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DEVELOPMENT OF CHALCOPYRITE CRYSTALS FOR NONLINEAR OPTICAL APPLICATIONS

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#### I. INTRODUCTION

During the first year, the chalcopyrite growth effort was directed at a single compound, CdGeAs<sub>2</sub>. The potential applications of this crystal in nonlinear optics is now fully evaluated. It promises to be a very useful nonlinear material providing that there is sufficient improvement in crystal quality. Past crystal growth has been by the Bridgman-Stockbarger technique. We are now preparing to grow crystals by the Czochralski method.

Recently we have started growth of a new chalcopyrite compound  $CdGeP_2$ , another potentially very useful nonlinear crystal. The choice of  $CdGeP_2$  was made after a study of all the  $II-IV-V_2$  chalcopyrites. estimating the optical properties from the measured properties of the III-V analogs. The results of this study are included in Appendix I.

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#### II. CRYSTAL GROWTH

#### A. CdGeAs,

#### (i) Bridgman-Stockbarger

The last series of boules have been grown from stoichiometric melt. The 0.5 - 1.0 weight percent excess As used previously does not improve the optical transmission. We also use slower growth rates  $(\sim 4^{\circ}/hr)$  and larger gradients  $(\sim 34^{\circ}/cm)$ . The growth gives fairly consistent results from boule to boule and we are planning impurity doping to investigate the effects on crystal properties such as resistivity, optical transmission, and index homogeneity. The orientation of large single crystal regions in a boule is usually with the chalcopyrite unit cell [111] direction within 10° of the boule axis. This agrees with the literature which reports the [111] direction as the fastest growth direction for the chalcopyrites.

There is a correlation between grain boundaries and crystal cracking. Large single crystal regions have usually few cracks. We therefore hope that the cracking problem may be solved with the growth of large homogeneous single crystals. The cracking might also be related to the constraints imposed by the walls of the quartz crucible. We are now measuring the thermal expansion coefficient and its anisotropy to gain some further insight.

For the last boule B6 , the synthesis and the growth were done in one step. Previously the synthesizing was done as a separate step. This nad the disadvantage that there was some vapor in the crucible which deposited on the walls when the synthesized material was quenched. It

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was impossible to retrieve this deposit. The one step process assures that no material is lost. However, we are faced with the problem of obtaining uniform mixing and achieving fully reacted material in the crucible as well as in the capillary before the growth starts. The first run showed incomplete mixing. An ultrasonic vibrator has been constructed to aid the mixing process in succeeding runs.

#### (ii) Czochralski

At present, initial experiments are being carried out to determine the correct growth conditions. In addition, a furnace is being assembled.

B. CdGeP

To date two boules have been grown. The  $CdP_2$  is synthesized first and then reacted with Ge to form  $CdGeP_2$ . The fully reacted material is then used to grow single crystals by the Bridgman-Stockbarger technique similar to the growth of  $CdGeAs_2$ . Due to observed Si vitrification, a carbon crucible is used to synthesize the  $CdGeP_2$ . The first boules have single crystal regions of approximately 1 mm<sup>3</sup> and they show the same cracking pattern as observed for  $CdGeAs_2$ .

A good etch for  $CdGeP_2$  is 10% Br<sub>2</sub> solution in ethyl alcohol. This reveals grain boundaries and twin lines after etching for about 15 sec.

3.

#### III. IMPURITY ANALYSTS OF CdGeAs,

Table I shows the results of an impurity analysis of three slices from boule #33. The slices were from different sections of the boule and they had different resistivity and optical transmission. The impurity analysis was performed by the Behl and Howell Electronic Materials Division in Pasadena using spark fource mass spectrometry. There appears to be very little correlation between the impurity analysis and the optical transmission. A possible explanation is that only a small fraction of the boule cross section was probed and homogeneity problems may have obscured the results. The probed area was less than one mm<sup>2</sup> and only a few tenths of a milligram was analyzed. The unusually large oxygen and carbon concentrations are most probably due to hydrocarbons and possibly an oxide layer on the surface.

