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Tunable white emission of silver-sulfur-zeolites as single-phase LED phosphors

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Abstract

Metal clusters confined inside zeolite materials display remarkable luminescent properties, making them very suitable as potential alternative phosphors in white LED applications. However, up to date, only single-color emitters have been reported for luminescent metal-exchanged zeolites. In this study, we synthesized and characterized white emitting silver-sulfur zeolites, which show a remarkable color tunability upon the incorporation of silver species in highly luminescent sulfur-zeolites. Via a combined steady-state and time-resolved photoluminescence spectroscopy characterization, we suggest that the observed luminescence and tunability arise from the presence of two different species. The first associated to an orange-red emitting silver cluster (Ag-CL), whereas the second is related to a blue-white emitting S-Ag-species. The relative contribution of both luminescent species depends on the synthesis procedure. It was shown that the formation of the blue-white emitting S-Ag-species is favored upon a heat-treatment of the samples.

1. Introduction

Light-emitting diodes (LEDs) display high efficiencies combined with low operational costs and long lifetimes, while they also do not contain harmful mercury [1]. Therefore, white light-emitting LEDs (WLEDs) are nowadays considered as the next generation of conventional lighting devices, of which remote phosphor converted WLEDs (pc-LEDs) are the most common type. The first generation of commercial WLEDs was based on a blue InGaN LED combined with a yellow Ce³⁺ doped yttrium-aluminum garnet (YAG:Ce³⁺) phosphor. However, these WLEDs suffered from high correlated color temperatures (CCT) and low color rendering index (CRI), which results in cool white light [2]. CCT and CRI values for pc-WLEDs were subsequently improved by adding a second red phosphor to the YAG:Ce³⁺-blue LED [3] or by combining the blue LED with a green and orange phosphor [4]. The most reported method to warm the color temperature (lower CCT) is the use of near-ultraviolet LEDs (NUV-LEDs) instead of blue LEDs. Warm white pc-WLEDs based on NUV-LEDs are more convenient compared to their blue-LED based counterparts, [5, 6] since in the former case, the CCT and CRI of the WLED are independent of the phosphor layer thickness [5].

W Baekelant *et al*

Nevertheless, the proposed warm WLEDs based on a combination of different single-color emitting phosphors (blue, green and red for the NUV-LEDs), display difficulties related to the phosphor blending during the manufacturing, reabsorption by the red and green phosphors and a variability in the photobleaching of each single-color phosphors causes color temperature instabilities over time. A way to overcome these difficulties is the use of a single-phase white emitting phosphor. These types of phosphors have often been proposed in literature [7–14], displaying a broad emission peak spanning the whole visible range. However, the reported phosphors often lack high efficiency and photostability, containing either toxic metals or critical raw materials [15], such as lanthanides elements, in their structure. Furthermore, many non-lanthanide-based single-phase phosphors suffer severely from the aforementioned reabsorption problems due to small Stokes shifts.

For the case of luminescent metal exchanged zeolites, especially Ag-exchanged zeolites, large Stokes shifts combined with high extinction coefficients and high quantum efficiencies have been reported [16-20], making them suitable candidates to overcome the difficulties encountered in remote-phosphors LEDs [6, 21]. Nevertheless, these silver clusters (Ag-CLs) confined in zeolites tend to display only broad singlecolor emission and up till now, no high efficient red emission has been reported for these materials. Nevertheless, red emission has been observed at room temperature for silver-sulfide species confined in zeolites [22–26]. Yet, the typical synthetic procedure of these species requires a reaction involving highly toxic and flammable H₂S gas to incorporate sulfur into the zeolite structure. Ruivo et al [27] showed an alternative approach to incorporate luminescent S-species into zeolite frameworks, following a solid-state reaction protocol where Na₂SO₄, NaCl and LTA zeolites were ball-milled and treated at high temperatures under a reductive atmosphere. These samples displayed phase transformations combined with the incorporation of yellow/orange luminescent S-species.

In this study, we show that the incorporation of Ag^+ into yellow/orange luminescent S-zeolites results in the formation of hybrid white-emitting sulfur-silver zeolites, with a tunable emission from cool bluish white to warm reddish white, depending on the synthesis and heat treatment conditions. The tunability of their emission properties was associated to two different emitting species, as evaluated by steady-state and time resolved photoluminescence spectroscopy.

