ELECTRICAL PROPERTIES OF SEMICONDUCTOR MATERIALS. CHROMIUM TRIOXIDE

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ABSTRACT

Since the $3d$ level of chromium trioxide is only partially filled, one might expect it to exhibit metallic conduction. However, this oxide exhibits relatively high specific conductivity of the order $10^{-6} \ \Omega^{-1}$ cm^{-1}, with a large increase in the value as a function of temperature indicating a semiconducting behaviour. This is attributed to the necessity for electron hopping from site to site. The energy gap width value is 4.32 eV.

The static dielectric constant E' and the dielectric loss E'' are 5.56 ± 0.02 and 0.65 ± 0.02, respectively. The increase of E' with temperature is a result of increase in both orientation and atomic polarization, and that of E'' is due to the migration of charge carriers. Their decrease with increasing frequency is attributed to the predominance of the energy loss connected with d.c. loss over the Debye loss. The specific conductivity calculated from the measured dielectric loss is of the same order of $10^{-6} \ \Omega^{-1}$ cm^{-1}.

INTRODUCTION

Compounds of transition metals represent a large group of materials with various types of chemical bond and crystal structure, and consequently with widely divergent physical properties. At present, chromium trioxide is of special importance because of its widely used application in technology.

From the band structure standpoint these materials are characterized by an incomplete $3d$ shell which results in a wide variety of magnetic, electrical, thermal and mechanical properties. Thus the electrical conductivity and the dielectric constant may serve as indicators of changes in a material, its transport properties and consequently its electron energy.

With respect to the electrical conductivity of CrO$_3$, contradictory results are stated in the literature. Chromium trioxide was stated by Moissan [1] to be a good conductor. Bleekrode [2] described it to be a nonconductor if pure. However, Hittorf [3] showed that CrO$_3$ is a conductor only when contaminated with impurities, particularly water, while the purified CrO$_3$ is a nonconductor. Both Buff [4] and Bleekrode [5] stated that molten CrO$_3$ is a good conductor for electricity. However, Van Arkel et al. [6] found that the electrical conductivity of molten CrO$_3$ was $2.958 \times 10^{-5} \ \Omega^{-1}$ cm^{-1} at 218°C and $8.964 \times 10^{-3} \ \Omega^{-1}$ cm^{-1} at 262°C. The

activation energy was found to be 72.5 kcal mole^{-1} (3.14 eV). Therefore, it must be stated that the problem is not yet solved.

As far as the authors are aware, there is no mention in the literature concerning the dielectric properties of CrO_3, although Srivastova and Srivastova [7,8] and Samakhvalov [9] have measured these properties for other chromium oxides such as Cr_2O_3.

In view of the scarcity of quantitative information, it was felt desirable to augment the observation by direct experimental measurements of the electrical conductivity and the dielectric constant and loss factor as a function of temperature and frequency. A correlation between the high frequency electrical conduction and dielectric loss may give more information about the mechanism of conduction in the $3d$ transition metal oxides.

EXPERIMENTAL

Chromium trioxide (Merk) was used. For the electrical measurements, test specimens were pressed at 5 ton cm^{-2} into pellets 1 cm in diameter and 3 mm thick. For the dielectric measurements, the sample was pressed at 1200 kg cm^{-2} into a cylindrical disc 59 mm in diameter and 4 mm thick. The shape and the dimensions of the sample were chosen so as to fit the cells used for the measurements.

The electrical conductivity was measured by applying the same technique described previously [10]. The resistance dispersion curves at different temperatures were established. A frequency of 20 kc s^{-1} was found to be suitable for obtaining the bulk resistance within the whole temperature range. The dielectric constant E' and dielectric loss E'' were measured with an accuracy of ± 0.02 using the technique described previously [11]. Heating of the samples at 60°C for at least 2 h under vacuum of 10^{-3} mm Hg was found to be quite enough for the sample to be free from any moisture before carrying on any measurement, without any change in the stoichiometry of the sample.

RESULTS AND DISCUSSION

The variation of the electrical conductivity with $1/T$ is illustrated in Fig. 1. Curve a represents the behaviour of a fresh sample of CrO_3 within the temperature range 20–182°C. The conductivity value at 25°C is found to be very high and decreases with increase in temperature. This may be due to the presence of OH$^-$ groups, especially because of their highly hygroscopic nature. This should not cause us to overlook the possibility that other defects may play their part in the low temperature conduction. Many trials were carried out to remove H_2O. The sample was first heated to 100°C for 2 h, but the same behaviour was obtained. The experiment was repeated directly after cooling the sample from the previous run to room temperature, i.e. the sample was previously heated to 172°C, but the same

decrease in conductivity with rise in temperature was observed. In the following experiment the sample was heated to 60°C for 2 h under vacuum of 10^{-3} mm Hg. This was done to ensure that any water present was totally removed. The variation of the resistance with temperature was then followed. The room temperature conductivity value was found to be $10^{-6}\ \Omega^{-1}\ cm^{-1}$, very low if compared with the corresponding value for the hydrated sample. The behaviour as a function of temperature is also quite different. An increase of conductivity is observed which is represented on curve b of Fig. 1.

