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Electronic and nonlinear-optical properties of some mixed thiogallates, selenogallates, and tellurogallates as candidates for laser device applications

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The refractive index, optical nonlinearity, and other related parameters of some mixed-defect compounds for the first time have been evaluated using the bond-charge model of Levine and the approach of Samanta *et al.* and the results are compared with available experimental values. We have further discussed the device feasibility and the construction of narrow-band tunable optical filters using these compounds which are very important nowadays for various sophisticated frequency-mixing processes.

I. INTRODUCTION

The ternary chalcopyrite semiconductors[1] and their mixed versions[2,3] are of considerable technological interest to the industry as they provide the opportunities for tailoring the lattice constants, energy band gap, refractive index, birefringence, thermal-expansion coefficient, nonlinear-optical susceptibilities, and other important physical and chemical properties to satisfy the requirements of specific applications in nonlinear laser devices, optoelectronics and heterojunction solar cell materials, and, very recently, in the development of future high-speed transistor technology. The importance of $A^{II}B^{IV}C_2^{V}$ and $A^{I}B^{III}C_2^{VI}$ ternary compounds over their binary analogs $A^{III}B^{V}$ and $A^{II}B^{VI}$ are already well established but because of some interesting physical properties of these ternaries and with the possible applications, a third type of materials, namely, $A^{II}B_2^{III}C_4^{VI}$, has attracted attention[4] recently.

These compounds attracted much interest because of their high photosensitivity, intense luminescence, and high nonlinear susceptibility coupled with natural birefringence. The Cd and Hg thiogallates particularly having direct band gaps are useful for developing light-emitting diodes and lasers while the residual conductivity of these compounds appears to be useful for developing memory cells. Also these compounds can be used as photodetector, switches, and narrow-band optical filters.[5,6] Apart from having a high transparent region and nonlinearity the birefringence is the key parameter which results in favorable phase matching of these compounds for nonlinear laser devices.

Studies on single-crystal samples show the high application potential of some of the crystals like $CdGa_2S_4$, $CdGa_2Se_4$ and $HgGa_2S_4$. Komarov *et al.*[7] was able to obtain efficient conversion of CO_2 laser using $HgGa_2S_4$ while Andreev *et al.*[8] reported up-conversion of CO_2 laser when pumped with a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser using a $Cd_xHg_{1-x}Ga_2S_4$ crystal and found that phase-matching angle changes from 41° to 62° as the concentration x varies from 0.0 to 0.4. Because of increasing trend of applications of these crystals we have studied for the mixed system $CdGa_2(S_xSe_{1-x})_4$, $HgGa_2(S_xSe_{1-x})_4$, $Cd_{1-x}Hg_xGa_2S_4$, $Cd_{1-x}Hg_xGa_2Se_4$, $CdGa_2(Se_xTe_{1-x})_4$ $HgGa_2(Se_xTe_{1-x})_4$ and $Cd_{1-x}Hg_xGa_2Te_4$ and evaluated for the first time the linear- and nonlinear-optical properties together with the band-structure parameters as they play a key role in characterizing the optical properties in that the end crystals do not always satisfy the stringent device requirements while the physical parameters like band gaps, the refractive index, and nonlinearity can be set to a desired value changing the concentration and finally the nonlinearity of a mixed quinary alloy has been presented together with the possibility of difference frequency mixing (DFG) using a $HgGa_2S_4$ crystal.

II. STRUCTURAL FEATURES

Regarding the structure of the ternary compounds, $A^{II}B_2^{III}C_4^{VI}$, the same can be derived by successive substitution from the sphalerite (zinc-blende) structure as shown in Fig. 1. The chalcopyrite unit cell is obtained by doubling the sphalerite unit cell by replacing two group-III atoms with group-II and -IV atoms satisfying always the basic requirement (Grimm-Sommerfeld rule) for these structures that valence-electron concentration (VEC) is equal to 4. The unit cell of such a compound usually known as defectlike $CdGa_2S_4$ contains two formula units and the primitive cell contains seven atoms. With the present ternary defect compound ($A^{II}B_2^{III}C_4^{VI}$) there are

