements of the X-ray diffraction pattern of the final product obtained.

Each two component system was mechanically mixed. The two mixes were:

(I) Sb_2O_3 (25%) + Sb_2Se_3 (75%)

(II) Sb_2S_3 (25%) + Sb_2Se_3 (75%)
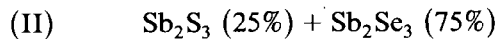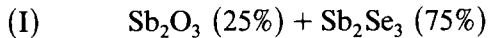
Each mix was then ground and passed through 200 mesh sieve.

The powdered material was then dry compressed in the form of disks using a stainless steel mould 5.9 cm. in diameter and kept in a vaccum desiccator. This was performed at a suitable saturated pressure of 200 kg cm^{-2} to fit the experimental requirements for dielectric measurements.

Dielectric measurements

The MFM 5T-type measuring cell with micrometer electrode for solids was used in this investigation. The specimen plate was of constant thickness (1–10 mm) and its surface was absolutely plane and parallel.

The readings were taken three times for each temperature equilibration of the cell with the test sample.

To determine the dielectric constant, ϵ', a recent calibration curve was established. The curve represents values of the scale readings (SR) in μV. against sample thickness for a series of standard plates. From this curve values of the dielectric constant were obtained by placing the plexiglass arm of the calibration diagram so that the pointer line intersects the curve of the sample thickness. The perpendicular of the abscissa corresponding to the

measuring instrument scale reading then crosses the pointer line at the level of the corresponding value ΔC on the ordinate.

The dielectric loss, ϵ'', is calculated from the dielectric constant, ϵ', resistance R_x, capacitance ΔC of the sample obtained and the frequency f (MHz) at which measurements were taken

$$\epsilon'' = \frac{\epsilon'}{2\pi f(R_x \Delta C)}$$

where ΔC = scale reading (SR) $\times$ 0.0112 $-$ 2.4 and π is taken as 3.14 or 22/7. ϵ' is the previously obtained dielectric constant. The a.c. resistance, R_x, was also measured on the same samples under the same variable frequency and temperature.

In this investigation, the measurements were performed in the frequency range 0.2–10 MHz and the temperature range 30–100°C on waiting 15 min after each temperature equilibration.

RESULTS AND DISCUSSION

The values of the dielectric constant obtained for the various specimens are listed in Table 1. From this table, it is clear that values of the dielectric constant of the pure antimony trioxide prepared (12.5) and of the antimony trisulphide (11.5) are in good agreement with those given by previous authors [2,3]. However, there is a considerable increase in the values obtained for the two modified specimens. Accordingly, the two mixes possess a high dielectric efficiency.

In contrast to the behaviour of the temperature dependence of the dielectric constant of pure antimony trioxide [9] there is a noticeable increase in the value of dielectric constant ϵ' with increasing temperature (Figs. 1 and 2). This may be attributed to the increase in mobility of polar groups and hence the development of more polarization at elevated temperature [10,11] which may take place as a result of the occurrence of a dispersed phase of increased conductivity (Sb_2Se_3) in a solid matrix [12], a phenomenon which takes place to a greater extent in the case of mix (II). This may be

TABLE 1

The values of the dielectric constant obtained for the various materials

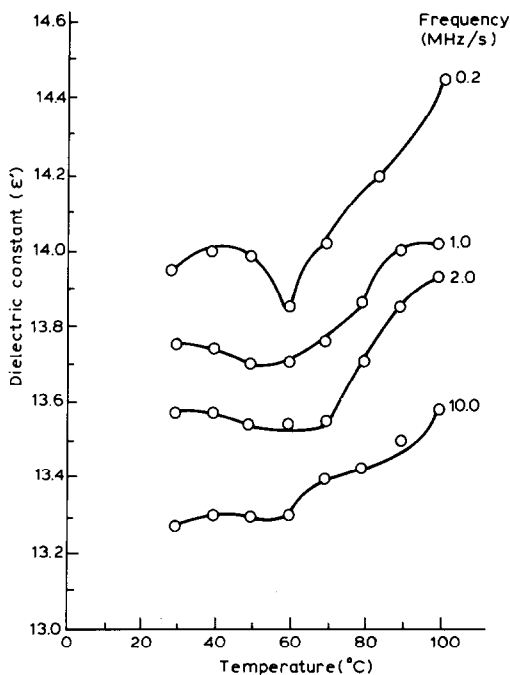| Antimony trioxide (Sb_2O_3)	Modified mix (I) (25% Sb_2O_3 + 75% Sb_2Se_3)	Antimony trisulphide (Sb_2S_3)	Modified mix (II) (25% Sb_2S_3 + 75% Sb_2Se_3)
12.50	14.20	11.20	18.40

