JOURNAL OF SOLID STATE CHEMISTRY 23, 205–211 (1978)

Electrical Properties of β-Ga_2O_3 Single Crystals. II

T. HARWIG AND J. SCHOONMAN

Solid State Chemistry Department, Physical Laboratory, State University, Sorbonnelaan 4, Utrecht, The Netherlands

Received April 29, 1977; in revised form July 5, 1977

The influence of aliovalent dopants (Mg, Zr) on the electrical conductivity of quenched and equilibrated β-Ga_2O_3 single crystals has been established. In the quenched crystals, frozen-in defects govern the electrical properties. In the quenched Zr-doped crystals optical absorption by free charge carriers is observed in the infrared spectral region. Above 580°K, the crystals can be equilibrated in air. Equilibration of the crystals markedly influences the electrical properties. In conjunction with data reported on undoped β-Ga_2O_3, it is proposed that the electronic conduction occurs via a hopping mechanism. The data reveal that doping influences the activation enthalpy for the conduction.

1. Introduction

The ionic and electronic conductivities of nominally pure β-Ga_2O_3 single crystals have been reported in the literature (*1*, *2*). The electronic conductivity of polycrystalline samples has been studied at high temperatures as well (*3*–*6*). In addition to ionic conductivity via gallium ion vacancies, *n*-type semiconductivity has now been well established. The influence of aliovalent cationic dopants on the electrical properties of β-Ga_2O_3 crystals has received only little attention. Harwig *et al.* (*2*) noticed that incorporation of ZrO_2 substantially increases, whereas incorporation of MgO decreases the electrical conductivity of β-Ga_2O_3 crystals. These data were obtained from single-heating runs on Verneuil-grown crystals. One may expect a high-temperature equilibrium to be frozen-in in such crystals and, consequently, ill-defined conductivities at low and moderate temperatures.

The present paper reports on the temperature dependence of the electronic contribution to the conductivity of doped β-Ga_2O_3 crystals. Attention is paid to the difference between the electrical conductivity of quenched and equilibrated crystals. Transmission spectra of doped and undoped crystals show that the higher electronic conduction of quenched Zr-doped crystals is related to an absorption in the infrared region of the spectrum.

2. Experimental

The melting point of β-Ga_2O_3 is 2068 ±20°K (*7*). Nominally pure and doped crystals were grown by the Verneuil method using β-Ga_2O_3 powder (Alusuisse 99.99% pure) as starting material. The growth of the crystal was terminated by stopping the powder flow and lowering the crystal. As soon as the crystal was outside the muffle (after about 7 min) the flame was extinguished and the crystal was left to cool down to room temperature. More details of the crystal growth will be given elsewhere (*8*). Mg and Zr were introduced as the oxides MgO and ZrO_2, respectively. All Mg-doped crystals were colorless, whereas all Zr-doped crystals were blue. Transmission spectra with the radiation

0022–4596/78/2312–0205$02.00/0

Printed in Great Britain

incident normally to the (100) plane of the crystals were recorded at room temperature with a Perkin–Elmer EPS/3T double-beam spectrophotometer. Spectrochemical analysis of several doped crystals revealed that if 1000 ppm of ZrO_2 or MgO had deliberately been added to β-Ga_2O_3, only a few hundred parts per million of Zr or Mg had actually been incorporated. The major impurities detected in undoped crystals were Si (100–200 ppm), Ca (20–50 ppm), Mg (20–50 ppm), and Al (50–100 ppm). The concentrations of the different impurities varied considerably in the various crystals. The accuracy of the analysis, however, was poor and excluded a quantitative interpretation of the compositional dependence of the conductivity. For convenience the deliberately added, weighed concentrations of dopants will be used throughout this paper.

