Materials Science-Poland, Vol. 22, No. 1, 2004

Luminescence properties of nanophosphors: metal ion-doped sol-gel silica glasses*

M. MORITA[1**], D. RAU[1], S. KAJIYAMA[1], T. SAKURAI[1], M. BABA[2], M. IWAMURA[1]

[1]Department of Applied Chemistry, Seikei University, Kichijoji, Musashino-shi,Tokyo 180-8633, Japan

[2]ISSP, The University of Tokyo, Kashiwa 277-8581, Chiba, Japan

Photoluminescence of xerogel and sol-gel SiO_2 glasses doped with metal ions, metal complexes and semiconductor nanocrystals are investigated at 300 K and 10 K to clarify the optical properties and the electronic structures of nanophosphors. Sol-gel glasses doped with 3d, 4d and 5d transition metal ions exhibit a bright luminescence with various colours due to the ^{3}LMCT transition associated with closed -shell molecular complex centres. Luminescence from rare earth(III) complexes doped in the same matrix serve as a sensitive probe to determine axial and chiral complex structures. Luminescence properties are investigated of doped semiconductors ZnS: Cu, Al dispersed as nanocrystalline green phosphors in xerogel with various lifetime components. The sol-gel silica-based phosphors are characterized by unusual valence states of the transition metal ions, stable centres in organic-inorganic hybrid hosts and the 500 ps lifetimes of D-A pairs due to spd hybridization effects in semiconductor nanocrystals.

Key words: *luminescence; sol-gel glass; nanocrystal; LMCT; phosphor*

1. Introduction

The sol-gel technique has developed very quickly in recent years, becoming an essential chemical method to prepare very small particles of nanometre sizes. Bhargava et al. [1] reported novel luminescence properties of nanocrystalline ZnS: Mn^{2+} and demonstrated an ultra-short emission lifetime of the orange band obtained with a high quantum efficiency. Several papers have appeared since then on luminescence of nanocrystalline materials related to quantum confinement effects in semiconductors [1, 2]. Reisfeld and her group have reported optical properties of luminescent species, such as semiconductor quantum size particles and rare earth ions in sol-gel glasses

---

[*] Paper presented at the International Conference on Sol-Gel Materials, SGM 2003, Szklarska Poręba, Poland.

[**] Corresponding author, e-mail: morita@ch.seikei.ac.jp.

and zirconia films which are characterized by quantum confinement effects [3–6]. Moreover, organic dye-based lasers were developed by the sol-gel technology [7]. We have investigated luminescence properties of sol-gel xerogel and silica glasses doped with transition metal and rare earth ions in order to develop nanocrystalline phosphors in which the surface enhancement effect induces unusual band shifts to blue and shortening of lifetimes due to surface defects or spd mixing effects [8]. In this paper, we present sol-gel derived nanoparticles such as metal ions and nanocrystals dispersed in xerogel and sol-gel SiO_2 glasses for phosphors with interesting luminescence properties. The particles with a diameter of 5–10 nm emit in the blue-green-red spectral regions. In the following, we characterise the optical properties, lifetimes, Stokes shifts, and temperature dependences of various materials.

2. Experimental procedures

We have prepared phosphors according to the following sol-gel procedures. TEOS (tetraethooxysilane $Si(OC_2H_5)_{4)},$ DEDMS (diethoxydimethylsilane), metal nitrate (1–0.5 mol %) were dissolved in a solution of water and ethyl alcohol and the solution was stored at room temperature. Xerogel was obtained after 2–3 months as wet solid blocks which, after annealing at 600 °C for one day, turned into transparent and isotropic sol-gel glasses containing dopants. By optimizing the preparation conditions, we can obtain glassy materials of desired optical qualities. Luminescence and luminescence excitation spectra, time-resolved spectra and lifetimes were measured in the temperature range between 10 and 300 K using a computer controlled luminescence spectrophotometric system combined with a Spex 1401 double monochromator and N_2 laser (337.1 nm) as an excitation source, developed in our laboratory [8]. The luminescence in the near infrared spectral region was measured using a computer-controlled SPEX 1702 single monochromator with a cryogenic system [9]. For rapid availability of luminescence and time resolved luminescence data, we also utilized an ICCD detection system. In addition, ultra-short luminescence lifetimes between 50 ns and 10 ps were detected by a single photon counting system and a streak camera using a pico-second YAG: Nd^{3+} laser excited dye laser second harmonic (300 nm, 250 fs) as an excitation source.

