

## Characterization of some quaternary defect chalcopyrites as useful nonlinear optical and solar-cell materials

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(Received 12 October 1989)

The ternary chalcopyrite semiconductors together with a few ternary defect compounds have emerged as useful nonlinear materials for nonlinear laser devices. We have studied some quaternary defect compounds and evaluated the dielectric constant as well as refractive indices and optical nonlinearities of these materials (since compounds with high value of refractive indices have higher nonlinearity) using the quantum dielectric theory of Phillips and Van Vechten and the bond-charge model of Levine and its modification for multinary compounds by Samanta *et al.* Other important band-structure parameters such as crystal-field splitting ( $\Delta_{CF}$ ) and spin-orbit splitting ( $\Delta_{s.o.}$ ) have been evaluated and the contribution of tetragonal distortion to birefringence has been discussed. We have been able for the first time to show a correlation between the band-gap energy and tetragonal distortion, and finally the importance of these crystals in context to nonlinear laser devices and solar cells has been pointed out.

### I. INTRODUCTION

The studies of ternary compounds in recent years are being carried out with continuously growing interest. The ternary chalcopyrite semiconductors such as  $A^{II}B^{IV}C_2^V$  and  $A^I B^{III} C_2^{VI}$  are being investigated with greater emphasis because of their wide variety of applications<sup>1-3</sup> in optoelectronic devices, light-emitting diodes (LED), heterojunction solar-cell materials,<sup>4</sup> and phase-matched nonlinear laser devices. These compounds provide fertile ground for studying several physical properties of tetrahedrally coordinated semiconductors. Chela<sup>5</sup> extended the Phillips-Van Vechten dielectric theory to ternary compounds to estimate the average linear susceptibility—hence refractive indices—and the bond-charge model of Levine<sup>6,7</sup> for nonlinear optical properties. Levine also calculated the nonlinear optical properties of some  $A^{II}B^{IV}C_2^V$  and  $A^I B^{III} C_2^{VI}$  compounds consisting of noble metal elements such as Cu and Ag taking into account the “*d*” electron contribution and also for some other crystal structures. Later Samanta and Bhar<sup>8,9</sup> estimated the linear and nonlinear optical properties of some chalcopyrites ( $A^I B^{III} C_2^{VI}$ ), defect chalcopyrites ( $A^{II} B^{III} \square C_4^{VI}$ ), stannite ( $A^I B^{II} C^{IV} D_4^{VI}$ ), and famatinite ( $A^I_3 B^V C_4^{VI}$ ) crystals and discussed the suitability for device design. Studies on ternary defect compounds such as  $CdGa_2S_4$  (Ref. 10) and  $HgGa_2S_4$  (Ref. 11) show that although the former has sufficient nonlinearity, it cannot be used in phase-matched nonlinear devices because of the lack of suitable birefringence, whereas the latter emerged as the useful one in the devices. In addition to the single crystals, the mixed crystals<sup>12,13</sup> are also emerging as useful nonlinear materials. The defect compounds are characterized as (i) being difficult to dope, (ii) showing very strong photoconductivity, and (iii) being stable under irradiation—a very useful property particularly when working with high-power lasers. It is not clear to what

extent these properties are “intrinsic,” related to the vacancy nature of structure, or “extrinsic,” due to defects or impurities. Again the applications of those crystals are limited due to the lack of availability of obtaining a crystal of suitable size and optical quality. In this light we therefore have undertaken a detailed study of quaternary defect compounds first grown by Hughes *et al.*<sup>14</sup> to evaluate several of their important physical parameters which, in turn, help to shed more light on the actual processes taking place in these compounds and also on their suitability in device design.

### II. STRUCTURAL FEATURES

Regarding the structure of these compounds, the same can be derived by successive substitution from the sphalerite (zinc blende) structure. The chalcopyrite cell is obtained by doubling the sphalerite unit cell by replacing the two group-III atoms with a group-II and a group-VI atom, i.e., by cationic substitution always maintaining an average valence-electron concentration (VEC) of 4. The unit cell of a quaternary defect chalcopyrite such as  $AgAlGaSe_4$  contains two formula units and the primitive cell contains seven atoms. In the chalcopyrite ( $ABC_2$ ), the ordering gives two cation sublattices, *A* and *B*, but with the present quaternary compounds there are four different cations if the lattice vacancy is incorporated, and hence three possible arrangements can be made, i.e., the *A* and *B* sublattices can be occupied by (i) (I- $\square$ ) and (III-IV), (ii) (I-III) and (IV- $\square$ ), or (iii) (I-IV) and (III- $\square$ ). The superlattice lines described above show that the occupancy of the separate *A* and *B* lattices is random and that no further ordering occurs. The different structures are shown in Fig. 1.

