

Shallow Acceptor States in ZnTe and CdTe

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The group VA element P and the group IA elements Li and Na give rise to shallow acceptor centers in ZnTe and in CdTe. An analysis of the carrier concentration data for Li-doped ZnTe and P-doped ZnTe on the basis of a single-level acceptor and nondegenerate statistics indicates that P and Li produce shallow, hydrogenic-type acceptor levels in ZnTe. Annealing studies demonstrate that the shallow levels in Li-doped ZnTe and CdTe may be removed by heat treatment at 250°C for tens of hours. The concentrations of shallow acceptors in P-doped ZnTe and Na-doped ZnTe are relatively unchanged by the annealing procedure. The effective mass for holes in ZnTe as deduced from the Hall analysis is $0.36m$, where m is the free-electron mass.

I. INTRODUCTION

ZINC telluride and cadmium telluride are cubic semiconductors (zinc blende structure) with direct band gaps of 2.3 and 1.5 eV, respectively, at 300°K. These two compounds are also the only members of the zinc and cadmium chalcogenides which can be made even moderately p type. By applying the concept of tetrahedral bonding to substitutional impurities in these compounds,¹ one may deduce that acceptor states should be introduced by a group VA element substituting for Te or by a group IA or IB element substituting for the cation (zinc or cadmium). In addition, stoichiometric defects may also lead to acceptor activity—e.g., a cation vacancy or an interstitial tellurium atom. Some of the properties of Cu, Ag, and Au acceptors in ZnTe² and in CdTe^{3,4} have been described. These group-IB substitutional acceptors produce relatively deep levels in these two compounds. Shallow levels exist in relatively pure ZnTe, and it has been suggested that these levels are due to a stoichiometric defect.^{2,5} The experiments of Aven and Segall have indicated that the stoichiometric defect in ZnTe is a doubly ionizable center (probably a zinc vacancy) with acceptor levels 0.05 and 0.13 eV above the valence band.² Similar results were obtained by Shiozawa and Jost, who analyzed Hall data from the shallow levels observed in nominally undoped ZnTe grown from the vapor phase.⁶ These authors concluded that the shallow acceptor exhibited a decrease in effective ionization energy with increasing acceptor concentration and that the ionization energy of this acceptor at infinite dilution was 0.075 eV. The degeneracy factor of this center which was most consistent with their over-all analysis was $\frac{3}{2}$, and the density-of-states mass of a hole in ZnTe was found to be 0.44 m . The degeneracy factor observed is

consistent with the identification of the acceptor as a doubly ionizable defect, for which the appropriate degeneracy factor for the first ionization should be 1.5.⁷ The high-temperature conductivity studies of ZnTe equilibrated under a known Zn pressure conducted by Thomas and Sadowski provide additional confirmation of the existence of a doubly ionizable zinc vacancy acceptor.⁵

The situation in CdTe with respect to native acceptor defects is similar in that the cadmium vacancy has been postulated to be a double acceptor which possesses a shallow level.^{3,4}

Shallow levels in ZnTe and CdTe have also been reported to be produced by doping with the group VA substitutional acceptor, phosphorus.⁸ This paper describes a more detailed analysis of the electrical transport properties of the shallow level introduced by phosphorus (a group VA acceptor) and by lithium (a group IA acceptor) in ZnTe. Experimental results obtained for these elements in CdTe and for sodium in ZnTe and CdTe are also presented.

II. EXPERIMENTAL

Single crystals of CdTe and of ZnTe were grown from melts containing excess Te and the desired doping agent (Li, P, or none as the case may be). A modified Bridgman technique was employed in which the crystals were grown at the rate of 0.8 to 1.5 in. per day. The resulting crystals were therefore in effect slow cooled under a Te overpressure. Subsequent heat treatments of portions of these single crystals were conducted in sealed, evacuated (to about 10^{-6} Torr) quartz ampoules. If a known elemental overpressure was desired, a chip of high-purity metal or Te was placed in the sample ampoule in a quartz plug. Samples which were heat treated were quenched by immersing the ampoule in a water bath in order to freeze in the atomic disorder more characteristic of the elevated firing temperature.

Electrical measurements were made by using the van der Pauw technique for obtaining resistivities and

¹ See, for example, R. Newman and W. W. Tyler, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1959), Vol. III, Chap. 3.

