JOURNAL OF SOLID STATE CHEMISTRY 31, 209–216 (1980)

Electrical and Optical Properties of High-Purity p-Type Single Crystals of $GeFe_2O_4$

PIERRE STROBEL, FRANS P. KOFFYBERG,* AND AARON WOLD†

Department of Chemistry, Brown University, Providence, Rhode Island 02912

Received January 5, 1979

Single crystals of the spinel $GeFe_2O_4$, grown by the chemical vapor transport technique, are p-type semiconductors with an acceptor ionization energy of 0.39 eV. The material is a heavily compensated band-type semiconductor, with a typical hole concentration of 10^{14} cm^{-3} near room temperature, and a temperature-independent Hall mobility of 2 $cm^2/V{\cdot}sec$. Optical absorption measurements show the optical band gap to be ≥ 2.3 eV; the octahedral field splitting of the Fe^{2+} d-levels is 10 200 cm^{-1}. Magnetic measurements show that n_{eff} is 5.26, from which a trigonal field splitting of 950 cm^{-1} is derived.

Introduction

The experimental study of the electrical properties of transition metal oxides is beset by three main problems: (i) The requirement of homogeneous single crystals, (ii) the difficulty in interpreting Hall effect measurements in magnetically ordered materials, and (iii) the striking influence of minor variations in the actual chemical composition. These difficulties have been pointed out in many studies of oxides with the rock salt or the spinel structure, recently reviewed by Parker (*1*).

Previously studied spinels were mixed-valency systems of the type $M^{2+}_{1-x}Fe^{2+}_xFe^{3+}_2O_4$, where the conduction mechanism is best described by electrons hopping between B-site Fe^{2+} and Fe^{3+} ions (*2*). No spinels without mixed valencies on the B-sites have been studied so far. On the other hand, not all transition metal oxides are hopping semiconductors, as has been shown for Li-doped NiO (*3*).

We report here the study of a stoichiometric spinel oxide, $GeFe_2O_4$. This compound is a normal spinel (*4*). Magnetic and Mössbauer studies have shown that it is antiferromagnetic with $T_N = 10°K$ (*5–7*). Its ir (vibrational) spectrum has been measured (*8*); all these studies used polycrystalline samples. Neither crystal growth nor the electrical properties have been reported so far. We describe here the preparation of single crystals of $GeFe_2O_4$, its optical spectrum in the visible and near ir, and its electrical properties. Our results show that the crystals are low-mobility band-type semiconductors.

Experimental

Single-Crystal Preparation

Polycrystalline $GeFe_2O_4$ was obtained by solid state reaction between appropriate mixtures of GeO_2, Fe_2O_3 (Johnson–Matthey), and Fe (Leico), previously heated

* Department of Physics, Brock University, St. Catharines, Ontario, Canada.

† To whom all correspondence should be addressed.

0022-4596/80/020209-08$02.00/0
Copyright © 1980 by Academic Press, Inc.
All rights of reproduction in any form reserved.
Printed in Great Britain

in hydrogen. The mixture was heated in evacuated silica tubes for 40 hr at 800°C, then 24 hr at 950°C with intermittent grinding.

Crystals were grown by chemical vapor transport in evacuated silica tubes (12 mm id., 15–20 cm long), using a two-zone furnace. The transporting agent was $TeCl_4$ (1.0 mg/cm^3), introduced as metallic Te and gaseous Cl_2. Special attention was paid to corrosion problems. The silica tubes were reheated to the softening point before use; they were protected with an inner carbon coating obtained by pyrolysis of acetone, and outgassed before sealing. Finally, the growth zone was cleaned *in situ* by back-transport for 20 hr.

After thermal equilibrium was established in the tube at 920°C, the transport was allowed to proceed by decreasing slowly the growth zone temperature (~2°C/hr) to 760°C. Reproducible results were obtained using different furnaces under the actual conditions listed in Table II. The transport rate was ~1.5 mg/hr. Attempts at temperatures higher than 930°C showed a sharp increase in the reaction of the charge with the silica tubes.

After slow cooling, the crystals were removed from the tubes, washed in 1 *M* hydrochloric acid in order to dissolve any condensed chloride or TeO_2 and finally rinsed with distilled water and ethanol.