3. Experimental results and discussions

Various sol-gel derived doped luminescent materials have been developed in our laboratory. The dopants were classified into three groups: (1) transition metal and rare earth ions, (2) metal complexes, and (3) semiconductors. In order to emphasize their versatile applications, we describe their luminescence properties and the electronic structures by fluorescence colours in red, green, blue, white and NIR (Near-Infrared).

These materials are considered to be usable as nanoparticles in fabrication of displays, lamps and storage phosphors while their optical properties, the quantum efficiencies and the saturation currents are not as yet examined under cathode-ray irradiation or under electric fields applied.

3.1. Phosphors due to metal ion dopants

Phosphors with red colours can be obtained from Cr^{6+} ion centres. Luminescence due to surface-activated SiO_2: V, Cr centres was reported by Anpo et al. [10]. As a typical example, luminescence of chromium ions doped in sol-gel silica glass No. 1 (SiO_2: Cr^{6+}) at 10 K is shown in Fig. 1.

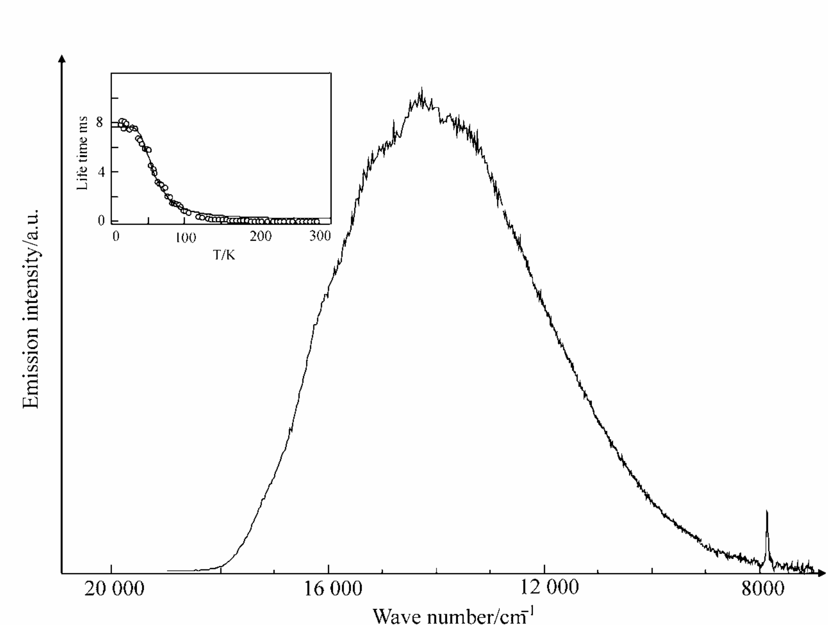

Fig. 1. Luminescence spectrum of the sol-gel glass SiO_2: Cr (sample No. 1) at 10 K, annealed at 800 K for 24 hrs, under N_2 laser excitation. The inset shows the temperature dependence of the average lifetime

The broad red band centred at 15 400 cm^{-1} is due to highly oxidized chromium(VI) ions in tetrahedrally coordinated $[CrO_4]^{2-}$ complex centres. The bright emission has a lifetime of 8 ms and 0.02 ms at 10 K and 300 K, respectively. This emission was once ascribed to chromium(V) ions with a single d-electronic configuration in view of the band shape and its position [11]. Later, the temperature dependence of lifetimes and ESR data were found to be consistent with a model scheme of tetrahedrally oxo-coordinated $[MO_4]$ centres of chromium(VI) ions with the closed-shell electronic structure. Luminescence is associated with the ^{3}LMCT (Ligand to Metal Charge Transfer) transition mechanism. The progressive structure of the broad band results from vibronic interaction of the M–O stretching mode [12]. In the course of redox reaction, chromium(III) is oxidized to chromium(VI) ions. Therefore, the xerogel and glasses should contain residual chromium ions with the intermediate valence, i.e. chromium(IV) and chromium(V). Strek et al. reported the luminescence of a similar SiO_2: Cr glass, which was completely oxidized by annealing at 1300 K under oxygen gas flow [13].