² M. Aven and B. Segall, *Phys. Rev.* **130**, 81 (1963).

³ D. de Nobel, *Philips Res. Rept.* **14**, 361 (1959).

⁴ M. R. Lorenz and B. Segall, *Phys. Letters* **7**, 18 (1963).

⁵ D. G. Thomas and E. A. Sadowski, *J. Phys. Chem. Solids* **25**, 395 (1964).

⁶ L. R. Shiozawa and J. M. Jost, Aeronautical Research Laboratory Contract No. AF 33(657)-7399; final report dated May 1965 (unpublished).

⁷ S. Teitler and R. F. Wallis, *J. Phys. Chem. Solids* **16**, 71 (1960).

⁸ F. F. Morehead and G. Mandel, *Phys. Letters* **10**, 5 (1964).

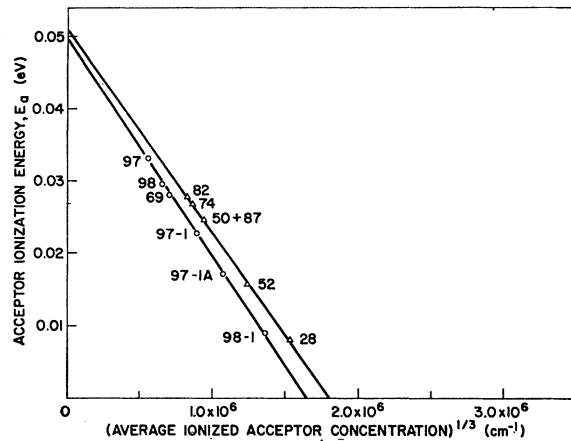


FIG. 1. Temperature dependence of the hole concentration of ZnTe crystals doped with P (triangles); with Li (circles); and of an undoped ZnTe crystal equilibrated under Zn at 400°C. Theoretical curves, obtained by applying Eq. (1) to the least-squares adjusted parameters obtained from Eq. (2), are shown as the solid lines in the figure.

Hall coefficients.⁹ The single crystals were lapped and polished into the form of disks approximately 0.5 mm thick and several millimeters wide. Contact to the samples was made either by soldering Indalloy No. 13 to chemically formed Au patches or by directly fusing dots of Indalloy No. 13 into the crystal. The electrical measurements were made with a conventional direct current potentiometric circuit employing a Leeds and Northrup Type K-3 potentiometer in conjunction with either a galvanometer or an electrometer as a null indicator, depending on the source impedance. A magnetic field of 7 kG was employed in the Hall measurements. The Hall apparatus was capable of providing constant temperature during measurement over the range of 70 to approximately 400°K.

III. RESULTS AND DISCUSSION

The starting point for the analysis of the carrier-concentration data is the well-known formula for non-degenerate statistics of a single level¹⁰

$$p(p+N_d)/(N_a-N_d-p) = (N_v/g) \exp(-E_a/kT). \quad (1)$$

Here p is the hole concentration at a temperature T °K due to an acceptor present in concentration N_a cm⁻³ with an ionization energy E_a relative to the valence-band edge. The acceptors are partially compensated by N_d cm⁻³ donors. The constant N_v is given by $2(2\pi m_v kT/h^2)^{3/2}$, where m_v is the density-of-states mass. The degeneracy factor g depends upon the impurity state involved and the band edge in question. In principle, one may apply the method of least squares to Eq. (1) and the experimental data (normally 15 to 20 values of p and of $10^3/T$) in order to obtain best-fit

values for the parameters E_a , g , m_v , N_d , and N_a . In practice, the procedure utilized in this paper is simpler.

For analytical purposes, Eq. (1) is rearranged into a linear form:

$$\log[p(p+N_d)(10^3/T)^{3/2}/(N_a-N_d-p)] = [20.182 + \log(1/g)(m_v/m)^{3/2}] - 5.04E_a(10^3/T). \quad (2)$$

