

Electro-optic behavior and dielectric constants of ZnGeP₂ and CuGaS₂

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The constant-strain electro-optic coefficients and dielectric constants of two ternary semiconductors (CuGaS₂ and ZnGeP₂) with the chalcopyrite structure have been measured. The magnitudes of the coefficients are similar to those of the binary analogs (ZnS and GaP). However, the signs of the CuGaS₂ coefficients appear to be positive whereas the ZnS coefficient is negative. The ZnGeP₂ coefficients are found to have opposite signs to each other.

INTRODUCTION

We report here the results of measurements of constant-strain dielectric constants and linear electro-optic coefficients of the ternary compounds ZnGeP₂¹ and CuGaS₂.² The only other electro-optic measurements we are aware of on this large class of compounds is a low-frequency measurement,³ which indicated the electro-optic behavior of AgGaS₂ was not unlike that of zinc-blende and wurtzite semiconductors. Similarly, we find the magnitudes of the ZnGeP₂ coefficients to be close to that of its binary analog GaP, while the CuGaS₂ coefficients have the same size as the ZnS coefficient. We have also determined the signs of the coefficients of the ternaries relative to piezoelectric signs and compare them with the known^{4,5} binary-compound signs. This comparison shows that the electro-optic behavior of the analogs is not in fact the same, since there is an apparent sign reversal in the sulfide compounds and the two ZnGeP₂ coefficients themselves have opposite signs. Our results, together with previously reported⁶⁻⁸ measurements of the linear and nonlinear optical properties of these materials, are used to isolate the lattice-related contributions to the electro-optic coefficients. The unusual sign behavior then is shown to arise from the relative strengths of purely electronic and lattice portions of the electro-optic effect.

CRYSTALS AND PIEZOELECTRIC ORIENTATION

Both CuGaS₂ and ZnGeP₂ have point-group symmetry $\bar{4}2m$. Thus, there are two independent linear electro-optic coefficients r_{63} and $r_{41} = r_{52}$, as well as two piezoelectric coefficients d_{36}^{PE} and $d_{14}^{PE} = d_{25}^{PE}$. The samples were oriented as shown in Fig. 1. This orientation permits the magnitudes of r_{41} and r_{63} to be measured and their signs to be found relative to an assumed piezoelectric sign. In Fig. 1 the sample axes x'_i are normal to the sample faces and their relation to the crystallographic

axes is shown. The choice of the positive [001] is arbitrary, but once this choice has been made, piezoelectric tests are used to decide whether x'_1 is parallel to a [1 $\bar{1}$ 0] axis or to a [110] axis as shown.

Silver-paint electrodes were applied to opposite pairs of sample faces and the sense of the voltage developed between these electrodes was noted when compressive stress was applied in each of the three directions. In the primed or sample coordinate system, 11 of 18 elements of the transformed piezoelectric matrix are nonzero. Five of these correspond to torsional stresses and are unimportant if moderate care is taken to keep the applied stress uniform. The polarization P'_i developed in the x'_i direction is

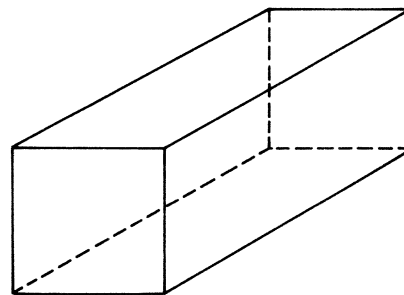
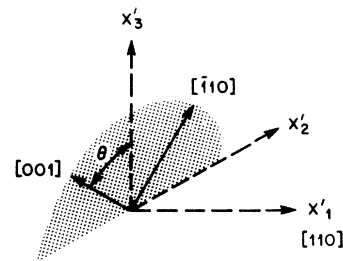


FIG. 1. Sample orientation showing relation of crystal axes to sample axes.