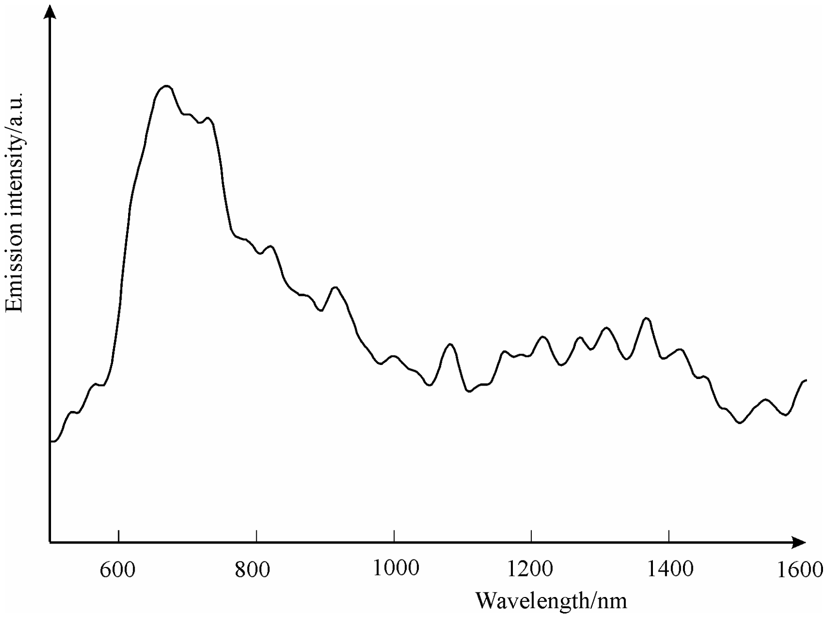

Fig. 2. Luminescence spectrum of SiO_2: Cr (sample No. 2) sol-gel glass at 10 K in the NIR spectral region. The sample was prepared at 1300 K under oxygen gas flow

Figure 2 shows the VIS-NIR luminescence at 10 K of the Cr-doped sol-gel silica glass sample (No. 2) (SiO_2: Cr) prepared by Strek and his group. The asymmetric band shape around 700 nm suggests the presence of complex centres in the glass. By taking into account the ESR data, the emission band in the deep-red (650–850 nm) region was ascribed to tetrahedrally coordinated Cr(VI) ions associated with Cr(V) ions. We have found vibronic structures and the associated side band at 1300 nm in the emission spectra. The side band is tentatively assigned to Cr^{4+} ions, known in forsterite (Mg_2SiO_4: Cr^{4+}) as a band at 1.13–1.36 μm.

Further experiments are needed to obtain spectroscopic evidence of Cr(VI, V) centres. We have investigated the luminescence at 10 K of chromium(V) ions doped in sol-gel PLZT ceramics (Pb, Ln)(Zr,Ti)O_3 [14]. Figure 3 displays the luminescence of PLZT: Cr with a small peak and a broad emission band at about 740 and 1000 nm, respectively. The former is assigned to R lines of Cr(III) ions while the latter to Cr(V) ions of a nearly octahedral [MO_{12}] centre at the A site. If we assume the presence of tetrahedral $[Cr(V)O_4]^{3-}$ centres in SiO_2, the emission band should be found at a wavelength longer than 1000 nm, by taking into account the crystal field splitting. We also prepared chromium-doped silica (90%)–alumina (10%) composites, $90SiO_2{\cdot}10Al_2O_3$: Cr. We found at 10 K a broad emission band at around 12 000 cm^{-1} (830 nm). It is assigned to the U-band emission of chromium(III) ions in the $[AlO_6]$ site because the band position and long lifetimes are close to those reported in Cr-doped aluminosilicate glasses [15]. The alumina (Al_2O_3) doped in silica affords the Cr ion many chances to occupy the Al site and it does not promote efficiently the generation of Cr(VI) and Cr(V) ions while the valence of Cr^{3+} remains unchanged in the condensation and redox reaction processes.