### III. THEORY AND METHOD OF EVALUATION

The dielectric constant, as well as the refractive index, is a very important physical parameter both for funda-

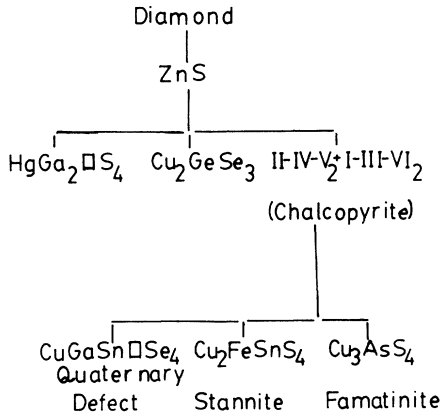


FIG. 1. Splitting diagram for different structures.

mental as well as applied considerations. These properties enter in an important way into the physics underlying the optical, transport, and lattice-dynamical properties of semiconductors and are also important for considering the defect and impurity states of the same. According to the quantum dielectric theory of Phillips and Van Vechten (PV theory), the dielectric properties are described by a single energy gap  $E'_g$  which is composed of a covalent part also known as homopolar energy  $E_h$  and an ionic part  $C$  known as heteropolar or antisymmetric energy. For a crystal consisting of different types of bonds  $l$  the total low-frequency electronic susceptibility  $\chi$  may be written as

$$\chi = \sum F^l \chi^l, \quad (1)$$

with

$$\chi^l = \frac{1}{4\pi} \frac{(\hbar\Omega_p)^2 D^l A^l}{(E'_g)^2}, \quad (2)$$

where  $\chi^l$  is the total macroscopic susceptibility,  $F^l$  is the fraction of the bonds of type  $l$  composing the actual crystal plasma frequency  $\hbar\Omega_p^l$ , and  $D^l$  is the core correction factor, and  $A^l$  is related to Fermi energy and the PV gap.

Considering a single bond, i.e., omitting  $l$ , the expression for low-frequency electronic susceptibility takes the form

$$\chi = \frac{1}{4\pi} \frac{(\hbar\Omega_p)^2 D A}{(E'_g)^2}, \quad (3)$$

where

$$(E'_g)^2 = E_h^2 + c^2$$

and ionicity of the bond

$$f'_i = c^2 / (E'_g)^2 \quad \text{with} \quad E_h = \frac{39.74}{d^{2.48}} \quad (4)$$

and

$$c = 14.4be^{-K_s r_0} \left[ \frac{z_\alpha}{r_\alpha} - \frac{z_\beta}{r_\beta} \right], \quad (5)$$

where  $d$  is the nearest-neighbor distance (i.e.,  $d = r_\alpha + r_\beta$  consisting of two atoms  $\alpha$  and  $\beta$ ),  $z$  is the number of valence electrons on cation,  $e^{-K_s r_0}$  is the Thomas-Fermi screening factor, and  $b$  is a correction factor introduced to account for the true screening behavior of a solid which is more complex than the simple Thomas-Fermi screening factor. Since all the compounds discussed contain the noble metals (either Cu or Ag), it is necessary to take into account the contribution of  $d$  electrons for evaluating these parameters, and hence the effective number of valence electrons for Cu and Ag. Thus evaluating all the quantities, it is possible to calculate  $\chi$ , hence the dielectric constant, as  $\epsilon = 1 + 4\pi\chi$ , and hence the refractive index since  $n = \sqrt{\epsilon}$ .

To calculate the susceptibility ( $\chi$ ) of a whole compound such as  $\text{AgAlGaSe}_4$  we have to consider individual bonds such as  $\text{AgSe}$ ,  $\text{AlSe}$ , etc., and the method followed has already been discussed in Refs. 8 and 9 and all parameters such as  $E_h$ ,  $C$ ,  $E_g$ ,  $f_i$  ( $\hbar\Omega_p$ )<sup>2</sup>, etc. have been evaluated to find out  $\chi$  of the individual bond. Again for a compound of the type  $ABCD_4$ , the total  $\chi$  of the system is given by

$$\chi_{ABCD_4} = \frac{1}{4}(\chi_{AD} + \chi_{BD} + \chi_{CD} + \chi_{\square D}), \quad (6)$$