Since the $3d$ level of chromium trioxide is only partially filled, one might expect that if the wave function of the metal overlapped sufficiently, the oxide would exhibit metallic conduction. However, this is not the case and CrO_3 exhibits relatively high conductivity of the order $10^{-6}\ \Omega^{-1}\ cm^{-1}$, with a large increase in the value as a function of temperature indicating a typical semiconducting behaviour. This may be attributed to the necessity for electron hopping from site to site, as was stated by Minomura and Drickamer [12].

The relation $\sigma = \sigma_0\ e^{-E/2KT}$ is applicable and the values of ΔE calculated from the slope of the linear parts are 0.4 and 0.48 eV with an exhaustion region at 142°C. It is observed that the oxide melts sharply at 195°C. Following the variation of conductivity of the sample with more rise in temperature over the melting point of CrO_3, a straight line relation still exists up to 215°C. The slope of the curve gave an
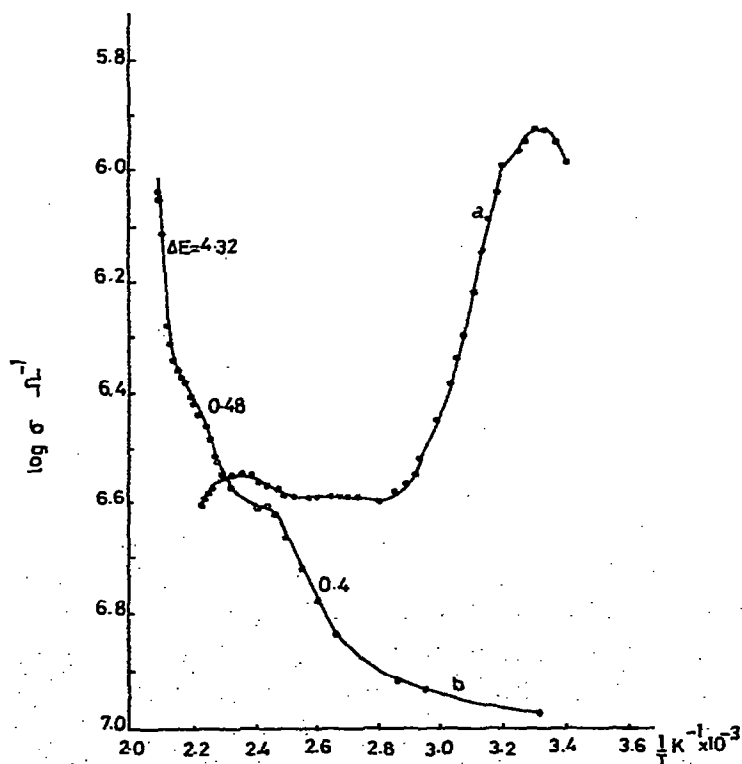

Fig. 1. Variation of the electrical conductivity with temperature for chromium trioxide.

activation energy value of 4.32 eV. This value may represent a value for the gap width for CrO_3, especially because it is reproducible and does not depend on the previous treatment of the sample.

It must be noticed here that measurements up to 215°C still represent the intrinsic CrO_3 region, because the first substoichiometric oxide is obtained at 225°C [13,14] and this was confirmed by DTA [15]. The value 4.32 eV can be reasonably accepted as an energy gap value of CrO_3 according to its position in the periodic table. This is supported by the following facts.

Comparison of the IR absorption curves of CrO_3 [15], MoO_3 [16] and WO_3 [17] manifested an increase in covalent character in the M–O bond from CrO_3 to WO_3. The ionic component is responsible for the increased bond strength. With increasing ionicity the difference between the maximum and minimum values of the crystal potential increases and it was pointed out by Welker [18] that this leads to an increase in the energy gap. The energy gaps of CrO_3, MoO_3 [19–21] and WO_3 [22,23] are 4.32, 3,45 and 2.73 eV, respectively—a shift in direction commonly observed in the value of the gap width with a family of compounds with increasing atomic weight [24]. Also, ZnO, CdO [24] and HgO [25] have gap width values of 3.2, 2.5 and 2.1 eV, respectively. The same degradation was also found between other oxides, sulphides, selenides and tellurides of elements of the same group. Thus Sb_2O_3, Sb_2S_3, Sb_2Se_3 and Sb_2Te_3 have gap width values of 4.19, 1.61, 1.19 and 0.32 eV [26], respectively.

