

Electronic Properties of Semiconducting Cd_2GeO_4

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Cd_2GeO_4 has been prepared from CdO and GeO_2 by solid state reaction at 850°C as a low resistivity ($\rho \approx 1 \Omega \cdot \text{cm}$) *n*-type semiconductor. Its conductivity is increased by doping with trivalent metal ions and decreased by heating oxygen. The electrons originate from shallow donors and their mobility is determined by a combination of large polaron formation and impurity scattering. From photoelectrolysis data the band gap is determined to be indirect, at 3.15 eV; the first direct transition occurs at 4.1 eV. The relations between conditions of preparation, defect structure, and carrier concentration have been examined, but the available data do not allow an unambiguous identification of the nature of the donor center.

Introduction

Among the compounds of cadmium and oxygen, CdO (1), Cd_2SnO_4 (2), CdSnO_3 (3), and CdIn_2O_4 (3) are *n*-type semiconductors with high conductivity. These materials have large band gaps and the carriers originate from shallow donor defects which are related to the oxygen-deficient stoichiometry. The electrons move in a wide conduction band, formed mainly from Cd (5s) orbitals, with fairly high mobility (4). The combination of high conductivity and large band gap makes these materials potentially useful as transparent conductors (5).

In the compounds mentioned above the metal-oxygen bonding is predominantly ionic. In contrast, in Cd_2GeO_4 which crystallizes in a distorted olivine structure (6) the bonding is at least partly covalent, since the

coordination of the O atoms around the Ge atom is the typical tetrahedral arrangement found in the analogous silicates. The oxygen coordination around the cadmium atoms is still octahedral. Cd_2GeO_4 has been prepared previously by hydrothermal synthesis as one of a series of cadmium germanates, the structures of which are closely related to the corresponding silicates (7); its electronic properties have not been measured to date.

The purpose of this paper is to show that Cd_2GeO_4 can be prepared, by solid state reaction, as a low-resistivity *n*-type semiconductor. Analysis of the conductivity and Hall effect data shows that the donor ionization energy is small (0.03 eV), and that the carrier mobility is limited by the formation of large polarons and, at low temperatures, by impurity scattering. The dependence of the carrier concentration on the conditions of sample preparation will be discussed in

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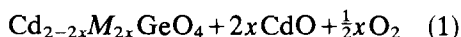
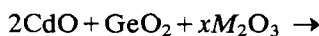
detail; however, from the limited data available it has not been possible to identify unambiguously the donor defects. Finally, data on the photoelectrolysis of water with a Cd_2GeO_4 electrode has been used to determine the band gap.

Experimental

Preparative Techniques

The starting materials were GeO_2 (Johnson–Matthey Specpure) and CdO (Fisher Certified Reagent, 99.99%) which were both heated to 600°C in air prior to use. The materials were mixed thoroughly by intensive grinding in an agate mortar and pressed as 150-mg tablets in a 3/8-in.-diameter steel die at 90,000 psi. The resulting disks were then placed in fused silica tubes, which were either evacuated to a pressure of $\approx 10^{-5}$ atm or filled with 1 atm pressure of O_2 ; the tubes were sealed with a H_2/O_2 torch. In some experiments CdO was placed in a separate portion of the tube, so that it could be heated to a temperature different from the Cd_2GeO_4 firing temperature. The disks were heated slowly from room temperature to 700°C and kept there for 5 hr, then heated at 750°C for 12–16 hr, and finally kept for 3–5 hr at 850°C . The tubes were then quenched to room temperature in an air blast. The physical properties of samples fired under vacuum did not depend on whether the samples were quenched or slowly cooled to room temperature; however, this was not the case for samples fired in oxygen. The original dark brown color (CdO) of the disks changed to the white, off-white, or light blue (if In_2O_3 doped) color of the product. When products were subsequently refired in oxygen or under vacuum, the disks were heated directly from room temperature to 850°C and kept there for 15 hr again in sealed quartz tubes. Small amounts of In_2O_3 , Gd_2O_3 , Y_2O_3 , and Na_2CO_3 were used to dope the Cd_2GeO_4 with the respective metal ions. Serial dilution

