# SPECIFICATION OF EMISSION COLOUR OF Li-DOPED ZnO COLLOIDS

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**Abstract**

Zinc oxide is a versatile material with many applications. Doped nanosized zinc oxide is capable of exhibiting fluorescence. The emission colour of such doped nanoparticles is dependent on the selected dopant, ratio of dopant to zinc oxide, and size of the nanocrystal or aggregate. In this work, we present zinc oxide colloids with different emission colours and a method of evaluation of the obtained colours. First step is the preparation of the precursor which is done according to Spanhel's and Anderson's sol-gel method [L. Spanhel, M.A. Anderson, J Am Chem Soc, 113, 2826, 1991]. Second step is the condensation process of the precursor with various concentrations of lithium hydroxide to form the ZnO colloid. The optical properties were studied using UV-VIS spectrophotometry and fluorescence measurements. The relative spectral intensities of emission were recalculated into CIExyY and CIELAB colorimetric models to determine the colour of fluorescence in a correct way.

**Keywords:** zinc oxide, lithium hydroxide, fluorescence, colour, nanoparticles

## 1. INTRODUCTION

Zinc oxide nanoparticles can be obtained by several approaches [1-5] which can lead to uniform morphology and size of nanoparticles [6]. Most solution-based methods use zinc salts dissolved in water or alcohols in which these salts undergo a hydrolysis process [7]. A lot of researches is aimed at ZnO quantum dots for their three-dimensional confinement of carrier and photon. This allows continuous tuning of optoelectric properties and improvement of device performance as well.

ZnO colloids or films can exhibit different emission colours depending on the doping and particle size. The results of fluorescence measurements therefore might show a broad band with one peak [7], several discrete peaks of different magnitudes [8, 9], or even peaks with shoulders which broaden the emission band [10]. Typically, the colour of fluorescence is specified only by maximal peak of emission or subjectively by the naked eye of the observer in an undefined environment.

Colorimetry explains the difference of colour as difference in colour attributes in corresponding colour space [11-13]. Thus, the colorimetric description serves as an objective tool for colour comparison. Classically, CIExyY and CIELAB colorimetric models are used for reflective materials or displaying devices. In case of objective specification of samples' colour, spectral representation of the colour stimuli in the visible region is converted to these models that mathematically describe the resultant colour of the sample.

In this study, we present application of colorimetric methods for objective colour evaluation of ZnO colloids doped with lithium (allowing to tune the emission colour [14]). These methods are applicable to each type of colloids or films and therefore could contribute to more exact evaluation of colour throughout the chemistry of fluorescent compounds.

## 2. EXPERIMENTAL

**Materials and conditions.** Zinc acetate dihydrate ($(CH_3COO)_2Zn.2H_2O$, 99.0 %, hereinafter ZnAc) and lithium hydroxide monohydrate ($LiOH.H_2O$, 98.0 %, hereinafter LiOH) were purchased from Sigma-

Aldrich. Anhydrous ethanol (99.8 %, max. 0.003 % $H_2O$, hereinafter EtOH) was purchased from VWR. Compounds were used as received without further purification. Temperature in the laboratory was maintained between 20–25 °C and the relative humidity under 40 %.

**Precursor.** Precursor solution $Zn_4O.6H_2O$ (hereinafter precursor) was prepared similarly to Spanhel's and Anderson's sol-gel method [6]. ZnAc powder was put into a round-bottomed flask with EtOH. The powder of ZnAc is not dissolving autonomously in EtOH, thus the flask is first put for 10 minutes into ultrasound bath. At low concentrations of ZnAc, the solution will turn clear. Afterwards the evaporation process is initiated and kept at constant ratio of evaporation for 3 hours. The resultant precursor is then refilled with fresh EtOH to 25 mM to maintain the ZnO colloids without any turbidity.

