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A few common misconceptions in the interpretation of experimental spectroscopic data

M.G. Brik^{a,b,c,d,f,*}, A.M. Srivastava^e, A.I. Popov^{f,g}

a School of Optoelectronic Engineering & CQUPT-BUL Innovation Institute, Chongqing University of Posts and Telecommunications, Chongqing, 400065, PR China

^b Institute of Physics, University of Tartu, W. Ostwald Str. 1, Tartu, 50411, Estonia

^c Faculty of Science and Technology, Jan Długosz University, Armii Krajowej 13/15, PL-42200, Częstochowa, Poland

^d Academy of Romanian Scientists, Ilfov Str. No. 3, 050044, Bucharest, Romania

^e Current Lighting Solutions, LLC, Cleveland, OH, 44110, USA

^f Institute of Solid State Physics, University of Latvia, Kengaraga Street 8, LV-1063, Riga, Latvia

^g Faculty of Physics and Technical Sciences, L.N. Gumilyov Eurasian National University, Nur-Sultan, 010008, Kazakhstan

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ABSTRACT

Proper presentation and interpretation of the experimental spectroscopic data is critical to understanding of the luminescence of solids that can increase fundamental scientific knowledge and serve as a practical guide to the development of commercially useful phosphors and other functional optical materials. We find prevalence of erroneous interpretation of the spectroscopic data in scientific reports that are caused by mistakes related to the estimation of the experimental band gaps, location of the defect levels in the band gaps, decomposition of the wide spectral bands into individual Gaussians and meaningful comparison of full widths at half maximum (FWHM). We hope that citing these issues will help researchers avoid making these common mistakes in the interpretation of the spectroscopic data.

1. Introduction

Recent decades have witnessed an enormous increase in scientific publications, evidenced by ever growing number of research conferences (both online and onsite) and by the introduction of new journals with different modes of publication (hard copies, electronic versions only, open access etc). Not always, unfortunately, the increased publication activity has been accompanied by a necessarily increased scientific rigor specifically in the analysis of the raw spectroscopic data Here and there, in many research papers published worldwide, one can find serious mistakes which lead to incorrect interpretation of the experimental results. The danger is that such mistakes when repeated many times take deep roots and becomes established among researchers. For example, as reviewers of various international scientific journals, we often encountered the situation where the authors attempt to overcome our critical remarks by stating in their rebuttal letters: "we have seen such things published in your and other journals (here some citations follow) and we have previously used such an interpretation in our publications (again some citations), so why are you against that?"

In this short communication, we make an attempt to articulate

forcefully some basic mistakes that are being made in the evaluation of the recorded spectral data. The reason for the incorrect interpretation is not so obvious to us but we are surprised as to how often such mistakes are encountered in the archival literature. Deliberately, we do not give any references to such papers so as tonot cause any offenses and/or hostility. It is our firm believe and hope that this short communication will be useful to the scientific community and will help researchers to provide better quantitative analysis of the raw data while simultaneously deepening their understanding of experimental and theoretical spectroscopic results.

2. Defect states in the insulator band gap

In the archival literature, diffuse reflectance spectroscopy of undoped and doped host lattices is used as a standard technique for measuring the absorption properties of the compounds and more specifically for determining the optical band gap energy. From the diffuse reflectance data, it is possible to extract the optical band gap by using the Kubelka-Munk function. For the undoped material the intrinsic band gap is then correctly determined. However, we frequently encounter the

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^{*} Corresponding author. Institute of Physics, University of Tartu, W. Ostwald Str. 1, Tartu, 50411, Estonia. *E-mail address:* mikhail.brik@ut.ee (M.G. Brik).

situation where authors present measurements determining the "band gap energy" of doped compounds and interpret the data as indicating that the band gap has decreased upon insertion of the impurity ion. This is an incorrect conclusion which is illustrated by discussing the band structure of pure YAlO₃ and Ce³⁺ doped YAlO₃ in the following.