Equation (2) is of the form

$$y = mx + b, \quad (3)$$

where y is the left-hand side of Eq. (2), x is $(10^3/T)$, and b is the quantity, $[20.182 + \log(1/g)(m_v/m)^{3/2}]$. The advantage of using Eq. (2) for analytical purposes instead of Eq. (1) is that the values of g , (m_v/m) , and E_a do not have to be known. For any particular values of N_a and N_d and experimental data on p and $(10^3/T)$, the method of least squares can be applied to determine the best values of m and of b [and, hence, of E_a and of the product $(1/g)(m_v/m)^{3/2}$]. The measure of the quality of the fit for particular values of N_a and N_d is given by

$$R = \left[\sum_{i=1}^N (y_i - mx_i - b)^2 / (N-2) \right]^{1/2}, \quad (4)$$

where the summation is over the N experimental points used in the analysis. The best values of N_a and N_d are thus taken to be those for which the value of R is a minimum. The value of $(N_a - N_d)$ almost certainly lies within the range of the value of p at 300°K and $10p$, if the level involved is shallow. For each of several values of $(N_a - N_d)$ in the above range, values of $[N_d/(N_a - N_d)]$ between 0 and 300 were employed in the computation of m , b , and R . The values of N_d and N_a which produce the best straight-line fit were quickly determined by observing the behavior of R . The use of a digital computer in the calculations made this procedure feasible. An additional check on the applica-

TABLE I. Least-squares adjusted parameters obtained from carrier analysis for ZnTe and CdTe single crystals.

Sample	Dopant	N_a (cm ⁻³)	N_d/N_a	E_a (eV)	$(1/g)(m_v/m)^{3/2}$
ZnTe 64	Undoped ^a	8.25×10^{16}	0.03	0.050	0.141
ZnTe 69	Li	4.55×10^{17}	0.71	0.028	0.175
ZnTe 97	Li	4.13×10^{17}	0.28	0.033	0.149
ZnTe 97-1	Li	1.95×10^{18}	0.23	0.023	0.153
ZnTe 97-1A	Li	2.38×10^{18}	0.41	0.017	0.183
ZnTe 98	Li	4.95×10^{17}	0.45	0.029	0.141
ZnTe 98-1	Li	5.10×10^{18}	0.41	0.009	0.155
ZnTe 28	P	5.80×10^{18}	0.50	0.008	0.165 ^b
ZnTe 50	P	2.21×10^{18}	0.23	0.025	0.165 ^b
ZnTe 52	P	4.05×10^{18}	0.33	0.016	0.165 ^b
ZnTe 74	P	1.40×10^{18}	0.29	0.027	0.165 ^b
ZnTe 82	P	1.26×10^{18}	0.29	0.028	0.165 ^b
ZnTe 87	P	1.82×10^{18}	0.29	0.025	0.165 ^b
CdTe 158	Li	1.36×10^{17}	0.44	0.034	0.095
CdTe 161	Na	2.45×10^{17}	0.72	0.028	0.133

^a Equilibrated under a Zn overpressure at 400°C and quenched to room temperature.

^b This product was fixed at this value in obtaining the least-squares values for E_a , N_d , and N_a .

⁹ L. J. van der Pauw, Philips Res. Rept. 13, 1 (1958).

¹⁰ See, for example, J. S. Blakemore, *Semiconductor Statistics* (Pergamon Press, Inc., New York, 1962), p. 139.

bility of Eq. (1) to the experimental data was made by computing the root-mean-square difference between the observed values of p and those calculated from Eq. (1) using the values of N_d , N_a , E_a , and $(1/g)(m_v/m)^{3/2}$ from the least-squares analysis and the observed values of $(10^3/T)$. This check served as a verification of the fact that the parameters N_d , N_a , E_a , and $(1/g)(m_v/m)^{3/2}$ which gave the best straight-line fit to Eq. (2) also produced the best fit to the experimentally observed values of p as a function of $10^3/T$. This agreement would not be obtained, for example, if the actual situation was such that a second level contributed appreciably to the observed carrier concentration in the temperature range used for analysis.

For simplicity, the carrier concentration was taken to be given by $(1/|R_H e|)$, where R_H is the Hall coefficient and e the electronic charge. The ratio of the Hall mobility to the drift mobility is thus taken to be unity over the entire temperature range. For the special case of carrier mobility limited primarily by optical-mode lattice-vibration scattering, this choice is not unreasonable. Aven and Segall have shown that this mechanism is probably the most important source of scattering in undoped ZnTe,² in the temperature range of interest here (80 to 300°K). For the more highly doped samples studied in the present work, the influence of scattering by charged impurities also becomes important.