and the expression for Miller's  $\delta$  using the bond-charge model becomes

$$\Delta_{pqr} = \sum F[\Delta_{pqr}(C) + \Delta_{pqr}(E_h)], \quad (7)$$

where  $F$ ,  $\Delta$ ,  $E_h$ , and  $C$  refer to a particular bond with

$$F\Delta(E_h) = \frac{23.2G\chi^2 E_h^2 (r_\alpha - r_\beta)}{N_b (E'_g)^2 q d^2 \chi_{av}^3}, \quad (8)$$

$$F\Delta(C) = \frac{600G\chi^2 |e| b e^{-K_s r_0} (z_\alpha + z_\beta) C}{N_b (E'_g)^2 q d^2 \chi_{av}^3}, \quad (9)$$

with  $\chi_{av}$  being the average principal linear susceptibility of the whole compound and all other quantities refer to a particular bond as already defined in Refs. 12 and 15.

Again, the band-structure parameters such as the crystal-field splitting  $\Delta_{CF}$  and spin-orbit splitting  $\Delta_{s.o.}$  are of utmost importance as they play a vital role in lifting the degeneracy of the  $p$ -like valence bands in chalcopyrite crystals. The crystal-field splitting  $\Delta_{CF}$  of the valence-band maxima can be expressed by the relation  $\Delta_{CF} = 1.5b(2 - c/a)$  where  $b$  is the deformation potential and  $a, c$  are the lattice parameters. On the other hand, the nature of the transition in an atomic spectra is governed by the spin-orbit splitting parameter  $\Delta_{s.o.}$ . The expression for  $\Delta_{s.o.}$  following Hubner and Unger,<sup>16</sup> and modified accordingly for multinary compounds by Samanta *et al.*<sup>12</sup> may be written as

$$\Delta_{s.o. | ABCD_4} = \frac{1 - f_i}{2} \left[ \frac{\Delta_A + \Delta_B + \Delta_C}{3} \right] + \frac{1 + f_i}{2} \Delta_D, \quad (10)$$

where  $\Delta_A, \Delta_B, \Delta_C, \Delta_D$  are the atomic spin-orbit splittings of the elements and  $f_i$  is the ionicity of the compound.

$\Delta_{s.o.}$  for all other elements, except for Cu and Ag, is known. Using the experimental values of ternary compounds, we have found the  $\Delta_{s.o.}$  for Cu and Ag,  $-1.49$  and  $-2.04$ , respectively, and then evaluated the  $\Delta_{s.o.}$  of all these compounds. For compounds containing the noble metals Cu and Ag, the  $d$ -electron contributions are to be taken into account the same as for Cu compounds by Yamamoto *et al.*<sup>17</sup> and hence the crystal-field splitting  $\Delta_{CF}$  and spin-orbit splitting  $\Delta_{s.o.}$  take the form

$$\Delta_{CF} = \alpha \Delta_{CF}^p + (1 - \alpha) \Delta_{CF}^d, \quad (11)$$

with

$$\Delta_{CF}^p = \frac{1}{2} b_p (2 - c/a)$$

and

$$\Delta_{CF}^d = \frac{1}{2} b_d (2 - c/a)$$

together with

$$\Delta_{s.o.} = \alpha \Delta_p + (1 - \alpha) \Delta_d, \quad (12)$$

where  $1 - \alpha$  is the fraction of  $d$  character and  $\alpha$  is the  $p$  character in the valence band, while  $b_p$  and  $b_d$  are the deformation potentials of the  $p$  and  $d$  orbitals, respectively. These values are taken to be  $-1.0$  and  $-3.15$  for Cu compounds and  $-1.0$  and  $-1.15$  for Ag compounds.  $\Delta_{s.o.}$  has been evaluated using Eq. (10) and as its value is influenced due to the presence of  $d$  electrons the same has been discovered remembering that  $\Delta_p$  is the spin-orbit splitting observed in  $p$ -like binary analogs and  $\Delta_d$  is the negative spin-orbit splitting of the  $d$  levels themselves.

As birefringence is the key parameter for phase-matched nonlinear laser devices, it is one of the most im-

portant characteristics of the chalcopyrite compounds, so it is quite natural to assume that the former has some sort of dependence on the tetragonal distortion  $(2 - c/a)$ , as has been discussed in detail in Chap. IV of Ref. 18.