Fig. 1. The temperature dependence of the dielectric constant of system (I): Sb_2O_3 (25%) + Sb_2Se_3 (75%).

attributed to the greater polarization as a result of the greater partial ionicity of the bond and/or the existence of excess sulphur in the case of mix (II).

From the results in Figs. 3 and 4, it can easily be seen that the dielectric constant increases markedly with a decrease in frequency in the region below 3 MHz, for the two modified specimens.

In this study, modified mix (I) consists of 25% Sb_2O_3 and 75% Sb_2Se_3 whereas modified mix (II) contains 25% Sb_2S_3 and 75% Sb_2Se_3. It is of interest to notice that within the same specimen the frequency dependent character of the dielectric constant increases with increasing temperature. This dependence is pronounced for mix (II). This is evidence of greater polarization existing in mix (II) than in mix (I). Thus, this may result in a high dielectric constant and temperature dependent character.

The sharp increase in the dielectric loss at low frequency (Figs. 5 and 6) is attributed to d.c. conductivity and is not connected with a dipole relaxation process. This criterion is more pronounced in mix (II) than in mix (I). Therefore, the dielectric loss must be considered as proportional to the total measured a.c. electrical conductivity minus the d.c. conductivity.

From Figs. 7 and 8 it is clear that the effect of temperature on dielectric loss ϵ' is almost equivalent to frequency. The position of the maxima of the curves and their attendant minima are different for the two mixes under the
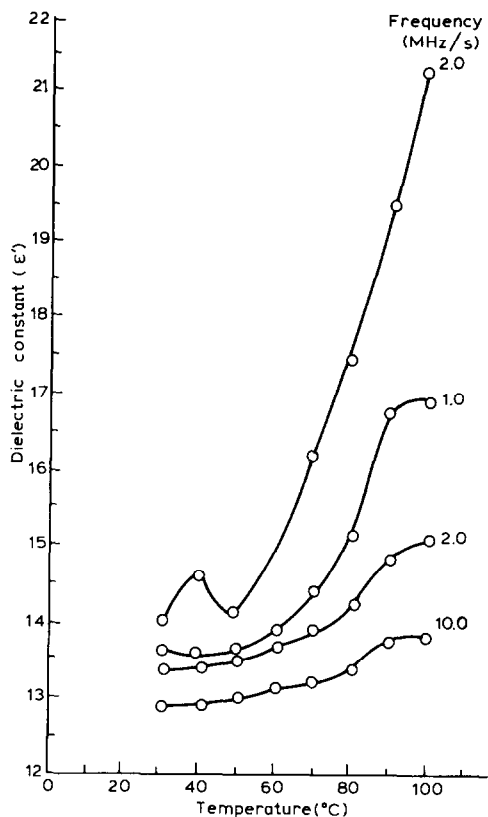
Fig. 2. The temperature dependence of the dielectric constant of system (II): Sb_2S_3 (25%) + Sb_2Se_3 (75%).
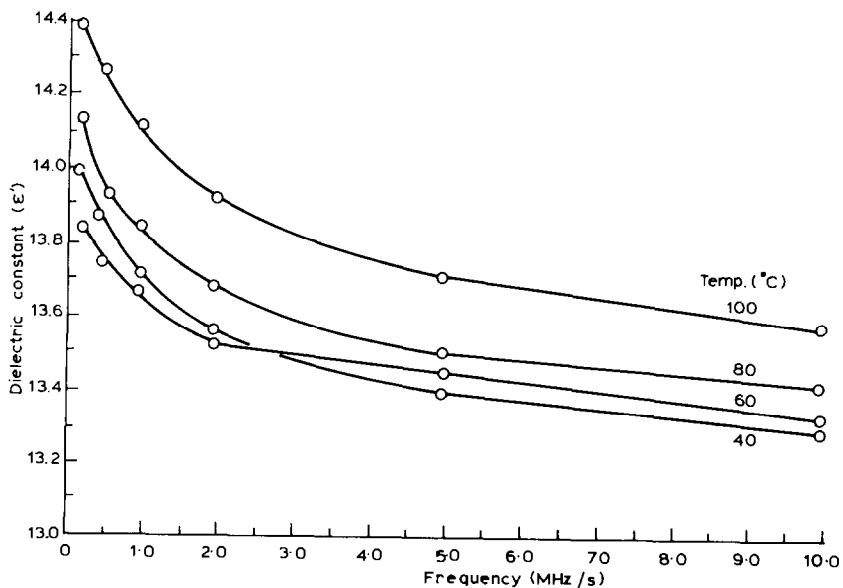

