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NONSTOICHIOMETRIC COMPOUNDS

Optical band gap in the system $ZnO_{1-x}S_x$. An experimental and quantum chemical study

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Abstract The synthesis of single crystalline and polycrystalline material is reported in the system $ZnO_{1-x}S_x$. Substitution of oxygen by sulphur yields hexagonal wurtzite-type mixed crystals in the range $0 \le x \le 0.05$. The cubic zincblende structure is observed for oxygen incorporation into ZnS for $0.96 \le x \le 1$. At intermediate compositions, the system is two-phase. For both types of anion substitution, the band gap energies, as determined from optical transmission and remission experiments, are found to decrease from the pure end members. Quantum chemical calculations at density functional level identify local structural changes as the main factor responsible for the reduction of band gap energies.

Introduction

Zinc oxide is of particular practical importance. It is of miscellaneous use, e.g. as pigment, fungicide, additive at the vulcanisation of rubber, curing retardant in cementation, as photosemiconductor in photocopying paper, or as UV absorber, e.g. in sun repellents. The latter application of zinc oxide is due to its very steep absorption edge at about 390 nm; UV radiation of shorter wavelength is absorbed completely. On the other hand, the material is already almost transparent for UV-radiation at 400 nm. Another noteworthy peculiarity of the system ZnO-ZnS is to be seen in the fact that this is one of the very few systems with mixing of O^{2-} and S^{2-} ions on the same sublattice, rather than the thermodynamically favourable formation of sulfates or of sulphur dioxide, SO_2.

The modification of zinc oxide and its optical properties by substitution of the zinc, and/or, oxygen atoms, respectively, by other atoms has been an object of topical interest in solid state physics for a couple of years [1–6]. Especially the recent interest in spintronics has motivated numerous investigation into the substitution of zinc by transition metal ions in the wide band gap semiconductor ZnO [1, 7, 8]. In contrast, information on anionic substitutions in ZnO and notably on that of oxygen by sulphur is scarce. Even most basic information on the phase diagram and on the extent of substitution that can be achieved in the system ZnO–ZnS is not available. Recently, Yoo et al. [9] reported on the synthesis of $ZnO_{1-x}S_x$ films by pulsed laser deposition (PLD) with $0 < x < 0.15$. By means of rf reactive sputtering, Meyer et al. [4] have been able to extend the composition range even to $0 \le x \le 1$. Structural characterisation by X-ray diffraction revealed that the thin films possess the wurtzite symmetry. These authors also demonstrated that the band gap energies, as determined from the optical absorption edge, decrease from both end members of the solution series and go thorough a pronounced minimum at about $x = 0.5$.

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The fact that thin films of $ZnO_{1-x}S_x$ can be prepared by various thin-film techniques does not allow the conclusion that these materials are thermodynamically stable, that they possess equilibrium structures and that they can be prepared as bulk materials as well. Consequently, the interest of the present work is directed to the preparation of bulk $ZnO_{1-x}S_x$ mixed crystals and to the determination of the homogeneity range of the system. One of the main objectives is to answer the question, how an anion substitution influences the band gap, respectively the absorption edge in the ZnO–ZnS system. Obviously, this substitution must be accompanied by considerable changes in the electronic structure, as is evident, e.g., if the band gap energies of ZnO and ZnS are considered which take values of about 3.2 eV [4, 10, 11] and 3.6 eV [12], respectively.

The new and further developments in optoelectronics as well as the aspect of UV protection provided essential motivation for the present work. In view of the practical interest in such materials, the chemical preparation of these materials appears to be a very worthwhile aim. We report here on procedures for the production of $ZnO_{1-x}S_x$ in the form of single crystals and powders, on its optical absorption properties as well as on results of quantum chemical electronic structure calculations, which shed light into the changes of electronic structure occurring upon anion substitution.

Experimental

Chemical transport reactions are a well-established preparative technique for the synthesis of polycrystalline and single crystalline material of high purity [13]. The chemical transport experiments in the system ZnS/ZnO have been carried out in quartz ampoules (inner diameter 18 mm, length 190 mm). In order to remove traces of water, the ampoules were baked out for about 10 min by heating with a forced-air burner in high vacuum. Afterwards the argon-ventilated ampoules were filled with zinc oxide and zinc sulphide in proportions reported in Table 1.