**Condensation.** Solution of LiOH was prepared before the condensation process in different concentrations shown in Table 1 and the range of pH was between 9.5 and 12.5. Clear LiOH solutions were obtained by processing them in ultrasound bath. All samples of LiOH solutions were afterwards put onto a magnetic stirrer and stirred vigorously for a day.

**Table 1** Concentration of LiOH solution for condensation

| Sample | A | B | C | D | E | F | G | H | I |
|---|---|---|---|---|---|---|---|---|---|
| $c_{LiOH}$ (mM) | 100.0 | 80.0 | 62.5 | 50.0 | 45.5 | 42.6 | 39.8 | 28.4 | 25.0 |

**Measurements and conditions used.** Conductometry and pH measurements were performed via 3540 pH & Conductivity Meter from Jenway. UV-vis spectrometry was performed on Specord 210 (Analytic Jena). Emission spectra (excitation at 340 nm) were measured with 1 nm resolution and constant photomultiplier voltage using Luminescence Spectrometer (Aminco Bowman Series 2).

**Evaluation.** The resultant colloids were evaluated with UV-vis spectrophotometry and using fluorescence measurements. For colour determination the obtained results from fluorescence measurements were recalculated to CIExyY and CIELAB colorimetric models.

The trichromatic values of a selfluminous object, essential for any colour evaluation, are obtainable from spectral radiance factor according to the Equation 1 [11, 12]:

$$X = k\sum_{\lambda}\phi_{\lambda}(\lambda)\bar{x}(\lambda)\Delta\lambda; \quad Y = k\sum_{\lambda}\phi_{\lambda}(\lambda)\bar{y}(\lambda)\Delta\lambda; \quad Z = k\sum_{\lambda}\phi_{\lambda}(\lambda)\bar{z}(\lambda)\Delta\lambda \tag{1}$$

Where $\phi_\lambda$ is spectral radiance factor, $\bar{x}$, $\bar{y}$, and $\bar{z}$ are the trichromatic functions of standard observer and $k$ is a constant. Trichromatic values then serve as an input in calculation of chromaticity coordinates in CIExyY and CIELAB space [11, 12].

The intensity of light emission is dependent on the concentration of colloids and the voltage on the photomultiplier. Photometric evaluation would require calibration of the signal intensity by a standardized light source [11]. Since the intensity of recorded light is relatively low, computed colours would be evaluated as very dark. Due to these reasons we applied a slightly different approach. Parameter $k$ in Equation 1 allows to normalize trichromatic values. For calculation of trichromatic values of all prepared colloids a $k_F$ constant was applied, by which the emission maximum of sample A after 144 hours was normalized to value equal to 1. The computation of $L^*$ (lightness), $a^*$, $b^*$, $C^*_{ab}$ (chroma), and $h^*_{ab}$ (hue) parameters in CIELAB space requires that the trichromatic values of colour stimuli are divided by a corresponding trichromatic value of a white point (due to the extent of calculation see [11, 12]). In our case, calculation of the white point used D65 standard illuminant with a constant $k_{D65}$, by which the maximum of D65 relative spectral power distribution was normalized to value equal to 1. Spectral data of D65 standard source and 2° observer's colour matching functions in 1 nm resolution were used [12].

The evaluation of colour change is mainly focused on dominant wavelengths, which were calculated from the *x* and *y* chromaticity coordinates [11, 12] in CIExyY space, and on hue in CIELAB space.

## 3. RESULTS AND DISCUSSION

Condensation process and development of photoluminescence in the colloids is a matter of a few hours or days. All colloids start fluorescing in the blue region. Growth of the particles and their extent of doping leads to shifts of the emission colour towards the red region resulting in colours as cyan, green, and yellow. Growth of nanoparticles in colloids can be observed in UV-vis spectra shown in **Fig. 1**. The band gap is shifting during the growth to lower energies.