The first species is related to a red-emitting Ag-CL, which was also observed in silver-exchanged S-free sodalite (SOD) zeolites. The second species is tentatively ascribed to a S-Ag species which displays whiteblue emission. The formation of the latter species is favored by a heat-treatment during the synthesis procedure.

2. Experimental section

2.1. Sample preparation

Luminescent S-zeolite composites were prepared following the procedure previously described by Ruivo et al [27]. Commercially obtained Na-LTA zeolites (UOP) were heat-treated for 1 h in the presence of Na₂SO₄ and NaCl at 900 °C under a reductive atmosphere (5% H_2 in Ar), using nominal molar ratios of S/ Cl between 0.21 and 0.33. The S-zeolites were washed to remove the excess of Cl- and subsequently exchanged with Ag⁺ using AgNO₃ solutions following two different synthetic routes. For the first route, 200 mg of the as-synthesized S-zeolites were grinded thoroughly using a mortar and pistil. Subsequently, the grinded powder was exchanged with 20 mg of AgNO₃, dissolved in 200 ml of milliQ (MQ) water and stirred overnight in an end-over-end shaker oven. After filtration, the powder was dried at 50 °C for 1 h. This sample is called sample A. Sample B was prepared similarly as sample A but instead of drying the powder, it was heat-treated at 250 °C overnight. Sample C was prepared similarly to sample A but avoiding the grinding step.

The synthesis of the S-free sodalite zeolite sample was adapted from the protocol of Breck [28]. 2.013 g of NaAlO₂ (Technical grade, Sigma Aldrich) and 10.352 g of NaOH (\geq 97 %, Sigma Aldrich) were dissolved in 37.391 g of milliQ (MQ) water and the solution was cooled down to 0 °C in an ice bath. Next, this was added to a solution of 2.5036 g Na₂SiO₃ prepared from a sodium silicate solution (26.5 % SiO₂, Sigma Aldrich) in 37.442 g MQ water and 10.4149 g NaOH $(\geq 97 \%)$, Sigma Aldrich). The mixture was heated to 100 °C for 150 min, followed by a rapid cooling in an ice bath to reach 0 °C. Next, the powder was filtered and thoroughly washed with MQ water until the wash water reached pH = 7.0. Then, the sample was dried overnight in a convection oven at 100 °C. In a final step, the SOD zeolites were exchanged with certain weight percentages of AgNO3 (Sigma Aldrich, \geq 99.0 %) followed by a heat-treatment at 450 °C in a muffle oven. The heat-treatment starts at room temperature with a heating rate of 5 °C min⁻¹. To avoid framework destruction by fast water removal, two 30 min intervals at 80 °C and 110 °C were included. The samples were cooled down to room temperature under ambient conditions [19].

2.2. Characterization of steady-state optical properties

Steady-state luminescent properties, such as 2D excitation/emission plots and EQEs, were recorded on an Edinburgh FLS980 fluorimeter. To measure the absolute EQE, the fluorimeter is equipped with an integrating sphere from Labsphere, connected to the fluorimeter via optical fibers. A barium sulfate sample was used as reference during EQE measurements.



Figure 1. Emission of the S-zeolite and both AgS-zeolite samples under 350 nm illumination.

Diffuse reflectance spectra (DRS) were determined using a Perkin Elmer Lambda 950 instrument equipped with a 150 mm integrating sphere, using a barium sulfate sample as 100 % reflective sample and carbon black as the 0 % reflection reference. To remove the influence of the luminescence, a UG5 filter from Schott, which has transmission in the UV and absorbs visible light from 400 to 700 nm, was employed during the measurements of the UV-region of the spectra. The reflectance percentage of the DRS spectra were finally converted to Kubelka-Munk (K-M) [29].

2.3. Time-resolved photoluminescence characterization

The nanosecond to millisecond time-resolved luminescence data were recorded using a 355 nm pulsed laser (8 ns, 10 Hz, Quanta-Ray INDI-40, Spectra Physics) to excite the samples, which were placed in a 1 mm thick quartz cuvette. The excitation light was focused on the sample by a 150-mm focal length lens and a small part of this light was sent to a fast photodiode to generate a trigger signal. Right angle configuration between excitation and light collection paths was used and the luminescence was collected, filtered and focused on the entrance slit of a 30 cm focal length monochromator. A SpectroPro-300i monochromator/spectrograph was used to disperse the emitted light and select the desired wavelength. The optical signal was detected by a PMT (Hamamatsu, R928) and the transient electrical signal was amplified and sent to a computer-controlled oscilloscope. An in-house made, Labview-based software was used to control and trigger the instruments, read, average and store the transient data.