Table 1 Chemical transport of ZnO:ZnS

Composition of starting material ZnO : ZnS (mol %)	Transported product phase(s)
80 : 20	$ZnO_{1-x}S_x$ ($x = 0.96$)
85 : 15	$ZnO_{1-x}S_x$ ($x = 0.96$) $ZnO_{1-x}S_x$ ($x = 0.05$)
90 : 10	$ZnO_{1-x}S_x$ ($x = 0.96$) $ZnO_{1-x}S_x$ ($x = 0.05$)
95 : 5	$ZnO_{1-x}S_x$ ($x = 0.05$)

Bromine is used as transport agent (0.5 bar initial pressure). The transport reaction, in a temperature gradient $T_2 \rightarrow T_1$ (1000 $\rightarrow$ 900 °C), was carried out in a horizontal furnace equipped with two separate heating zones. The reaction time in each case was 148 h, the transport rate was 0.3 mg/h. The reaction rates of ZnS and ZnO were 10.2 mg/h and 0.15 mg/h, respectively. Therefore, an enhancement of ZnS during the transport process is expected and observed. After reaction, the ampoules were removed from the furnace and air-cooled. As given in Table 1, from a ZnO/ZnS mixture of proportion 80:20, the only phase obtained by chemical transport is sulphur rich $ZnO_{1-x}S_x$ with $x = 0.96$. With increasing proportion of ZnO, two phases are deposited: one oxygen rich and one sulphur rich phase. At a ratio of 95:5 we obtained a single $ZnO_{1-x}S_x$ phase with $x = 0.05$. The lattice parameters of the oxygen rich $ZnO_{1-x}S_x$ phases differ only slightly from those of ZnO. For pure ZnO, the following parameters apply: $a = 325.16(5)$ pm, $c = 520.91(6)$ pm, $V = 47.70(1) \cdot 10^6$ pm^3. For $ZnO_{1-x}S_x$ with $x = 0.05$, we obtain: $a = 325.31(2)$ pm, $c = 521.16(3)$ pm, $V = 47.76\ (4) \cdot 10^6$ pm^3. All information on lattice parameters given here and in what follows refers to room temperature.

The direct synthesis of $ZnO_{1-x}S_x$ powders is carried out by annealing mixtures of ZnO/ZnS at 950 °C in the presence of small amounts of bromine in the above described quartz ampoules (0 up to 8 mol% ZnS in 1 mol% steps). According to X-ray diffraction analysis, the products prove to be single phase $ZnO_{1-x}S_x$ containing up to 5% ZnS. An increased ZnS proportion in the ingots leads to the formation of an additional sulphur rich mixed crystal.

For X-ray analysis, a powder diffractometer (Stadi P with PSD, Stoe, Darmstadt, Cu-K$_\alpha$- radiation, 40 kV, 30 mA) was used. Diffractograms were evaluated using the WinXPow software (Stoe). Samples were analysed using scanning electron microscopy (FEI-Philips, XL 30, W-Cathode) equipped with an EDX (EDAX, SUTW-Detector) and by means of an electron microprobe (Cameca SX-100). Optical UV/Vis/NIR spectra were taken using a Lambda 900 photo spectrometer (Perkin-Elmer). For the measurement of diffuse reflection from polycrystalline samples the spectrometer was equipped with a "praying mantis" accessory (Harrick); KCl was used as reference material.

Results and discussion

Phases and structures

While ZnO crystallizes in the wurtzite type, ZnS is of the sphalerite type at temperatures below 1020 °C. Above this temperature it also assumes the wurtzite structure. Due to these structural differences and due to the fact that the anion radii differ considerably, complete miscibility of the two compounds is not to be expected. ZnO as well as ZnS can be obtained by chemical transport reactions [13]. $ZnO_{1-x}S_x$ might also be obtainable by this technique, which is known to produce pure, crystalline and at the same time thermodynamically stable solids. If it is possible to prepare $ZnO_{1-x}S_x$ in this manner, it can be assumed that the products represent equilibrium phases, which can be obtained by other thermal methods, too.