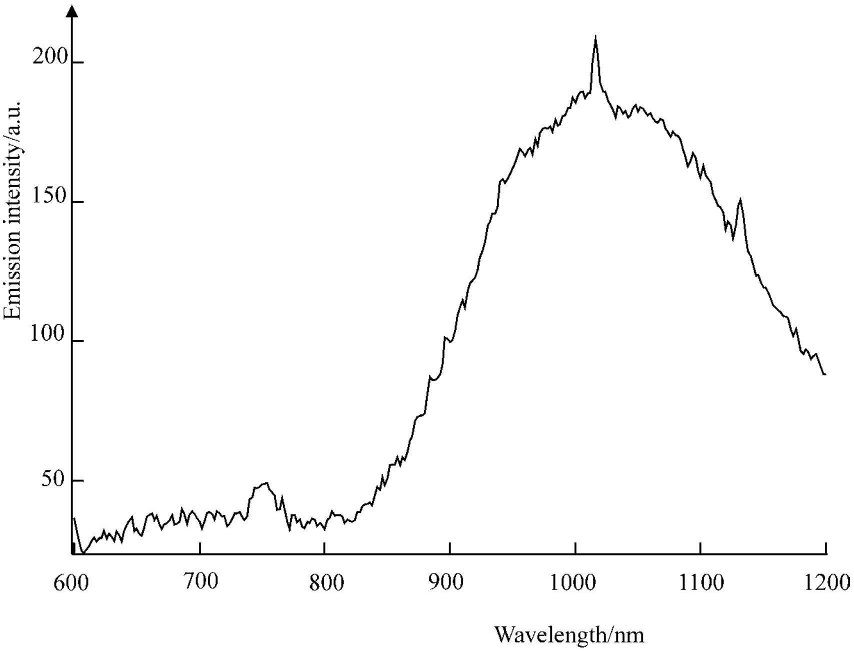

Fig. 3. Luminescence spectrum of PLZT(9/65/35); Cr (0.1%) at 10 K under Hg-arc (365 nm) excitation

Luminescence spectra of $KCrO_3Cl$ single crystals were measured at 10 K to elucidate luminescence characteristics of the $[Cr(VI)O_4]^{2-}$centre. The electronic structure of the centre is determined from the Stark experiments as a distorted tetrahedral $[Cr(VI)O_3Cl]$ centre of C_{3v} point symmetry [16]. As shown in Fig. 4, the emission spectra are composed of a main band centred at 800 nm and a side band at 1400 nm. In comparison with emission of SiO_2: Cr^{6+} (Fig. 2), two spectral profiles demonstrate a good correspondence while the band of $KCrO_3Cl$ shows a red shift of about 2000 cm^{-1} by lifting the orbital degeneracy in C_{3v} symmetry. By comparing these spectral features we conclude that the red band of Cr doped sol-gel silica glass is principally due to chromium(VI) ion being associated with Cr^{3+}, Cr^{4+} and Cr^{5+} centres.

We have described so far a red phosphor originating from Cr^{6+} in SiO_2. Extending this research we doped into sol-gel glasses other transition metal ions with 3d, 4d, and

5d electronic configurations. With increase of principal quantum numbers of dopants with $n = 3, 4, 5$, the spin-orbit interaction will be enhanced by the increase of atomic weight. Therefore the mixing of the wave function of the triplet and singlet states increases, resulting in the enhancement of lifetimes and of the fluorescence quantum efficiency. We have already reported luminescence spectral characteristics of 9 elements (Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, W) doped in sol-gels at room temperature [12]. In this paper, we compare host-dependent phosphor properties. We found an increase of the luminescence intensity and enhancement of vibronic progressions in the luminescence of V^{5+} in SiO_2 when a small amount of Al_2O_3 or TiO_2 was doped into SiO_2. As a result, quantum efficiency of this phosphor increased in the hybrid glass. In the case of a pure SiO_2 host, the dopant ion will occupy the substitutional centre in the tetrahedral structure of SiO_2. However, an addition of Al_2O_3 seems to efficiently strengthen the chemical bonding of the SiO_2 structure [10] because the transition metal ions will also be supported by the octahedrally coordinated centre. When the annealing temperature (T_a) of SiO_2: V was raised from 80 °C to 800 °C, luminescence quenching temperature (T_q) was found to be roughly proportional to the annealing temperature (T_a). In other words, we could use various parameters (T_a, T_q, activation energy, Stokes shift, electron-lattice interaction parameter S, etc.) as a measure of luminescence properties of sol-gel derived phosphors.