A. Hall Analysis of ZnTe and CdTe

Figure 1 shows the variation of the carrier concentration with temperature of typical ZnTe crystals melt doped with Li, with P, and undoped but equilibrated under a Zn overpressure and quenched. The solid curves in Fig. 1 are obtained from the Hall analysis given below. Figure 2 gives the temperature variation of the Hall mobility of ZnTe samples of Fig. 1.

The procedure outlined above for the least-squares analysis of carrier concentration data was applied to

TABLE II. Comparison of observed Hall mobility at several temperatures with concentration of ionized species as deduced from Hall analysis.

Sample	Dopant	N_d (cm ⁻³)	N_a average ionized (cm ⁻³)	Hall mobility (cm ² /V sec)		
				250°K	100°K	88°K
ZnTe 28	P	2.90×10^{18}	3.44×10^{18}	95	94	75
ZnTe 98-1	Li	2.10×10^{18}	2.68×10^{18}	85	100	90
ZnTe 52	P	1.35×10^{18}	1.86×10^{18}	75	105	95
ZnTe 97-1A	Li	0.98×10^{18}	1.30×10^{18}	85	150	150
ZnTe 50	P	0.51×10^{18}	0.84×10^{18}	85	150	150
ZnTe 97-1	Li	0.45×10^{18}	0.76×10^{18}	93	165	165
ZnTe 87	P	0.52×10^{18}	0.79×10^{18}	98	185	200
ZnTe 74	P	0.40×10^{18}	0.61×10^{18}	105	230	250
ZnTe 82	P	0.36×10^{18}	0.55×10^{18}	115	250	270
ZnTe 98	Li	0.22×10^{18}	0.30×10^{18}	115	390	500
ZnTe 97	Li	0.12×10^{18}	0.20×10^{18}	125	400	530
ZnTe 69	Li	0.19×10^{18}	0.23×10^{18}	130	560	750
ZnTe 64	Undoped	2.5×10^{16}	2.2×10^{16}	120	640	920

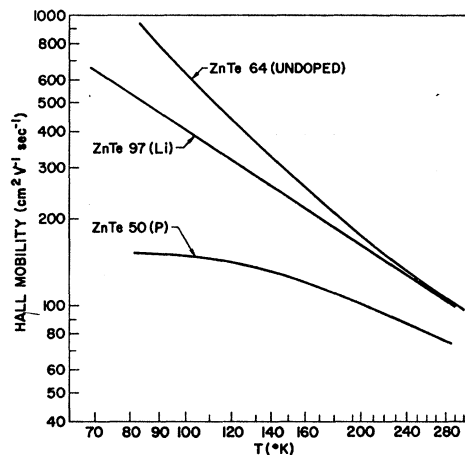


FIG. 2. Temperature dependence of the Hall mobility of ZnTe crystals doped with Li, with P, and nominally undoped. The temperature dependence of the hole concentration of these crystals is given in Fig. 1.

several samples of ZnTe and to a few samples of CdTe. In each case the doping level gave a hole concentration low enough for the use of nondegenerate statistics and was such that the major scattering mechanism limiting the carrier mobility was due to optical mode lattice vibrations. For such samples, the values of E_a , the product $(1/g)(m_v/m)^{3/2}$, and the values of N_d and N_a for the least-squares best fit were obtained and are listed in Table I.

In analyzing the data from ZnTe samples in which the mobility departed appreciably from that predicted on the basis of optical-mode lattice-vibration scattering, the least-squares procedure was modified to obtain best-fit values of E_a , N_d , and N_a for a fixed value of the product $(1/g)(m_v/m)^{3/2}$, namely, 0.165 (a value close to that observed for the majority of the Li-doped samples

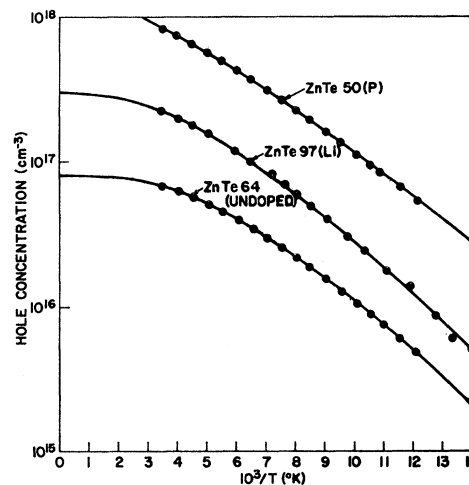


FIG. 3. Variation of the acceptor ionization energy of ZnTe crystals doped with Li (circles) and with P (triangles) with the cube root of the average ionized-acceptor concentration as deduced from a least-squares analysis of the Hall data using Eq. (2).