#### TABLE I

#### IMPURITY CONCENTRATIONS IN STANFORD CADMIUM GERMANIUM ARSENIDE

		·清朝第二帝的		J. S. S. S. S.
Element <sup>(a)</sup>	Detection Limit <sup>(b)</sup>	Opaque	Max T = 20%	Max T = 5%
Li	0.007	210.0	0.083	0.017
C	0.03	4.0=25	3,200 (75-10,000)	19
N	0.03	0.18	0.51	0.28
0	0.03	76	900	3,600
F	0.07	0.27	0.48	0.22
Na	0.01	0.35	8.3	0.73
Mg	0.3	N.D.	0.49	N.D.
Al	0.1	0.37	3.9	0.80
Si	1.	6.7	N.D.	N.D.
S	0.03	7.5	1 1	4.5

(IN PART'S PER MILLION ATOMIC)

0.19

0.074

(a)No analysis was made for hydrogen. Analyses for gold are not given since the samples were sparked against high purity gold counterelectrodes. Background lines of the matrix interfere with the analyses for Cl, Mn, and Fe. Other impurities not listed were not detected and have concentrations less than 0.3 ppma.

0.052

0.065

0.51 (6.6\*) 0.25 (3.3\*)

Determined for  $3 \times 10^{-7}$  coulomb exposure. (b)

0.01

0.03

- \* Seen on one exposure only.
- N.D. Not detected.

K

Ca

#### IV. ELECTRON PROBE MICROANALYSIS

We have completed an extensive microprobe analysis of several boules to investigate possible deviations from stoichiometric composition. The absolute accuracy of microprobe measurements are between 2 and 5 weight percent. For absolute calibration we use Cd , CdS, Ge , and GaAs as standards and determine the weight fraction  $W_u$  of the elements in the unknown (CdGeAs<sub>2</sub>) using the expression

$$W_{u} = W_{s} \frac{F_{s}}{F_{u}} \frac{I_{s}}{I_{u}} , \qquad (1)$$

where  $W_s$  is the weight fraction of the element in the standard,  $I_s$ and  $I_u$  are the X ray intensities from the standard and the unknown, and  $F_s$  and  $F_u$  corrects for the matrix absorption in the standard and the unknown. We have determined  $F_s/F_u$  from tables in Birks<sup>1</sup> for an accelerating voltage of 25 kV, electrons incident at 62.5°, and a takeoff angle  $\Psi$  of 38.5°. Table II gives the product  $W_s F_s/F_u$ .

The relative accuracy of the microprobe analysis can be as good as a few tenths of one percent. Table III lists some experimental results for CdGeAs<sub>2</sub>. Within the experimental error excess As does not perturb the stoichiometric composition. The results confirm what we would expect from our previous phase diagram studies, that CdGeAs<sub>2</sub> exists only in a narrow homogeneity region.

We have also studied carefully an etched boule cross section containing several grains, some optical transparent and some opaque. No variation in stoichiometry or irregularities at the grain boundaries could be observed within the experimental resolution.

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#### TABLE II

# MAGNITUDE OF W<sub>s</sub> F<sub>s</sub>/F<sub>u</sub> FOR MICROPROBE ANALYSIS OF CdGeAs<sub>2</sub>

Standard	Cd La	Ĝe <b>K</b> a	As <sub>Ka</sub>
Cd	115.26		
CdS	82.23		
Ge		101.99	
GaAs			49.37

-	TOT S	<b>)</b> T	10	1
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## MICROPROBE ANALYSIS OF CdGeAs2

Boule number	W <sub>Cd</sub> W <sub>Ge</sub>		WAB	Growth condition	Optical transmission		
16	31.33	22.2]	45.46	0.5 Wt % excess As	opaque		
26A (top of boule)	31.33	22.12	46.55	Stoichiometric	Max 40%		
260 /	31.34	22.29	46.36	Stoichiometric	Max 105		
31 7	31.64	22.03	46.34	0.5 Wt % excess As	Max 25%		
33 V	0.16	£6.,84					
CdCeAs	33.57	21.68	44.75				
2			1				

#### V. OPTICAL MEASUREMENTS

#### A. CdGeAs

We have determined the type I phasematching angle for doubling  $CO_2$  using a 1.95 mm crystal from boule #31. When the crystal is mounted normal to the laser beam, back reflections make the laser unstable. By motor scanning the crystal through the unstability and phasematching positions we can determine the phasematching angle very accurately with respect to the crystal front surface. The measured phasematching angle is  $31.7^{\circ} \pm 0.5^{\circ}$ , while the index of refraction data from boule #16 gives a calculated angle of  $35.6^{\circ}$ . The measured full width of the external angle at the half-power point was  $5.9^{\circ}$  in good agreement with an angle of  $6^{\circ}$  that we calculate using the expression

$$\Delta \theta_{\text{ext}} = \frac{\pi}{2.25 \, \ell \, \tan \rho}$$

(2)

with  $\ell = 1.95$  mm and  $\rho = 0.02313$  rad.