The ac conductivity measuring technique has been published before (*2*). Direct currents were recorded under potentiostatic conditions automatically as a function of temperature using an automatic ranging digital picoammeter (Keithley 445), which was commanded by a Solartron data transfer unit. Applied dc voltages were measured with a digital voltmeter (Schlumberger A220) in combination with a recorder drive-unit (Schlumberger A295). It was checked whether the conductivity remained constant over a time interval of 30 min if the temperature was kept constant. All measurements were performed in air.

3. Results

The temperature dependence of the electronic conductivity, σ_e, of several doped crystals is presented in Fig. 1. The conduction activation enthalpies are gathered in Table I. For comparison literature data obtained on undoped single crystals and powder specimens have been included.

The highest electronic conductivity is exhibited by the as-grown crystal Zr 1000. For temperatures above about 580°K its conductivity becomes time dependent. This behavior indicates the onset of an equilibration reaction with the surrounding atmosphere. Upon subsequent heating to temperatures above about 900°K equilibrium is rapidly reached, which is manifested by reproducible conductivity data obtained thereafter during temperature-cycling experiments. A similar behavior was observed for the other quenched crystals.

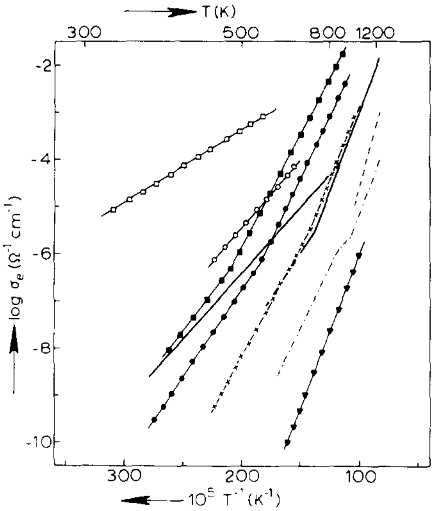

FIG. 1. The electronic conductivity (σ_e) versus reciprocal temperature for β-Ga_2O_3 single crystals with aliovalent dopants and measured in air. Literature data of undoped samples have been included for comparison. □, as grown crystal: 1000 ppm Zr; ○, as grown crystal: 100 ppm Zr; ■, ●, subsequent cooling and heating curves; ×, equilibrated crystal: 100 ppm Mg; ▼, equilibrated crystal: 1000 ppm Mg; – – –, polycrystalline undoped sample: Sasaki and Hijikata (*6*), 180 mm O_2; · — ·, polycrystalline undoped sample: Cojocaru *et al.* (*3*, *5*), probably 760 mm O_2; ——, two undoped crystals (apparently grown under slightly different oxygen pressure). Harwig *et al.* (*2*), air.

Below 550°K the conductivity of the equilibrated crystal Zr 1000 shows frequency dispersion. From the admittance plots (*2*) it is concluded that below about 550°K the ionic conductivity is of the same order of magnitude as the electronic conductivity. For the equilibrated Zr 100 crystal the ionic and the electronic conductivity are also of the same order of magnitude below about 575°K.

The equilibrated crystal Mg 1000 exhibits the lowest electronic conductivity. The electro-

TABLE I

ACTIVATION ENERGIES FOR ELECTRONIC CONDUCTION IN DOPED β-Ga_2O_3 CRYSTALS AND IN NOMINALLY PURE SAMPLES

Dopant	Temperature interval (°K)	ΔH(eV)	Remarks
Mg 1000	610–1040	1.26	Equilibrated in air
Mg 100	440– 625 625–1000	0.91 1.23	Equilibrated in air
Zr 100	365– 555 555– 910	0.74 1.04	Equilibrated in air
Zr 1000	380– 475 475– 895	0.64 0.95	Equilibrated in air
Zr 100	435– 625	0.58	As grown
Zr 1000	310– 575	0.33	As grown
Undoped polycrystalline	600– 900 900–1220	1.0 1.3	Cojocaru and Alecu (*3*)
Undoped polycrystalline	960–1220	1.8	Sasaki and Hijikata (*6*)
Undoped crystal	360– 830 555– 710 710–1250	0.56 0.71 1.31	Harwig *et al.* (*2*) as grown

nic conduction of the quenched Mg 1000 crystal was too low ($<10^{-10}\ \Omega^{-1}\ cm^{-1}$), at temperatures where no equilibration with the atmosphere occurs, to be measured reliably, indicating that the electronic conductivity of the quenched Mg 1000 crystal was not much higher than the electronic conductivity of the equilibrated crystal. At temperatures above 750°K, the ac conductivity shows little frequency dispersion for frequencies in the range dc—20 kHz. This indicates that the electronic conductivity of this crystal largely exceeds the ionic conductivity.