$$P'_i = d'_{ij} \sigma_j, \quad (1)$$

where σ_j is the stress in the x'_j direction and the d'_{ij} are piezoelectric matrix elements in the primed system. The matrix element

$$d'_{31} = \frac{1}{2} \cos \theta d_{36}^{PE} \quad (2)$$

allows identification of the x'_1 and x'_2 axes assuming the sign of d_{36}^{PE} is known. In each sample one of the five remaining transformed elements was used to get the sign of d_{14}^{PE} . The observed sign of the element

$$d'_{32} = \cos \theta (\sin^2 \theta d_{14}^{PE} - \frac{1}{2} \cos^2 \theta d_{36}^{PE}) \quad (3)$$

was used in the CuGaS₂ case. With $\theta = 32.7^\circ$ and $d_{36}^{PE} > 0$ as in ZnS,^{5,9} we found $d_{14}^{PE} > 1.2d_{36}^{PE}$. Similarly, the relation

$$d'_{23} = -\sin \theta (\cos^2 \theta d_{14}^{PE} - \frac{1}{2} \sin^2 \theta d_{36}^{PE}) \quad (4)$$

gave information about d_{14}^{PE} of Z:GeP₂: With $d_{36}^{PE} > 0$ ¹⁰ and $\theta = 54.2^\circ$, the observed sign of d'_{23} requires $d_{14}^{PE} > d_{36}^{PE}$. In each crystal the remaining piezoelectric tests yielded no new information but gave results consistent with those above.

ELECTRO-OPTIC MEASUREMENTS

Electro-optic measurements were made on CuGaS₂ at 0.6328 and 1.15 μm and on both materials at 3.39 μm . The heterodyne measurements were made at 55 MHz using fields of amplitude E'_3 applied in the x'_3 direction and with the laser beam propagating along x'_2 . Since the x'_2 axis lies in a mirror plane, possible difficulties arising from optical activity were avoided. In particular, the

near equality of the ordinary index n_1 and extraordinary index n_3 of CuGaS₂ at 0.6328 μm would have allowed appreciable polarization conversion.¹¹ With the beam polarized along x'_1 , first-order sidebands of amplitude $J_1(\eta_{63})$ are produced through the electro-optic effect. The unshifted carrier amplitude is given by $J_0(\eta_{63})$, where the J 's are Bessel's functions of the first kind. The ratio $J_1(\eta_{63})/J_0(\eta_{63})$ is found experimentally and this determines the value of the modulation index η_{63} . If the path length is L , we have

$$\eta_{63} = -\pi n_1^3 r_{63} E'_3 \cos \theta L \lambda^{-1}. \quad (5)$$

Using this relation we find the r_{63} coefficient. Repeating the experiment with beam polarization parallel to x'_3 we find a modulation index given by

$$\eta_{\text{eff}} = +\pi n_{\text{eff}}^3 \sin^2 \theta \cos \theta E'_3 (\gamma_{63} + 2\gamma_{41}) \lambda^{-1} L. \quad (6)$$

With the previously determined value for r_{63} we can then find r_{41} from Eq. (6). For n_{eff} we used

$$n_{\text{eff}} = \left(\frac{n_1^2 n_3^2}{n_1^2 \cos^2 \theta + n_3^2 \sin^2 \theta} \right)^{1/2}. \quad (7)$$

Although this neglects the effect of the double-refraction angle which is 0.66° in ZnGeP₂ and completely negligible in CuGaS₂, no appreciable error is introduced in n_{eff} . The values found for the coefficients appear in Table I.

The signs of the coefficients are also given in Table I. In order to determine signs the beam is directed through a "standard" LiNbO₃ crystal in series with the test sample, while the modulating voltage is applied simultaneously to both samples. The resulting modulation index is then either the

TABLE I. Summary of electro-optic and nonlinear optic properties of CuGaS₂, ZnGeP₂, and their binary analogs. Units expressed in 10^{-12} m/V.