of the dopant oxide in the $2\text{CdO}\text{--}\text{GeO}_2$ oxide mix was used to achieve the very small dopant concentrations. In samples 19 and 22 we compared doping with $\text{In}_2\text{O}_3 + \text{In}$ metal in a 1:1 ratio with doping with only In_2O_3 . The electronic properties of these samples were identical, showing that the small amount of oxygen liberated during the incorporation of the trivalent oxide according to the likely reaction



had negligible influence.

Samples prepared according to these procedures had reproducible physical properties. The results listed in Tables I and II have been obtained at least in duplicate. For duplicate samples carrier concentrations were within 15%; mobilities differed at most by a factor of 2.

Sample Characterization

The X-ray diffraction ($\text{CuK}\alpha$) pattern of our samples corresponded to the olivine-like structure of Cd_2GeO_4 prepared hydrothermally (7). In addition to the predicted Cd_2GeO_4 lines, the patterns sometimes showed a very weak line at $2\theta = 28.9^\circ$. This line corresponds to the strongest line from a sample made by firing equimolar amounts of CdO and GeO_2 at 850°C ; we ascribe it to the presence of a small amount of a CdGeO_3 phase.¹ This extra line was not present in sample 49 (prepared with 1% excess CdO), but was clearly detectable in sample 50 prepared with 0.4% excess GeO_2 . In the doped samples no X-ray evidence was found for the presence of a separate dopant oxide phase, with the one exception of sample 24 which showed a faint In_2O_3 line. This sample was first doped with In_2O_3 under vacuum and

¹ The diffraction pattern of our CdGeO_3 sample prepared by solid state reaction did not correspond to the reported pattern of CdGeO_3 made by hydrothermal synthesis (7).

TABLE I
CONDUCTIVITY PARAMETERS OF UNDOPED Cd₂GeO₄ AT 295°K

Sample No.	Prepared from	Firing conditions	ρ ($\Omega \cdot \text{cm}$)	n (cm^{-3})	μ ($\text{cm}^2/\text{V} \cdot \text{sec}$)
5 ^a	2CdO + 1GeO ₂	850°C, vacuum	1.26	7.1×10^{17}	7.0
49	2CdO + 1GeO ₂ + 1% CdO excess ^b	850°C, vacuum	0.57	9.3×10^{17}	11.8
50 ^a	2CdO + 1GeO ₂ + 0.4% GeO ₂ excess ^b	850°C, vacuum	0.33	1.3×10^{18}	15.0
40 ^a	2CdO + 1GeO ₂	850°C, vacuum	1.80	7.7×10^{17}	4.5 (separate CdO at 650°C)
42	2CdO + 1GeO ₂	850°C, vacuum	1.27	5.9×10^{17}	8.3 (separate CdO at 750°C)
43	2CdO + 1GeO ₂	750°C, vacuum	1.11	6.8×10^{17}	8.3 (separate CdO at 650°C)
23	No. 5	850°C, 1 atm O ₂	$>10^5$	$<5 \times 10^{14}$	—
32	No. 23	850°C, vacuum	1.18	7.0×10^{17}	7.6
7	2CdO + 1GeO ₂	850°C, 1 atm O ₂	$>10^5$	$<5 \times 10^{14}$	—
34 ^a	No. 7	850°C, vacuum	0.70	6.2×10^{17}	14.3 (heated for only 0.5 hr)

^a Very weak CdGeO₃ line observed in X-ray pattern.

^b wt% w.r.t. Cd₂GeO₄.