Fig. 3. The frequency dependence of the dielectric constant of system (I): Sb_2O_3 (25%) + Sb_2Se_3 (75%).
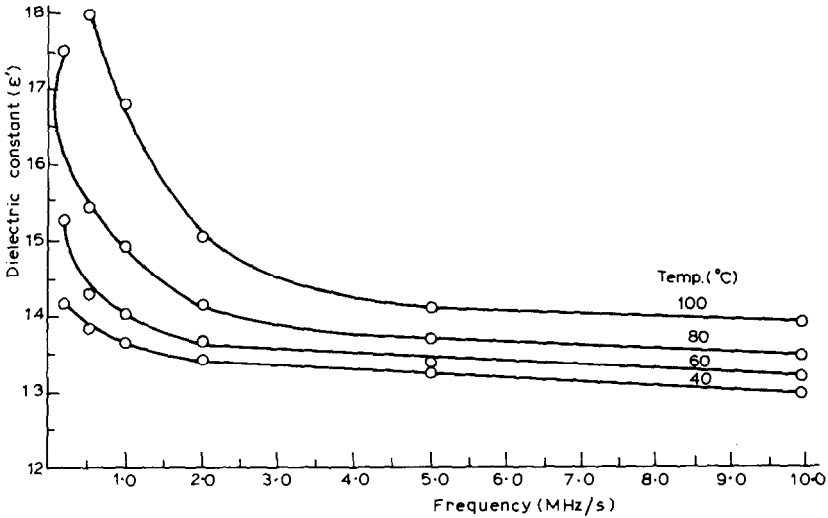
Fig. 4. The frequency dependence of the dielectric constant of the system (II): Sb_2S_3 (25%) + Sb_2Se_3 (75%).

same conditions. This may be attributed to the contribution of structure difference and/or differences in lattice imperfections for the two mixes. Lattice imperfections are caused by one component of the mix being dispersed in the other. In agreement with the results of Kocharli and Imanov [1] the frequency dependence of the dielectric loss explains the ohmic nature of the loss.
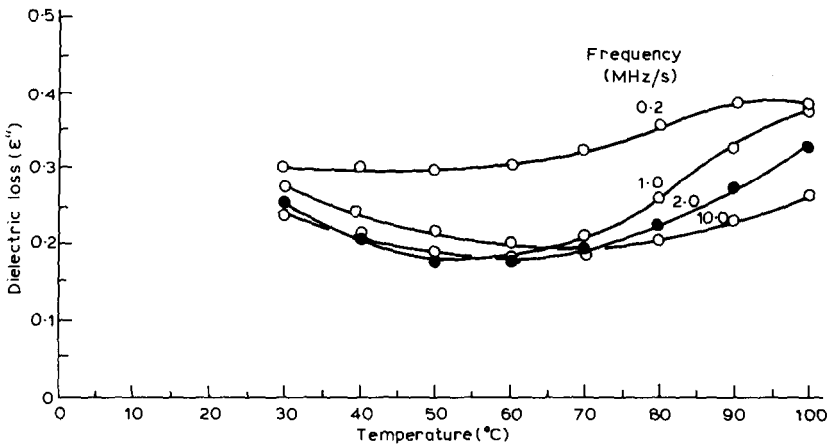