Material	λ (μm)	ij	r_{ij}	d_{ji}^{e}	d_{ji}^{o}	$d_{ji}^i q$	δ_{ji}^D	δ_{ji}^C
CuGaS ₂ ^a	0.6328	63	+1.35	-17.2	+20.9	-38.1	+0.12	-0.24
	0.6328	41	+1.76	-22.4	+20.9	-43.3	+0.12	-0.32
	1.15	63	+1.66	-17.2	+16.7	-33.9	+0.12	-0.27
	1.15	41	+1.9	-19.6	+16.7	-36.3	+0.12	-0.35
	3.39	63	+1.05	-10.1	+15.1	-25.2	+0.12	-0.22
	3.39	41	+1.1	-10.4	+15.1	-25.5	+0.12	-0.27
ZnS ^b	0.6328	63	-1.6	+12.3	+12.1	+0.2	+0.14	≈ 0
	1.15	63	-1.4	+9.6	+10.5	-0.9	+0.14	-0.02
	3.39	63	-1.4	+9.2	+9.9	-0.7	+0.14	-0.01
ZnGeP ₂ ^c	3.39	63	-0.8	+19	+114	-95	+0.17	-0.49
	3.39	41	+1.6	-37	+113	-150	+0.17	-0.33
GaP ^d	3.39	63	-0.97	+20	+78	-58	+0.16	-0.47

^aOptical properties from Ref. 7.

^bLinear optical properties from W. L. Bond, J. Appl. Phys. **36**, 1674 (1965). Dielectric constant from D. Berlincourt, H. Jaffe, and L. R. Shiozawa, Phys. Rev. **129**, 1009 (1963).

^cOptical properties from Ref. 6.

^dG. D. Boyd, T. J. Bridges, M. A. Pollack, and E. H. Turner, Phys. Rev. Lett. **26**, 387 (1971).

sum or the difference of the individual indices. Since the sense of the crystalline axes is known, the sign of the coefficient is fixed. The signs of the pertinent LiNbO₃ constant-strain coefficients r_{33} and r_{13} had been found earlier¹² to be positive (as are the low-frequency coefficients¹³) by comparison with a GaP sample.

Dielectric constants were measured at frequencies between 10 and 70 MHz. The same sample of ZnGeP₂ that was used for piezoelectric and electro-optic tests was used here also. With the x'_1 faces painted silver we found $\epsilon_1 = 15$. A composite of ϵ_1 and ϵ_3 was measured with the x'_3 faces coated, and from this and the known ϵ_1 we calculate $\epsilon_3 = 12$. A thin platelet of CuGaS₂ with the optic axis normal to the surface and using evaporated gold electrodes was used to measure $\epsilon_3 = 10.0$ and a similar platelet containing the axis was used to find $\epsilon_1 = 9.3$.¹⁴ These measured values are used in the data reduction in Table I.

Both materials are *p* type and have carrier concentration less than 10^{16} cm⁻³ at room temperature.¹⁵ Approximate values of radio-frequency resistivity, which were determined while measuring dielectric constants, indicate the free-carrier concentration is less than 10^{15} cm⁻³.

DISCUSSION

For purposes of comparison we have included in Table I values and signs of coefficients of the cubic binary analogs although the only new result here is the 1.15- μ m measurement of ZnS. The d_{ij}^o coefficients which are simply related to the usual r_{ji} ($d_{36}^o = -\frac{1}{4}n_1^4 r_{63}$ and $d_{14}^o = -\frac{1}{4}n_1^2 n_3^2 r_{41}$) are also tabulated, as are its component parts the purely electronic d_{ij}^e and lattice related d_{ij}^l . The effect of linear electronic and ionic susceptibilities on the d_{ij}^o and d_{ij}^l quantities was removed by the normalization prescription of Garrett.¹⁶ The resulting electronic δ_{ij}^e and ionic δ_{ij}^i , which should be less wavelength dependent, are also included in Table I. The pertinent relations for d_{ij}^o are

$$\begin{aligned} d_{14}^o(-\omega_A, \omega_B, \omega_C) &= \chi_1^e(\omega_C) \chi_3^e(\omega_B) \chi_1^e(\omega_A) \delta_{14}^D, \\ d_{36}^o(-\omega_A, \omega_B, \omega_C) &= \chi_3^e(\omega_C) \chi_1^e(\omega_B) \chi_1^e(\omega_A) \delta_{36}^D. \end{aligned} \quad (8)$$