It was indeed found possible to obtain mixed phases of $ZnO_{1-x}S_x$ by chemical transport of ZnO/ZnS mixtures. For $0 < x \leq 0.05$, light green, translucent crystals were obtained, which, in their habit, evidently differ from the transparent, colorless and needle-shaped ZnO crystals (Figs. 1, 2). These crystals exhibit the hexagonal wurtzite structure. The present chemical analyses and X-ray investigations of single and polycrystalline samples lead to the conclusion that $ZnO_{1-x}S_x$, with x between 0 and 0.05, is thermodynamically stable at 900 °C. On the other hand, we obtained a cubic, sulfur-rich mixed phase in chemical transport experiments using higher amounts of ZnS in the starting material (see Experimental section). The analytical investigations reveal that the solubility of ZnO in ZnS is comparable to that of ZnS in ZnO: $ZnO_{1-x}S_x$ with $0.96 < x \leq 1$. The system ZnO–ZnS therefore exhibits an approximately symmetrical region of immiscibility between 5 mol% and 96 mol% ZnS at 900 °C. This shows that thin $ZnO_{1-x}S_x$ films produced for example by sputtering, as described by Meyer et al. [4] for $0 \leq x \leq 1$, can be metastable in extended ranges of composition.

Fig. 1 ZnO crystals (length of the crystals up to 10 mm)

Fig. 2 $ZnO_{1-x}S_x$ crystals ($x = 0.05$) (diameter of the crystals up to 5 mm)

Optical spectroscopy

Optical spectra of $ZnO_{1-x}S_x$ single crystals and powders have been studied at room temperature. Fig. 3 shows the spectrum of a small single crystal. The graph displays the absorbance A

$$A = \log(I_0/I) \qquad (1)$$

where I_0 and I are the intensities of incoming and transmitted light, respectively. In addition to the Lambert-Beer contribution, the experimental absorbance also contains a contribution A_R due to reflectance

$$A = \alpha d + A_R \qquad (2)$$

Here, α represents the (linear decadic) absorption coefficient and d is the thickness of the absorber.

The spectra shown in Fig. 3 are almost featureless, apart from the absorption edge at high energies. In the edge region, the absorption coefficient is given by [14]

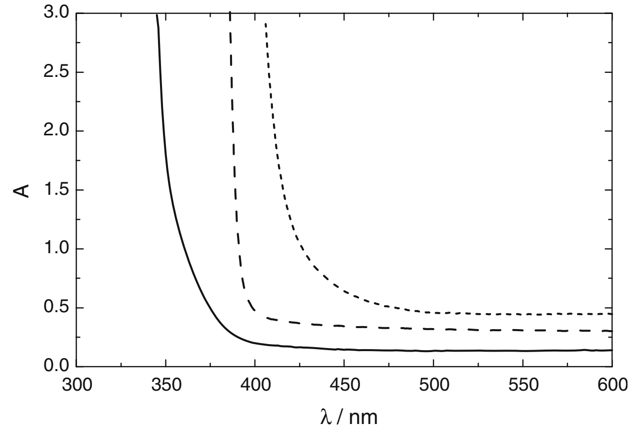

Fig. 3 UV/Vis spectra of single crystalline ZnO, ZnS, and $ZnO_{1-x}S_x$ ($x = 0.05$). Solid line: ZnS; dotted line: ZnO; fine dotted line: $ZnO_{1-x}S_x$. A displacement was applied in *y*-direction of 0.15 units for ZnO and of 0.3 units for $ZnO_{1-x}S_x$. Thickness of crystals approx. $d = 150\ \mu m$

$$\alpha \cdot E = B(E - E_g)^r \tag{3}$$

where B is a constant, $E = h\nu$ the photon energy, and E_g the band gap energy. The numerical value of the parameter r depends on the type of transition under consideration. For a direct transition, $r = 1/2$ holds, for an indirect transition $r = 2$ [14, 15]. Since the absorption edges in the system $ZnO_{1-x}S_x$ are due to direct transitions (see Quantum chemical calculations), the band gaps can be determined from a plot of $(A–A_R)^2 \cdot E^2$ versus photon energy E from the intercept with the *x*-axis, where $(A–A_R)^2 \cdot E^2 = 0$. Figure 4 shows the respective plots for ZnO, $ZnO_{0.95}S_{0.05}$, and ZnS. For the pure end members one obtains gap energies of $E_g(ZnO) = 3.19$ eV and $E_g(ZnS) = 3.54$ eV, which are in good agreement with literature values of 3.2 eV and 3.6 eV for ZnO and ZnS, respectively (300 K) [10–12]. With increasing sulphur content in $ZnO_{1-x}S_x$ ($0 \leq x \leq 0.05$), the absorption edge shifts to lower energies, see e.g. $E_g(ZnO_{0.95}S_{0.05}) = 3.03$ eV in Fig. 4. However, while the absorbance of ZnO shows a very steep increase at the edge, in the cases of ZnS and $ZnO_{0.95}S_{0.05}$ some kind of band tailing seems to be present or an absorption in the band edge region, Fig. 3, which may be due to some unknown impurities. This is also reflected in Fig. 4, where, however, band gap energies are determined from extrapolation of the linear part of the plot.

