Solid-State Chemistry

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Luminescent Semiconductors

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The investigation of the optical properties of inorganic solids is currently a very topical theme, not least because of the dramatic changes being made in the use of illuminants. In fact, the energy saved by replacing incandescent bulbs and even energy-saving lamps with the highly efficient light-emitting diodes (LEDs) is considerable,[1,2] since approximately 20% of the electric energy is used for illumination purposes. In this context two different technologies are employed to produce white light:[3] either three semiconductor diodes in the colors blue/green/red are used (multi-chip LED), or a blue diode is coated with a yellow phosphor (usually Ce-YAG; Figure 1) or with a green and red phosphor (phosphor-converted LEDs). In each case the primary radiation is brought about by semiconductor luminescence. Semiconductors that emit efficiently in the long wavelength range have been known for some time, yet surprisingly the great breakthrough in their use in lighting technology did not come until the semiconductor Ga/InN, which emits in the near UV/blue/green range, was developed in the 1990s.[4] For other applications too, such as display backlighting, general and medical sensor technology, or photovoltaics, luminescent inorganic semiconductors are the future materials of choice owing to their usually high-temperature and long-term stability, environmental tolerance, and their non-toxicity.

Figure 1. Green- and blue-emitting ($(Ga_{1-x}In_x)N$) LEDs (left and center) and a blue LED coated with the yellow illuminant Ce-YAG ($Y_3Al_5O_{12}:Ce^{3+}$, right).

From a chemical materials viewpoint the number of semiconductor materials with a large band gap used in the optical area is, however, rather limited.[5] Normally these are typically binary II/VI or III/V semiconductors or their mixed crystals. Thus ZnO, ZnS, and CdS have been investigated thoroughly at a relatively early stage, whereas today III/V semiconductors are more likely to be used. GaN, which emits in the near-UV (NUV) range at a wavelength of 364 nm, is particularly suitable for applications with short wavelength emissions. Moreover, there is an adequately efficient emission since unlike GaP, GaN is a direct band-gap emitter, that is, the transition takes place with conservation of momentum. With indirect emitters, the electrons in the conduction band have a different momentum than the holes in the valence band, the transitions are therefore forbidden, and such materials are unsuitable for applications as illuminants. In addition, GaN is relatively insensitive towards defects so that a high efficiency can also be achieved with a high defect concentration. Substitution of some of the Ga ions by In leads to a decrease of the band gap so that depending on the In content blue and green light-emitting diodes, up to an emission wavelength of $\lambda_{max} = 540$ nm, can be obtained (Figure 1).

Modern red and yellow LEDs also contain III/V semiconductor compounds, for example, (AlGaIn)P, in which the wavelength can be varied by variation of the cation ratio. At 650 nm an internal efficiency of almost 100% is achieved, which however, falls considerably at shorter wavelengths. Moreover, to date it is not possible to obtain efficient high-performance LEDs with these materials since the luminescence is quenched significantly at the higher temperatures reached. For these reasons it would be desirable to find materials with more suitable properties.

It is conspicuous that only non-complex inorganic semiconductors are being investigated in detail for their optical properties, and developed and exploited in applications. Even simple investigations of the optical properties of more complex semiconductors have rarely been described, although such semiconductors are possibly quite suitable for applications. Even for the formation of thin films and nanoparticles whose optical properties are highly dependent upon the particle size only the established systems are being used.

For this reason it is most welcome that Kanatzidis et al. have recently described the structures and properties of a series of novel, highly promising complex semiconductors with large band gaps.[6] These are the compounds $AZrPS_6$ ($A = K, Rb, Cs$). They crystallize in two different polymorphic forms, α- and β-$AZrPS_6$. $KZrPS_6$ crystallizes in the α-form isotypical to the corresponding selenide[7] in the polar space group $Pmc2_1$, whereas $CsZrPS_6$ was obtained in the β-form with the non-centrosymmetric space group $P1$. The Rb compounds could be prepared in both forms depending on

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the reaction conditions. The previously unknown structures of the β-compounds, which form small, highly twinned, single crystals, were elucidated by synchrotron measurements.

The two polymorphs crystallize in similar structures.[6,7] In each case anionic $1/\infty[\mathrm{ZrPS_6}]^-$ chains are formed along the *a* axis (Figure 2c), which are linked through the alkali-metal ions (Figure 2b). The $\mathrm{Zr^{4+}}$ ions are in each case coordinated in a distorted bicapped trigonal-prismatic fashion by S atoms and are also connected by corner-sharing $\mathrm{PS_4}$ units. (Figure 2d). The differences in the two forms essentially amount to the arrangement of these building blocks relative to one another.