Measurement Procedures

The density was measured by a hydrostatic technique (*9*) using 1-methyldecalin as the density fluid, calibrated with a high-purity silicon crystal.

Both powders and ground single crystals of $GeFe_2O_4$ were analyzed by slow-scan (0.25°/min) X-ray diffraction with a Si internal standard. A Norelco X-ray diffractometer with a high-intensity Cu source ($\lambda_{CuK\alpha_1} = 1.5405$ Å) and a graphite monochromator in the diffracted beam was used.

The magnetic susceptibility of ground single crystals was determined in the temperature range 55–300°K using a Faraday balance previously described (*10*) and calibrated with platinum. The maximum field value was 10.5 KOe.

For optical measurements, thin slices were carefully cut and ground from single crystals (final polishing with 1 μm alumina). Only two crystals yielded useful samples, because of the extreme difficulty of polishing the brittle, thin crystals. The optical absorption was measured with a single-beam instrument using the sample-in, sample-out method.

The dc conductivity and Hall effect were determined by the Van der Pauw technique (*11*) with readouts on a Keithley 610 electrometer (input impedance 10^{14} Ω). Contacts made with ultrasonically applied Indalloy (No. 3) were found to be ohmic under our experimental conditions.

Results and Discussion

(*a*) *Single Crystals*

The chemical transport technique produced octahedral crystals, with edges up to 4 mm (Fig. 1). Bulky crystals appeared black, but thin and crushed ones were light brown in color, in contrast with powdered $GeFe_2O_4$ obtained from solid state reaction, which is black, probably because of traces of Fe^{3+} as in $Fe_{1-x}O$.

Structural results are summarized in Table I. The structure and cell parameter from Durif-Varambon *et al.* (*4*) were confirmed. We note that small amounts of Fe^{3+}, if present at all, cannot be detected by X-ray diffraction since the cell parameters of $GeFe_2O_4$ and Fe_3O_4 (*12*) differ by less than 0.2%. A value of 8.408 Å was reported for natural $GeFe_2O_4$ (Brunogeirite), which contains ~10% Fe_3O_4 (*13*).

(*b*) *Magnetic Susceptibility*

Our magnetic susceptibility results are very similar to those obtained by Blasse and Fast

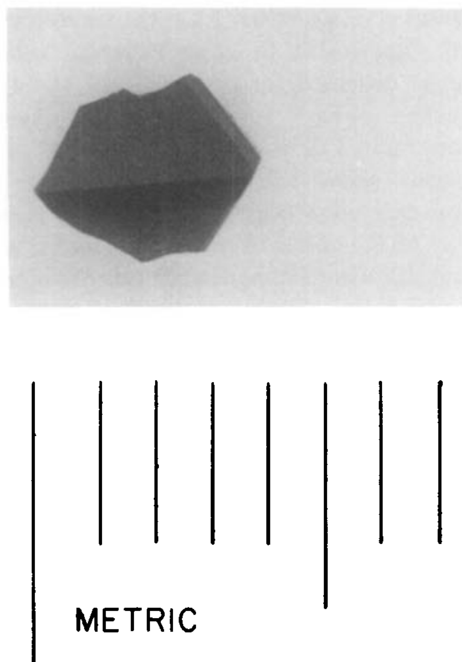

FIG. 1. Monocrystalline sample of $GeFe_2O_4$ grown by chemical vapor transport (series 7).

(*5*) with a nonlinear variation of χ^{-1} vs T below ~110°K, where we observe a slight field dependence of χ. Experimental asymptotic Curie temperatures and effective numbers of Bohr magnetons (n_{eff}) are given in Table I.

As there is spin–orbit coupling in Fe^{2+}, n_{eff} is related to the trigonal field splitting δ of the t_{2g} levels of B-site cations. This allows a further comparison of magnetic results with δ values obtained from Mössbauer spectra, as discussed by Hartmann-Boutron (*14*). Values of δ, calculated using Hartmann-Boutron's assumptions, are presented in Table I, which shows a good agreement between our results and the Mössbauer δ value. The difference between the results of Blasse and Fast and our results may be due to the lower Fe^{3+} content of our samples.