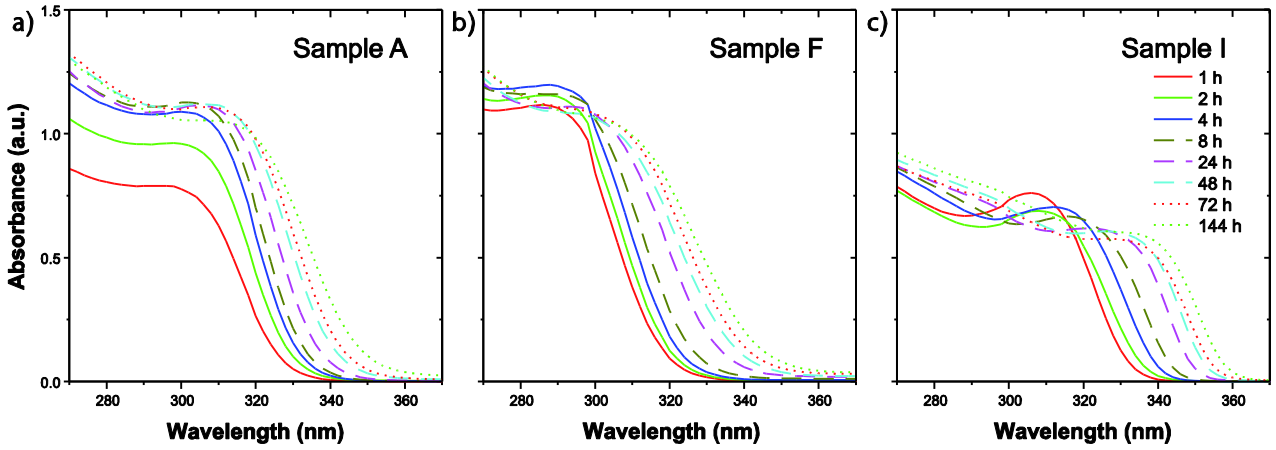


**Fig. 1** Absorbance spectra of samples a) A, b) F, and c) I over time

Subjective specification of colloids' colour is highly sensitive to the environment in which one is attempting to perform it. The second factor is the subjective perception of the observer which again can lead to different results of colour description. Taking images with a camera is an issue as well; this is because the settings of the white balance and the exposition time can alter the resultant colour and intensity of the colloids' colour. Therefore, objective characterisation of the particular colloid's colour using a standardized colorimetric model seems to be advantageous.

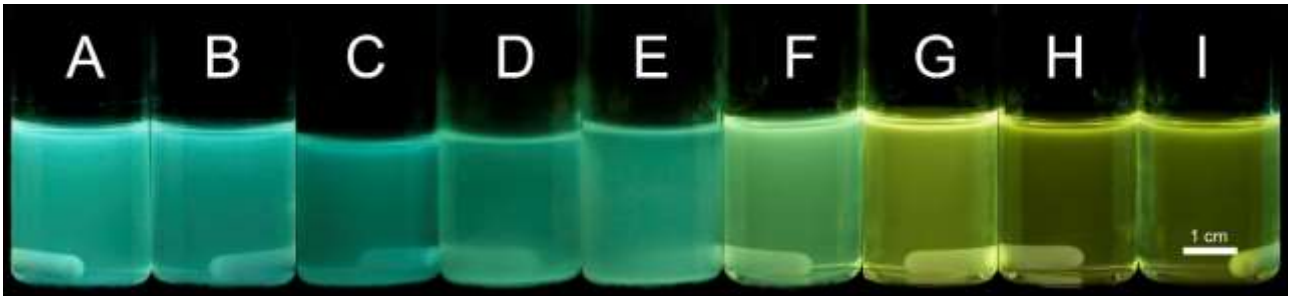


**Fig. 2** Colloids under UV light illumination at 365 nm after 144 hours of stirring

In **Fig. 2**, the fluorescence of the colloids under UV-light exposure is shown. Each image is taken through a cut-off filter to cut the reflexion of UV light under 400 nm from the glassware. This is also an important task due to alteration of the resultant colour of colloids. Also, turbidity of the colloids affects the emission intensity and colour of the colloids. In **Fig. 2**, samples A to E are turbid to various extents; observed by naked eye, samples D and E showed highest turbidity among the samples.

