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FURTHER INVESTIGATIONS ON THE EFFECTS OF TEMPERATURE, FREQUENCY AND PHASE CONSTITUTION ON THE DIELECTRIC PROPERTIES OF ANTIMONY TRIOXIDE SPECIMENS

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In the present manuscript, freshly prepared and also pure chemical grade (BDH) antimony trioxide specimens were investigated. Numerous measurements were carried out on these specimens, comprising chemical, spectral and X-ray analyses, pycnometric and X-ray density measurements and observations of the behaviour of the dielectric constant and dielectric loss factor (ϵ' and ϵ'') as functions of temperature and frequency. The results obtained gave values of 12.4 and 10 for the dielectric constant for the freshly prepared and commercial antimony trioxide specimens, respectively. The results were compared in correlation with the phase constitution and degree of compactness for both specimens. Finally, the data are discussed on the basis of the interactions of the field frequency and temperature with the electric dipoles and electronic polarization of the test specimens.

The physico-chemical properties of antimony trioxide have been studied previously by the present author [1, 2]. The dependence of the dielectric properties of this substance on the mode of preparation and the crystal structure was the major goal of this and previous investigations [3–5]. Very few authors have investigated the dielectric constant of Sb_2O_3. Thus, in 1932 Guentherschulze and Keller [3] gave a value of 12.8 for the dielectric constant of antimony trioxide polycrystals. They noted that the breakdown of the film is associated with shock ionization of impurities. As regards the crystal structure, antimony trioxide exists in a cubic and an orthorhombic modification, depending on the method of preparation [5].

As far as the author is aware, no work concerning the dependence of the dielectric properties of antimony trioxide on the crystalline modifications is to be found in the literature. Accordingly, it is worth-while to examine this problem.

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Experimental

Material synthesis and specimen preparation

A wet method very similar to that of Roberts and Fenwick [5] was applied for the preparation of pure antimony trioxide. The product was heat-treated at 590° for 15 hr in order to obtain pure orthorhombic antimony trioxide, as proved by X-ray measurements.

Another pure chemical sample was supplied by Johnson–Matthey (London), which was found (via X-ray measurements) to be a mixture of 30% cubic and 70% orthorhombic antimony trioxide.

The different specimens were finely ground and mesh-sieved to have nearly the same average grain size ($\simeq$ 200 mesh sieve), as the dielectric properties are highly dependent on the average grain size of the test specimen.

The resulting ground material was compressed in the form of cylindrical discs without binder, by using a stainless steel mould 59 mm in diameter, to produce a sample thickness of 0.2–0.4 mm. This was done under a suitable pressure of 200 kg/cm^2, which was chosen after many trials to give as compact specimens as possible.

X-ray diffraction measurements

A Cu–K_α X-ray diffraction study was undertaken for each specimen with a Philips X-ray diffractometer at room temperature.

Dielectric constant (ϵ') and dielectric loss (ϵ'') measurements

A DK06 Multi-Dekameter MFM5T measuring cell with micrometer electrodes for solids was used in the present investigation. The cell is suitable for plates of various thickness, with a diameter of 59 mm, or a strip of about 59 mm width. A fresh calibration curve for the cell was frequently constructed. This curve depicts values of scale readings against the sample thickness of a series of standard plates with well-known dielectric constant (ϵ'). The cell is connected to the measuring instrument. The sample plate was smoothly pushed through the slit into the cell. The readings were taken twice after 15 minutes for each temperature equilibration of the cell with the specimen. Values of ϵ' could be obtained from the above calibration curve by balancing at the corresponding sample thickness.

The dielectric loss factor (ϵ'') could thus be calculated from ϵ', the resistance (R_x), the constant ΔC and the frequency F (Mc/s):

$$\epsilon'' = \frac{\epsilon'}{2\pi F R_x \Delta C}$$

where C = the capacitance of the specimen.

The accuracy of the apparatus for ϵ' is ± 0.03–0.5% and that for ϵ'' ± 3–5%. In this investigation, the measurements were undertaken in the frequency range from 0.2 to 10 MC/s and in the temperature range from 30° up to 100° for both specimens.