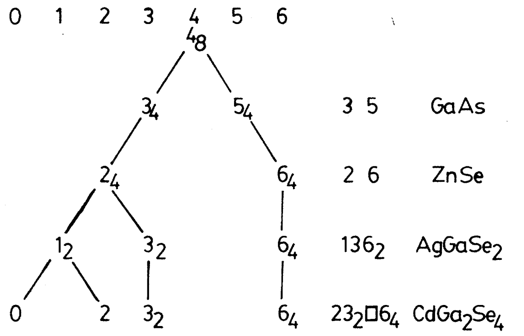

FIG. 1. Schematic splitting diagram for the derivation of a structure satisfying the Grimm-Sommerfeld rule. The shorthand labels in the hierarchy may be interpreted as follows: 4_8 (A_8^{IV});3_4 (A_4^{III}) and 5_4 (B_4^{V}), yielding 3 5 ($A^{\mathrm{III}}B^{\mathrm{V}}$);$2_4$ (A_4^{II}) and 6_4 (B_4^{VI}), yielding 2 6 ($A^{\mathrm{II}}B^{\mathrm{VI}}$);$1_2$ (A_2^{I}),3_2 (B_2^{III}), and 6_4 (C_4^{VI}), yielding 1 3 6_2 ($A^{\mathrm{I}}B^{\mathrm{III}}C_2^{\mathrm{VI}}$); and 0_1 (□), 2_1 (A^{II}), 3_2 (B_2^{III}), and 6_4 (C_4^{VI}), yielding 2 3_2□6_4 ($A^{\mathrm{II}}B_2^{\mathrm{III}}\square C_4^{\mathrm{VI}}$).

four different cations if the lattice vacancy is incorporated and two possible arrangements can be made, i.e., the A and B sublattice can be occupied by (i) (A^{II}-□) and (B^{III}-B^{III}) and (ii) (A^{II}-B^{III}) and (B^{III}-□). Usually one uses the formula $A^{\mathrm{II}}B_2^{\mathrm{III}}\square C_4^{\mathrm{VI}}$ for this type of compound where the symbol □ denotes the empty lattice point and this is an ordered defect and various attempts to fill up this vacancy emerged out as unsuccessful pointing to the conclusion that it is "inherent" to the structure. The VEC for this structure is 4.57 and in a cation sublattice there are 25% ordered defects. Many of the compounds grown by Hahn *et al.*[9] though have chalcopyrite structure, some of them are spinel, layered, and pseudocubic. These compounds having vacancy incorporated in the ideal structure (i) are very difficult to dope, (ii) show very strong photoconductivity, and (iii) are very resistant under irradiation—a property very useful 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 defect or impurities. Again the major mode of defect in chalcopyrite crystals compared to the common pseudobinaries is the cation disorder as valences usually differ by 2 in the case of ternary compounds whereas there is no such difference for binary compounds.

III. THEORY AND METHOD OF EVALUATION

The dielectric constant as well as the refractive index of tenary compounds is very useful both from fundamental and applied consideration and is central to the property of semiconductors. A thorough knowledge of the refractive index is therefore not only of fundamental interest but also highly relevant for the development of various sophisticated semiconductor devices. On the other hand the optical nonlinearity is a key parameter for assessing the performance potential of materials for various nonlinear frequency-mixing devices and a compound with a high refractive index usually has higher nonlinearity ($d=\chi^3\Delta$) thus necessitating the study for the search of materials with higher indices. Out of various approaches for evaluating the nonlinearity of material the bond-charge model of Levine[10] has been found to be useful and Samanta *et al.*[11] have found out the optical nonlinearity of some ternary mixed systems with necessary modifications. With the use of defect chalcopyrites in various nonlinear laser devices we found it useful to evaluate the optical nonlinearity of various mixed versions of this type. According to Levine the expression for Miller's Δ for $A^{\mathrm{II}}B_2^{\mathrm{III}}C_4^{\mathrm{VI}}$ crystals can be written as