Change in colour of fluorescence during the growth of particles is shown in **Fig. 3**. Here, one can see different kinetics of the growth according to the concentration of LiOH into which the precursor was

poured. Fluorescence can be observed first in colloids with the lowest concentration of LiOH (close to precursor : LiOH 1 : 1 ratio). The growth of the nanoparticles is an ongoing process due to Ostwald ripening [15] causing changes in emission colour of colloids.

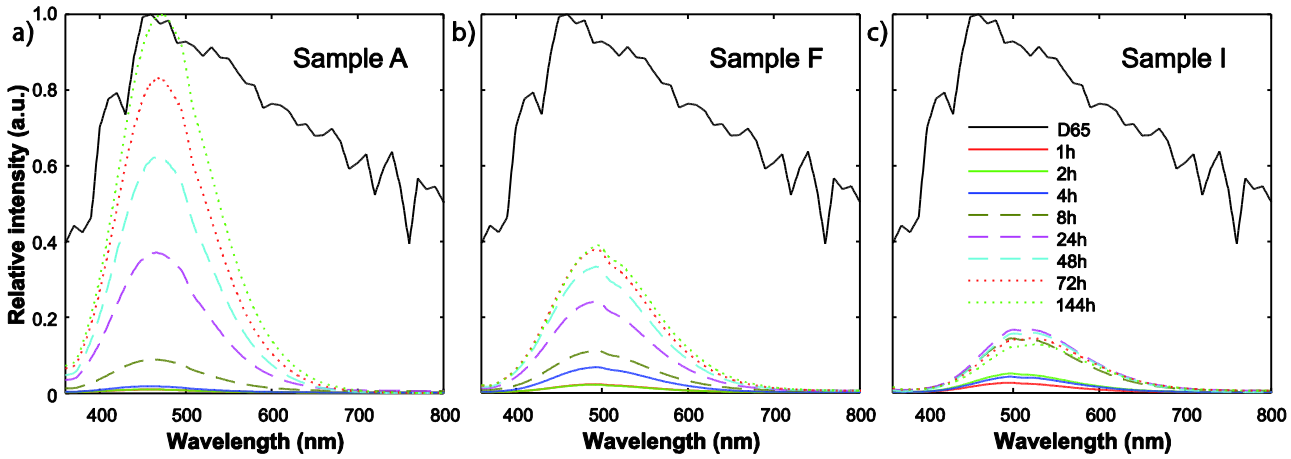


**Fig. 3** Normalized fluorescence spectra of samples a) A, b) F, and c) I over time

Using only the peaks of emission spectra of colloids is not sufficient for colour evaluation. For example, in sample A one can see mainly a discrete peak, in other samples a more pronounced shoulder is forming at approx. 550 nm and in sample I already reaches the intensity level of the peak at approx. 500 nm. For clearer colour description where the whole spectrum is considered into the colour evaluation, CIExyY model can be used. From this model, one can find the dominant wavelengths of emission. These dominant wavelengths are compared with the peak maxima determined from fluorescence spectra in **Fig. 4**. Due to the process of particle development the individual peak maxima do not show clear shifts in colour (as illustrated in Fig. 4a). After recalculating the spectral intensities through the CIExyY model the colour change is smoother and also shows a shift to higher values of wavelengths (Fig. 4b).