A vast majority of optical materials are wide-band gap insulators, doped with various impurity ions with unfilled electron shells, such as transition metal ions and rare earth ions in different charge (oxidation) states. The concentration of these impurities is usually not more than a few percent at most. The band gaps of such host materials are usually wide enough to accommodate some number of the impurity ion energy levels. The electronic transitions between the impurity ion energy levels or between the intrinsic bands of the host crystals (valence and conduction bands) are then utilized in fundamental investigations and practical applications.

The main point to be kept in mind in this connection is that the impurity ion electronic levels are the *localized* states appearing within the band gap, and the results of the experimental data (diffuse reflectance) on the doped material cannot be interpreted to indicate that the *band gap of the host has decreased* upon insertion of the impurity ion.

Below we provide a graphical illustration of this fact, by comparing and contrasting the YAlO₃ and YAlO₃:Ce³⁺ electronic band structures (Figs. 1 and 2). By definition, in solid state physics, the band gap of a crystalline material is the energy difference between the highest occupied state (which corresponds to the top of the valence band) and the lowest empty state (which is then the bottom of the conduction band). As a rule, the valence band is made by the occupied s, p anion orbitals, such as oxygen, fluorine, chlorine etc., whereas the conduction band consists of the unoccupied s, p, d states of cations (usually metals). For pure YAlO₃, the top of the valence band is composed of the oxygen 2p orbitals and the bottom of the conduction band is composed of the Y 4d orbitals (Fig. 1).

Let us now consider Ce^{3+} -substituted YAlO₃. The impurity ion has the 4f¹ electronic configuration. As seen from Fig. 2, the presence of the Ce^{3+} ion introduces localized 4f states at about 3.5 eV above the top of the valence band. More importantly, the presence of these localized states within the band gap of YAlO₃ does not change the band gap, whose value of about 8 eV remainsthe same in pure and Ce^{3+} -doped YAlO₃. Therefore, a small amount of impurity ion cannot modify the hosts electronic bands, but can only produce flat (nearly dispersionless) states within the band gap.

The band gap can be altered in a process that is termed in the literature as band gap engineering. This can be realized by forming solid solutions based on a partial or complete cation (more often) or anion substitution, for example, $Mg_{1-x}Zn_xO$, x = 0 ... 1. In this particular case, gradual replacement of Mg by Zn allows to smoothly tune the band gap from the MgO value (7.8 eV) to the ZnO value (3.37 eV).

Special care should be taken when using the density functional theory (DFT)-based approaches for calculations of the electronic properties of solids with substitutional defects. It is well-known that the DFT methods underestimate the band gap value. Many DFT-based softwares



Fig. 1. Calculated band structure of pure YAlO3.



Fig. 2. Calculated band structure of Ce³⁺-doped YAlO₃.

automatically place the zero of energy at the highest occupied energetical state. Then, due to the band gap underestimation, the ground impurity state (or zero of energy) can ironically be found in the host's conduction band, thus resulting (mathematically!) in a zeroth value of the band gap. Moreover, this may lead to an incorrect conclusion pertaining tothe conducting nature of a newly formed doped material. This fact should not be understood as a transformation of an insulator into a conductor, and an utmost care should be taken when analyzing the results of calculations of electronic structure of defects in solids.

3. Experimental determination of the band gap from the absorption spectra

Experimental absorption spectra are widely used to determine the band gap value for crystalline solids. The idea is very simple: for an ideal crystal, non-zero absorption is detected in the range of the band-to-band (valence band to conduction band) absorption transitions. However, in spite of this seeming simplicity, there are several important physical aspects which can adversely affect the experimental results. In fact, this is the reason why the experimental data for the band gaps of many crystals can vary significantly.

First of all, there are no *ideal* crystals in the nature (we hope that the crystal growth specialists will excuse us for such a statement), but there are crystals of *high optical quality*. Still there are some defects (even unintentional ones, like uncontrollable impurities, vacancies, interstitial atoms, adsorbed atoms on the crystal surfaces etc.), which – as we saw in Fig. 2 – may have some of their energy levels in the band gap. If these levels are located close to the conduction band bottom, then absorption associated with these defects will mask the true host absorption, leading to an underestimation of the true band gap.

Secondly, the temperature at which the spectra are taken is very important. With increased temperature due to thermal expansion the interatomic distances are increased and the band gaps tend to decrease (at least, the direct band gaps). Therefore, even for the same crystal the low temperature band gaps can be greater than the high temperature ones.