$$\Delta_{ijk}(x)=F\{\Delta_{ijk}^{\mathrm{II\text{-}VI}}(C(x))+\Delta_{ijk}^{\mathrm{II\text{-}VI}}(E_h(x))+2[\Delta_{ijk}^{\mathrm{III\text{-}VI}}(C(x))+\Delta_{ijk}^{\mathrm{III\text{-}VI}}(E_h(x))]\}\ , \tag{1}$$

with

$$F\Delta(C(x))=\frac{0.288be^{-k_s r_0(x)}(Z_\alpha+Z_\beta)[\chi_k^l(x)]^2C^l(x)V_k^l(x)}{E_g^2(x)d^2(x)[q(x)/e](\chi_{\mathrm{compound}})^3}\ , \tag{2}$$

and

$$F\Delta(E_h(x))=\frac{0.232f_c(x)(\chi_k^l(x))^2\rho(x)V_k^l(x)}{d(x)[q(x)/e](\chi_{\mathrm{compound}})^3}\ , \tag{3}$$

where the total nonlinearity (Miller's Δ) is the sum of the individual contributions from different types of bond and can be written as

$$\Delta=\sum[F\Delta(E_h(x))+F\Delta(C(x))]\ . \tag{4}$$

The quantities F, Δ, $E_h(x)$, and $C(x)$ refer to a particular type of bond and all other quantities in Eqs. (2) and (3) have their usual meaning as defined in Levine[10] and Samanta *et al.*[11,3,12] and the method of evaluation of various parameters has been discussed in detail in the works of the latter. The χ_{compound} of the mixed system can be evaluated as has already been done by Samanta and Bhar[11] and the refractive index of the compound can be found using the relation $\epsilon=1+4\pi\chi_{\mathrm{compound}}$. On the other hand, the bond length of the atoms in a mixed crystal have been evaluated by utilizing the relation of the form first suggested by Van Vechten and Bergstrasser[13] and thus ultimately leading to the evaluation of nonlinearity of the mixed compound.

Again the crystal-field splitting of a valence-band maxima may be written as $\Delta_{\mathrm{CF}}=1.5b(2-c/a)$, where b is the deformation potential and c and a are the lattice parameters which vary with concentration and these have been evaluated using Vagerd's law. On the other hand the observation of spin-orbit splitting is one of the most reliable ways to find the nature of transition as in atomic spectra. The spin-orbit splitting parameters $\Delta_{\mathrm{s.o.}}$ have been evaluated using the relation of Hubner and Unger[14] and modifying accordingly for the mixed crystal knowing the atomic spin-orbit splitting of the individual elements. The expression for spin-orbit splitting $\Delta_{\mathrm{s.o.}}$ for a compound of the type $AB_2[(C_1)_x(C_2)_{1-x}]$ can be written as,

$$\Delta_{\text{s.o.}}=\frac{1-f_i}{2}\left[\frac{\delta_A+2\delta_B}{3}\right]+\frac{1+f_i}{2}[x\delta_{C_1}+(1-x)\delta_{C_2}] \tag{5}$$

and a similar expression for the cationic variation (amalgamated type) where f_i is the ionicity of the compound and δ_A, δ_B, etc. are the atomic spin-orbit splitting of the elements.

IV. RESULTS AND DISCUSSIONS

The results of our calculation of optical nonlinearity, spin-orbit splitting, crystal-field splitting energy, and the refractive indices are shown in Table I. It is observed that the optical nonlinearity increases for anion variation from sulfur to tellurium through selenium at a steady rate for both the mixed compounds containing Cd and Hg. On the other hand for the cationic variation from Cd to

TABLE I. Calculated values of the refractive index, nonlinearity, spin-orbit splitting ($\Delta_{\text{s.o.}}$), and crystal-field splitting (Δ_{CF}) at different concentrations together with available experimental values of the refractive index.