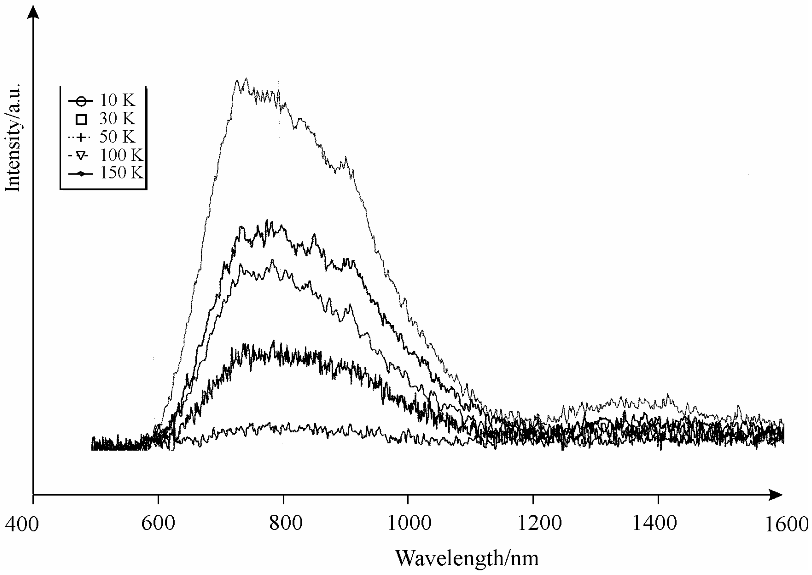

Fig. 4. Luminescence spectra of $KCrO_3Cl$ single crystal at 10 K under Hg-arc (365 nm) excitation as a function of temperature between 10 and 150 K

The phosphor in the NIR spectral region can be in principle realised by doping rare earth ions to make cooperative transitions possible. We have investigated the luminescence and lifetimes of sol-gel silica glasses co-doped with Eu^{3+} and other lanthanide ions by luminescence and lifetime measurements. The rate of energy transfer from Eu^{3+} to other ions is found to be strongly dependent on the trapping-limited relaxation processes in the solid [17]. Therefore, doping of more than two rare earth ions into the sol-gel silica glass is in principle not good enough to develop NIR phosphors. Instead, we have to improve chemical compositions of the host glasses [18].

3.2. Phosphors due to metal complex centres

Red phosphors are fabricated using Eu^{3+} ions and complexes embedded in the sol-gel matrix. We first consider Eu(III) (15-CE-5)-doped sol-gel silica glasses where CE stands for a crown ether. This complex has a planar and pentagonal oxo-ligand with a C_{5h} symmetry. The metal complex can be stabilized in the glasses if prepared under mild chemical conditions. The material is a composite of the organic ligand of (15-CE-5) and the inorganic Si and Eu(III) ions. In our experiments, we have not detected luminescence due to Eu(II) ions from xerogel [19]. By monitoring the splitting and the shift of Eu(III) ions in the $^5D_0 \rightarrow {}^7F_1$ transition, crystal field parameters have been determined in various samples as a function of annealing temperatures between 80 °C and 800 °C [8]. The metal complex was found to keep its axial symmetry when annealed at temperatures below 120 °C. Monitoring a variety of spectral changes, observed in the sol-gel glasses doped with the complex, we can establish the conditions of chemical preparation of new phosphors. If Eu is replaced by other rare earth ions and the ligand is chemically modified, improvements of colours, quantum efficiency, lifetimes and others become possible.

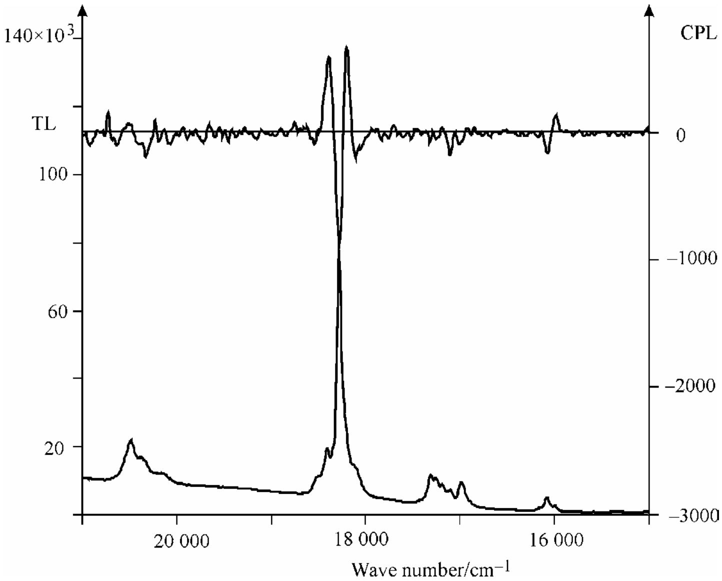

Fig. 5. Total luminescence (lower half) and circularly polarized luminescence (CPL; upper half) spectra of Tb(III)-(S)-cyclene derivative complex in xerogel at room temperature

To prepare a green phosphor, we started with Tb(III) ions or Tb complexes dissolved in sol-gel silica glasses. Luminescence spectrum of Tb(III) (15-CE-5) in the glass at 10 K shows a green band due to the host itself and associated peaks of Tb^{3+}. The quantum efficiency of this green band is not comparable to the commercial phosphor Y_2O_3: Tb^{3+}. However, the splitting of the sharp lines can clarify the electronic configuration of the green colour centre in the chiral host [8].