Thirdly, very often the Tauc plots are used to estimate the band gaps (Fig. 3). In this method, the photon energy ($h\nu$) on the abscissa and the quantity ($\alpha h\nu$)^{1/2} on the ordinate are plotted (α is the absorption coefficient of the material). A tangent line to the absorption spectrum curve in the vicinity of the steepest absorption rise is extrapolated to the photon energy axis. The intersection point yields the band gap energy. The issue is that the tangent line can be drawn in several ways, as shown in Fig. 3. Depending on how that straight line is plotted, the difference in the estimated band gap energies in the considered example can well be within 0.5–1 eV. Therefore, if such a method is used, it is recommended to extract the data corresponding to the absorption edge range and clearly indicate the "best" position of the tangent line. The techniques for proper extrapolation have been discussed in recent literature [1].

Sometimes it is possible to meet a statement that "the band gap was calculated from the Tauc plot". Again, it is not entirely correct. The calculations imply application of certain equations and/or



Fig. 3. A hypothetic absorption spectrum in the vicinity of the absorption edge and several tangent lines, which would return the band gap values in the range from 6.6 eV to 7.0 eV.

computational methods, whereas determination of the band gap from the Tauc plot can be at its best referred to as an "estimation" only, but not the true "calculation".

4. Decomposition of the experimental spectra into individual Gaussians

Routine measurements of the excitation and emission spectra on commercial spectrofluorometers are made on a wavelength scale. Therefore, it is natural that the experimental spectroscopists are used to working on the wavelength scale. When they analyze the complicated shapes of the absorption/emission bands, they decompose those bands into a number of Gaussians, without converting the spectrum into the energy scale, and fundamentally, this is incorrect.

The origin of any spectral feature is the transition between two energetic states, with energies E_1 and E_2 . The probability of such a transition (or intensity, if we employ the experimentalists language) depends on the square of the matrix element of the transition operator calculated on the wave functions of those states. The energy of those states (and, ultimately, their difference) is a key parameter for such calculations. The analysis of the spectral features, search for the split sub-states etc. Would only be meaningful in the energy scale. Therefore, it is imperative to convert the spectra recorded in the wavelength scale to the energy scale prior to performing any decomposition of the spectral bands. We should also mention that for proper analysis of the experimental data, the intensity recorded in wavelength scale (the abscissa) must be scaled by the (λ^2/hc) factor when converting to the energy scale [2,3].

5. Full width at half maximum (FWHM)

A qualitative parameter that is widely used for a description of the spectral bands is the full width at half maximum (FWHM). In many cases, it is extremely important to have phosphor emission characterized by a small FWHM value, which would ensure high color quality. Again, experimentalists often give the FWHM values in nm, not paying attention to the fact that the same value of FWHM in nm corresponds to quite different FWHM values in the energy scale. For example, the FWHM of 50 nm for blue emission (450 nm) is equal to 2477 cm⁻¹, for red emission (620 nm) it is 1303 cm⁻¹, and for UV emission at 300 nm it is already 5594 cm⁻¹. These examples show that values of the FWHM in nm only is not sufficient to give a clear picture of a true width of the spectral lines. At least, in addition to this FWHM the position of the emission maximum should be clearly given.

6. Urbach rule, insulators band gaps and host absorption

The temperature- and energy-dependent absorption coefficient of an insulator in the absorption tail region is determined by the Urbach rule [4]:

$$A(E, T) = A_0 \exp\left\{-\frac{\sigma_s(T)(E_0 - E)}{kT}\right\},$$
(1)

where E_0 is the Urbach energy, E is the absorbed photon energy, σ_S is the non-dimensional steepness parameter, k and T are the Boltzmann's constant and temperature, respectively. The Urbach energy and steepness parameters are host-dependent. In addition, the value of σ_S depends on temperature as [5,6].

$$\sigma_{S}(T) = \sigma_{0} \frac{2kT}{\hbar\omega} \tanh\left(\frac{\hbar\omega}{2kT}\right),\tag{2}$$

where $\hbar\omega$ is the effective phonon energy that are involved into the formation of the absorption edge and σ_0 is the host-dependent parameter.