X-ray and pycnometric density measurements

The true density of the different antimony trioxide specimens was measured pycnometrically at 30° with *n*-hexane as the immersing fluid.

The X-ray true density (ϱ_x) was calculated via the well-known equation

$$\varrho = \frac{1.6604 \times M \times n}{V} \text{ g/cm}^3$$

where ϱ = true density,
M = molecular weight,
n = number of molecules per unit cell,
V = volume of unit cell in Å^3.

Results and discussion

Figure 1A shows the X-ray diffraction pattern of the freshly prepared antimony trioxide specimen. Analysis and comparison of the data with the A.S.T.M. cards

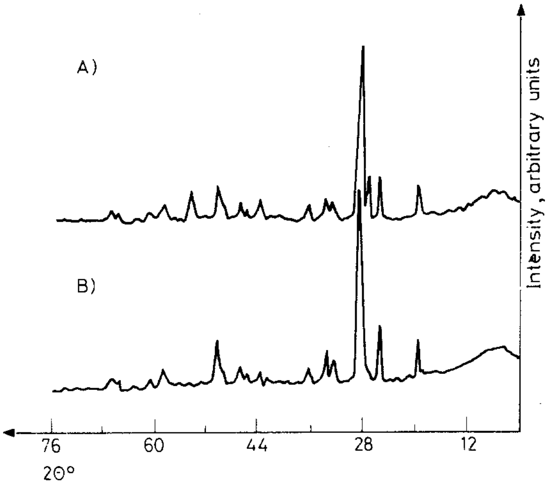

Fig. 1 The Cu–K$_\alpha$ X-ray diffraction patterns of: A) Antimony trioxide (supplied specimen), B) Antimony trioxide (freshly prepared specimen)

indicate that the material possesses a pure orthorhombic crystal form. On the other hand, the X-ray diffraction pattern of the commercial specimen (Fig. 1B) showed that the material consists of a mixture of cubic (30%) and orthorhombic (70%) crystal forms.

From the results on the dielectric properties, the absolute dielectric constant of the prepared orthorhombic antimony trioxide was found to be 12.4 at room temperature (22°). This value is in agreement with that obtained by previous authors [3]. On the other hand, the value of the absolute dielectric constant for the commercial sample, which is a mixture of the cubic and orthorhombic crystal forms, was found to be 10.0. Thus, the difference in the values may be due to the difference in structure and/or impurity content, as found by Zharikov [6] for other materials. Thus, the close packed arrangement (high density) of the prepared sample with the purely orthorhombic structure results in a high density and dielectric constant for the freshly prepared specimen (see Fig. 1 and Table 1).

Table 1 Room-temperature absolute pycnometric and X-ray densities of the different antimony trioxide specimens

Crystal form	Pycnometric density, g/cm^3	X-ray calculated density, g/cm^3
Orthorhombic antimony trioxide (prepared)	5.78	5.80
(Orth. + cubic)Sb_2O_3 (commercial)	5.55	5.58

Accordingly, the decrease of temperature throughout the entire temperature range results as usual in an increase of the dielectric constant (Figs 2 and 3). This could be attributed to the contributions of both increased density and decreased kinetic energy for both samples.

The general form of the Clausius–Mosotti–Debye equation is

$$\frac{\epsilon'-1}{\epsilon''+2}\frac{M}{d}=\frac{4\pi N}{3}\left(\alpha+\frac{\mu^2}{3kT}\right)$$

where ϵ' = dielectric constant,
M = molecular weight,
d = density,
N = Avogadro's number,
α = polarizability,
μ = dipole moment,
k = Boltzmann's constant.

The quantity given by either side of the equation is known as the total molar

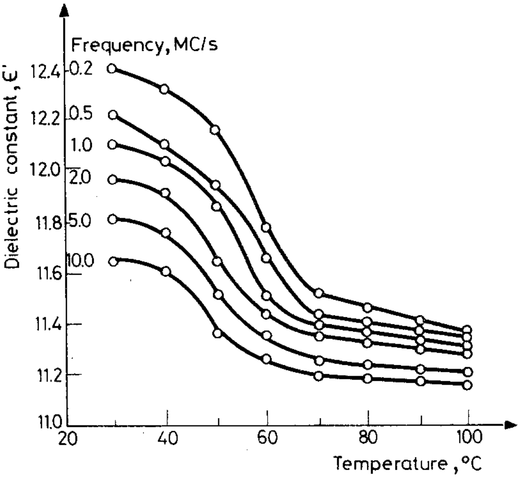

Fig. 2 A diagram showing the temperature dependence of the dielectric constant of antimony trioxide (prepared)