#### IV. RESULTS AND DISCUSSIONS

Results of our calculation of refractive indices as well as dielectric constants together with the values evaluated using Moss's formula  $n = (77/E_g)^{0.25}$  are shown in Table I, and are compared with the corresponding ternary analogs. The agreement between them is gratifying. An inspection of Table I shows that the refractive indices of the quaternary defect compounds are close to their ternary analogs as refractive indices of the ternary defect compounds follow from their binary analogs, and hence the trend from binary to ternary to quaternary follows. It is to be noted in this connection that the compound with a low band gap does not fit well into the above relation. Regarding the nonlinearity shown in Table II, it is observed that the Ag compounds have higher nonlinearity than the corresponding Cu ones. Again  $\Delta(\text{AgInGeSe}_4) > \Delta(\text{AgGaGeSe}_4)$  and also  $\Delta(\text{AgInSnSe}_4) > \Delta(\text{AgInGeSe}_4)$  and the same trend is also maintained in Cu compounds, thus confirming the experimental observation  $\Delta(\text{AgInSe}_2) > \Delta(\text{AgGaSe}_2)$  for the ternary version. Amongst the Ag compounds,  $\text{AgGaSnSe}_4$ ,  $\text{AgAlSnSe}_4$ , and  $\text{AgInSnSe}_4$  have higher nonlinearity because these have high refractive indices, while  $\text{CuAlSnSe}_4$ ,  $\text{CuInGeSe}_4$ , and  $\text{CuInSnSe}_4$  have amongst the Cu ones. Thus it is seen that the quaternary defect chalcopyrites usually have larger nonlinearities than their corresponding ternary analogs, which is particularly important in view of their phase-matching characteristics.

TABLE I. Comparison of calculated refractive indices of quaternary defect compounds with the corresponding ternaries (experimental) along with that evaluated using Moss's formula. The refractive indices of the ternary compounds are taken from Shay and Wernick, except for  $\text{AgAlSe}_2$ , for which those of Samanta have been utilized.

Ternary compounds	Refractive index	Quaternary compound	Refractive index	Refractive index using Moss's formula	Dielectric constant
$\text{AgAlSe}_2$	2.4	$\text{AgAlGeSe}_4$	2.4	2.5	5.76
		$\text{AgAlSnSe}_4$	2.6	2.6	6.76
$\text{AgGaSe}_2$	2.58	$\text{AgGaGeSe}_4$	2.5	2.5	6.25
		$\text{AgGaSnSe}_4$	2.6	2.6	6.76
$\text{AgInSe}_2$	2.63	$\text{AgInGeSe}_4$	2.4	2.6	5.76
		$\text{AgInSnSe}_4$	2.6	3.0	6.76
$\text{CuAlSe}_2$	2.47	$\text{CuAlGeSe}_4$	2.5	2.4	6.25
		$\text{CuAlSnSe}_4$	2.7	2.5	7.29
$\text{CuGaSe}_2$	2.71	$\text{CuGaGeSe}_4$	2.5	2.5	6.25
		$\text{CuGaSnSe}_4$	2.7	2.7	7.29
$\text{CuInSe}_2$	2.79	$\text{CuInGeSe}_4$	2.5	2.8	6.25
		$\text{CuInSnSe}_4$	2.7	3.2	7.29

TABLE II. Calculated values of spin-orbit splitting  $\Delta_{s.o.}$ , crystal-field splitting  $\Delta_{CF}$ , and nonlinearity together with the experimental values of the band gap of the compounds.

Ternary compound	Band gap $E_g$ (eV)	Quaternary compound	Band gap $E_g$ (eV)	$\Delta_{s.o.}$ (eV)	$-\Delta_{CF}$ (eV)	Nonlinearity $\Delta$ ( $10^{-6}$ esu)
AgAlSe <sub>2</sub>	2.54	AgAlGeSe <sub>4</sub>	1.89	0.29	0.38	1.84
		AgAlSnSe <sub>4</sub>	1.56	0.34	0.28	2.28
AgGaSe <sub>2</sub>	1.80	AgGaGeSe <sub>4</sub>	1.85	0.31	0.34	1.83
		AgGaSnSe <sub>4</sub>	1.70	0.35	0.24	2.27
AgInSe <sub>2</sub>	1.24	AgInGeSe <sub>4</sub>	1.53	0.39	0.19	2.27
		AgInSnSe <sub>4</sub>	0.94	0.40	0.12	2.56
CuAlSe <sub>2</sub>	2.50	CuAlGeSe <sub>4</sub>	2.34	0.33	0.23	1.74
		CuAlSnSe <sub>4</sub>	1.90	0.37	0.13	2.00
CuGaSe <sub>2</sub>	1.77	CuGaGeSe <sub>4</sub>	1.35	0.34	0.15	1.77
		CuGaSnSe <sub>4</sub>	1.42	0.39	0.12	1.98
CuInSe <sub>2</sub>	0.95	CuInGeSe <sub>4</sub>	1.23	0.38	0.06	2.11
		CuInSnSe <sub>4</sub>	0.71	0.33	0.0	2.25