2.4. Remote phosphor LED prototype fabrication

Prior to the device fabrication, fused-silica substrates $(2 \times 2 \text{ cm}^2)$ were cleaned consecutively by sonication for 10 min in alkaline-detergent water (Hellmanex solution), MQ water, acetone, and isopropanol to remove all (organic) impurities. For the fabrication of the device, a thin emissive zeolite-layer (10–20 μ m) was deposited on the cleaned silica substrates. This layer was prepared by mixing 60 mg of zeolite phosphor with a solution of 0.33 ml α -terpineol (90%, Sigma Aldrich) and 34 mg ethylcellulose (48% ethoxyl,

Sigma Aldrich) in 1 ml of acetone (Spectrograde, Sigma Aldrich), and coated on top of the substrate by doctor blade technique in two parallel adhesive Scotch tapes $(1 \times 1 \text{ cm}^2)$ [30, 31]. Subsequently, the prototype LED device was finished by placing the remote phosphor layer on top of a 340 nm UV-LED (figure S1 is available online at stacks.iop.org/MAF/8/024004/mmedia) from Thorlabs (0.33 mW, full-width at half maximum = 15 nm).

3. Results and discussion

3.1. Steady-state photoluminescence properties

Initially, we checked the stability of the S-zeolites with XRD after silver exchange and heat-treatment. XRD (figure S2) showed neither phase transitions nor structural damage for both sample A and B, indicating a high stability of the materials under the used conditions.

The orange emission originating from the presence of S-species inside the cages of SOD zeolites (Szeolites) [27], changes to a bright white emission upon the incorporation of Ag⁺-ions, under 350 nm illumination (figure 1). This change is also observed in the 2D excitation/emission plots of the AgS-zeolites (figure 2), displaying a broad emission across the whole visible range for both AgS-zeolite samples (sample A and B, see sample preparation). However, some differences are observed between the samples. For sample A, the main emissive species are observed upon 340 nm excitation, giving rise to a broad emission centered at about 485 nm with a FWHM of about 8493 cm⁻¹. Next to that, other minor luminescent species are observed when excited at 310 nm and 395 nm. The 310-nm species also displays broad emission with a maximum at 505 nm and a FWHM 8898 cm^{-1} , while the species excited at 395 nm displays an orange-red emission with a maximum emission at 630 nm and a FWHM of 4039 cm^{-1} .

Sample B, on the other hand, has its main excitable species at 315 nm, which slightly blue-shifts to 300 nm for higher emission wavelengths. These species also display a broad blue-white emission with a maximum around 495 nm and FWHM of 8321 cm⁻¹. This luminescent species observed for sample B shows some





remarkable resemblance with one of the minor species (310 nm-species) observed in sample A.

Furthermore, we can also see that the original orange luminescence with the peculiar vibronic structures of the S-zeolite sample (figure S3) is no longer observed in the AgS-zeolites [27]. We suggest that the incorporation of Ag⁺ leads to an interaction with the luminescent sulfur species, possibly forming hybrid sulfur-silver (S-Ag) species. This is also observed in the DRS spectra (figure S4), where the absorption peak related to the luminescent sulfur species centered around 390 nm [22] disappears completely and two other absorbing features appear between 300 and 360 nm. Absorption peaks at these wavelengths have been previously related to the presence of Ag-CL species in zeolites [31]. Even though, it is clear that the observed white luminescence does not originate from the S-species present in the parent materials. It is possible that next to S-Ag species, sulfur-free Ag-CLs are formed for stoichiometric reasons which are responsible for the white emission. Indeed, during exchange an average of 1.5 Ag⁺ ions for each S present in the parent S-zeolites were added. This parent S-zeolite has the SOD framework structure [27]. Therefore, we checked the luminescent properties of the Ag-exchanged S-free sodalite zeolites (Ag-SOD) with different Ag-loadings, all displaying an orange-red emission (figures 3 and S5). In the 2D excitation/emission plot we observe, for Ag-SOD sample, two distinct peaks: one centered at 365 nm excitation with emission at 595 nm and the other one at 400 nm excitation with emission maximum at around 620 nm.