Since the walk-off angle limits the maximum useful interaction length, the most attractive parametric oscillator construction would be a 90° phasematched oscillator with a tunable pump. Figure 1 shows the tuning curve for such a device. The tunable pump may be a LiNbO<sub>3</sub> or LiIO<sub>3</sub> parametric oscillator.

#### B. CdGeP

We have not yet obtained sufficiently large single crystals to measure the indices of refraction by the prism method. Boule #1 had

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Figure 1--Theoretical tuning curves for CdGeAs<sub>2</sub> for 90° phasematching.

a small transparent section which could be studied under an infrared microscope. The measured transmission range is between 7500 Å and 13  $\mu$ m with the reststrahl frequency located at approximately 26  $\mu$ m. By probing with a CO<sub>2</sub> laser beam we measured the transmission through the most transparent sections to be at least 30% for a 0.5 mm thick sample.

#### VI. ELECTRICAL MEASUREMENTS

### A. CdGeAs

We have experimented with ohmic contacts. Indium soldered contact works well down to at least  $77^{\circ}K$ . Some crystals of approximately  $1 \times 2 \times 7$  mm have been cut for Hall effect measurements.

B. CdGeP

The first boule was n-type with a resistivity of approximately  $10^4$  -  $10^5~\Omega cm$  .

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#### APPENDIX I

ESTIMATION OF THE OFFICAL PROPERTIES OF THE II-IV-V2 CHALCOPYRITE COMPOUNDS

ESTIMATION OF THE OPTICAL PROPERTIES OF THE II-IV-V2 CHALCOPYRITE COMPOUNDS\*

by

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#### ABSTRACT

Several of the II-IV-V<sub>2</sub> chalcopyrite compounds are attractive for nonlinear optical applications. In order to evaluate their potential, their optical parameters are determined using the close resemblance to the III-V analogs and their relative anisotropic bond polarizability which has been measured for a few of the chalcopyrites.

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ESTIMATION OF THE OPFICAL PROPERTIES

OF THE HI-IV-V, CHALCOPYRITE COMPOUNDS

by

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The II-IV-V2 compounds with a chalcopyrite structure have recently generated considerable interest as new infrared nonlinear crystals. 1,2 The nonlinear coefficients are large and compare with the III-V compounds and the chalcopyrites have the necessary birefringence for phasematching. The chalcopyrite point group symmetry is 42m which allows both type I and type IJ phasematching.<sup>2</sup> Unfortunately, the growth of high optical quality material presents problems and for best progress it seems reasonable to concentrate on a few compounds. In choosing which compounds to grow, the important considerations are transmission range, birefringence, and magnitude of the nonlinear coefficients. However, measured values exist only for a few of the chalcopyrites, and a method to estimate their properties would be very useful. We outline a procedure using the close resemblance between the II-IV-V, compounds and their III-V analogs. The predicted properties agree well with the few measured experimental values. By a different method using Levine's bond charge model, 3,4 Chemla<sup>5</sup> has also estimated the indices of refraction and Miller's delta for the chalcopyrites.

Table I lists the properties of the III-V compounds used to estimate the properties of the chalcopyrites in Table II. The optical bandgap

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	Unit cell volume [X <sup>3</sup> ]	Reststrahl frequency <sup>(a)</sup> [µm]	Index of refraction(a)	Nonlinear coefficient rel. GaAs <sup>(b)</sup>		
Alp	162:0	~ 15.6	2.95			
GaP	162.0	25	2.95	.58		
InP	202.1	28.5	3.1			
AlAs	181.5		3.2			
GaAs	180.7	34	3.3	1.00		
InAs	222.4	41.1	3.5	-2.22		

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#### TABLE I

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### OPTICAL PROPERTIES OF III-V COMPOUNDS