TABLE II
CONDUCTIVITY PARAMETERS OF DOPED Cd₂GeO₄ AT 295°K

Sample No.	Prepared from	Firing conditions ^a	ρ ($\Omega \cdot \text{cm}$)	n (cm^{-3})	μ ($\text{cm}^2/\text{V} \cdot \text{sec}$)	$n/[\text{dopant ions}/\text{cm}^{-3}]$
19 ^b	2CdO + 1GeO ₂ + 1.10% In ₂ O ₃ ^c	Vacuum	6.7×10^{-3}	1.0×10^{20}	9.2	0.33
22	2CdO + 1GeO ₂ + 0.63% In ₂ O ₃ + 0.28% In	Vacuum	3.7×10^{-3}	8.9×10^{19}	19.0	0.24
37	2CdO + 1GeO ₂ + 0.22% In ₂ O ₃	Vacuum	7.6×10^{-3}	8.5×10^{19}	9.8	1.42
41	2CdO + 1GeO ₂ + 0.02% In ₂ O ₃	Vacuum	7.2×10^{-2}	1.0×10^{19}	8.6	1.84
20	No. 19	1 atm O ₂	1.38×10^1	5.9×10^{17}	1.3	—
21	No. 20	Vacuum	8.1×10^{-3}	9.0×10^{19}	8.5	—
24 ^b	No. 19	1 atm O ₂ ^d	$>10^5$	$<5 \times 10^{14}$	—	—
27 ^b	2CdO + 1GeO ₂ + 1.0% Y ₂ O ₃	Vacuum	6.3×10^{-2}	1.8×10^{19}	5.5	0.055
44	2CdO + 1GeO ₂ + 0.2% Y ₂ O ₃	Vacuum	1.1×10^{-1}	6.0×10^{18}	9.3	0.090
45	2CdO + 1GeO ₂ + 0.04% Y ₂ O ₃	Vacuum	4.3×10^{-1}	1.8×10^{18}	8.4	0.14
30	No. 27	1 atm O ₂	1.7	2.6×10^{17}	13.9	—
28	2CdO + 1GeO ₂ + 1.0% Gd ₂ O ₃	Vacuum	8.6×10^{-3}	6.5×10^{19}	11.2	0.31
46 ^b	2CdO + 1GeO ₂ + 0.2% Gd ₂ O ₃	Vacuum	2.8×10^{-2}	2.6×10^{19}	8.8	0.61
56 ^b	2CdO + 1GeO ₂ + 0.04% Gd ₂ O ₃	Vacuum	1.57×10^{-1}	3.0×10^{18}	13.0	0.36
58	No. 28	1 atm O ₂	4.2×10^2	$<3 \times 10^{15}$	—	—
51	2CdO + 1GeO ₂ + 1.1% Na ₂ CO ₃	Vacuum	4.5	1.4×10^{17}	9.8	—

^a All samples fired at 850°C.

^b Very weak CdGeO₃ line observed in X-ray pattern.

^c All dopants in wt% w.r.t. Cd₂GeO₄.

^d Sample cooled to 295°K in 5 hr, instead of quenched; faint In₂O₃ line seen in X-ray pattern.

then fired in O_2 at $850^\circ C$ and slowly cooled to room temperature. This observation may indicate a limited solubility of In_2O_3 in Cd_2GeO_4 in an oxygen-rich atmosphere.

The density of the fired samples was at least equal to 90% of the theoretical density of 6.3 g/cm^3 (calculated from the unit-cell size). The grain size varied from 2 to $5 \mu m$.

Physical Measurements

The electrical measurements were made by the van der Pauw technique. Contacts, of ultrasonically applied indium, were ohmic except for $\rho > 10^4 \Omega \cdot cm$. The photoelectrolysis data were obtained using equipment described previously (8) in detail. The electrolyte was 0.2 M sodium acetate solution, saturated with hydrogen gas, and adjusted with NaOH to $pH = 12.7$; the counter electrode was platinum. The photocurrents were obtained at a bias of 0.6 V; light intensities were measured with a calibrated Si photodiode.