Figure 5 shows very special luminescence spectra of chiral phosphors: xerogel doped with optically active metal complexes of Tb-(S)-cyclene derivatives. The ordinate on the left side is the number of photons for total luminescence (TL) and the right ordinate is for the CPL signal. (CPL stands for circularly polarized luminescence which measures a differential signal between left- and right-handed circularly polarized luminescence.) If the optical active character of these complexes is maintained in the xerogel during the thermo-chemical treatments, we can see CPL spectral components clearly as those found for the complexes in solution. It is noteworthy that the existence of a chiral phosphor is demonstrated for the first time as a solid material.

Blue phosphors based on sol-gel glasses are not easy to prepare at present. This is because a blue to yellow band is inherent to the silica host itself. At lower temperatures, the host luminescence centred at 19 000 cm^{-1} is enhanced in intensity and we cannot measure the luminescence component of the dopant ions. Nevertheless, emission of Ce(III)(15-CE-5) doped in xerogel consists of two bands, located at 24 000 and 19 000 cm^{-1} with an interesting temperature-dependent spectral behaviour.

3.3. Phosphors due to semiconductor nanocrystals

Quantum confinement effects in luminescence of doped semiconductor nanocrystals are the most attractive topic of current research [20–22]. Our interest has been focused on nanocrystals embedded in ceramics and doubly doped nanocrystalline materials. Luminescence spectra of thin films of semiconductor CdS nanocrystals embedded in ZrO_2 ceramics were measured at 10 K [20]. The composite $80ZrO_2 \cdot 20CdS$ exhibits a broad band consisting of three emission bands originated from ZrO_2, CdS and defects. If Eu^{3+} is doped in addition, a red phosphor appears due to the f-f transition located at 16 300 cm^{-1}. We observed a very fast luminescence decay of a few ns from the sample at room temperature [23]. The presence of a few ns lifetime components is interpreted as due to a non-radiative relaxation to defect centres near the surface.

Zinc sulfide doped with Cu-Al is a very important green phosphor for CRT applications. The origin of the luminescence is established as being due to the donor-acceptor pair transition. In Figure 6, the emission spectra of the green phosphors are displayed. Materials of different particle sizes, i.e. bulk powders and nanocrystal xerogels, were studied. The nanomaterial was prepared as ZnS: Cu-Al phosphor dispersed into sol-gel matrices. The preparation conditions are described elsewhere [24]. The two luminescence bands are similarly located at 20 000 cm^{-1} with a bandwidth of 2500 cm^{-1}. Time-resolved luminescence spectra of this band show a red shift with the increase of delay times from 1 to 15 μs at room temperature. The red shift of the green band and decrease of intensity with the increase of delay times are a good