A word of caution about the Urbach energy. It is not exactly equal to the host band gap, although it is certainly related to it. Its value depends on temperature, on polarization (for non-cubic crystals) [7–9], on the presence of various defects such as antisite defects (exchange of crystal lattice positions between two different cations) [10], presence of impurity ions [11,12], traps and recombination centers [13]. Any of these defects and formation of excitons can cause non-zero and rather noticeable absorption at much lower energies than the true band-to-band transitions, leading to considerable underestimations of the band gap. In the case of wide band gap materials, the difference between experimentally reported band gaps for the same compound in various references may be more than 1 eV. In the case of narrow band gap semiconductors, the defects-related absorption can significantly mask the host absorption and result in very low (even close to zero) reported band gap values.

To avoid such a mistake, measurements of the absorption and excitation spectra in a wide spectral domain (including the UV range and even vacuum UV for the wide band gap materials) appears to be mandatory. In view of these arguments, the term "host absorption" seems to be more applicable than the "band-to-band" absorption. More details on the Urbach rule can be found in Refs. [14,15].

7. Conclusions

We have described in this short note several common mistakes which we have encountered many times in the scientific literature, when reading the papers or fulfilling our reviewer or editorial duties. We hope that this communication will help researchers to avoid making these mistakes. We also hope that this summary will advance our fundamental understanding of the luminescence phenomena and facilitate design of new optical materials.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- P.R. Jubu, F.K. Yam, V.M. Igbab, K.P. Beha, J. Solid State Chem. 290 (2020), 121576.
- [2] G. Blasse, B.C. Grabmier, Luminescent Materials,", Springer Verlag, 1994, p. 225.
- [3] J. Mooney, P. Kambhampati, J. Phys. Chem. Lett. 4 (2013) 3316.
- [4] F. Urbach, Phys. Rev. 92 (1953) 1324–1326.
- [5] T. Tomiki, F. Fukudome, M. Kaminao, M. Fujisawa, Y. Tanahara, T. Futemma, J. Lumin. 40–41 (1988) 379–380.
- [6] I. Studenyak, M. Kranjčec, M. Kurik, Int. J. Opt. Appl. 4 (2014) 76-83.
- [7] T. Tomiki, M. Kaminao, Y. Tanahara, T. Futemma, M. Fujisawa, F. Fukudome, J. Phys. Soc. Jpn. 60 (1991) 1799–1813.

- [8] T. Tomiki, Y. Ganaha, T. Shikenbaru, T. Futemma, M. Yuri, Y. Aiura, H. Fukutani, H. Kato, T. Miyahara, A. Yonesu, J. Tamashiro, J. Phys. Soc. Jpn. 63 (1994) 1976–1985.
- [9] T. Tomiki, Y. Ganaha, T. Futemma, T. Shikenbaru, H. Kato, Y. Aiura, M. Yuri, H. Fukutani, J. Tamashiro, T. Miyahara, A. Yonesu, J. Phys. Soc. Jpn. 63 (1994) 2269–2289.
- [10] T. Morimoto, M. Harima, Y. Horii, Y. Ohki, Nucl. Instrum. Methods Phys. Res. B 366 (2016) 198–205.
- [11] H. Gao, Y.H. Wang, Mater. Res. Bull. 42 (2007) 921-927.
- [12] Yu Zorenko, T. Zorenko, T. Voznyak, S. Nizhankovskiy, E. Krivonosov, A. Danko, V. Puzikov, Opt. Mater. 35 (2013) 2053–2055.
- [13] A.J. Wojtowicz, P. Bruyndonckx, W. Drozdowski, Z. Gałazka, J. Głodo, T. Łukasiewicz, P. Szupryczyński, S. Taverner, M. Wiśniewska, D. Wiśniewski, Nucl. Instrum. Methods Phys. Res. A 486 (2002) 482–485.
- [14] M. Kranjčec, I.P. Studenyak, M.V. Kurik, J. Non-Cryst. Solids 355 (2009) 54-57.
- [15] M.V. Kurik, Phys. Stat. Solidi A 8 (1971) 9-45.

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