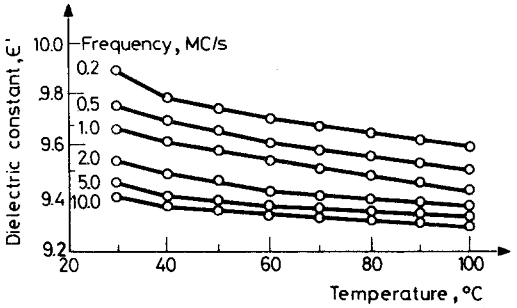

Fig. 3 An illustration showing the temperature dependence of the dielectric constant of antimony trioxide (supplied)

polarizability, denoted by P. It is considered to consist of four terms, as given by the following equation:

$$P = P_e + P_a + P_0 + P_s$$

P_e, P_a, P_0 and P_s are called the electronic, atomic, orientation (or dipole) and space charge polarization [7, 8], respectively.

From the results of the present investigation in Figs 4 and 5, it can readily be seen that ε' increases markedly with the decrease of frequency in the region below 0.3 MC/s and 0.5 MC/s for the commercial and prepared samples, respectively.

Figures 6–9 show that at temperatures up to 40° (for the commercial specimen)

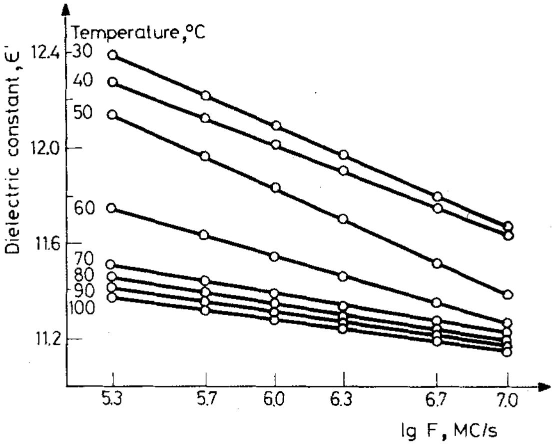

Fig. 4 A diagrammatical representation for the frequency dependence of the dielectric constant of antimony trioxide (prepared)

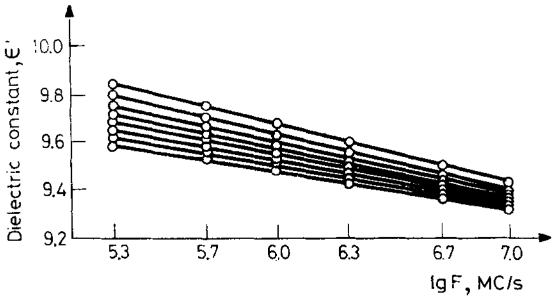

Fig. 5 A figure representing the frequency dependence of the dielectric constant of antimony trioxide (supplied)

and 60° (for the prepared specimen) ϵ'' at first decreases with increasing frequency, reaching a flat minimum (or constancy), and then rises again at high frequencies (above 1.0 MC/s). The sharp increase in ϵ'' at low frequencies can probably be attributed to the d.c. conductivity and is not connected with a dipole relaxation process. Therefore ϵ'' must be considered as proportional to the total measured a.c. conductivity minus the d.c. conductivity. In fact, the observed loss must be regarded as the sum of three distinct effects, namely:

$$\epsilon'' = \epsilon''_{\mathrm{d.c.}} + \epsilon''_{\mathrm{M.W.}} + \epsilon''_{\mathrm{D}}$$

where $\epsilon''_{(\mathrm{d.c.})}$ is the loss factor due to d.c. conductance. It is given as $\epsilon''_{(\mathrm{d.c.})} = \frac{1.8 \times 10^{10}\sigma}{F'}$, where σ is the real part of the complex conductivity. Thus, our