TABLE III. Resistivity and carrier concentration of ZnTe and CdTe samples before and after annealing at 250°C.

Sample	Dopant	Treatment	290°K		77°K	
			Resistivity (Ω cm)	p (cm ⁻³)	Resistivity (Ω cm)	p (cm ⁻³)
ZnTe 97	Li	Not annealed	0.10	8.5×10^{17}	0.97	4.1×10^{16}
		Annealed, 48 h ^a	2.8	2.8×10^{16}	1.4×10^6	2×10^{10}
ZnTe 82	P	Not annealed	0.09	8.0×10^{17}	1.3	1.0×10^{17}
		Annealed, 48 h	0.11	8.7×10^{17}	2.9	3.9×10^{16}
ZnTe 58	Na	Not annealed	0.86	8.8×10^{16}	0.87 ^b	1.3×10^{16b}
		Annealed, 90 h	0.73	9.9×10^{16}	0.67 ^b	2.0×10^{16b}
CdTe 70	Undoped	Not annealed	0.56	6.4×10^{16}	3.0	2.8×10^{15}
		Annealed, 48 h	7.2	1.0×10^{16}	9×10^5	...
CdTe 158	Li	Not annealed	0.34	2.3×10^{17}	1.7	1×10^{16}
		Annealed, 48 h	1.6×10^8	7×10^{13}

^a ZnTe 97(Li) crystal was almost opaque after annealing due to precipitation of a second phase.

^b Temperature of measurement was 110°K. Contacts were rectifying at 77°K.

of ZnTe and the undoped ZnTe in Table I). These results are also given in Table I.

A check on the semiquantitative consistency of the values of N_a and N_d obtained from the analysis would be desirable. Such a check is available, if one makes the reasonable assumption that the departure of the observed Hall mobility from that expected on the basis of polar scattering by optical-mode lattice vibrations is due to the increased importance of ionized-impurity scattering. This scattering mechanism is more important in samples with larger numbers of ionized impurities. Table II lists samples of ZnTe in order of increasing Hall mobility at 88°K, together with the average ionized-impurity concentrations as deduced from the values of N_d and N_a obtained from the least-squares analysis (Table I). The expected trend (samples with lower mobilities possessing larger numbers of ionized impurities) is observed, so that the results presented in Table II provide additional support for the values of N_d and N_a deduced from the Hall analysis.

Shallow, hydrogenic-type acceptor levels should exhibit a decrease in ionization energy with increasing acceptor concentration. This decrease should vary as the cube root of the ionized acceptor concentration averaged over the temperature range employed in the analysis.^{11,12} Figure 3 is a plot of the acceptor ionization energy E_a as a function of the cube root of the average ionized-acceptor concentration computed for the calculated values of N_a and N_d for Li-doped ZnTe and for P-doped ZnTe. For Li- and P-doped ZnTe, the rate of decrease is 2.8 to 3.0×10^{-8} eV cm. By comparison, the value calculated on the basis of simple considerations based on the reduction of the ionization energy by Coulombic interactions¹¹ is 2.3×10^{-8} eV cm for ZnTe.

The value of E_a at infinite dilution can be used to obtain an estimate of the effective mass, by applying the hydrogenic model:

$$E_B \gtrsim 13.6(m_0/m)/K_s^2 \text{ eV}, \quad (5)$$

where the binding energy E_B of the center may be

greater than the simple hydrogenic model because of central-cell corrections. The static dielectric constant K_s for ZnTe is 10.1.¹³ An upper limit on the effective mass for holes in ZnTe derived from E_B equal to 0.05 eV is therefore such that $(m_0/m) = 0.36$.