(*c*) *Optical Absorption*

The optical absorption coefficient of $GeFe_2O_4$ (uncorrected for reflectivity losses) in the range 500–1200 nm is shown in Fig. 2.

TABLE I

STRUCTURAL AND MAGNETIC DATA FOR $GeFe_2O_4$

	Durif-Verambon *et al.* (*4*) Imbert (*7*)	Blasse and Fast (*5*)	This work
Preparation	$Fe + Fe_3O_4$ $+ GeO_2$ 900°C	$Fe + Fe_2O_3$ $+ GeO_2$ 1000°C	$Fe + Fe_2O_3 + GeO_2$ 950°C + vapour transport via $TeCl_4$
Cell parameter (Å)	8.411		8.4118 ± 0.0001
Density (g/cm^3)			calc. 5.54 meas. 5.51
Asymptotic Curie temp. (°K)		−15	−25
Effective magnetic moment (μ_B)		5.40	5.26
Trigonal field splitting of Fe^{2+} t_{2g} levels (cm^{-1})	1020 (Mössb.)	600 (magn.)	950 (magn.)

We ascribe the broad band peaking at 980 nm (10 200 cm^{-1}) to the $^5\Gamma_5 \rightarrow {}^5\Gamma_3$ crystal-field transition of the Fe^{2+} ion, octahedrically coordinated with oxygen. This is in good agreement with the band observed at 10 400 cm^{-1} for $Fe(H_2O)_6^{2+}$ (*15*).

The sharply rising absorption edge at 550 nm suggests the onset of a band-to-band transition; the corresponding value of the optical band gap is therefore $E_g \geqslant 2.3$ eV.

(d) Conductivity and Hall Effect

The conductivities of single crystals of $GeFe_2O_4$ were measured in the range 200–320°K, corresponding to σ values ranging from 10^8 to 10^4 $(\Omega\ cm)^{-1}$; a typical σ vs T^{-1} curve is given in Fig. 3. All measurements fitted the relationship

$$\sigma = \sigma_0 \exp\left(\frac{E_\sigma}{kT}\right).$$

Values of ρ (295°K) and E_σ of different series of crystals, as well as actual conditions of growth, are given in Table II. Good agreement is observed between ρ and E_σ of various crystals, either from the same transport experiment or from different tubes. Values obtained for crystals from strongly attacked growth tubes (grown at higher temperatures or without inner surface protection) show the striking influence of impurities upon both ρ and E_σ. The lower value of E_σ obtained in series 3, which was grown for a much longer time than the others may be due to similar contamination.

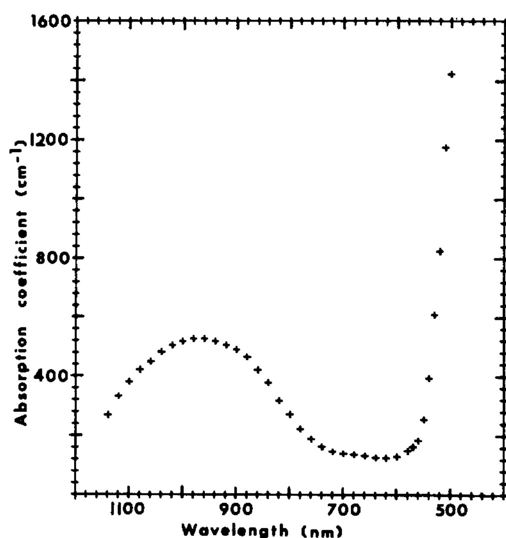

FIG 2. The optical absorption spectrum of $GeFe_2O_4$ at room temperature (crystal from series 3, thickness 57 ± 5 μm).

Discrepancies in the absolute values of ρ are mainly due to the uncertainties on the thickness of the samples, which were not in the ideal flat plate shape. Measurements on inner and outer parts of one sliced crystal were in good agreement.