The electronic conductivity of the equilibrated crystal Mg 100 is found between those of Zr 100 and Mg 1000 and close to the electronic conductivity of nominally pure crystals (see Fig. 1). For both the quenched and the equilibrated Mg 100 crystal frequency dispersion was observed over a wide temperature interval, which enabled the evaluation of the ionic conductivity, σ_i. After heating the crystal up to 1150°K, the ionic conductivity decreased with more than one power of ten. The slope of the $\log \sigma_i T$ vs T^{-1} curve did not change measurably (Fig. 2). For the activation enthalpy a value of (0.63 ± 0.01 eV) is calculated. It should be remarked that the ionic conductivity of the quenched crystal Mg 100 is found to be a factor of 6 larger than that of undoped crystals reported previously (*2*).

For the equilibrated crystals Zr 1000, Zr 100, and Mg 100 two linear regions can be discerned in the $\log \sigma_e$ vs T^{-1} curves. From Table I and Fig. 1 it is clear that the activation enthalpy for conduction, ΔH, decreases upon increasing isothermal conductivity values. Meyer and Neldel (*9*) have shown empirically

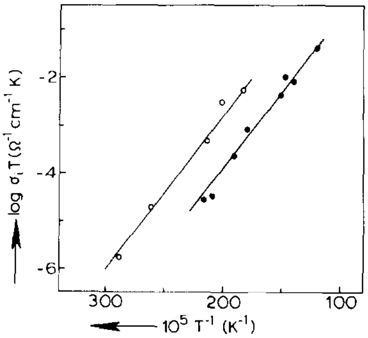

FIG. 2. The ionic conductivity, σ_i, of a crystal doped with 100 ppm Mg, plotted as log σ_i T versus $1/T$. ○, heating curve; ●, subsequent cooling curve.

that a wide variety of undoped semiconductors obey the relation:

$$-\log \sigma_T \sim \Delta H.$$

Eror and Wagner (*10*) showed that this relation is also valid for certain doped oxides. Our data obtained below 550°K fit in this relation.

Transmission spectra revealed that only the blue-colored crystals exhibit optical absorption in the near infrared. A transmission spectrum for a crystal with thickness of 0.0657 cm has been given in Fig. 3. Blue-colored crystals became colorless after a heat treatment at 1200°K in air or nitrogen, and the infrared absorption disappeared. Our attempts to obtain blue-colored crystals by heat-treating colorless crystals in a reducing atmosphere were unsuccessful: If the crystals were heated in a mixture of 70% nitrogen and 30% hydrogen the β-Ga_2O_3 crystals decomposed at temperatures above 1000°K. This is compatible with the observation that volatile Ga_2O is formed if β-Ga_2O_3 is heated in hydrogen (*11*, *12*).

4. Discussion

It is remarkable that dopant concentrations (especially zirconium) which are low compared with the impurity contents of the undoped crystals have such a great influence on the electrical properties. An important influence has also been noticed on the luminescence properties of crystals doped with relatively low concentrations of ZrO_2 (*13*). The ionic conductivity of the Mg 100 crystal is of the same order of magnitude as the ionic conductivity of undoped crystals. This is in agreement with the relatively low concentration of dopant. The activation enthalpy is equal within the experimental error to that reported for undoped quenched crystals for temperatures larger than 475°K, indicating that in the Mg 100 crystal the gallium ion vacancies constitute the mobile ionic species. Their activation enthalpy is 0.63 eV irrespective of thermal treatments. The ionic conductivity decreases in the sequence Zr 1000, Mg 100, Mg1000, in line with the proposed (*2*) gallium ion vacancy conduction, albeit that no conclusion can still be drawn as to the nature of the intrinsic defect compensating the charge of the gallium ion vacancy.