Results and Discussion

Electronic Conductivity

All samples of Cd_2GeO_4 were found to be *n*-type; their conductivity parameters are listed in Tables I and II. The carrier concentration n at $298^\circ K$ in all undoped samples prepared under vacuum was in the range $(6-12) \times 10^{17} \text{ cm}^{-3}$. Doping with the trivalent metals indium, yttrium, and gadolinium increased n , whereas doping with sodium had the opposite effect. Heating the samples in oxygen increased the resistivity by orders of magnitude. The implications of these results for the defect structure of Cd_2GeO_4 will be discussed in the next section; first we will analyze the temperature dependence of the conductivity to determine the electronic transport parameters.

The carrier concentration $n = (R_H e)^{-1}$ and the mobility $\mu = R_H / \rho$ as a function of temperature for sample 43 are shown in Figs. 1 and 2, respectively; these data are

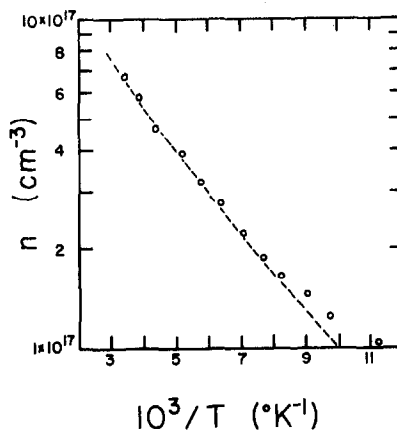


FIG. 1. The electron concentration n versus reciprocal temperature for sample 43. \circ , experimental values; ---, calculated from Eq. (2) with $N_D = 2.2 \times 10^{18} \text{ cm}^{-3}$, $(m^*/m_0) = 0.19$, and $E_D = 0.032 \text{ eV}$.

representative of all undoped samples prepared under vacuum. Both the magnitude and temperature dependence of μ show that in Cd_2GeO_4 the conductivity process is not by electron hopping between localized states, but that the carriers move in a relatively wide band, presumably formed mainly from Cd ($5s$) orbitals. The weak temperature dependence of n suggests a small donor ionization energy, E_D , and in analyzing the data

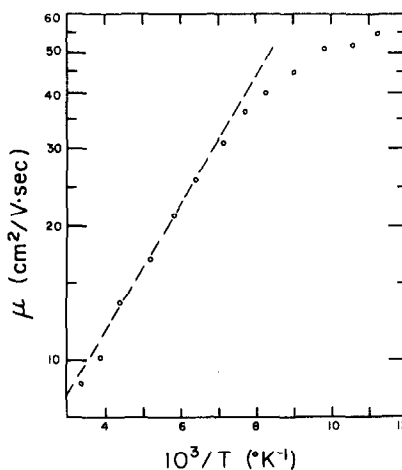


FIG. 2. The mobility μ versus reciprocal temperature for sample 43. \circ , experimental values; ---, large polaron mobility calculated from Eq. (3) with $\theta = 350^\circ K$, $\alpha = 4.3$, and $(m^{**}/m_0) = 2.5$.

we will specifically take into account the temperature dependence of the density of states of the conduction band.

For a single donor (density N_D) and negligible compensation the ionization equilibrium can be expressed (9) as:

$$n^2/(N_D - n)N_c = (m^*/m_0)^{3/2} D^{-1} \exp - E_D/kT, \quad (2)$$

where m^* is the density-of-states effective mass, m_0 , is the bare electron mass, D is the spin degeneracy of the donor level (assumed to be equal to 2), and $N_c = 2(2\pi m_0 kT/h^2)^{3/2}$. A semilog plot of the left-hand side of Eq. (2) versus $(T)^{-1}$ for various assumed values of N_D will be a straight line only for the correct N_D value; then the slope and intercept give E_D and m^* . Analyzing the data of Fig. 1 for $T > 120^\circ\text{K}$ in this way gives: $N_D = (2.2 \pm 0.5) \times 10^{18} \text{ cm}^{-3}$, $E_D = (3.2 \pm 0.2) \times 10^{-2} \text{ eV}$, and $(m^*/m_0) = 0.19 \pm 0.05$. Using these values we calculate that the Fermi level approaches the conduction band edge well within kT for $T < 120^\circ\text{K}$. The resulting degeneracy of the electron gas in the conduction band accounts for the difference at low temperature between the experimental n values and the values calculated from Eq. (2), since Eq. (2) is valid only for the nondegenerate case. The small value of (m^*/m_0) found for Cd₂GeO₄ is not unusual for cadmium-oxygen compounds; for CdO (m^*/m_0) equals 0.14 (1), whereas for Cd₂SnO₄ its value is approximately 0.05 (2).

The Hall coefficients of the samples doped with In, Y, and Gd were very weakly temperature dependent, increasing at most by a factor of 2 between 300 and 80°K. These samples are fully degenerate and a meaningful ionization energy could not be determined from the data.

The increase in μ with decreasing temperature (Fig. 2) is characteristic of scattering by phonons; however, the value of μ ($\approx 10 \text{ cm}^2/\text{V} \cdot \text{sec}$) at room temperature is

low compared to that of other oxides (CdO, $300 \text{ cm}^2/\text{V} \cdot \text{sec}$ (Ref.(4)); SnO₂, $100 \text{ cm}^2/\text{V} \cdot \text{sec}$ (Ref. (10))) with comparable donor concentrations and density-of-states effective masses. This indicates that the electron-phonon coupling in Cd₂GeO₄ is sufficiently strong so that the electrons move as large polarons. Therefore we will analyze the data using the theoretical calculation of the large polaron mobility given by Langreth (11); this theory has been applied successfully to lightly reduced WO₃ which has mobilities similar to those of Cd₂GeO₄ (12). According to Langreth, the large polaron mobility is given by:

$$\mu = \frac{e\hbar}{2\alpha m^{**}k\theta} \left[1 + \frac{1.53}{(\theta/T)} \right] \left[\exp(\theta/T) - 1 \right]. \quad (3)$$

Here α is the electron-phonon coupling constant, m^{**} is the polaron effective mass, and $\theta = \hbar\omega_{\text{LO}}/k$ is the characteristic temperature corresponding to the optical mode frequency ω_{LO} . α and m^{**} are related by:

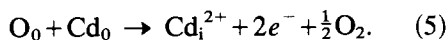
$$(m^{**}/m_0) = (1 - 0.008\alpha^2) / (1 - \alpha/6 + 0.0034\alpha^2). \quad (4)$$

For $T > 150^\circ\text{K}$ the temperature dependence of our experimental μ values obeys Eq. (3) very well with $\theta = 350 \pm 30^\circ\text{K}$; a fit of the absolute values of μ , together with Eq. (4), then gives $\alpha = 4.3$ and $(m^{**}/m_0) = 2.5$. These values for the coupling constant and the polaron mass should be considered as upper limits, since in the analysis we have assumed that the interaction of the carriers with the optical modes is the only factor limiting the mobility. In our polycrystalline samples scattering by grain boundaries may well have some influence on the mobility. In that case the true polaron mobility is larger than the measured mobility, which would lead to α and m^{**}/m_0 values smaller than those calculated above.

For $T < 150^\circ\text{K}$ the measured mobilities are smaller than the values calculated from Eq. (3); we ascribe this to the increasing influence of ionized impurity scattering at low temperatures. This is confirmed by the observation that in the doped samples the mobility at 100°K is approximately three times smaller than that in the undoped samples.