Fig. 5. The temperature dependence of the dielectric loss of the system (I): Sb_2O_3 (25%) + Sb_2Se_3 (75%).
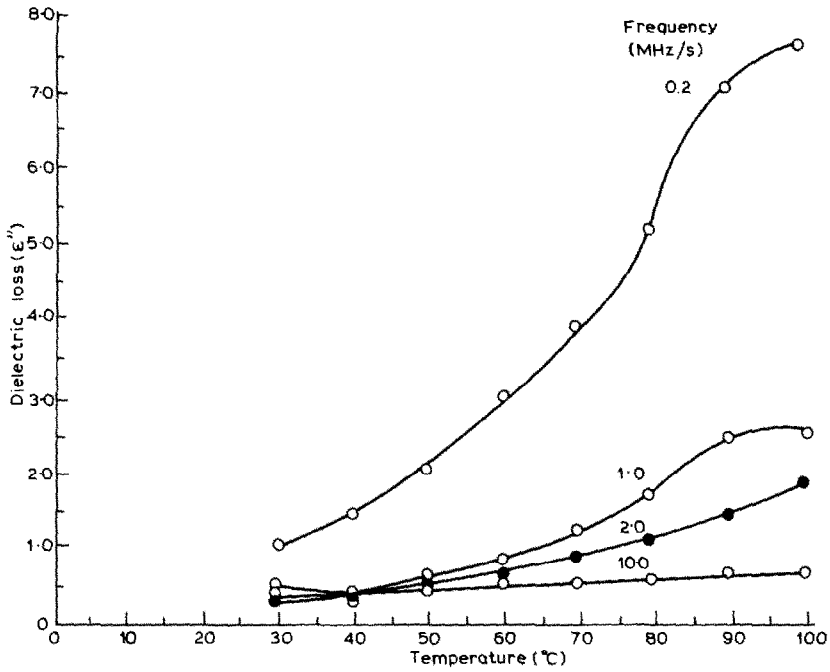
Fig. 6. The temperature dependence of the dielectric loss of the system (II): Sb_2S_3 (25%) + Sb_2Se_3 (75%).
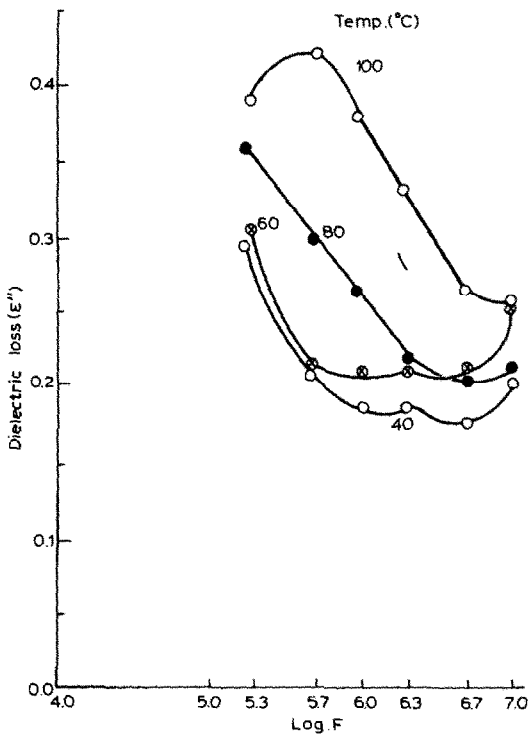