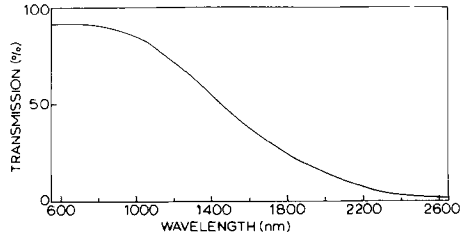

FIG. 3. Transmission of a quenched β-Ga_2O_3 crystal doped with 1000 ppm Zr (thickness 0.0657 cm), as a function of wavelength. The radiation was incident normally to the (100) plane.

It is evident that the as-grown crystals are not in equilibrium with the ambient used in this study. Equilibrium is established at temperatures above 580°K. Nevertheless the proposed model for the relation between aliovalent dopant and electronic conductivity still holds for equilibrated crystals.

It is apparent that the higher the concentration of gallium ion vacancies in the crystal, the more high-temperature defects are frozen-in. When the crystals are cooled from the growing temperature to room temperature equilibrium with the ambient demands the incorporation of oxygen according to

$$V_O^{\cdot\cdot} + 2e' + \tfrac{1}{2}O_2 \rightarrow O_O^{\times}, \qquad (1)$$

or

$$2Ga_i^{\cdot\cdot\cdot} + \tfrac{3}{2}O_2 + 6e' \rightarrow 2Ga_{Ga}^{\times} + 3O_O^{\times}, \qquad (2)$$

depending on the existence of a Schottky or a Frenkel disorder, respectively. Here and throughout this paper the defect notation of Kröger (*14*) is used. If the concentration of oxygen vacancies (interstitial gallium ions) is low as is the case in Zr-doped crystals, the rate at which the incorporation can take place is determined by the diffusion of oxygen vacancies (interstitial gallium ions) to the surface. Clearly this rate is too low to establish equilibrium with the gas phase if the Zr-doped crystals are quenched.

The infrared absorption of quenched Zr-doped crystals is attributed to free-carrier absorption, which is a common phenomenon in binary oxides in which the electron concentration has been increased either by doping or by heat treatments in a reducing atmosphere (*15–17*). After a heat treatment in air the infrared absorption has disappeared in accordance with the observed decrease in the electronic conductivity in equilibrated Zr-doped crystals.

Cojocaru and co-workers (*3–5*) and Sasaki and Hijikata (*6*) have shown that the conductivity of undoped polycrystalline β-Ga_2O_3 varies with $p_{O_2}^{-1/4}$ in the pressure range 1–760 mm Hg. Cojocaru and Prodan (*5*) assume that from 400 to 1000°K electroneutrality is preserved via the relation

$$3[Ga_i^{\cdot\cdot\cdot}] = [e'],$$

both species thus depending on the partial oxygen pressure. Sasaki and Hijikata assume the predominant defects to be either electrons and singly ionized oxygen vacancies or doubly ionized gallium ion interstitials, or the coexistence of both types of ionic defects and electrons. As can be readily observed from the interphase reaction

$$2Ga_{Ga}^{\times} + 3O_O^{\times} \rightleftarrows 2Ga_i^{m\cdot} + \tfrac{3}{2}O_2\,(g) + 2me';$$
$$K = [e']^{2m}\,[Ga_i^{m\cdot}]^2\,p_{O_2}^{3/2}, \tag{3}$$

the $p_{O_2}^{-1/4}$-dependence of the conductivity is for $m = 3$ only compatible with electrons being minority charge carriers, contrary to the assumption of Cojocaru and Prodan. Sasaki and Hijikata reported dissociative loss of oxygen above 950°K via Eq. (3) or via

$$O_O^{\times} \rightleftarrows V_O^{n\cdot} + \tfrac{1}{2}O_2\,(g) + ne';$$
$$K = [e']^n\,[V_O^{n\cdot}]\,p_{O_2}^{1/2}. \tag{4}$$

A $p_{O_2}^{-1/4}$-dependence is in their case obtained for $m = 2$ (Eq. 3) or for $n = 1$ (Eq. 4).