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#### TABLE II

#### ESTIMATED OPTICAL PROPERTIES OF THE CHALCOPYRITES

	2nSIP2	ZnGePa	ZnSnPg	C451P2	CasePa	CdSnPg	ZnSIAsg	ZnGeAsg	Ensnag	Casiang	CiGeAa	ClianAsa
III-V enslogs	GaP+Alp	Jup	OsP+InP	InPALP	InPiGaP	InP	GEAS+AlAs	Outs	OnAs+InAs	InAa+AlAs	Endotada	EnAs
Melting point (°C)	1370(e)	1052(P)	~950 <sup>(b)</sup>	~1150(p)	~790(e)	~670 <sup>(c)</sup>	~1090(e)	<sub>-980</sub> (ه)	~775 <sup>(d)</sup>	(e)	670 <sup>( e )</sup>	595 <sup>(4)</sup>
Unit cell volume (R <sup>3</sup> )	30%.5	¥1.7	3:0.7	. 156.3	355.1	400.9	342.5	3:3.8	400.7	376.8	325.1	142.1
Tetragonal compression(a) t = 2 - c	.065	.029	.000	.163	<b>.</b> 123	.018	.061	.034	.000	.193	:118	.044
••••x••1(f)	.076	.056	044	~.172	.132	.044	~.090	.07.6	044	~.164	.166	.044
Neasured Reststrahl Frequency (um)	18.7 <sup>(e)</sup>		27.2 <sup>(h)</sup>	/		<b>2</b> 3 <sup>(1)</sup>					36.5 <sup>(J)</sup>	
Estimated Restatentl frequency (um)		8	26.3	19.4	26.5	28.•		ų	л.)		37.3	41.1
Expected transmission Farge (um)	.54 <sup>(e)</sup> . 9		.84 <sup>(k)</sup> -13	.55 <sup>(a)</sup> .9	.72(1)-13	1.1 <sup>(n)</sup> .14	.:d <sup>(n)</sup> -	1.5 <sup>(a)</sup> .17	1.9 <sup>(a)</sup> -18	.23 <sup>(0)</sup> .	2. j <sup>(a)</sup> .18	6,8(e).20
Neasured	3.1 <sup>(e)</sup>	3.1 <sup>(p)</sup>	** 2.85(h)	ð.	3.7 <sup>(a)</sup> ·	3.3(1)				3.4(2)	<b>3.6</b> <sup>(s)</sup>	3.8 <sup>( *)</sup>
Estimated <sup>6</sup> ev	3.03	2.95	1.05	3.15	3.07	3. 11	3.33	J.JI	3,42	3.68	3.44	3.51
Measure1 Direfringence	.05 <sup>(R)</sup>	.039(b)			.11 <sup>(q)</sup>	.04 <sup>(*)</sup>					.095(=)	.16 <sup>(e)</sup>
Estimatei Direfrirgenae n <sub>e</sub> - n <sub>o</sub>	.05	.04	•.02	.14		.04	.05	.03	•.œ	.11	.095	.03
Measured monlinear coefficient rel. CaAs		.83	Carlos -								3.4	
Estimated Nonlinear coefficient rel. Cada		.6					Ų.	1.0	1.7			2.2
Fatinates nonlinear conflicient from Miller's 5	.6	.5	.6	.1	.6	<b>, 1</b> ,	1.1	1.0	1.)	1.5	1.9	1.5

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frequency and two phonon absorption determine the transmission range of the chalcopyrites. In CdGeAs<sub>2</sub>, i.e., the two phonon absorption at room temperature is about 20 cm<sup>-1</sup>. The three phonon absorption is much weaker and is approximately 0.4 cm<sup>-1</sup>. We take the two phonon absorption frequency to be half the reststrahl frequency. For the reststrahl frequency  $\omega_r$  we use the experimental value or an estimate from the reststrahl frequencies  $\omega_a$  and  $\omega_b$  of the III-V analogs using the relation

2

$$\omega_r = \frac{1}{2} \sqrt{\omega_a^2 + \omega_b^2} \quad (1)$$

By assigning bond polarizabilities to the II-V and the III-V bonds, we derive expressions for the indices of refraction and for the birefringence by summing over the thirty-two bonds within the chalcopyrite unit cell. With a linear polarizability tensor  $\tilde{a}$  and a second order polarizability tensor  $\tilde{\beta}$ , we write the induced polarization of a bond as

$$\overline{p}(t) = c_{\alpha}\overline{a}\cdot\overline{E}(t) + \overline{\beta}\cdot\overline{E}(t)\overline{E}(t) . \qquad (2)$$