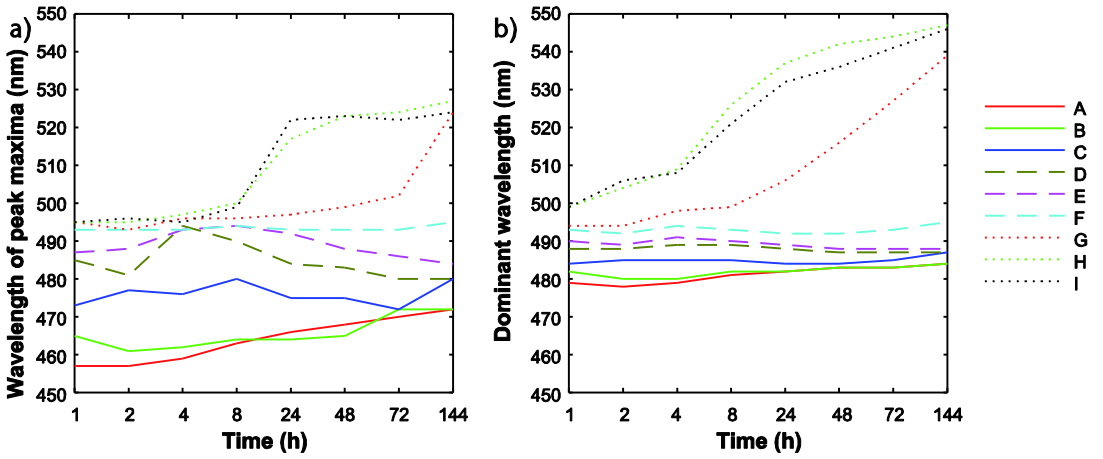


**Fig. 4** Shifts of a) wavelength of peak maxima and b) dominant wavelength in all colloids over time

**Fig. 5**a shows the resultant colloids' colours after 144 hours of synthesis. From **Fig. 5**b it is obvious that that the colour change over time in samples A, F, and I does not occur to the same extent. In sample A, the dominant wavelengths are situated within a small interval of change which means that the colour is more or less the same throughout the synthesis. Sample F already shows a slight shift of colour toward yellow. On the other hand, in the case of sample I the colour change from cyan to yellow clearly occurs.

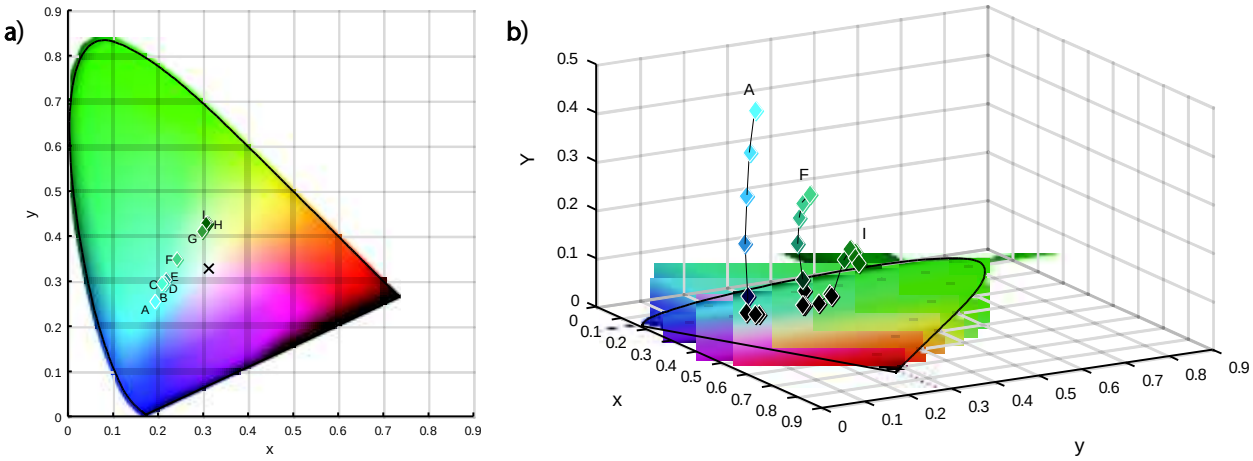


**Fig. 5** CIExyY colorimetric model showing a) trichromatic positions of all samples after 144 hours of stirring and b) colour change in time of samples A, F and I where the start of the synthesis process is at the lowest values of *Y*; for a clearer view, the volume of CIExyY space for $Y > 0$ was not rendered