The measured Hall constants R_H were found to be independent of the applied field up to 7 kOe (Fig. 4, inset). We note that our measurements were performed in a temperature region far above the magnetic ordering range ($T/T_N > 25$). The sign of the Hall effect indicated *p*-type conduction. Measured values of the hole concentration $p = (eR_H)^{-1}$ and of the Hall mobility $\mu_H = \sigma R_H$ are shown in Figs. 3 and 4. We found that p is thermally activated, with an activation energy E_H very close to E_σ (Fig. 3); consequently, μ_H is essentially independent of T in the range 250–320°K.

In previously studied spinels (*1*), the conduction was ascribed to small polarons hopping between cations of different valencies on the *B*-sites. In such a hopping model, the drift mobility is very small (experimental value for holes in cobalt ferrite: 1.4×10^{-6} $cm^2/V{\cdot}sec$) (*2*) and thermally activated; the carrier concentration is basically temperature independent. The Hall mobility, although not equal to the drift mobility, should also be very small and thermally activated. In contrast, in $GeFe_2O_4$, it is the carrier concentration p that is thermally activated, and the Hall mobility is well above the limit (~ 0.1 $cm^2/V{\cdot}sec$ (*3*)) below which hopping conduction may take place.

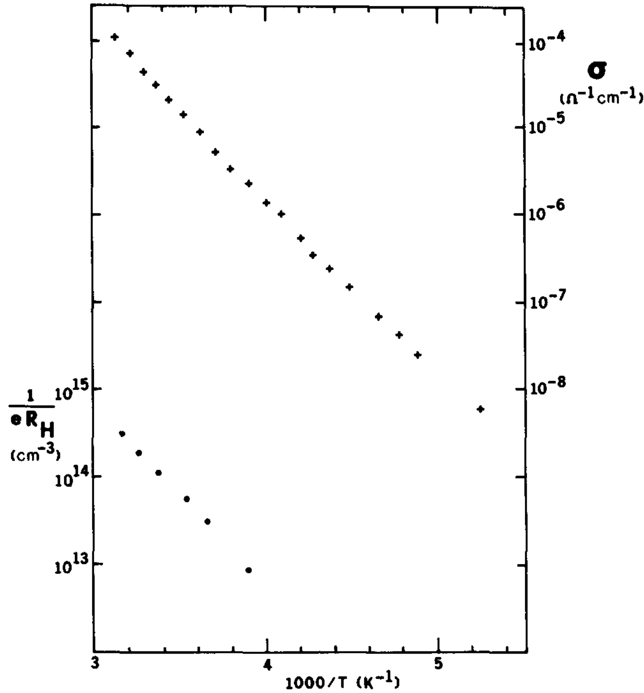

FIG. 3. The conductivity (+) and hole concentration (●) of $GeFe_2O_4$ as a function of temperature (crystal from series 7).

We therefore conclude that $GeFe_2O_4$ is a band conductor; the low mobility may be due to a narrow valence band and/or large polaron formation, as has been found in *p*-type NiO (*3*).

Two further possibilities arise in the case of band conduction. In nearly intrinsic conduction, the activation energies of the conductivity (E_σ) and of the Hall constant (E_H) should be equal to $E_g/2$. our data show

TABLE II

ELECTRICAL PROPERTIES OF SINGLE CRYSTALS OF $GeFe_2O_4$

Crystal growth series	Transport temp. (°C)	Duration of growth (days)	Resistivity at 295°K (Ω-cm)	Activation energy (eV)	
				Conductivity	Hall const.
1	925/760	10	1.5×10^5	0.370	
			1.4×10^5	0.386	
2	920/745	12	1.3×10^5	0.406	
			9.6×10^4	0.396	
3	900/730	20	2.6×10^5	0.355	
4	910/745	11	2.6×10^5	0.435	
			2.4×10^5	0.450	
5	925/760	11	7.6×10^4	0.421	0.442
6	910/740	11	1.4×10^5	0.406	
7	920/745	12	3.5×10^4	0.418	0.422
Crystals from strongly attacked tubes			10^1–10^2	0.05–0.15	(magn)

