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ELECTRICAL PROPERTIES OF β-Ga_2O_3 SINGLE CRYSTALS

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Direct current and alternating current conductivity measurements have been performed on β-Ga_2O_3 single crystals in the temperature range 300–1250 K. Up to about 900 K the crystals exhibit ionic as well as electronic conductivity. Above 900 K the conductivity is predominantly electronic. From the conductivity of crystals doped with the aliovalent cations Zr^{4+} or Mg^{2+}, and structural considerations it is concluded that gallium ion vacancies are the mobile point defects in β-Ga_2O_3.

THE ELECTRICAL CONDUCTIVITY of nominally pure β-Ga_2O_3 single crystals has been investigated from 4.2 to 300 K by Lorenz, Woods and Gambino.[1] They obtained blue conducting crystals under reducing growth conditions, whereas oxidizing growth conditions led to colorless insulating materials. Cojocaru and Alecu[2] reported on d.c. conductivity measurements on compressed pellets of nominally pure β-Ga_2O_3 in vacuum between 555 and 1000 K. The oxygen pressure dependence of the conductivity was studied at high temperatures by Cojocaru[3] and by Sasaki and Hijikata:[4] the relation between conductivity (σ) and oxygen partial pressure (p_{O_2}) was found to be:

$$\sigma \sim p_{O_2}^{-0.25}.$$

The conductivity measurements on β-Ga_2O_3 crystals presented in this paper were carried out as part of a program to clarify the luminescence mechanism in these crystals.[5]

1. EXPERIMENTAL

Nominally pure and doped crystals were grown by the Verneuil method using β-Ga_2O_3 powder (Alusuisse, 99.99% pure) as starting material. As dopants the aliovalent cations Mg and Zr were used. They were introduced as the oxides MgO and ZrO_2, respectively. All crystals were quenched in air directly after growth. The undoped crystals were colorless or light blue. All Mg-doped crystals were colorless, whereas all Zr-doped crystals were light blue. The conductivity measurements were performed in the temperature range 300–1250 K in air. Thin platelets were cleaved from the boules along the (100) plane. The area of the samples varied from 0.20 to 0.60 cm^2, the thickness from 0.1 to 0.2 cm. Contact between the platinum electrodes and the cleaved surfaces was established with a platinum paint (Leitplatin, Degussa). All experiments were carried out in a conductivity cell as described previously.[6] The direct voltages applied to the crystal never exceeded 1 V. Voltage–current characteristics were recorded from an autoranging Keithley digital electrometer (model 616). Admittance parameters were measured over the frequency range 0.4–20 kHz with a General Radio impedance bridge (1608 A) with external oscillator (G.R. 1210 C) and an amplifier–null detector (G.R. 1232 A).

2. RESULTS AND DISCUSSION

The electronic contribution to the total conductivity was calculated from steady-state current–voltage characteristics which were linear up to 350 mV. A.c. conductivities showed frequency dispersion over the frequency range employed up to about 900 K. The absence of a frequency dependence at higher temperatures was confirmed by the observation that experimental direct currents showed no time-dependence over the voltage-range employed. These results indicate predominantly electronic conductivity at $T > 900$ K in accordance with the results of Sasaki and Hijikata.[4] For temperatures below 560 K conductances were only slightly dependent on frequency. d.c. polarization currents, however, strongly decayed as a function of time. Above about 560 K a semicircular shape appeared in the complex admittance plots: $Y = G + jB$. Typical admittance plots are shown in Fig. 1. By extrapolating these curves to higher frequencies one obtains values for the total bulk conductivity whereas the values obtained by extrapolation to zero frequency coincided with experimentally observed d.c.-conductances.

Figure 2 shows the temperature dependence of the ionic conductivity (σ_i), and the electronic conductivity (σ_e) for two undoped crystals. The ionic contribution to the total conductivity is within 40% the same for all undoped crystals, whereas the electronic conductivity varies over 2 decades from sample to sample below 740 K. Above 870 K no reliable values for the ionic contribution to the total conductivity could be obtained due

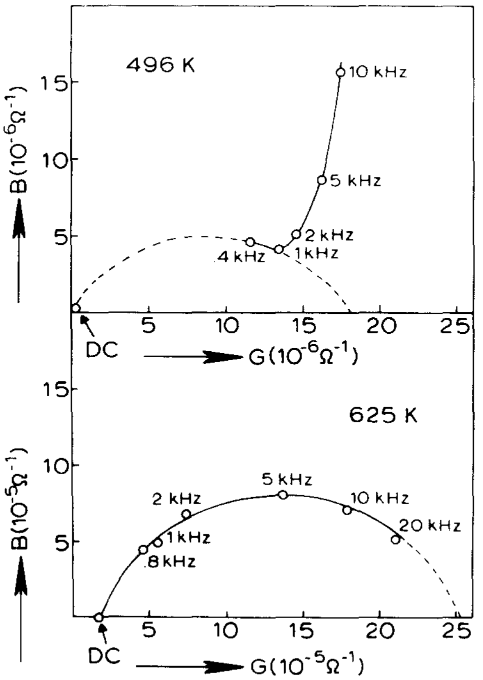

Fig. 1. Admittance plots for a nominally pure β-Ga_2O_3 crystal.