Decreasing band gap energies with increasing substitution displayed by the single crystalline material is also shown by the spectra of polycrystalline mixed crystals. In this case, the band gap energy can be determined from an analogous use of the Kubelka-Munk quantity F(R)

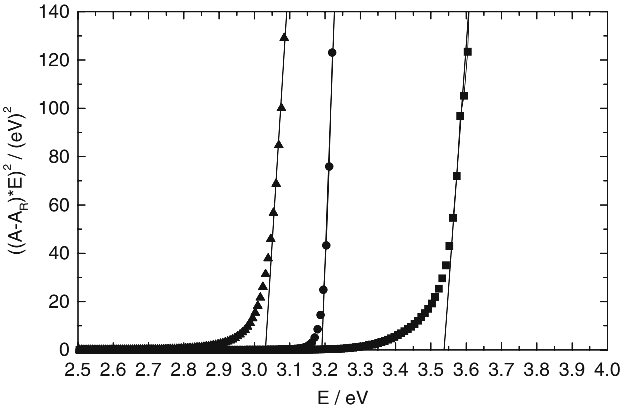

Fig. 4 Determination of the band gap in single crystals of ZnO, ZnS, and $ZnO_{1-x}S_x$ ($x = 0.05$), under the assumption of a direct band-to-band transition. Squares: ZnS ($E_g = 3.54$ eV), Square: ZnO ($E_g = 3.19$ eV), triangle: $ZnO_{1-x}S_x$ ($E_g = 3.03$ eV)

$$F(R) = (1 - R)^2/(2R) \tag{4}$$

where R is obtained from measurement of diffuse reflection [16]. Figure 5 shows the band gap energy as a function of sulphur content of the $ZnO_{1-x}S_x$ mixed crystals determined for single crystalline as well as for polycrystalline material. Figure 6 demonstrates the good agreement observed between the spectra of a single crystal and a high purity powder of ZnO (Ventron, 99.99%), yielding band gaps of 3.19 eV and 3.20 eV respectively.

Meyer et al. [4] determined the band gap energies in $ZnO_{1-x}S_x$ ($0 \leq x \leq 1$) for a series of thin films on

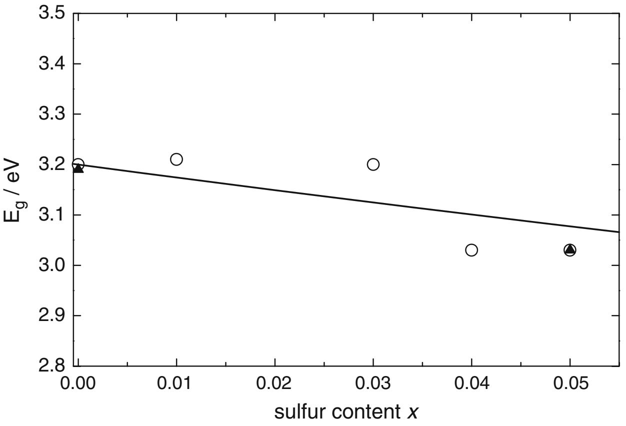

Fig. 5 Band gaps of $ZnO_{1-x}S_x$ determined from the optical spectra of single crystals and powders of different composition. Squares: single crystals; circles: polycrystalline materials. The solid line shows Eq. (5) with $b = 3$ eV, $E_g(ZnS) = 3.54$ eV, and $E_g(ZnO) = 3.19$ eV

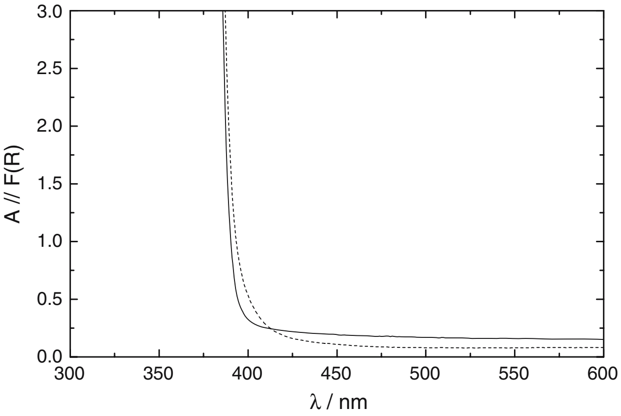

Fig. 6 UV/Vis spectra of ZnO. Solid line: single crystal (*A*), dotted line: polycrystalline material (*F(R)*)