Compound	Concentration x	Nonlinearity (10^{-6} esu)	$\Delta_{\text{s.o.}}$ (eV)	$-\Delta_{\text{CF}}$ (eV)	Refractive index n	
					Calc.	Expt.
$\text{CdGa}_2(\text{S}_x\text{Se}_{1-x})_4$	0.00	2.10	0.53	0.23	2.42	2.45[a]
	0.25	2.09	0.43	0.25	2.38	
	0.50	2.03	0.34	0.26	2.33	
	0.75	1.98	0.24	0.28	2.28	
	1.00	1.95	0.15	0.30	2.24	2.28[b]
$\text{CdGa}_2(\text{Se}_x\text{Te}_{1-x})_4$	0.00	2.17	1.11	0.24	2.71	
	0.25	2.14	0.96	0.23	2.64	
	0.50	2.13	0.81	0.23	2.57	
	0.75	2.11	0.67	0.23	2.50	
	1.00	2.10	0.53	0.23	2.42	2.45[a]
$\text{HgGa}_2(\text{S}_x\text{Se}_{1-x})_4$	0.00	2.15	0.59	0.23	2.60	2.60[c]
	0.25	2.18	0.49	0.23	2.52	
	0.50	2.17	0.40	0.24	2.44	
	0.75	2.15	0.30	0.24	2.36	
	1.00	2.04	0.20	0.25	2.28	2.28[c]
$\text{HgGa}_2(\text{Se}_x\text{Te}_{1-x})_4$	0.00	2.43	1.12	0.01	2.85	
	0.25	2.36	0.98	0.06	2.79	
	0.50	2.27	0.85	0.11	2.73	
	0.75	2.20	0.72	0.17	2.66	
	1.00	2.15	0.59	0.23	2.60	
$\text{Cd}_{1-x}\text{Hg}_x\text{Ga}_2\text{S}_4$	0.00	1.95	0.12	0.30	2.24	
	0.25	1.99	0.13	0.29	2.25	
	0.50	2.02	0.13	0.27	2.26	
	0.75	2.03	0.14	0.26	2.27	
	1.00	2.04	0.15	0.25	2.28	
$\text{Cd}_{1-x}\text{Hg}_x\text{Ga}_2\text{Se}_4$	0.00	2.10	0.50	0.23	2.42	
	0.25	2.11	0.50	0.23	2.47	
	0.50	2.12	0.51	0.23	2.51	
	0.75	2.13	0.52	0.23	2.57	
	1.00	2.15	0.52	0.23	2.60	
$\text{Cd}_{1-x}\text{Hg}_x\text{Ga}_2\text{Te}_4$	0.00	2.17	1.08	0.24	2.71	
	0.25	2.20	1.07	0.18	2.75	
	0.50	2.24	1.07	0.12	2.78	
	0.75	2.33	1.06	0.06	2.81	
	1.00	2.43	1.06	0.01	2.85	

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Hg, a change in the same direction is observed but at a rather slow rate than the former which are consistent with the earlier observations in the case of $A^{\mathrm{I}}B^{\mathrm{III}}C_2^{\mathrm{VI}}$ and $A^{\mathrm{II}}B^{\mathrm{IV}}C_2^{\mathrm{V}}$ chalcopyrites. It is seen that when an element of a lower atomic number is replaced by a corresponding element of a higher one, the nonlinearity increases and this in turn makes the contribution from the more ionic bond much greater than that from the less ionic one. The effect is much more predominant when Cd is replaced by Hg and S or Se replaced by Te. Calculated values of nonlinearity for $\mathrm{Cd}_{1-x}\mathrm{Hg}_x\mathrm{Ga}_2\mathrm{S}_4$ for $x=0$ and 1 is found to agree well with the experimental values[15,16] 1.97×10^{-6} and $(2.34\pm25\%)\times10^{-6}$ esu. Compounds (both cationic and anionic variation) are found to obey a parabolic variation with composition whereas the cationic variation (amalgamation-type compounds) produces an optical energy gap bowing with concentration but for anionic variation (persistence type) the linear relationship is found to obey. An effort has been made to evaluate the optical nonlinearity of the quinary $\mathrm{Cd}_y\mathrm{Hg}_{1-y}\mathrm{Ga}_2(\mathrm{S}_x\mathrm{Se}_{1-x})_4$ system following the technique of Moon *et al.*[17] which in its $x=y$ form reduces to

$$\Delta(x)=2.15+0.16x-0.55x^2+0.19x^3\ . \qquad (6)$$

A three-dimensional plot of the functional dependence of nonlinearity with composition is shown in Fig. 2 and its shaded region represents the same for the $x=y$ quinary compound.