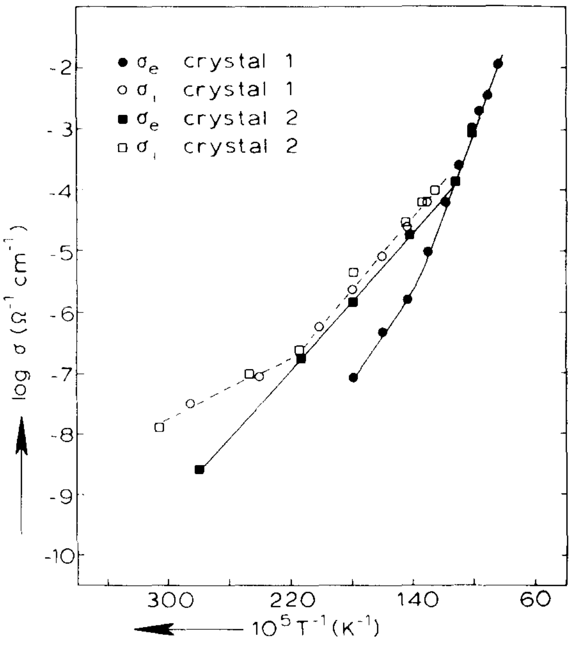

Fig. 2. The ionic conductivity (σ_i) and the electronic conductivity (σ_e) of two undoped β-Ga_2O_3 crystals plotted as log σ vs T^{-1} (measured in air).

to the high electronic contribution. Doping with Zr results in a substantial increase in the whole temperature range considered in ionic as well as electronic conductivity as compared to these partial conductivities in nominally pure material. Doping with Mg has the opposite effect on both ionic and electronic conductivity. The electronic contribution to the conductivity of the Zr-doped crystal never exceeded the ionic contribution. From this observation and the general assumption that the mobility of electrons is much higher than the mobility of ionic point defects we conclude that the electrons are minority charge carriers.

Assuming that Zr is incorporated substitutionaly the incorporation mechanism using Krögers notation[7] can then be described in two ways as follows:

$$3ZrO_2 \rightarrow 3Zr_{Ga}^{\cdot} + V_{Ga}''' + 6O_O^x \quad (1)$$

$$2ZrO_2 \rightarrow 2Zr_{Ga}^{\cdot} + O_i'' + 3O_O^x. \quad (2)$$

Since available interstitial sites in the β-Ga_2O_3 structure[8] do not allow for mobile interstitial oxide ions, we propose that the increase in ionic conductivity on doping with Zr can be attributed to the formation of gallium ion vacancies according to reaction (1). It is not known at present whether intrinsic ionic point defects in β-Ga_2O_3 are thermally generated according to a Schottky or a Frenkel mechanism. An increase in the concentration of gallium ion vacancies $[V_{Ga}''']$ however, means that either the concentration of oxide ion vacancies $[V_O^{\cdot\cdot}]$ (Schottky disorder) or the concentration of interstitial gallium ions $[Ga_i^{\cdot\cdot\cdot}]$ (Frenkel disorder) will decrease, and will consequently lead to a higher concentration of free electrons, as can be seen from the equilibria (3) and (4)

$$O_O^x \rightleftharpoons V_O^{\cdot\cdot} + 2e' + 1/2O_2(9) \quad (3)$$

$$2Ga_{Ga}^x + 3O_O^x \rightleftharpoons 2Ga_i^{\cdot\cdot\cdot} + 6e' + 3/2O_2(9). \quad (4)$$

This anticipated increase in the concentration of free electrons $[e']$ is in accordance with experimental observations for the Zr-doped crystals. Incorporation of Mg will result in a decrease in concentration of gallium ion vacancies either through an increase in the concentration of interstitial gallium ions, or through an increase in the concentration of oxide ion vacancies:

$$6MgO + Ga_2O_3 \rightarrow 6Mg_{Ga}' + 2Ga_i^{\cdot\cdot\cdot} + 9O_O^x$$

$$2MgO \rightarrow 2Mg_{Ga}' + V_O^{\cdot\cdot} + 2O_O^x.$$

A decrease in $[V_{Ga}''']$ will involve a decrease in $[e']$ according to (3) and (4).

In the experimental relation between log σ_i and T^{-1} two linear regions can be discerned for all undoped samples. Below 475 K the activation enthalpy calculated from the relation log $\sigma_i T$ vs T^{-1} has the value 0.28 eV, above 475 K the value 0.62 eV is obtained. From the log σ_e vs T^{-1} plots an activation enthalpy of 0.56 eV at relatively low temperatures and of 1.3 eV at high temperatures was calculated. The measurements on doped crystals show that the temperature region where the ionic conductivity is governed by an intrinsic process (formation of point defects according to a Schottky or

Frenkel mechanism) is not reached. This may be attributed to a high energy of formation of these defects. Annealing experiments and more elaborate measurements on doped crystals are required for a detailed interpretation of the ionic conductivity.

Due to the high band gap energy of β-Ga_2O_3 (4.7 eV[9]) intrinsic semiconduction cannot account for the observed increase in electronic conductivity with temperature. According to Lorenz *et al.*[1] the first ionization of the donors is complete at 200 K. Independent of the choice of gallium interstitials or oxide ion vacancies as donors the increase in electronic conductivity up to 740 K might be attributed to a second ionization of the donors. Above 740 K we expect oxygen loss from the lattice in agreement with the interpretation of Sasaki and Hijikata, resulting in an increasing concentration of dissociated donors and free electrons. The observed differences in electronic conductivity in various undoped crystals point to a difference in the concentration of donors, which could be the result of growing under slightly different oxygen pressures. In agreement with Lorenz *et al.*[1] we obtained the highest values for the electronic conductivity for blue crystals. None of our crystals, however, showed the reported[1] metallic conductivity.

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