Defect Chemistry

At first glance the data of Tables I and II seem to suggest the following simple defect structure of Cd_2GeO_4 : samples prepared under vacuum are oxygen deficient, containing either oxygen vacancies (V_O^{2+}) or cadmium interstitials (Cd_i^{2+}) which act as donor defects. In the olivine structure defects involving Ge atoms are unlikely because of the strong covalent bonding in the GeO_4 tetrahedra; on the other hand the structure will probably accommodate Cd interstitials in the relatively large interstices of the Ge-O framework. The n -type conductivity can then be understood on the basis of the reaction:



Substitution of Cd by In, Gd, or Y produces a positive defect M_{Cd}^+ , whereas doping with Na gives Na_{Cd}^- . The dopants change the carrier concentration according to the electroneutrality equation:

$$[\text{M}_{\text{Cd}}^+] + 2[\text{Cd}_\text{i}^{2+}] = n + [\text{Na}_{\text{Cd}}^-]. \quad (6)$$

However, this simple description of the defect structure cannot be complete. It neglects that in the samples the Cd/Ge ratio may not be exactly equal to 2. CdO is slightly volatile at 850°C and may be lost from the disks during the high-temperature preparation. Even small losses may produce large defect concentrations; for example, a CdO/GeO₂ ratio of 1.999 corresponds to cadmium and oxygen vacancy concentrations of $2 \times 10^{19} \text{ cm}^{-3}$. Then the electrons would be a minority defect, and n should

be rather sensitive to small changes in the CdO/GeO₂ ratio. However, a comparison of samples 49, 50 and 5 shows that the deliberate addition of excess CdO and GeO₂ to the starting material does not produce samples with markedly different carrier concentrations. This may indicate that deviations of the ideal CdO/GeO₂ ratio are accommodated in the crystal structure as electrically neutral defects, for example, as ($\text{V}_{\text{Cd}}^{2-}\text{V}_{\text{O}}^{2+}$) complexes. The defect structure of Cd_2GeO_4 would then be similar to that of BaTiO_3 , where BaO deficiencies are accommodated as neutral defect complexes (13). On the other hand the homogeneity range of Cd_2GeO_4 may be extremely narrow, so that attempts to change the Cd/Ge ratio results in the formation of a two-phase system consisting mainly of Cd_2GeO_4 with a small amount of CdGeO_3 . The appearance of a very weak X-ray line of CdGeO_3 in the diffraction pattern of sample 50 (and some other samples listed in Tables I and II) supports the latter explanation.

In ternary oxides the phase rule requires that, in addition to the temperature and hydrostatic pressure, two additional parameters must be fixed in order to establish a well-defined defect concentration in thermodynamic equilibrium for pure samples (14). These can be, for example, the partial pressures of two volatile components (P_{Cd} and P_{O_2}), or one partial pressure and the Cd/Ge ratio in the solid. In order to test this, we have heated Cd_2GeO_4 in an evacuated tube with separate CdO; CdO is sufficiently volatile under these conditions so that it establishes well-defined P_{Cd} and P_{O_2} in the tube. Between samples 40 and 42 P_{Cd} and P_{O_2} over the sample were varied by a factor of 25 (as calculated from the temperature dependence of the vapor pressures over CdO (15)); between samples 40 and 43 P_{Cd} and P_{O_2} were kept constant but the temperature of the Cd_2GeO_4 was varied. However, a comparison of the carrier concentration of