We have tried to calculate the electron concentrations using mobility values from literature sources. From the Hall coefficient and resistivity measurements on light-blue conducting crystals Lorenz *et al.* (*1*) determined the electron mobility μ_e to be 80 cm²/Vsec at room temperature, and approximately 110 cm²/Vsec at 160°K. The room temperature electron concentration was found to be about 10^{18} cm^{-3}. Details regarding the ambient were not provided. From thermoelectric power and conductivity data on polycrystalline β-Ga_2O_3 *in vacuo* Cojocaru and Alecu (*3*) obtained for μ_e at 900°K the value 1×10^{-4} cm²/Vsec and for the electron concentration, the value 3.0×10^{17} cm^{-3}. At 650°K, μ_e has the value 7×10^{-6} cm²/Vsec. If the Hall mobility is used to obtain the concentration of the electrons at room temperature in the quenched Zr 1000 crystal (highest electronic conductivity), the low value of 3.2×10^{11} cm^{-3} results. This low concentration violates the observation of frozen-in defects in the quenched crystals. If, on the contrary, the drift mobility data of Cojocaru and Alecu are used in conjunction with the present conductivity data of equilibrated, doped crystals, the following concentrations can be inferred:

Dopant	$[e']$ cm^{-3} (650°K)	$[e']$ cm^{-3} (900°K)
Mg 1000	2.82×10^{14}	1.11×10^{16}
Mg 100	7.09×10^{17}	1.76×10^{19}
Zr 100	2.24×10^{19}	2.79×10^{20}
Zr 1000	2.00×10^{20}	1.40×10^{21}

In view of the concentration of gallium ions, viz., 4×10^{22} cm^{-3}, and the actual amounts of incorporated ZrO_2 the latter concentrations are unrealistically high. It should be remarked that the mobility data used have been obtained on polycrystalline β-Ga_2O_3. It has been recognized for oxide semiconductors that the charge-carrier mobility can be larger in crystals (*18*). The magnitude of this effect is small, however, and no substantial decreases in the calculated concentrations of electrons are to be expected. The values of [e'] calculated for the Zr 1000 crystal at 650 and 900°K indicate that the room temperature electron concentration is much higher than the value of 3.2×10^{11} cm^{-3}. The huge discrepancy originates from the use of the Hall mobility. This mobility is always characteristic of the conduction band motion of charge carriers. The present data, therefore, indicate that the electronic conduction mechanism can be regarded as a hopping-type process, i.e., an activated mobility. It is well known that for localized electrons, drift mobilities can be orders of magnitude smaller than the Hall mobility (*19*).

Moreover, a compositional influence on the drift mobility may exist if the concentration or even the nature of the immobilization centers is influenced upon doping. The values of [e'] calculated above suggest that not only the electron concentration, but also the mobility, decreases in the sequence Zr 1000, Zr 100, Mg 100, Mg 1000. In regard of the composition of the crystals, it is likely that the nature of the immobilization centers is different in the Zr-doped and Mg-doped crystals. In the Zr-doped crystals, $\mathrm{Zr}_{\mathrm{Ga}}^{\cdot}$ seems to be a reasonable choice, whereas either $V_{\mathrm{O}}^{\cdot\cdot}$ or $\mathrm{Ga}_i^{\cdot\cdot\cdot}$ would be appropriate for the Mg-doped crystals. In view of the higher effective charges of the defects in the latter case, the larger effect of doping with 1000 ppm Mg on the conductivity may be ascribed partly to a much more effective localization, i.e., a strongly reduced electron mobility as compared with the Zr-doped crystals in which localization of the electrons is assumed to be small.