Al_2O_3 substrates deposited by reactive sputtering techniques. The energies determined by these authors exhibit a minimum of about 2.55 eV at $x \approx 0.5$. To good approximation, the data can be represented as

$$E_g(x) = x \cdot E_g(\text{ZnS}) + (1-x) \cdot E_g(\text{ZnO}) - b \cdot x \cdot (1-x) \tag{5}$$

with an optical bowing parameter of $b \approx 3.0$ eV [4]. If Eq. (5) is applied in the homogeneity range $0 \le x \le 0.05$ of the mixed crystals determined in the present work, a reduction is predicted from $E_g(\text{ZnO}) = 3.20$ eV to 3.08 eV, which is in reasonable agreement with the data shown in Fig. 5.

In the context of optical absorption in the edge region of the mixed crystals, the following considerations appear of interest. On the one hand side, the experimental reduction of the band gap energy with sulphur content may be due to a homogeneous change of crystal properties, e.g., the lattice parameters. On the other hand, new electronic states may be created within the forbidden zone, leading to an apparent reduction of the band gap. The latter situation appears to be met, e.g., in the case of titania, TiO_2, doped with nitrogen [17]. Here, a region of doping-related intermediate absorption below the original absorption edge is observed extending to lower energies. In the present case, such a structured absorption edge is not observed, which may indicate that the experimental changes in the edge region are brought about by homogeneous changes in the electronic structure of the mixed crystals.

In conclusion, the investigations of the optical behaviour of $ZnO_{1-x}S_x$ have shown that zinc oxide can be modified by partial substitution in the anion lattice thereby extending the range of absorption of electromagnetic radiation to lower energies. Thus, the efficiency of such a modified zinc oxide as UV absorber is improved considerably.

Quantum chemical calculations

The reasons for the strong reduction of the optical excitation energy in $ZnO_{1-x}S_x$ mixed crystals [4] – in comparison to the pure end members – were investigated by means of quantum chemical calculations. Zinc oxide, zinc sulfide, as well as the mixed phases $ZnO_{0.9375}S_{0.0625}$, $ZnO_{0.875}S_{0.125}$, $ZnO_{0.125}S_{0.875}$ and $ZnO_{0.0625}S_{0.9375}$ were modeled by periodic supercell calculations using the crystalline orbital program CRYSTAL03 [18]. Based on our earlier work on the $ZnS_{1-x}Se_x$ system [19], a Hartree-Fock density functional hybrid method was applied together with optimized atomic basis sets. With this approach, band gaps of 3.34 eV and 3.84 eV were obtained for ZnO and ZnS, respectively, which are in reasonable agreement with the experimental values of 3.2 eV and 3.6 eV [10–12], respectively, and those obtained in the present study (see above). For the comparison of experimental and theoretical band gaps it must be taken into account that the former are obtained at 300 K while the latter correspond to 0 K. Temperature effects tend to decrease the band gap considerably. Theis has measured the optical band gap of ZnS as 3.78 eV at 19 K [20]. This low temperature value is in good agreement with the calculated results.

The calculated lattice parameters *a* and *c* of the ZnO wurtzite lattice are 326.3 pm and 522.0 pm, respectively, in close agreement with the present experimental values 325.2 pm and 520.9 pm as mentioned above. For the mixed phase $ZnO_{0.875}S_{0.125}$ the calculated lattice parameters increased to 333.8 pm and 535.4 pm, respectively. This effect is much larger than that observed experimentally for x = 0.05. In $ZnO_{0.875}S_{0.125}$, the substitutional sulfur atoms are coordinated by four zinc atoms at distances ranging from 224 pm to 227 pm in a distorted tetrahedral arrangement. The S–Zn distances are about 5% shorter than calculated for ZnS (236 pm). The Zn–O distances of zinc atoms near S dopant atoms range between 198 and 200 pm and are, thus, close to pure ZnO, whereas all others are larger by approximately 1% (201 to 203 pm).