We assume uniaxial bond symmetry and write the transverse and the longitudinal linear bond polarizabilities as  $\alpha_{\perp}$  and  $\alpha_{\parallel}$ . Defining an average bond polarizability as  $\alpha = \frac{1}{3}(2\alpha_{\perp} + \alpha_{\parallel})$  and the anisotropy as  $\gamma = (\alpha_{\parallel} - \alpha_{\perp})$ , we follow Chemla and obtain for the susceptibility

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tensor that

$$\mathbf{\bar{x}} = \mathbf{\bar{e}} - 1 = \frac{16}{\mathbf{V}} (\alpha_{AC}^{+} \alpha_{BC}^{+}) \mathbf{1} + \frac{16}{9\mathbf{V}} \left[ \gamma_{AC}^{-} (\tau + \sigma) + \gamma_{BC}^{-} (\tau - \sigma) \right] \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} , \quad (3)$$

where AC and BC denote the two different bonds and V is the unit cell volume. The parameters  $\tau$  and  $\sigma$  characterize the chalcopyrite structure. Since the II and IV cations have different covalent radii, the anion is not exactly in the center of the cation tetrahedra. It is positioned a distance  $a(x - \frac{1}{4})$  off the center closer to the cations with the smallest radii.<sup>7</sup> With the lattice parameters a and c we have  $\tau = 2 - c/a$  for the tetragonal compression and  $\sigma = 4x - 1$ . In Eq. (3) BC denotes the bond to the smallest cation. Assuming the bond polarizability is approximately the same as for the III-V analogs, we have for the average susceptibility of the chalcopyrites that

$$X_{av} = \frac{V_a}{v} X_a + \frac{V_b}{v} X_b, \qquad (4)$$

where  $V_a$  and  $V_b$  are the unit cell volume of the III-V analogs and  $X_a$  and  $X_b$  are the measured susceptibilities. The average estimated index in Table II agrees well with experimental values.

For the relative birefringence we obtain from Eq. (3) that

$$\frac{\Delta n}{n} = \frac{n_e - n_o}{n} = \frac{\chi_e - \chi_o}{2(1 + \chi_{av})} \approx -\frac{\gamma_a(\tau + \sigma) + \gamma_b(\tau - \sigma)}{6(\alpha_a + \alpha_b)}, \quad (5)$$

since  $X_{av}$  is always much greater than one. For the II-IV-V<sub>2</sub> compounds, **t** and  $\sigma$  have about the same magnitude so we can approximate Eq. (5)



$$\frac{\Delta n}{n} \approx -\frac{1}{6} \frac{\gamma_a}{\alpha_a + \alpha_b} (\tau + \sigma) \quad . \tag{6}$$

The maximum positive birefringence occurs when  $\alpha_1 \gg \alpha_1$ . This gives

by

$$\left(\frac{\Delta n}{n}\right)_{\max} = + \frac{1}{h} \frac{\tau + \sigma}{1 + \alpha_{1b}/\alpha_{1a}} \qquad (7)$$

Trustworthy measurements of the birefringence exist only for a few of the chalcopyrites. Figure 1 shows a plot of the relative birefringence versus  $\tau + \sigma$ . According to Eq. (6) the birefringence depends mainly on the anisotropic polarizability of the AC bond. Consequently, since A is the cation with the largest radius, the birefringence of  $2nSiP_2$ and  $2nGeP_2$  should be determined mainly by the anisotropic polarizability of the ZnP bond. This is confirmed by a linear dependence in Fig. 1. Figure 1 also indicates approximately the same relative anisotropic bond polarizability for the Zn and Cd bonds to the same anion. This needs to be confirmed, however, by more experimental points for the As compounds. In Table II we estimate the birefringence using  $\Delta n/n =$  $K(\tau + \sigma)$  with K equal to 0.14 for the P compounds and 0.10 for the As compounds.