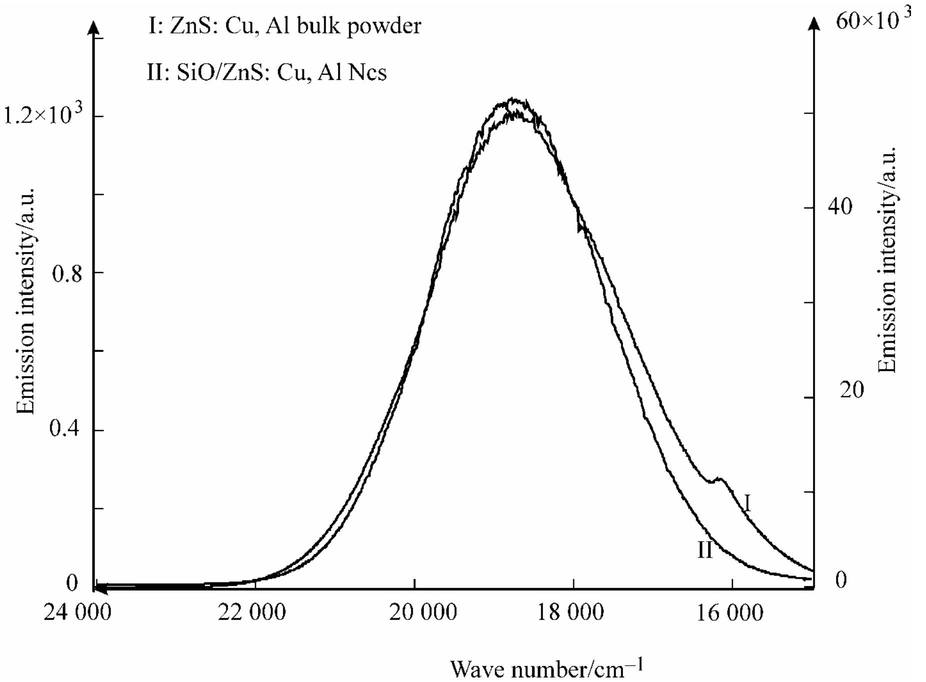

Fig. 6. Luminescence spectra ZnS: Cu, Al as bulk powder (I) and nanocrystals in xerogel (II) at room temperature under N_2 laser excitation

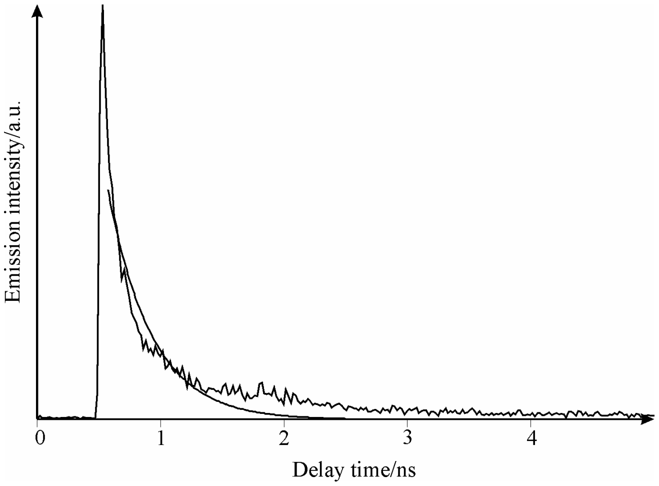

Fig. 7. Luminescence decay profile of ZnS: Cu, Al nanocrystals in xerogel at room temperature with a pico-second YAG: Nd^{3+} laser exciting dye laser second harmonic (300 nm, 250 fs) as the excitation source. The lifetime is 355 ps assuming a single exponential decay curve

evidence of the donor-acceptor pair transition mechanism. However, the green phosphor in sol-gel glasses was found to reveal lifetimes of 500 ps at 10 K.

Figure 7 shows the luminescence decay profile of ZnS: Cu, Al nanocrystals in xerogel at room temperature. As an excitation source, the second harmonic of a dye laser excited with a pico-second YAG: Nd^{3+} laser (300 nm, 250 fs) was employed. The lifetime is 355 ps by assuming a single exponential decay curve. The ultrafast relaxation processes were also found in ZrO_2/CdS: Eu and they are considered to be due to surface-bound defect centres. The fact that few µs and 0.5 ns lifetimes coexist in the same powdery material does support Bhargava's experimental findings. The green phosphor ZnS NCs is applicable to new storage phosphors of very fast optical response [25]. Preparation of this green phosphor is not so easy at the moment because the ZnS phosphor has Wurtzite structure at room temperature while the donor-acceptor mechanism is possible in the high temperature phase of the Zinc Blende structure. The material embedded in poly(vinyl alcohol) (PVA) matrices shows a blue luminescence due to SA (self-activated) centre. When the concentration of codopants (Cu, Al) is low, luminescence from the SA centre is dominant. Improvements of the preparation conditions are required.

4. Summary

We have presented chemical and optical properties of new phosphors based on xerogel and sol-gel silica glasses as host materials. In nanoporous and amorphous structures there exist traps, defects and killer centres which prevent efficient luminescence processes in amorphous solids. In the case of transition metal ions, broad and efficient luminescence bands in the visible spectral range (white and red) were found. They are due to LMCT transitions associated with dangling bonds on the surface. Quantum size-confinement effects were reported for nanocrystalline semiconductor materials. However, we could not find the same quantum effects in glasses because of the presence of trapping centres. Sol-gel SiO_2 glasses doped with rare earth(III) complexes are sensitive luminescence probes for monitoring structural changes of planar Eu(III) and chiral Tb(III) complexes. Luminescence properties of nanocrystalline phosphors were investigated in sol-gel SiO_2 glasses doped with ZnS: Cu, Al. These green phosphor nanocomposites have revealed a donor-acceptor transition within 0.02 ms decay times. The doped sol-gel xerogel and silica-based phosphors are characterized by the unusual valence states of the transition metal ions or stable rare earth complex centres in organic-inorganic hybrid hosts. Luminescence of green phosphors ZnS: Cu, Al in xerogel is characterized by the presence of 500 ps lifetimes due to spd mixing effects in semiconductor nanocrystals.