The CIELAB results depict the changes in three attributes as shown in **Fig. 6**, where $L^*$ is the lightness, $a^*$ represents the greenness-redness and $b^*$ the blueness-yellowness of the colour stimuli. In this study, parameter $b^*$ is of highest importance and **Fig. 6**b shows that the colour of colloids is significantly changing from blue region to yellow whereas parameter $a^*$ changes only slightly and $L^*$ shows a decreasing trend with increasing concentration of LiOH. Lightness of samples D and E is lower than expected (according to the tendency) due to their high turbidity.

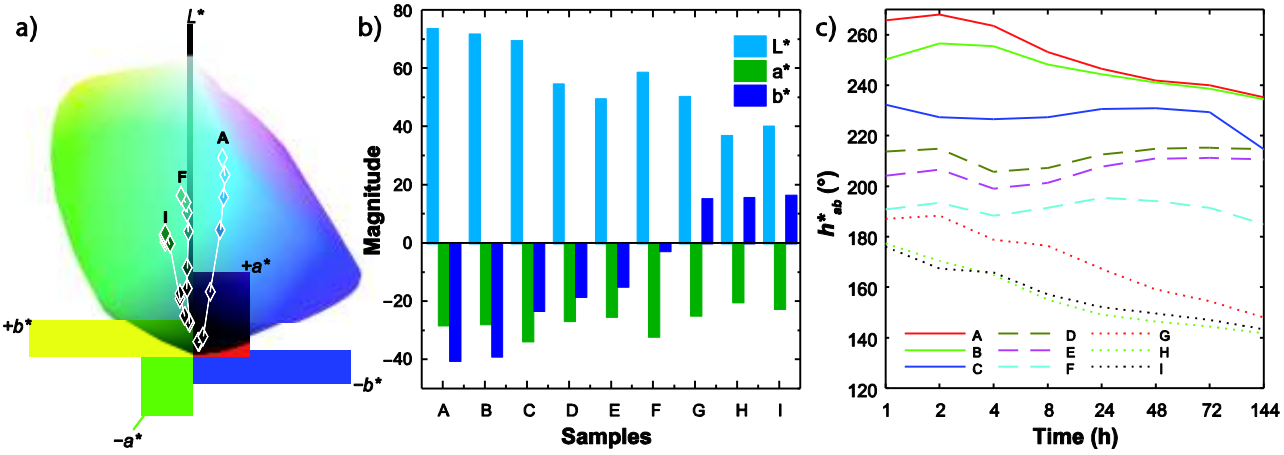


**Fig. 6** CIELAB values of a) samples A, F, and I with their change in time in CIELAB colour space, b) of all samples after 144 hours of stirring, and c) hue $h^*_{ab}$ parameter of all samples over time.

The colour change over time can be visualised also through hue parameter $h^*_{ab}$ (Fig. 6c). In contrast to the evaluation in CIExyY colour space (see also Fig. 4c), the extent of hue change after 144 hours in sample A is comparable to that of sample I. Although the CIELAB colour space is more perceptually uniform, the magnitude of change in hue (namely for samples A and B) could be influenced by certain nonuniformities in blue part of CIELAB colour space [11].

## 4. CONCLUSION

We have successfully synthesised ZnO colloids and measured their fluorescence in the visible region of the spectra. The evaluation shows that the colour of fluorescence can be described with several colorimetric methods which give a better understanding of the colour change than a simple reading of

spectra. These models give the opportunity to compare the results of fluorescence of ZnO and other fluorescent compounds in clearer and more accurate manner.

## ACKNOWLEDGEMENT

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