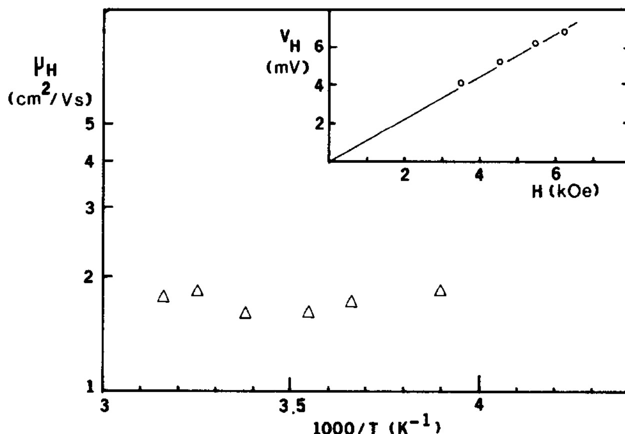

FIG. 4. Temperature dependence of the Hall mobility μ_H of $GeFe_2O_4$ (crystal from series 7); inset, variation of the Hall voltage V_H with applied magnetic field.

$E_\sigma \simeq E_H \ll E_g/2$. Furthermore, the purity required for intrinsic conduction at room temperature is unlikely to be reached.

Extrinsic *p*-type conduction requires the presence of acceptors A, which ionize according to

$$A = A^- + p.$$

In real crystals, the acceptors are partly compensated by ionized donors or positively charged defects D^+. If N_A and N_D are the total concentration of acceptors and donors, $N_A = [A] + [A^-]$, and charge neutrality requires that

$$[A^-] = N_D + p.$$

From the acceptor ionization equilibrium, we obtain:

$$p = \beta N_v \frac{[A]}{[A^-]} \exp\left(\frac{E_A}{kT}\right),$$

where E_A is the ionization energy of acceptors, β their spin degeneracy, and N_v the density of states in the valancy band (*16*). Rearranging A, A^-, and N_v, we obtain:

$$p = \frac{N_A - (p + N_D)}{(p + N_D)} a\beta \left(\frac{m_p^*}{m_0}\right)^{3/2} T^{3/2} \exp\left(\frac{E_A}{kT}\right),$$

where a is a numerical constant equal to 4.832×10^{15} cm^{-3} °K$^{-3/2}$, and (m_p^*/m_0) is the relative effective mass of holes.

This equation can be further simplified, depending on the degree of compensation: In the lightly compensated case, we have $N_D \ll p$, whereas in the heavily compensated case $N_D \gg p$. Resulting equations are compared in Table III, together with the experimental values for p vs T relationships. In the further calculation of N_A or N_D/N_A, we have assumed $\beta = 2$ and $m_p^* = m_0$; the order of magnitude of these values is certainly correct, and the main conclusions are not changed if the assumed β and m_p^*/m_o values are varied.

Evaluating our data according to the light compensation case leads to unreasonable values of N_A and E_A; compared to the total Fe^{2+} concentration in $GeFe_2O_4$ (2.7×10^{22} cm^{-3}), an acceptor concentration of 1.5×10^{22} cm^{-3} is unacceptable. Moreover, 0.81 eV is an unrealistically large value for an acceptor ionization energy. The parameters assuming the heavy compensation case appear much more acceptable; the ionization energy is now 0.39 eV, and a compensation ratio of 0.10 is not unusual. With $p \simeq 10^{14}$ cm^{-3} at room temperature there seems to be no difficulty in satisfying the basic assumption $N_A > N_D > p$ for the heavy compensation case.

We have no actual information as to the nature of the acceptors and compensators.

TABLE III
RESULTS WITH EXTRINSIC MODEL

	Light compensation	Heavy compensation
Basic assumption	$N_A \gg p \gg N_D$	$N_A \gg N_D \gg p$
p vs T (theory)	$pT^{-3/4} = C_1 \exp\left(-\frac{E_A}{2kT}\right)$	$pT^{-3/2} = C_2 \exp\left(-\frac{E_A}{kT}\right)$
	$C_1 = N_A^{1/2} a^{1/2} \beta^{1/2} \left(\frac{m_p^*}{m_0}\right)^{3/4}$	$C_2 = \left(\frac{N_A - N_D}{N_D}\right)_{a\beta} \left(\frac{m_p^*}{m_0}\right)^{3/2}$
Fitted values	$E_A = 0.81$ eV $C_1 = 1.21 \times 10^{19}$ (cgs)	$E_A = 0.39$ eV $C_2 = 8.32 \times 10^{16}$ (cgs)
Assuming $\beta = 2$ $m_p^* \simeq m_0$	$N_A = 1.5 \times 10^{22}$ cm^{-3}	$\frac{N_D}{N_A} = 0.105$

However, we think it likely that the acceptors are Fe^{3+} ions on the spinel B-sites, whereas the compensators probably are traces of Cl^- incorporated during the crystal growth or charged oxygen vacancies.