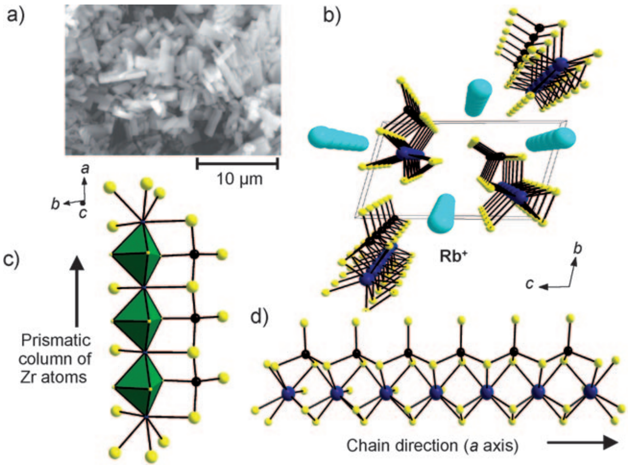

Figure 2. a) Scanning electron microscope image of microcrystals of α-$\mathrm{KZrPS_6}$. b) Crystal structure of β-$\mathrm{RbZrPS_6}$ along [100], Zr: dark blue; S: yellow; P: black; Rb: turquoise. c,d) Projections of the $1/\infty[\mathrm{ZrPS_6}]^-$ chains along the *a* axis.

The optical properties of the compounds are most remarkable. The absorption spectra show a steep increase at the same energy, independent of the alkali-metal ion and of the structure, which corresponds to a band gap of approximately 2.1 eV (17 000 $\mathrm{cm^{-1}}$) (Figure 3a), in agreement with the orange color of the compounds. The potential of these materials is demonstrated by the observation of intense red luminescence even at room temperature, with a maximum at approximately 1.9 eV (Figure 3c); unfortunately no quantum yields are reported. The small Stokes shift leads to the conclusion that they are direct band-gap emitters, which means they have the short lifetime and the resulting efficient emission that are prerequisites for applications. The asymmetric shape of the emission bands and the nonlinear dependence of the emission intensity on the excitation energy confirm that the emissions are caused by donor–acceptor transitions.

That the emission maxima of the individual compounds are displaced only insignificantly in relation to one another (Figure 3) is noteworthy and shows that the states of the valence and conduction bands involved do not vary with the alkali-metal ions. The lifetimes in the nanosecond range support the hypothesis of direct emission, however the lifetime falls with decreasing size of the alkali-metal ions through nonradiative processes. These findings are an interesting example of the structure–property relationships of semiconducting materials. The high stability of the compounds even allows the preparation of thin, monodisperse luminescent films of good quality (Figure 3b).

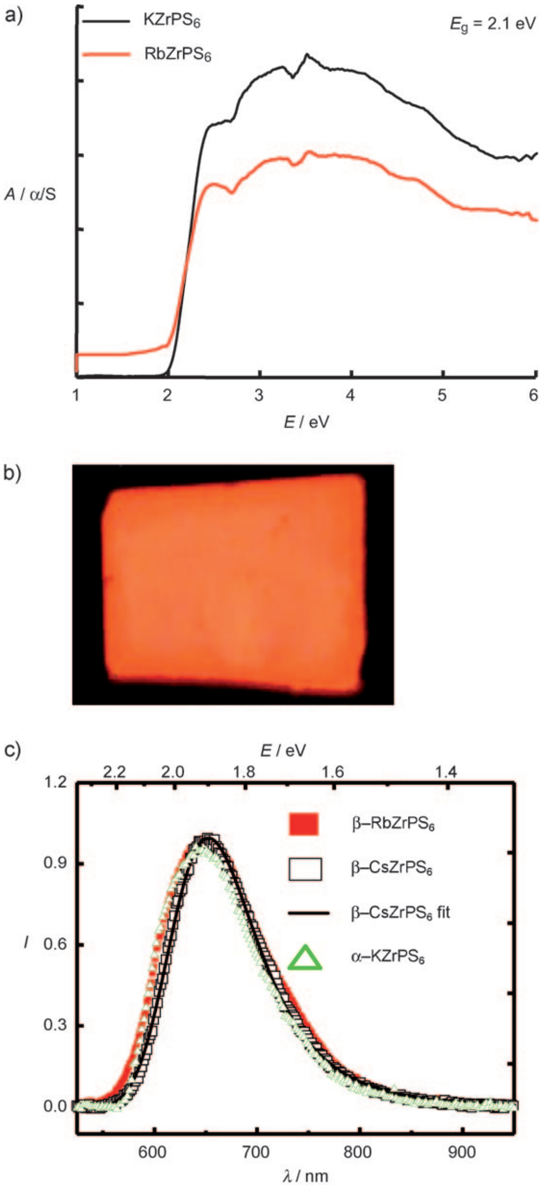

Figure 3. a) Absorption spectra of $\mathrm{AZrPS_6}$, b) red-emitting film of $\mathrm{KZrPS_6}$ on Si (10×8 mm), c) emission spectra of $\mathrm{AZrPS_6}$.

Since the compounds crystallize in non-centrosymmetric space groups, the luminescent properties could be associated with nonlinear optical properties. Thus, if the second harmonic generation (SHG) effect is suitably efficient, excitation with IR laser radiation could lead to electronic excitation and subsequent red emission through frequency doubling. The semiconductors described are certainly interesting materials for further optical investigations.

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