Acknowledgements

We are very grateful to W. Stręk for allowing us to use the sample No. 2 for measurements and to H. Kuroda for his continuous encouragement.

References

[1] Bhargava R.N., Gallagher D., Hong X., Nurmikko A., Phys. Rev.Lett., 72 (1994), 416.

[2] Kushida T., Tanaka M., Bull. Stefan Univ., 14 (2002), 60 and references therein.

[3] Reisfeld R., Joergensen C.K., *Optical properties of colorants and luminescence species in sol-gel glasses*, [in:] *Structure and Bonding*, Vol. 77, R. Reisfeld and C.K. Joergensen (Eds.), Springer -Verlag, Berlin, 1992, pp. 207–256.

[4] Reisfeld R., Zelner M., Saraidarov T., Minti H., *Semiconductor quantum size particles and rare earth ions (Eu^{3+}, Tb^{3+}), in amorphous sol-gel films*, [in:] *Advances on Energy Transfer Processes*, B. Di Bartolo, Xuesheng Chen (Eds.), World Scientific Publishing, 2001, p. 341.

[5] Reisfeld R., Gaft M., Saraidarov T., Panczer G., Zelner M., Materials Letters, 45 (2000), 154.

[6] Reisfeld R., J. Alloys Compds, 341 (2002), 56.

[7] Reisfeld R., *Lasers based on sol-gel technology*, [in:] *Structure and Bonding*, Vol. 85, R. Reisfeld and C.K. Joergensen (Eds.), Springer-Verlag, Berlin, 1996, pp. 215–233.

[8] Morita M., Rau D., Kai T., J. Lumin., 100 (2000), 97.

[9] Herren M., Morita M., J. Lumin., 66–67 (1996), 268.

[10] Dzwigaj S., Matsuoka M., Anpo M., Che M., J. Phys. Chem., B104 (2000), 6012.

[11] Herren M., Nishiuchi N., Morita M., J. Chem. Phys., 101 (1994), 4461.

[12] Morita M., Kajiyama S., Rami D., Sakurai T., Iwamura M., J. Lumin., 102–103 (2003), 608.

[13] Stręk W., Dereń P.J., Łukowiak E., Hanuza I., Drulis H., Bednarkiewicz A., Gaishun V., J. Noncryst. Solids, 288 (2001), 56.

[14] Murakami S., Herren M., Rau D., Sakurai T., Morita M., J. Lumin., 83–84 (1999), 215.

[15] Grinberg M., Holliday K., J. Lumin., 92 (2001), 277.

[16] Hφg J.H., Ballhausen C.J., Solomon E.I., Mol. Phys., 32 (1976), 807.

[17] Sharma P.K., Jilavi M.H., Nass R., Schmidt H., J. Lumin., 82 (1999), 187.

[18] Buddhudu S., Morita M., Murakami S., Rau D., J. Lumin., 83–84 (1999), 199.

[19] Zaitoun M.A., Goken D.M., Bailey L.S., Kim T., Lin C.T., J. Phys. Chem., B104 (2000).

[20] Bol A.A., Meijerink A., J. Phys. Chem., B105 (2001), 8861, 10197.

[21] Bol A.A., Ferwerda J., Bergwerff J.A., Meijerink A., J. Lumin., 99 (2002), 325.

[22] Konishi M., Isobe T., Senna M., J. Lumin., 93 (2001), 1.

[23] Morita M., Rau D., Fujii H., Minami Y., Murakami S., Baba M., Yoshita M., Akiyama H., J. Lumin., 87–89 (2000), 478.

[24] Morita M., Baba M., Rau D., Koike M., Takada K., Ishii T., Yoshita M., Akiyama H., Nonlinear Optics, 29 (2002), 697.

[25] Ihara M., Igarashi T., Kusunoki T., Ohno K., J. Electrochem. Soc., 149 (2002), 1172.

Received 16 July 2003
Revised 6 October 2003