The observed mobility is intermediate between the very small values observed for hopping conductors and the larger values observed in wideband semiconductors (*17*). Our values are of the same order of magnitude as those observed in p-type NiO (*3*). In that case, the small mobility values have been attributed to the formation of large polarons by the holes, and a similar condition may exist in $GeFe_2O_4$.

Conclusion

The chemical vapor transport technique allowed the growth of pure light-brown single crystals of the iron (II) spinel $GeFe_2O_4$. Magnetic and optical measurements confirmed the splitting of B-sites Fe^{2+} d-levels; experimental values are 10 200 cm^{-1} for the octahedral crystal field splitting, and 950 cm^{-1} for the trigonal field splitting. The crystals were p-type semiconuctors with an optical band gap $E_g \geq$ 2.3 eV. Conductivity and Hall effect measurements showed that the acceptor ionization energy is 0.39 eV, and that the mobility is moderately low (~2 cm^2/V·sec) and independent of temperature. A consistent interpretation of the data is obtained by applying the model of a heavily compensated band-type semiconductor. $GeFeO_4$ differs in that respect from previously reported hopping-type spinels; its electronic properties are analogous to antiferromagnetic NiO at high temperatures.

Acknowledgments

The authors wish to thank Mr. Kirby Dwight for numerous helpful discussions during the course of this work as well as Mr. Robert Kershaw for his help with the synthetic part of this work.

In addition the authors wish to acknowledge the partial support of the Office of Naval Research in Arlington, Virginia, as well as the support of Dr. Pierre Strobel by the National Science Foundation, Washington, D.C. (Grant GF 39737).

Acknowledgment is also made to the Materials Research Laboratory Program at Brown University.

References

1. R. PARKER, *in* "Magnetic Oxides" (D. J. CRAIK, Ed.), Part 1, Chap. 8, Wiley, New York (1975).

2. G. H. JONKER, *J. Phys. Chem. Solids* **9**, 165 (1959).
3. A. J. BOSMAN AND H. J. VAN DAAL, *Advanc. Phys.* **19**, 1 (1970).
4. A. DURIF-VARAMBON, E. F. BERTAUT, AND R. PAUTHENET, *Ann. Chim. (Paris)* **13**, 526 (1956).
5. G. BLASSE AND J. F. FAST, *Philips Res. Rep.* **18**, 393 (1963).
6. K. B. MATHUR, *Solid State Commun.* **3**, 401 (1965).
7. P. IMBERT, *C. R. Acad. Sci. Paris, Ser. B* **263**, 184 (1966).
8. P. TARTE, *Spectrochim. Acta* **19**, 49 (1963).
9. R. ADAMS, Ph.D. thesis, Brown University (1973).
10. B. L. MORRIS AND A. WOLD, *Rev. Sci. Instrum.* **89**, 1937 (1968).
11. L. J. VAN DER PAUW, *Philips Res. Rep.* **13**, 1 (1958).
12. H. E. SWANSON, *Nat. Bur. Stand. Monogr.* **25**, (Sect. 5), 31 (1967).
13. J. OTTEMANN AND B. NUBER, *Neues Jahrb. Mineral. Monats.*, 263 (1972).
14. F. HARTMANN-BOUTRON, *CR. Acad. Sci. Paris, Ser. B* **263**, 188 (1966).
15. D. S. MCCLURE, *in* "Solid State Physics" (F. Seitz and D. Turnbull, Eds.), Vol. 9, p. 497, Academic Press, New York (1959).
16. J. S. BLAKEMORE, "Semiconductor Statistics," Chap. 2, Pergamon, Oxford (1962).
17. F. P. KOFFYBERG, *Canad. J. Phys.* **49**, 435 (1971).