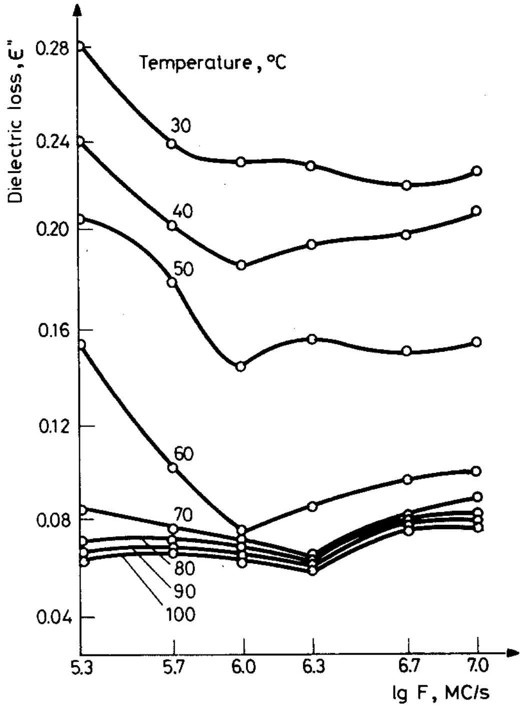

Fig. 6 The frequency dependence of the dielectric loss of Sb_2O_3 (prepared)

present material is an example of a dielectric for which this formula is practically applicable, since the value of ϵ'' is inversely proportional to frequency (Figs 6 and 7). $\epsilon''_{(M.W.)}$ is the Maxwell–Wagner or interfacial polarization loss factor [11].

Our present results obtained as given in Figs 6–9 indicate that both specimens show the same trend of behaviour of ϵ'' versus frequency.

From Figs 7 and 8, it can readily be seen that the actions of temperature and frequency on ϵ'' also have nearly the same trend of negative coefficient character. However, the situation of the curve minima and their attendant maxima vary for both specimens investigated here. This is probably correlated with the contribution of structure differences and/or lattice imperfections, which are plausibly caused by the existence of cubic antimonia (Sb_2O_3) incorporated in the orthorhombic antimonia lattice of the supplied specimen.

At frequencies from 0.2 up to 0.5 MC/s ϵ', ϵ'' falls sharply and then remains fairly constant up to 10 MC/s (sse Figs 4–7). This trend can plausibly be attributed to the increase of the ionic component of the dielectric polarization, in accordance with the earlier finding of Zharikov [6] for other materials. As the frequency increases, the electronic component thus tends to prevail.

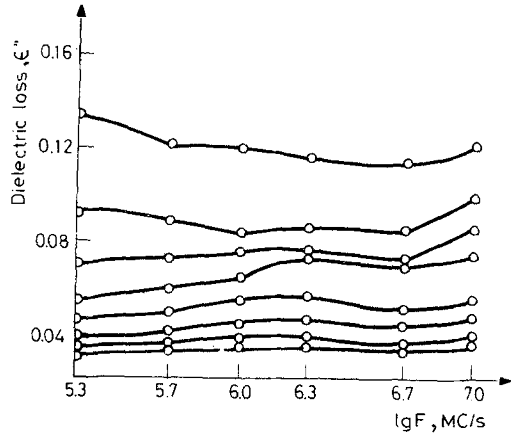

Fig. 7 The frequency dependence of the dielectric loss of Sb_2O_3 (supplied)

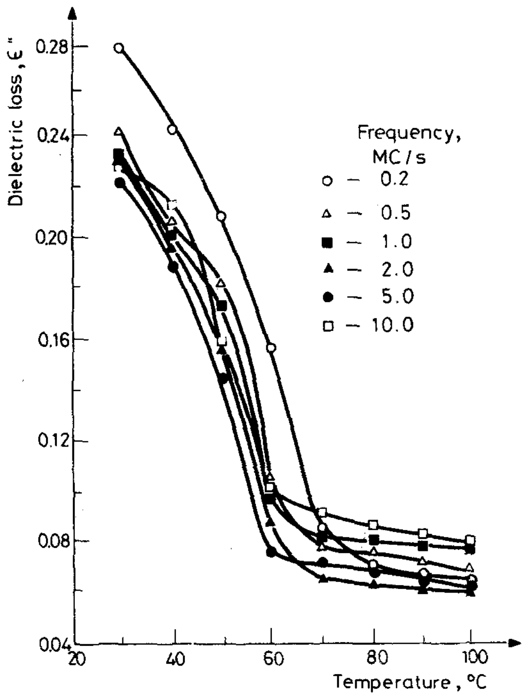

Fig. 8 The temperature dependence of the dielectric loss of Sb_2O_3 (prepared).