samples 40, 42, 43, and 5 (where no deliberate attempt was made to control the partial pressures) shows that n is insensitive to the conditions inside the tubes as long as large amounts of oxygen are absent. These results are readily understandable if one assumes that n is determined by accidental donor impurities, which are present in larger concentrations than electrically active defects (such as Cd_i^{2+}) related to any oxygen deficiency. In terms of the electroneutrality equation (Eq. (6)) this would mean $[\text{M}_{\text{Cd}}^+] = n$; consequently n should be independent of P_{O_2} , P_{Cd} , and T . However, it is clear from Tables I and II that n is strongly dependent on P_{O_2} , in both the undoped and doped samples. For example, comparison of samples 23 and 5 shows that n decreases by a factor of 10^3 on heating in 1 atm. oxygen; reheating under vacuum, even for a short time (samples 32 and 34) restores the original conductivity. These results seem to be inconsistent with the assumption that n is determined by donor impurities; nor do they support the opposite assumption. If n is determined by defects related to oxygen deficiency, such as Cd_i^{2+} (or V_o^{2+}), then it follows from Eqs. (5) and (6) that $n \sim P_{\text{O}_2}^{-1/6}$ for $[\text{M}_{\text{Cd}}^+] < [\text{Cd}_i^{2+}]$. Then changing P_{O_2} from $\approx 10^{-5}$ atm (under vacuum) to 1 atm should decrease n by one order of magnitude only; the experimentally found change in n is much too large to be explained as a consequence of a change in bulk defect concentrations with P_{O_2} .

A possible explanation of the anomalously large effect of oxygen, and of the ease with which it can be reversed, is to invoke chemisorption of oxygen at high temperatures on the surface of the Cd_2GeO_4 grains. In this case the interior of the grains would still be conducting but the absorbed oxygen, in the form of O^{2-} on the surface, would produce just below the surface a layer depleted of electrons and therefore insulating. The measured sample resistivity is then determined by the insulating depletion layers. The

effects of oxygen chemisorption on the conductivity have been observed in other polycrystalline oxides as well; for example, in In_2O_3 (16) and in extreme form in fine-grained ZnO (17). Its importance for the conductivity of polycrystalline Cd_2GeO_4 remains uncertain until comparative measurements can be made on single crystals.

For the deliberately doped samples we assume that the trivalent metal ions substitute for the Cd ions, since their ionic radii are rather similar. Charge compensation can then take place by electrons (one for each dopant ion), by charged atomic defects such as $\text{V}_{\text{Cd}}^{2-}$, or by a combination of both. The last column of Table II shows that for all samples (except two In-doped samples) prepared under vacuum the carrier concentration increased with dopant concentration but was never equal to it. Therefore, for these samples the solubility limit of the dopant in Cd_2GeO_4 was not exceeded, and charge compensation was only in part by electrons. Heating the doped samples in oxygen decreases n drastically; the original conductivity can be restored by a subsequent short firing under vacuum. For samples doped with In this decrease may be due to exsolution of In_2O_3 , since in sample 24, which was slowly cooled in oxygen instead of quenched, a very weak line of In_2O_3 was detected in the X-ray pattern. However, for all other doped samples no evidence for exsolution of the dopant oxide was found, although it was looked for carefully. This negative evidence, taken together with the similar behavior of the undoped samples, indicates that heating in oxygen reduces the conductivity in both doped and undoped samples by the same chemisorption mechanism.

Photoelectrolysis

In the experiments on the photoelectrolysis of water, Cd_2GeO_4 disks were used as the oxygen-producing anode in an electro-

chemical cell. Upon illumination of the disks with monochromatic light (photon energy $h\nu$, photon flux Φ), a current i flows through the cell due to the generation of hole-electron pairs in the Cd_2GeO_4 and subsequent production of hydrogen and oxygen. Recently it has been shown (18) that the quantum efficiency of this process, defined as $\eta = i/\Phi$, is proportional to the absorption coefficient α of the semiconducting anode. Therefore plots of $(\eta h\nu)^n$ versus $h\nu$ can be used to determine both the energy, E_g , of the band gap, and the nature of the optical transition (indirect, $n = 2$, or direct, $n = \frac{1}{2}$). In Fig. 3 we show the data for sample 5; other undoped or doped samples gave similar results. From these data we conclude that the band gap of Cd_2GeO_4 is indirect, and occurs at $E_g = 3.15 \pm 0.02$ eV; at higher energies there is evidence for a direct interband transition at 4.10 ± 0.05 eV.