The calculated band gap of $ZnO_{0.875}S_{0.125}$ is 2.68 eV, which is about 0.7 eV smaller than that calculated for pure ZnO. The changes of atomic positions in the defective lattice strongly affect the band gap. A test calculation of a $ZnO_{0.875}S_{0.125}$ cell with lattice parameters and atomic positions of the perfect ZnO lattice results in an almost unchanged band gap of 3.33 eV.

On the other hand, the computed band gap of a fictitious ZnO lattice with atomic positions taken from the optimized $ZnO_{0.875}S_{0.125}$ structure is only 2.78 eV. This indicates that the shift of energetic levels is mainly due to structural effects. The presence of sulfur anions with a larger radius compared to oxygen leads to a local distortion of the ZnO lattice and in turn to changes in the crystal field.

The calculated band gap increases from 2.68 eV ($x = 0.125$) to 2.75 eV in the $ZnO_{0.9375}S_{0.0625}$ cell ($x = 0.0625$, optimized lattice parameters $a = 330.1$ pm, $c = 529.5$ pm). The latter value is 0.26 eV smaller than the experimental excitation energy of 3.01 eV for a mixed crystal with $x = 0.05$. To a minor part, this discrepancy may be due to the slight difference in composition. But it also has to be noted that the periodic supercell calculations correspond to highly ordered structures which might be different from the real materials used in the experiments. In the supercells of the mixed systems, one oxygen atom was replaced by a sulfur atom or vice versa. Thus, $ZnO_{0.9375}S_{0.0625}$ and $ZnO_{0.875}S_{0.125}$ were modeled by $Zn_{16}O_{15}S$ and Zn_8O_7S supercells, respectively. In this way, the dopant anions always form a regular sublattice with the largest possible distances from each other, corresponding to the dimensions of the supercells. It is possible that this special arrangement which might be different from the situation present in real crystals, also affects the calculated electronic structure. In our previous study of the related system $ZnS_{1-x}Se_x$ [19] we tested this possibility by comparing different anion distributions explicitly. Indeed, it was found that the calculated band gap in this system can vary by up to 0.13 eV when the anion–anion distances are changed accordingly. Therefore, the discrepancy between theory and experiment can be partly related to the anion ordering in the supercells, but the qualitative picture emerging from the calculations is expected to remain unchanged.

For oxygen substituted zinc sulfide $ZnO_{0.125}S_{0.875}$ the lattice parameter a is calculated as 536.3 pm, which is 2% smaller than that of pure ZnS (544.8 pm). The Zn–O distances, 210 pm, are about 5% larger than in bulk ZnO, while the Zn–S distances, 233–240 pm, are similar to those in bulk ZnS. The calculated band gap of fully optimized $ZnO_{0.125}S_{0.875}$ is 2.59 eV. This is 1.25 eV smaller than that calculated for pure ZnS. The smallest energy gap corresponds to a direct Γ-transition. The lowest conduction band has a large dispersion of 2.4 eV, which is similar to $ZnO_{0.875}S_{0.125}$. The corresponding fictitious ZnS structure with all atoms located at the optimized coordinates of $ZnO_{0.125}S_{0.875}$ does not show a reduction of the band gap (3.78 eV) with respect to perfect ZnS. The observed decrease of the band gap in $ZnO_{0.125}S_{0.875}$ is therefore a direct effect of the presence of the oxygen anions. If the oxygen concentration is decreased to 6.25% ($ZnO_{0.0625}S_{0.9375}$) the calculated band gap increases to 3.40 eV.

In conclusion, the quantum chemical calculations of the effects of atomic substitution in the system ZnO–ZnS reproduce the experimentally observed decrease of band gap energies for substitution into the end members. The optical effect caused by anion substitution falls off much faster on the sulfur-rich side than on oxygen-rich side, which is in qualitative agreement with the observations of Meyer et al. [4] made on thin films of $ZnO_{1-x}S_x$ produced by sputtering techniques.

Conclusions

The anion substituted system Zn(O,S) has been studied in respect to the region of existence of the mixed system. For the temperature of preparation of 900 °C, an almost symmetric solubility of about 5 mol% has been determined with crystals possessing the zincblende and the wurtzite structure for oxygen and sulphur rich mixed crystals, respectively. Optical spectra of single crystalline and polycrystalline samples show absorption edges shifting to decreasing energies with increasing doping level. The same trend is obtained with periodic quantum chemical calculations performed at density functional level. The calculated changes of the band gap due to doping are larger than the experimental ones, which can be attributed to ordering effects. Local structural changes are identified as the main factor responsible for the reduction of band gap energies.

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