As regards to the spin-orbit splitting and crystal-field splitting, the same trend has been observed as found in nonlinearity. An inspection of Table I reveals that the systems $\mathrm{CdGa}_2(\mathrm{Se}_x\mathrm{Te}_{1-x})_4$, $\mathrm{HgGa}_2(\mathrm{Se}_x\mathrm{Te}_{1-x})_4$, and $\mathrm{Cd}_{1-x}\mathrm{Hg}_x\mathrm{Ga}_2\mathrm{Te}_4$ possess higher values of spin-orbit splitting energy at all concentrations. And this is due to the fact that each of the above compounds contain Te which itself has a very high value of spin-orbit splitting (1.26 eV); a value nearly 10 times greater than the corresponding value for the sulfur atom.

The refractive indices of the compounds at various concentrations evaluated from the corresponding bond susceptibilities are also shown in Table I, the analysis of which reflects an increase in the refractive index in the direction S→Se→Te and Cd→Hg. The results are found to agree well with available experimental values. It is to be noted in this connection that both $\mathrm{HgGa}_2\mathrm{S}_4$ and $\mathrm{CdGa}_2\mathrm{S}_4$ have refractive index crossings, i.e., an isotropic point[18] where the birefringence changes its sign and this in turn can be utilized for the construction of a narrow-band tunable optical filter (NBTOF). On the other hand $\mathrm{CdGa}_2\mathrm{Se}_4$ has no such isotropic point. But it is now possible to design a suitable NBTOF by properly changing the composition, i.e., either by amalgamation or by persistence method. It is interesting to note in this connection that using a $\mathrm{HgGa}_2\mathrm{S}_4$ crystal, the phase matching angle in the difference frequency generation can be varied from 38° to 48° when the pump wavelength varies from 1.06 to 0.6943 μm.

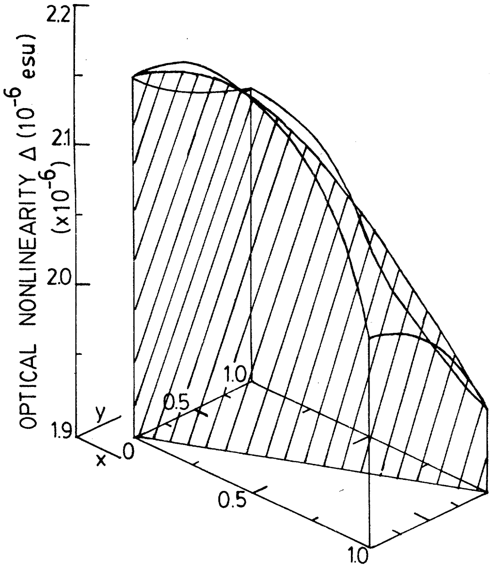

FIG. 2. A three-dimensional plot of optical nonlinearity of the quinary $\mathrm{Cd}_y\mathrm{Hg}_{1-y}\mathrm{Ga}_2(\mathrm{S}_x\mathrm{Se}_{1-x})_4$ as a function of concentration (x,y).

V. CONCLUSION

We have evaluated the optical nonlinearity, band-structure parameter, and refractive indices of some mixed defect compounds, of which $\mathrm{CdGa}_2(\mathrm{S}_x\mathrm{Se}_{1-x})_4$ and $\mathrm{Cd}_{1-x}\mathrm{Hg}_x\mathrm{Ga}_2\mathrm{S}_4$ emerged as suitable materials for nonlinear-optical laser devices. Further detailed study of these compounds will be very helpful for solving the technological problems for the crystal growers who want to select the most promising candidates for growing and for the optoelectronic device designers who want to choose the most appropriate ones for their specific device design. Knowledge gained from such studies would undoubtedly help not only to enhance the performance of existing devices but also to realize new combinations and configurations of semiconductor materials which will be important for various practical applications.

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