Degenerate parametric oscillators or second harmonic generation (SHG) require the largest birefringence. The phasematching angle for SHG is approximately given by

 $\sin \theta_{I} \approx \sqrt{D/B}$ 6

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(8)

for type I phasematching and

$$\sin \theta_{II} \approx \sqrt{2D/B}$$
 (9)

for type II, where  $B = n_e - n_o$  is the birefringence and  $D = n_o^{2\omega} - n_o^{\omega}$ is the dispersion. For type II phasematching the necessary birefringence is approximately 0.6 to 0.7 for 90° phasematching. For propagation at angles less than 90° to the c-axis the walkoff angle limits the effective crystal length  $\ell_{max}$  for the nonlinear interaction. For confocal focusing we have

$$\ell_{\rm max} = \frac{r}{2n\rho^2}$$
 (10)

with the walkoff angle  $p \approx -\frac{B}{n} \sin 2\theta$ . A crystal with a large birefringence, e.g. 0.1 for CdGeAs<sub>2</sub>, is phasematchable for parametric interaction and second harmonic generation over most of its transparency range. Maximizing the nonlinear interaction, however, requires a crystal with a smaller birefringence to ensure phasematching closer to 90°.

The chalcopyrites have only one independent nonlinear coefficient since  $d_{14} = d_{36}$  according to the Kleinman symmetry condition.<sup>8</sup> Assuming the second order bond polarizability  $\beta_{ijk}$  satisfies the overall permutation symmetry, we express the nonlinear coefficient for the chalcopyrites as<sup>5,9</sup>

$$d_{14} = d_{xyz} = \frac{8}{V} \frac{1}{3\sqrt{3}} \left[ (\beta_{\parallel} - 3\beta_{\perp})_{AC} + (\beta_{\parallel} - 3\beta_{\perp})_{BC} \right] , \quad (11)$$

where  $\beta_{\parallel} = \beta_{333}$  and  $\beta_{\perp} = \frac{1}{2}(\beta_{113} + \beta_{223})$  are the longitudinal and the transverse second order bond polarizabilities. For the III-V compounds, Flytzanis and Ducuing<sup>9</sup> state that the main contribution to the nonlinear coefficient is from  $\beta_{\parallel}$ , even though the linear polarizability tensor is almost isotropic with  $a_{\parallel}$  slightly larger than  $a_{\perp}$ . Chemla's calculations for the chalcopyrites include only  $\beta_{\parallel}$ . This approximation may not be valid since the transverse component of the linear polarizability tensor is larger than the longitudinal component. However, we shall make the same approximation so that we may use the measured nonlinear coefficients for the III-V analogs to estimate the nonlinear coefficients for the chalcopyrites using the expression

$$d_{14} = \frac{v_a}{v} (d_{14})_a + \frac{v_b}{v} (d_{14})_b$$
 (12)

Table II also lists the nonlinear coefficients calculated from  $d_{14} = 6(X_{av})^3$ , assuming the Miller's 6 is the same for all the chalcopyrites. This assumption is probably true within a factor of two for most chalcopyrites.<sup>10</sup>

It follows from Table II that all the chalcopyrites have roughly the same figure of merit  $d^2/n^3$ . Therefore, for nonlinear orders applications it is more important to consider transmission range wirefringence, and crystal quality. The transparency region sets in upper limit for the tuning range of a parametric oscillator. It a fixed idler frequency the gain of a parametric oscillator varies linearly proportional to the pump frequency for walkoff limited interaction lengths.<sup>11</sup> It is therefore advantageous to use the shortest pump wavelength permitted by the bandgap and phasematching condition. An attractive pump source for infrared parametric oscillators is the Nd<sup>3+</sup>:YAG laser in cases where the bandgap cutoff is shorter than one micron. The nonlinear crystal then also has applications in infrared up-conversion schemes for low noise signal processing<sup>12</sup> or image up-conversion.<sup>13</sup> Materials with bandgaps shorter than a micron are also attractive from a crystal growth point of view since this allows visual detection of crystal imperfections.

In conclusion we have estimated the optical properties of the  $II-IV-V_2$  compounds based on the analogous III-V compounds. The estimated birefringence and transparency range agrees very well with the few values that have been measured. Several of the chalcopyrites have potential for nonlinear optics applications. The values listed in Table II should assist in the selection of the crystal most suited for a particular application.

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#### FIGURE CAPPIONS

Figure 1 Relative birefringence of the chalcopyrites.

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