Summary

n -Type Cd_2GeO_4 is a wide-band semiconductor with an indirect band gap of 3.15 eV. The carriers originate from shallow donors; their mobility is limited by strong electron-phonon interaction leading to the formation of large polarons. At low

temperatures and large dopant concentration impurity scattering of the carriers becomes important. When doped with trivalent metal oxides to carrier concentrations larger than 10^{18} cm^{-3} the material becomes a degenerate semiconductor. For samples prepared under vacuum the carrier concentration is nearly independent of the temperature of preparation, of the Cd and O_2 pressures over the samples, and of the CdO/GeO_2 ratio; this indicates that the donor centers are impurities, even in the undoped material. The large increase in the resistivity on heating in 1 atm of oxygen, for both the undoped and the doped samples, cannot be rationalized in terms of changes in the bulk defect concentrations; chemisorption of oxygen on the surface of the grains may be the cause of this effect.

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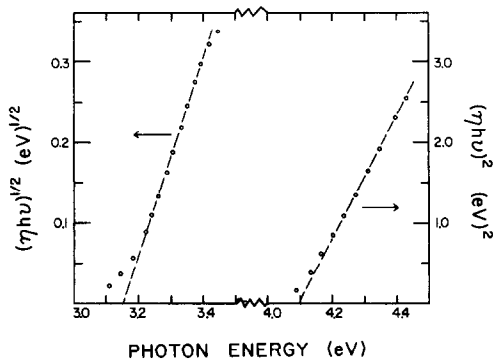


FIG. 3. The quantum efficiency η for photoelectrolysis of sample 5. Left scale: plotted as $(\eta h\nu)^{1/2}$ in the region of the indirect gap at 3.15 eV. Right scale: plotted as $(\eta h\nu)^2$ in the region of the direct transition at 4.1 eV.

References

1. F. P. KOFFYBERG, *J. Solid State Chem.* **2**, 176 (1970).
2. A. J. NOZIK, *Phys. Rev. B* **6**, 453 (1972).
3. R. D. SHANNON, J. L. GILLSON, AND R. J. BOUCHARD, *J. Phys. Chem. Solids* **38**, 877 (1977).
4. F. P. KOFFYBERG, *Canad. J. Phys.* **49**, 435 (1971).
5. G. HAACKE, *Appl. Phys. Lett.* **28**, 622 (1976).
6. E. L. BELOKONEVA *et al.*, *Sov. Phys. Crystallogr.* **17**, 177 (1972).
7. E. L. BELOKONEVA *et al.*, *Sov. Phys. Crystallogr.* **18**, 610 (1974).
8. S. N. SUBBARAO *et al.*, *Mater. Res. Bull.* **13**, 1461 (1978).
9. J. S. BLAKEMORE, "Semiconductor Statistics," Chap. 3, Pergamon, New York (1962).
10. J. A. MARLEY AND R. C. DOCKERTY, *Phys. Rev. A* **140**, 304 (1965).

- 11 D. C. LANGRETH, *Phys. Rev.* **159**, 717 (1967).
- 12 J. M. BERAK AND M. J. SIENKO, *J. Solid State Chem.* **2**, 109 (1970).
- 13 N. G. EROR AND D. M. SMYTH, *J. Solid State Chem.* **24**, 235 (1978).
- 14 H. SCHMALZRIED, in "Progress in Solid State Chemistry" (H. Reiss, Ed.), Vol. 2, p. 265, Pergamon, New York (1965).
- 15 O. GLEMSE AND U. STÖCKER, *Ber. Bunsenges. Phys. Chem.* **67**, 505 (1963).
- 16 J. H. W. DEWIT, G. VAN UNEN, AND M. LAHEY, *J. Phys. Chem. Solids* **38**, 819 (1977).
- 17 J. W. ORTON AND M. J. POWELL, *Phil. Mag. B* **38**, 491 (1978).
- 18 F. P. KOFFYBERG, K. DWIGHT, AND A. WOLD, *Solid State Commun.* **30**, 433 (1979).