Here $\chi_k^e(\omega)$ is the *k*-axis electronic susceptibility at frequency ω . In Table I the values of δ_{ij}^D were obtained from published second-harmonic-generation values of d_{ij}^o , with $\omega_A = \omega_B = \frac{1}{2}\omega_C$. The d_{ij}^o contribution to d_{ij}^o at frequency ω is then found using Eq. (8) with $\omega_A \approx 0$ and $\omega_B \approx \omega_C = \omega$. The δ_{ij}^C 's in Table I are calculated from

$$\begin{aligned} d_{14}^i &= \chi_1^e(\omega) \chi_3^e(\omega) \chi_1^i(0) \delta_{14}^C, \\ d_{36}^i &= \chi_1^e(\omega) \chi_1^e(\omega) \chi_3^i(0) \delta_{36}^C, \end{aligned} \quad (9)$$

where χ^i is the ionic susceptibility.

The values of d_{36}^o for ZnS were obtained by multiplying the *corrected*¹⁷ experimental value⁵ of d_{33}^o found on a hexagonal polytype of ZnS by $\sqrt{3}/2$. The d_{36}^o obtained in this way is smaller than other values in the literature.¹⁸⁻²⁰ The fact that d_{36}^o and d_{36}^e have the same sign is well established,⁵ and their near equality makes the sign of the small quantity d_{36}^l very uncertain. The small lattice contribution d_{36}^l is now in excellent agreement with Raman scattering results²¹ which show the transverse-optic (TO) phonon scattering intensity at 0.6328 μ m to be less than 1% of that of the longitudinal phonon in cubic ZnS. In addition, the TO intensity in hexagonal ZnS goes through zero²² in the vicinity of 0.6328 μ m.

Since not only the sign but the magnitude of the d_{ij}^l depend on the correct signs of d_{ij}^e and d_{ij}^o , some comments on the reasons for our choices are needed. The fact that the d_{ij}^o 's of ZnGeP₂ are smaller than d_{ij}^e shows at once that d^i and d^o have opposite signs. For energies well below the band edge this seems to be the case in all tetrahedrally coordinated compounds, although, as pointed out above, ZnS is somewhat uncertain. In addition the sign of d^o has also been measured⁸ relative to the piezoelectric sign, so all signs are consistent with $d_{36}^{PE} > 0$. The absolute sign of d^o is also consistent with theoretical²³ predictions. The signs given for CuGaS₂ are consistent with $d_{36}^{PE} > 0$ as well as the general rule $d^i/d^o < 0$. Again, the absolute sign of d^o fits theoretical prediction.²³ Finally, preliminary measurements of the temperature dependence of dielectric constant and electro-optic coefficient as was done on CuCl₂²⁴ indicate that $|d^i| > |d^o|$, which is in keeping with the size of d^i resulting from our sign choices.

Inspection of Table I shows that the initially surprising difference in sign of the ZnGeP₂ coefficients is merely due to differences in size of the opposing electronic and lattice portions. The normalized δ_{ij}^C and δ_{ij}^D of the analogous GaP are, in fact, very similar to those of the ternary compound. On the other hand, the δ 's of the sulfide analogs are quite different. The smaller δ_{ij}^D of CuGaS₂ has been accounted for theoretically²³ as arising from the influence of the copper *d*-electrons. It seems likely that the even larger discrepancy between δ_{ij}^C terms is also related to the *d*-electron shells, since the cuprous halides also show an enhanced ionic contribution.

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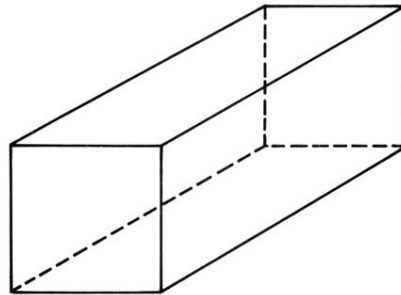
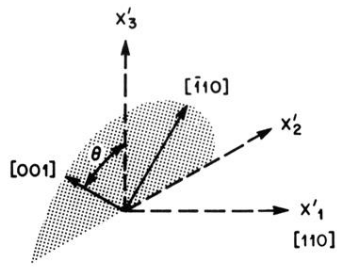


FIG. 1. Sample orientation showing relation of crystal axes to sample axes.