B. Annealing Studies of ZnTe and CdTe

The results of the above Hall analysis indicate that Li substituting for Zn and P substituting for Te in ZnTe give rise to shallow, hydrogenic acceptors in which the ionization energy at infinite dilution is 0.05 eV. The value of the effective mass of holes in ZnTe is deduced to be about $0.4m$, and the corresponding g value for the centers in Li-doped ZnTe and in P-doped ZnTe is about $\frac{3}{2}$. These values are close to those which have been observed for the shallow level ascribed to the native acceptor in ZnTe.^{2,6} However, it is known that the shallow levels in nominally undoped ZnTe may be removed by heat treatment at low temperatures (200 to 300°C) for extended periods of time (a few days).⁶ For this reason, annealing studies of ZnTe and CdTe doped with various elements were performed. Table III is a compilation of the resistivities and carrier concentrations at 290 and 77°K for two samples of each doping agent which had been given comparable treatments, except that one of the two samples was annealed at 250°C for a period of time as a final step. The marked decrease in free carriers in ZnTe and in CdTe doped with Li upon annealing is consistent with the rapid diffusion of this species accompanied by precipitation within the crystal as a second phase. The Li-doped ZnTe, which had been annealed at 250°C, was almost opaque because of a precipitated second phase. Samples doped with P and with Na, by comparison, exhibited only relatively minor changes upon annealing for long periods of time at 250°C. The behavior of the P-doped samples is consistent with the slow rate of diffusion of P in these compounds (see Ref. 8, for example). The observations on the Na-doped samples indicate

¹¹ G. L. Pearson and J. Bardeen, Phys. Rev. **75**, 865 (1949).

¹² P. W. Debye and E. M. Conwell, Phys. Rev. **93**, 705 (1954).

¹³ D. Berlincourt, H. Jaffe, and I. R. Shiozawa, Phys. Rev. **129**, 1009 (1963).

TABLE IV. Electrical properties of Li-doped ZnTe before and after heat treatment at 1050°C.

Sample	Treatment	290°K			77°K		
		Resistivity (Ω cm)	p (cm^{-3})	Hall mobility ($\text{cm}^2/\text{V sec}$)	Resistivity (Ω cm)	p (cm^{-3})	Hall mobility ($\text{cm}^2/\text{V sec}$)
ZnTe 97 (Li)	As-grown crystal	0.29	2.2×10^{17}	97	2.1	4×10^{18}	640
ZnTe 97 (Li)	Fired 1050°C Zn overpressure Rapid quench	0.04 ₅	1.9×10^{18}	72	0.05 ₀	1.4×10^{18}	90

either that Na is also a slow diffuser relative to Li at these temperatures or that the solubility of Na in ZnTe is as high at 250°C as at the temperatures characteristic of the growth process used in crystal preparation.

The precipitation of Li in Li-doped ZnTe is evidence of a lower solubility of this element at the annealing temperature than at temperatures characteristic of the final stages of crystal growth (approximately 500°C). If Li is more soluble at elevated temperatures, one might expect to obtain higher carrier concentrations in material which is fired at elevated temperatures and rapidly quenched. This expectation is realized, as the results in Table IV indicate. The sample of Li-doped ZnTe which was fired at 1050°C under a Zn overpressure is degenerate, or very nearly so. The Li concentration in these samples, as determined from emission spectroscopy, is 1 to 2 times 10^{18} cm^{-3} , which is in reasonable agreement with the carrier concentration in the fired and quenched sample.

IV. SUMMARY

The group-VA element P and the group IA elements Li and Na give rise to shallow acceptor levels in ZnTe and in CdTe. These shallow levels appear to be hydrogenic in nature, i.e., the ionization energy of the level decrease with increasing acceptor concentration approxi-

mately as the cube root of the average ionized-acceptor concentration. The effective mass of holes in ZnTe as deduced from the Hall analysis is $0.4m$. The corresponding g values for acceptor centers in Li-doped ZnTe and in P-doped ZnTe are close to $\frac{3}{2}$. Annealing at moderate temperatures (250°C) for tens of hours removes the shallow levels from Li-doped ZnTe and from Li-doped CdTe. The concentrations of shallow levels in P-doped ZnTe and in Na-doped ZnTe are not appreciably changed by this annealing treatment. In ZnTe, the solubility of Li is apparently higher at elevated temperatures than at 250°C. In order to obtain most of the Li present in the crystal in an electrically active form, one must fire the crystal at an elevated temperature (approximately 1000°C) and rapidly quench to room temperature. ZnTe which is very nearly degenerate may be obtained in this fashion.

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