As the ternary  $A^{II}B^{IV}C_2^V$  compounds are too covalent and have small band gaps, they cannot be used in the visible spectral region as useful nonlinear materials. But the quaternary compounds, on the other hand, such as AgGaSnSe<sub>4</sub> and CuAlSnSe<sub>4</sub> having larger nonlinearity and appropriate band gaps, may be used as a suitable nonlinear material in the visible region, particularly in the red part of the spectrum, while AgInSnSe<sub>4</sub> and CuInSnSe<sub>4</sub> can be used in the near-infrared region. An inspection of the band gap of the compounds reveals that CuGeSnSe<sub>4</sub> and CuInGeSe<sub>4</sub> satisfies the stringent require-

ment of a photovoltaic active semiconductor (PVAS) for solar cells.

Table II also depicts the calculated values of  $\Delta_{s.o.}$  and  $\Delta_{CF}$  for the quaternary compounds for which the contribution due to  $d$  electrons has been taken care of.

Table III compares the tetragonal distortion ( $2-c/a$ ) of these compounds along with the corresponding ternary analogs and their birefringences. The tetragonal distortion for the quaternary is found to decrease if the Al atom of AgAlGeSe<sub>4</sub> is replaced by an element of higher atomic weight, thus confirming the experimental observa-

TABLE III. Comparison of the tetragonal distortions and birefringence of ternary compounds along with the quaternary compounds.

Ternary compound	Tetragonal distortion	Birefringence (Shey and Vernick, 1975)	Quaternary compound	Tetragonal distortion
AgAlSe <sub>2</sub>	0.20		AgAlGeSe <sub>4</sub>	0.245
			AgAlSnSe <sub>4</sub>	0.179
AgGaSe <sub>2</sub>	0.183	-0.03	AgGaGeSe <sub>4</sub>	0.218
			AgGaSnSe <sub>4</sub>	0.157
AgInSe <sub>2</sub>	0.09	+0.002	AgInGeSe <sub>4</sub>	0.123
			AgInSnSe <sub>4</sub>	0.080
CuAlSe <sub>2</sub>	0.06	-0.013	CuAlGeSe <sub>4</sub>	0.084
			CuAlSnSe <sub>4</sub>	0.046
CuGaSe <sub>2</sub>	0.038	-0.006	CuGaGeSe <sub>4</sub>	0.053
			CuGaSnSe <sub>4</sub>	0.042
CuInSe <sub>2</sub>	0.00		CuInGeSe <sub>4</sub>	0.020
			CuInSnSe <sub>4</sub>	0.00

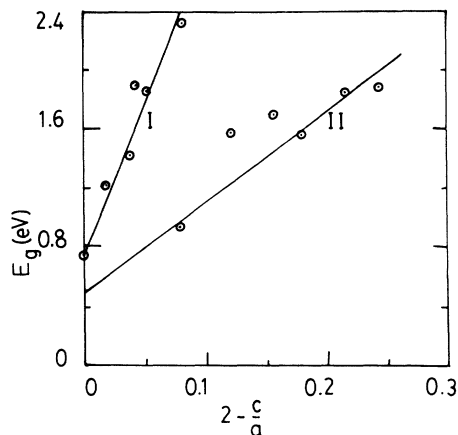


FIG. 2. Plot of band-gap energy ( $E_g$ ) vs tetragonal distortion ( $2 - c/a$ ): I, Cu compounds; II, Ag compound.

tion with the corresponding ternary chalcopyrites. It is worth mentioning in this connection that the compound  $\text{AgAlSnSe}_4$  having tetragonal distortion 0.179 might possess birefringence of about  $-0.03$  as that of  $\text{AgGaSe}_2$  (having the same tetragonal distortion) and the same argument might be extended for other quaternary compounds also.