By comparing the 2D plot of the Ag-SOD sample with that of sample A, we observe a remarkable overlap between the orange-red emitting species with maximal emission around 620–635 nm. Even more, comparing the emission spectra at 340 nm excitation of sample A, B and Ag-SOD as depicted in figure 4, it seems that the sample A is a combination of sample B and the Ag-SOD sample. This would mean that the orange-reddish part in the luminescence might result from the presence of pure Ag-CLs. This 620-635 nm emission, on the other hand, could also be related to S-species excitable at 380 nm and emitting at around 650 nm as observed by Ruivo et al [27]. However, as already mentioned, the vibronic structure in the AgSzeolites and the absorption peak related to S-species in the DRS spectra are no longer observed in the AgSzeolites. This, together with the fact that Ag⁺-ions were added in excess, makes the presence of S-species less-likely. To further prove this hypothesis, we performed XPS (figure S6) showing that for sample A the binding energy of Ag displays a similar value as for luminescent Ag-CLs previously reported [17]. This may indicate that the silver species in the samples studied in this manuscript could possess a similar electronic configuration as for those already reported for luminescent Ag-CLs. Furthermore, the bluish part in the emission of sample A results from the same luminescent species observed in sample B. This blue luminescence, which is not observed in the S-free samples, most probably results from the formed S-Ag species. This would also mean that upon heat-treatment the S-Ag species are formed, rather than the red-emitting Ag-CLs. This could result from the enhanced ion mobility of Ag at elevated temperatures, favoring a better interaction between Ag and S.

3.2. Time-resolved photoluminescence properties

To corroborate the results observed in the steady state luminescence, we performed an analysis of the excited state dynamics of the observed species by time-



Figure 3. 2D excitation-emission plot of the Ag-exchanged SOD zeolites with 18.9 wt% of AgNO3.



resolved luminescence experiments on the AgS-zeolites. The luminescence decays were determined for sample A, sample B and Ag-SOD zeolite on a ns-ms time scale using an excitation wavelength between 340 and 360 nm and detection wavelengths ranging from 400 to 700 nm. The luminescence decay traces of the different samples (figure S7) show the presence of only long decay times in the μ s-time range. From these luminescence decay traces a decay associated spectrum (DAS) was composed for each sample, as shown in figure 5.

Sample A shows 3 different decay times in the μ stime range, namely 0.18 μ s, 2.63 μ s and 20.9 μ s component. The 0.18 μ s component gives rise to the orange-red emission with a small tail in the blue, while the two longer components only give rise to the bluewhite emission as also observed in figure 4 for the steady-state luminescence. Sample B displays three decay components, with decay times of 0.99 μ s, 7.41 μ s and 34.3 μ s, which are all three contributing to the luminescence of the blue-white emission. The Ag-SOD sample on the other hand, has only one decay time observed in the DAS, with a 0.14 μ s decay time, contributing to the luminescent properties of the sample.

By analyzing the results of the time-resolved spectroscopy, we can see that there is a strong correspondence between the shortest decay time of sample A (0.18 μ s) and the decay time of Ag-SOD sample (0.14 μ s). This also confirms that the S-free Ag-CLs are responsible for the orange-red emission. However, upon heat-treatment of the sample this decay time related to the Ag-CLs disappears and only the luminescence of blue-white emitting-species remains, as observed in sample B. These are most probably the S-Ag-species as mentioned before.





A third AgS-zeolite sample was prepared (see Experimental section sample C) with higher and lower Ag-content sections, in order to further corroborate our previous statement. The results displayed in figures 6 and S8, indeed show a large similarity with sample A. However, due to the lower Ag-content, the orange-red emitting species are less pronounced, resulting in a better overlap in its emission with the sample B for the deeper UV excitation wavelengths (below 365 nm). Next, when 365 nm excitation or higher was used (figure S8), the orange-red emission becomes more favored, since in some particles the silver concentration is higher and thus the formation of pure Ag-CLs is favored. The analysis of the timeresolved data of this sample shows a large similarity with sample A, having three similar decay times of 0.14 μ s, 2.84 μ s and 26.3 μ s. The shortest decay time, which is similar to the observed decay time of Ag-SOD, corresponds again to the orange-red emission. While the

two longer decay times can be linked to the blue-white emission. We also provide a tentative diagram (figure S9) for the different luminescent pathways. However, further investigation needs to be conducted to get a more complete and robust diagram.