Fig. 7. The frequency dependence of dielectric loss for the system (I): Sb_2O_3 (25%) + Sb_2Se_3 (75%).
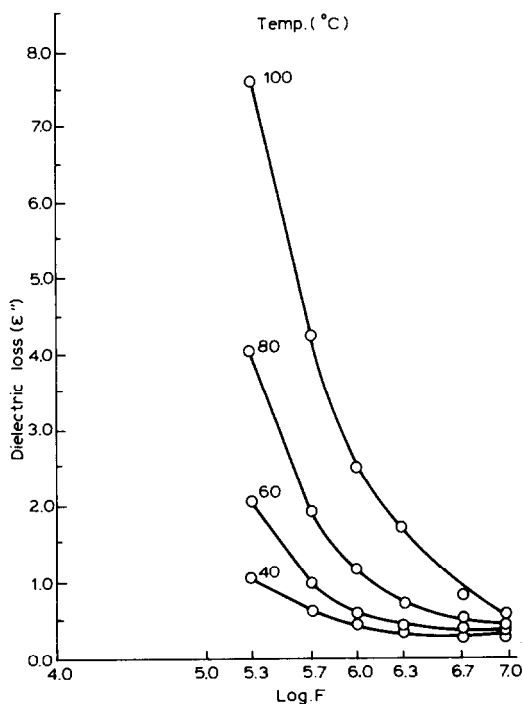
Fig. 8. The frequency dependence of dielectric loss for the system (II): Sb_2S_3 (25%) + Sb_2Se_3 (75%).

CONCLUSION

Finally, the following conclusions are drawn.

(1) There is good agreement between our results and those given by the previous authors: values of 12.5 and 11.20 for the dielectric constants of antomony trioxide and antimony trisulphide respectively.

(2) The two-component systems exhibit a higher dielectric efficiency than the pure one-component material.

(3) The observed frequency dependence of the dielectric loss for each mix explains the ohmic nature of the loss.

(4) The sudden increase in the values of the dielectric constant with decreasing frequency in the range of 0.2–5.0 MHz could be correlated with space-charge polarization.

(5) The sudden increase in dielectric loss at relatively low frequency as a function of temperature is caused by d.c. conductivity.

(6) These foundations occurred pronouncedly for mix II indicating that its dielectric loss falls close to zero at increased frequencies of up to 10.0 MHz. Therefore, mix II constitutes a modified quality for attaining semiconductor dielectrics, although it contains the same proportion of Sb_2Se_3 as that for mix I.

REFERENCES

1 K.Sh. Kocharli and L.M. Imanov, Uch, Zap. Azerb. Gos. Univ. Ser. Fiz. Mat. Khim. Nauk., 6 (1961) 49.
2 A. Guntherschulze, A. and F. Meller, Z. Phys., 75 (1932) 78.
3 J.L. Rosenholtz and D.T. Smith, Am. Mineral., 21 (1936) 115.
4 G.P. Zharikov and, S.M. Kirova, Uch. Zap. Azerb Gos. Univ. Ser. Fiz. Mat. Khim.. Nauk., 3 (1960) 75.
5 J. Roberts and F. Fenwick, J. Am. Chem. Soc., 50 (1928) 2133.
6 R. Frickes and E. Donges, Z. Anorg. Allgem. Chem., 250 (1942) 202.
7 J. Black, E.M. Conwell and C.W. Spencer, J. Phys. Chem. Solids, 2 (1957) 240.
8 N.W. Tideswell, F.H. Kruse and J.D. McCullough, Acta Crystallogr., 10 (1957) 99.
9 M.M. Abou Sekkina, Tech. Sci. Ser., (1957) 66.
10 C.J.F. Böttcher, Theory of Dielectric Polarization, Elsevier, Amsterdam 1952.
11 O. Fuchs and K.L. Wolk, Dielectrische Polarization und Jahr der Chemischen Physik, Teil 6 Leipzig, 1935.
12 K. Wagner, Ark. Electrotech., 2 (37) (1914); Electrotech. Z., 36 (1915) 111, 121, 135, 163.