A detailed study about the variation of the band gap ( $E_g$ ) with tetragonal distortion yields no result for the ternary compounds whereas a reasonably good dependence was obtained with these quaternary compounds. Figure 2 shows such a correlation, but with different slopes for two different noble-metal compounds, viz., Cu and Ag. Such different slopes again show the strong  $d$ -electron contribution (hybridization of  $p$  and  $d$  levels)

which is different for the two noble-metal elements. Considering the band gap of the quaternary compounds  $\Delta E_g$ , i.e.,  $E_g|_T - E_g|_Q$  is positive for the Sn-substituted compound as the band gap of the ternary is larger than that of the quaternary, but mostly negative for Se-substituted compounds except for the two Al ones. The positive value for  $\Delta E_g$  for the two compounds amongst all other Al compounds suggests that there is some critical value of the band gap for the ternary which is near 2 eV. Further, the reduction of the band gap for the Sn-substituted quaternary compound compared to the Ge one is due to the tendency of the former towards metalization.

## V. CONCLUSIONS

The extensive study presented here on refractive index, birefringence, nonlinearity, and band-structure parameters about the quaternary defect compounds shows that  $\text{AgGaSnSe}_4$  and  $\text{CuAlSnSe}_4$  having higher nonlinearity might be suitable as useful nonlinear materials, while  $\text{CuGeSnSe}_4$  and  $\text{CuInGeSe}_4$  might be suitable as solar-cell materials, thus helping the crystal grower and technologists to concentrate their efforts to grow high quality and suitable sizes of this type of crystal for their specific device applications. Further characteristic properties, such as photoconductivity and difficulty in doping, are related to the vacancies and the growth of a much higher quality of single crystals would shed more light on these aspects.

## ACKNOWLEDGMENTS

The authors note, with appreciation, that this work was partially financed by the University Grants Commission (UGC) through its DRS Programme granted to Burdwan University.

<sup>1</sup>J. L. Shay and J. H. Wernick, *Ternary Chalcopyrite Semiconductors, Growth Electronic Properties and Applications* (Pergamon, New York, 1975).  
<sup>2</sup>R. C. Smith, *J. Phys. (Paris) Colloq.* **36**, C3-89 (1976).  
<sup>3</sup>S. Wagner, in *Ternary Compounds*, Inst. Phys. Conf. Ser. No. 35 (IOP, Bristol, 1979).  
<sup>4</sup>N. Romeo, *Jpn. J. Appl. Phys.* **19**, Suppl. 19-3, 5 (1980).  
<sup>5</sup>D. S. Chemla, *Phys. Rev. Lett.* **26**, 1441 (1971).  
<sup>6</sup>B. F. Levine, *J. Chem. Phys.* **59**, 1463 (1973).  
<sup>7</sup>B. F. Levine, *Phys. Rev. B* **7**, 2591 (1973).  
<sup>8</sup>L. K. Samanta and G. C. Bhar, in *Proceedings of the 1st Symposium on Lasers*, IIT, Kanpur, India, 1975 (unpublished).  
<sup>9</sup>L. K. Samanta and G. C. Bhar, *Phys. Status Solidi A* **41**, 331 (1977).  
<sup>10</sup>L. M. Suslikov, Z. P. Gadmasi, D. Sh. Kovah, and V. Yu. Slivka, *Opt. Spectrosc.* **53**, 283 (1982).  
<sup>11</sup>V. V. Badikov, L. N. Matveev, S. M. Pshenichnikov, O. V.

Rychik, N. K. Trotsenko, N. D. Ustinov, and S. I. Shcherbakov, *Kvant. Elektron. (Moscow)* **7**, 2233 (1980) [*Sov. J. Quantum Electron.* **10**, 1300 (1980)].  
<sup>12</sup>L. K. Samanta, D. K. Ghosh, and G. C. Bhar, *Phys. Rev. B* **33**, 4145 (1986).  
<sup>13</sup>L. K. Samanta, D. K. Ghosh, and G. C. Bhar, *Phys. Rev. B* **35**, 4519 (1987).  
<sup>14</sup>O. H. Hughes, J. C. Wooley, S. A. Lopez Rivera, and B. R. Pamplin, *Solid State Commun.* **35**, 573 (1980).  
<sup>15</sup>L. K. Samanta, D. K. Ghosh, and G. C. Bhar, *Cryst. Res. Technol.* **23**, K16 (1988).  
<sup>16</sup>K. Hubner and K. Unger, *Phys. Status Solidi B* **54**, K65 (1972).  
<sup>17</sup>N. Yamamoto, H. Horinaka, and T. Miyauchi, *Jpn. J. Appl. Phys.* **18**, 225 (1979).  
<sup>18</sup>L. K. Samanta, Ph.D. dissertation, Burdwan University, 1981 (unpublished).