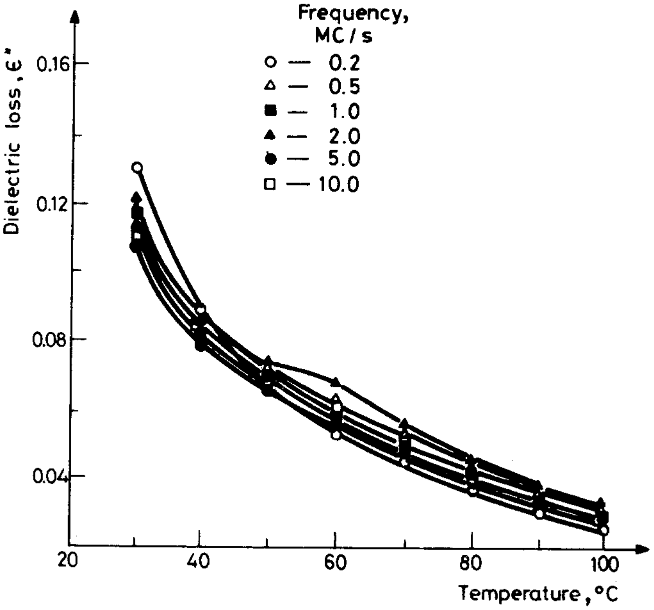

Fig. 9 The temperature dependence of the dielectric loss of Sb_2O_3 (supplied).

In conclusion, the difference in behaviour and values of ϵ' and ϵ'' for the prepared and supplied antimonia specimens investigated can probably be correlated with differences in their phase constitutions, lattice imperfections, electronic polarizations and dipole moments of the electric dipoles.

Accordingly, the interaction of both temperature and applied field frequency with the electric dipoles of the antimonia lattices for both test specimens were evaluated and established for the first time.

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Zusammenfassung — Es wurden frisch präparierte und auch chemisch reine (BDH) Antimontrioxidproben untersucht. An diesen Proben wurden zahlreiche Untersuchungen durchgeführt, einschließlich chemischer, spektraler und Röntgenbeugungsanalyse, Pyknometer- und Röntgen-Dichteuntersuchungen und Beobachtungen des Verhaltens der Dielektrizitätskonstante und des dielektrischen Verlustfaktors (ϵ' und ϵ'') in Abhängigkeit von Temperatur und Frequenz. Die erhaltenen Ergebnisse lieferten einen Dielektrizitätskonstantenwert von 12,4 bzw. 10,0 für frisch präparierte bzw. kommerziell erhältliche Antimontrioxidproben. Die Ergebnisse wurden in Wechselbeziehung mit der Phasenkonstitution und dem Kompaktheitsgrad der Proben verglichen. Letztendlich werden die Daten auf der Grundlage der Wechselbeziehungen zwischen Feldfrequenz und Temperatur mit den elektrische Dipolen und der elektrischen Polarisation der Testproben diskutiert.

Резюме — Исследованы свежеприготовленные, а также химически чистые образцы оксида трехвалентной сурьмы, с которыми были проведены многочисленные измерения, включая химический, спектральный и рентгенографический анализы, рентгенографическое и пикнометрическое измерение плотности и поведение диэлектрической постоянной и фактора диэлектрических потерь (ϵ' и ϵ'') в зависимости от температуры и частоты. Значения диэлектрической постоянной для свежеприготовленных и продажных образцов окиси сурьмы были, соответственно, равны 12,4 и 10. Результаты были сопоставлены в связи с фазовым составом и степенью совместимости для обоих видов образцов. Полученные данные обсуждены на основе наложения частоты магнитного поля и температуры на электрические диполи и электронную поляризацию испытанных образцов.