The value 4.32 eV can therefore be safely defined as a gap width value for CrO_3. This needs further support which will be the subject of a future study through optical measurements. The value 72 kcal mole^{-1} (3.14 eV) obtained by Van Arkel et al. [6] does not represent CrO_3 because it was obtained between 218 and 262°C which does not represent the stoichiometric region of CrO_3 [13,14].

It is found that the value of the dielectric constant E' and the dielectric loss factor E'' at 2 Mc s^{-1} and 20°C are 5.56 ± 0.02 and 0.65 ± 0.02, respectively. The variations of E' and E'' with temperature at different frequencies are tabulated in Table 1. It is observed that as the temperature increases both E' and E'' increase. Also the rate of change is small at low temperature and increases markedly at higher temperatures, especially at the low frequencies of 0.2 Mc s^{-1} and 0.5 Mc s^{-1}.

It is well known that the total polarization P of the molecule can be represented by

$$P = P_e + P_a + P_o$$

where P_e, P_a and P_o are the electronic, atomic and orientation polarization, respectively. These three mechanisms of polarization are due to charges that are locally bound in atoms, in molecules or in the structure of solids.

As the temperature increases, the space between the molecules of CrO_3 increases, giving rise to free rotation of the polar molecules with the applied electric field. The free rotation of these molecules raises the orientation polarization and leads to an increase in the dielectric constant. Also, when the temperature increases, the associated molecules of CrO_3 break to monomer molecules. The number of polarized

Table 1

Variation of the dielectric constant E' and the dielectric loss E'' with temperature at different frequencies for CrO_3

Frequency (Mc s⁻¹)	Temperature (°C)									
	10		20		30		40		50	
	E'	E''	E'	E''	E'	E''	E'	E''	E'	E''
0.200	6.70	1.8055	6.95	1.7676	7.15	1.8700	7.85	2.2210	8.36	2.2800
0.500	6.07	1.1341	6.22	1.1299	6.44	1.2570	6.81	1.4751	8.38	1.8541
1.0	5.80	0.8520	5.91	0.8452	6.20	0.9990	6.35	1.1916	6.74	1.4609
2.0	5.50	0.6502	5.56	0.6501	5.63	0.7432	5.84	1.0101	6.10	1.3050
5.0	5.25	0.5144	5.35	0.5100	5.38	0.5501	5.47	0.7020	5.60	0.8886
10.0	5.14	0.5126	5.13	0.5088	5.18	0.5676	5.25	0.5590	5.3	0.6220

molecules per unit volume increases. Thus the orientation polarization P_0 and the polarization around the Cr–O bond P_0 increases and consequently the dielectric constant increases. The ability of these spaces to increase and the appearance of monomers are larger at high temperature, so that the variation of the dielectric constant with temperature is faster than that at low temperature.

Besides the three polarization types mentioned above, a fourth type resulting from charge carriers can be added. Usually these charge carriers can migrate for some distance through the dielectric material. When such carriers are hindered in their motion, either because of being trapped in the material or in interfaces, or because they can be freely discharged or replaced at the electrodes, space charges and a macroscopic field distortion result. Hence the increase in the dielectric loss factor of CrO_3 E'' with temperature may be attributed to the increase in the migration of these charge carriers [27].

The variations of dielectric constant E' and the dielectric loss factor E'' with frequency at different temperatures are shown in Table 1. It is observed that both E' and E'' decrease with increasing frequency. This decrease may be due to the predominance of the energy loss connected with d.c. loss over Debye loss.

The measured dielectric loss E'' has two components, the dielectric loss and the conductivity loss [28]

$$E''_{measured} = E''_{dielectric\ loss} + E''_{conductivity\ loss}$$

The conductivity loss $= 1.0 \times 10^{12} K_s / f$, where K_s is the specific conductivity at frequency f. $E''_{conductivity}$ can be calculated from the measured dielectric loss [29] by plotting the product fE'' measured against f and extrapolating the resulting curve to zero f (at this frequency the loss is mainly due to the conductivity component, and the dielectric component disappears).

By dividing fE'' extrapolated to zero frequency over the employed frequency, the conductivity loss can be calculated. The obtained value for the specific conductivity by this method lies in the same order of magnitude of 10^{-6} Ω^{-1} cm^{-1} as that previously measured by a.c. conductivity.

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