Cojocaru ascribes the kink in the temperature-dependence curves of the electronic conductivity to a dissociative loss of oxygen and hence a temperature-dependent electron concentration. The temperature region where equilibration occurs in the quenched crystals indicates that this may be the cause of the kink in the conductivity curves for these crystals too.

5. Conclusions

Due to frozen-in oxygen vacancies and electrons quenched Zr-doped crystals show a higher electronic conductivity than equilibrated Zr-doped crystals. In equilibrated crystals the electronic and the ionic conductivity decrease both in the sequence Zr 1000, Mg 100, Mg 1000, in accordance with the influence of aliovalent dopants on the concentration of point defects and with the proposition of mobile gallium vacancies. From the observed relations between $\log \sigma_e$ and T^{-1} and from literature values for μ_e it is concluded that the electronic conduction occurs via a hopping-type process, which implies a thermally activated electron mobility. Moreover this mobility is less in Mg-doped crystals than in Zr-doped crystals due to a much more effective localization in the Mg-doped crystals.

Acknowledgments

The valuable criticism of Prof. Dr. G. Blasse during the preparation of the manuscript is thankfully acknowledged. Thanks are due to Mr. H. Kuyt, who participated in the conductivity measurements.

Thanks are also due to Mrs. P. Anten and T. van de Kraats of the Vening Meinesz Laboratory of this University for the spectrochemical analyses.

The investigations were performed as a part of the research program of the "Stichting voor Fundamenteel Onderzoek der Materie (FOM)" with financial support from the "Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (ZWO)."

References

1. M. R. Lorenz, J. F. Woods, and R. J. Gambino, *J. Phys. Chem. Solids* **28**, 403 (1967).
2. T. Harwig, G. J. Wubs, and G. J. Dirksen, *Solid State Commun.* **18**, 1223 (1976).
3. L. N. Cojocaru and I. D. Alecu, *Z. Phys. Chem.* **84**, 325 (1973).
4. L. N. Cojocaru, *Rev. Roum. Phys.* **18**, 409 (1973).
5. L. N. Cojocaru and A. Prodan, *Rev. Roum. Phys.* **19**, 209 (1974).
6. T. Sasaki and K. Hijikata, *Proc. Inst. Nat. Sci. Nihon Univ.* **9**, 29 (1974).
7. S. J. Schneider and J. L. Waring, *J. Res. Nat. Bur. Standards Sect. A* **67**, 19 (1963).

8. T. Harwig, Thesis, Chap. 2, University of Utrecht, The Netherlands (1977).

9. W. Meyer and H. Neldel, *Z. Tech. Phys.* **18**, 588 (1937).

10. N. G. Eror and J.B. Wagner Jr., *Phys. Status Solidi* **35**, 641 (1969).

11. A. Brukl and G. Ortner, *Z. Anorg. Allg. Chem.* **203**, 23 (1931).

12. M. Saurat and A. Revcolevschi, *Rev. Int. Hautes Temp. Refract.* **8**, 291 (1971).

13. T. Harwig and F. Kellendonk, *J. Solid State Chem.* to appear.

14. F. A. Kröger, "The Chemistry of Imperfect Crystals," North–Holland, Amsterdam (1974).

15. H. Koch, *Phys. Status Solidi* **3**, 1619 (1963).

16. M. W. Schafer, J. B. Torrance, and T. Penney, *J. Phys. Chem. Solids* **33**, 2251 (1972).

17. H. Köstlin, R. Jost, and W. Lems, *Phys. Status Solidi A* **29**, 87 (1975).

18. R. N. Blumenthal and R. J. Panlener, *J. Phys. Chem. Solids* **31**, 1190 (1970).

19. W. Schockley, "Electrons and Holes in Semiconductors," Van Nostrand, Princeton, N.J. (1950).