3.3. Remote phosphor LED prototype fabrication

The luminescent properties observed under NUVlight pointed out the potential applicability of the AgSzeolite composite materials as single-phase whiteemitting phosphors in LED applications. Additionally, they also show some remarkable degree of tunability. The prepared prototype LEDs, as depicted in figure 7, show that a thin layer (10–20 μ m) of different AgSzeolite samples is sufficient to absorb the 340 nm primary NUV-light and to produce a white emitting remote phosphor LED. Although, in the pictures it seems that at this excitation wavelength, all samples show similar white light emission, however, there are



Figure 7. Prototype single phase white light emitting pc-LEDs based on the different AgS-zeolite samples and a 340 nm NUV-LED (left) and their 1931 CIE coordinates at 340 nm excitation (right) for sample A (1), sample B (2) and sample C (3).

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	@340 nm excitation		@365 nm excitation	
	EQE (%)	CIE ^{a (X, Y)}	EQE (%)	CIE ^{a (X, Y)}
Sample A	24 ± 2	(0.299, 0.337)	19 ± 2	(0.330, 0.340)
Sample B	30 ± 2	(0.266, 0.312)	19 ± 2	(0.256, 0.287)
Sample C	20 ± 2	(0.285, 0.313)	19 ± 2	(0.352, 0.333)

^a 1931 CIE coordinates as determined by Edinburgh F980 software.

clear differences in the EQE and 1931 CIE, as depicted in table 1 and shown in figure 7.

Even though the 340 nm light used in these prototypes is preferred for the efficiency of the Ag-S-zeolite phosphors as displayed in Figure S10, the use of this type of LEDs is commercially less favorable compared to NUV-LEDs between 365 and 400 nm [6]. Looking at the evolution in the EQE and 1931 CIE color space, the use of a 365 nm NUV-LED would be preferred in commercial white LEDs. At this excitation wavelength all three samples have an EQE of about 19 \pm 2 % (table 1). For sample A and C, the 1931 CIE coordinates of (0.330, 0.340) and (0.352, 0.333), respectively, approach very well the optimal value (0.333, 0.333) of pure white emission when compared to 340 nm excitation. Only for sample B the CIE coordinates show that the emission, when excited at 365 nm, is really shifted to more bluish white compared to the excitation at 340 nm. For sample C the EQE increases when going to higher excitation wavelengths (figure S10) reaching a maximum value of 24 \pm 2 % at an excitation of 400 nm. However, at these excitation wavelengths the sample displays a single-color orange-red emission.

These results demonstrate the proof of concept of these materials for their applicability as single-phase white-emitting phosphors in LEDs for general illumination purposes. However, further optimization of these samples is still needed. The EQE requires to be optimized as well as the tuning of the excitation wavelengths. Therefore, a full understanding of the structure-to-luminescent properties of these zeolites is essential in order to develop rational design protocols to synthesize improved materials. This can be done throughout a fine-structural characterization using a combination of conventional transmission and X-ray excited optical luminescence EXAFS techniques. These techniques have already proven their usefulness in linking the luminescent properties of Ag-CLs inside zeolite materials with the structure of the emissive species [17, 18, 20, 31].

4. Conclusion

The incorporation of Ag^+ ions into the framework of orange luminescent S-zeolites leads to the generation of single-phase white emitting phopshors which display a broad white emission upon excitation with NUV-light between 300 and 400 nm. A detailed steady-state and time-resolved photophysical characterization of the samples showed that the luminescent properties most probably originate from the presence of two different emitters: a pure S-free Ag-CLs, which displays an orange-red emission with a maximum around 595 nm emission and a S-Ag species which displays a white-blue emission with a maximum around 495 nm. Depending on the synthesis procedure, the warmth of the white color can be tuned. For instance, a heat treatment at 250 °C enhances the formation of the blue-white emissive species, leading to a cooler white emission. By using a thin layer of these AgS-zeolite phosphor we were able to produce a white emitting pc-LED, with EQEs for the phosphor going up to 30 %. Even though this study shows the large potential for these types of materials, further optimization through rational design protocols is necessary for their commercial use. Therefore, a complete structure-to-luminescence characterization of these Ag-S-zeolites will be the subject of a follow-up research.

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The authors have declared that no conflicting interests exist.

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