Research Article

Luminescence Properties of Eu- and Mg-Codoped Sol-Gel SiO_2 Glasses

Martin O. Onani,[1] Paul Mushonga,[1] Lehlohonolo F. Koao,[2] and Francis B. Dejene[2]

[1] *Department of Chemistry, University of Western Cape, Private Bag X17, Bellville 7535, South Africa*
[2] *Department of Physics, University of the Free State, Qwaqwa Campus, Private Bag X13, Phuthaditjhaba 9866, South Africa*

Correspondence should be addressed to Martin O. Onani, monani@uwc.ac.za

A series of SiO_2 nanostructures codoped with Eu^{3+}; Mg^{2+} ions were obtained by a sol-gel method. The gels synthesized by the hydrolysis of $Si(OC_2H_5)_4$, $Eu(NO_3)_3 \cdot 6H_2O$, and $Mg(NO_3)_2$ were heated in air at $600°C$ for 2 hours. Firstly, the total amount of Eu^{3+} ions was varied from 0 to 2.0 mol% to investigate the effect of self-damping, while in the second case, the Eu^{3+} ions were kept constant in the experiment at 0.5 mol% total doping and Mg^{2+} ions varied. The samples were characterized by X-ray diffraction, TEM, EDS, and UV lamp-excited luminescence spectroscopy. The Eu^{3+} ions were homogeneously dispersed in the silica and interacting with the small (1–5 nm) amorphous silica matrix. Strong red emissions located at 614 nm and 590 nm for doped and codoped SiO_2 were observed from the UV light excitation at room temperature. The composition of around 1.25 mol% Eu^{3+} gave highest emission intensity. SiO_2; Mg^{2+} ions portray strongly enhanced emissions due to energy transfer from Mg^{2+} to Eu^{3+}, which is due to radiative recombination. An increase in luminescence intensity was observed as the Mg^{2+}-to-Eu^{3+} ratio increased for the range investigated. The results show Eu^{3+} ion is located inside or at the surface of disordered SiO_2 nanoparticles.

1. Introduction

The sol-gel technique that involves the simultaneous hydrolysis and condensation reaction of the metal alkoxide is one of the most common methods of synthesizing silica nanoparticles [1]. It is an efficient technique for the synthesis of phosphors due to the good mixing of starting materials and relatively low reaction temperature resulting in more homogenous products than those obtained by the solid-state reaction synthesis method. Lanthanide ions have been employed as optically active centers due to unique electronic configurations, which result in special spectroscopic properties. Thus, these ions have played prominent role in lighting and light conversion technologies. However, their optical properties, not only depend on the nature of the active ions, but also on the site environment provided by the host lattice. Rare earth ions or lanthanides in a silica host matrix have a wide range of applications in active materials for solid-state lasers, amplifiers, electro-optic devices and

sensors because of their well-known fluorescing property [2–9]. In particular, europium is of great interest since it displays both a sharp luminescence in the orange-red as trivalent ion and a broad band one from UV to blue-green in its divalent configuration. Eu^{3+} ions are widely used as activators in various materials for their allowed optical transitions of 4f–5d. A strong overlap of the activator 5d orbitals with ligand orbital causes high sensitivity of their spectral characteristics to the local environment structure. The luminescence of Eu^{3+} doped silica is influenced by factors such as the modification of the ligand field around the Eu^{3+} ions in the silica, presence of hydroxyl ions, energy transfer by cross-relaxation, and the concentration of dopants as well as the preparation process [10]. It is therefore of great interest to distinguish between the luminescence arising from Eu^{3+}-ions and that arising from defect centers in the silica matrix and also investigate the possibility of energy transfer from the matrix to the activators. Thus, the purpose of this paper, firstly, was to study the absorption and luminescent properties

(a)

(b)
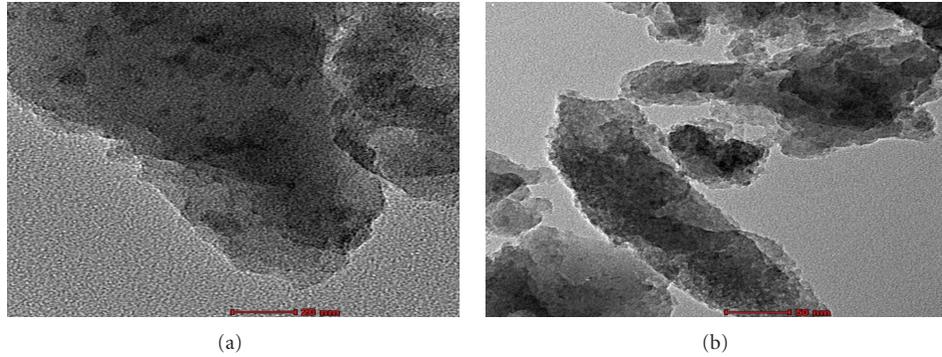
FIGURE 1: TEM images of (a) 2 mol% Eu-doped silica samples; (b) 2 mol% Eu- and 2 mol% Mg-doped silica samples at 64000 times magnification.


■ Acquire EDX
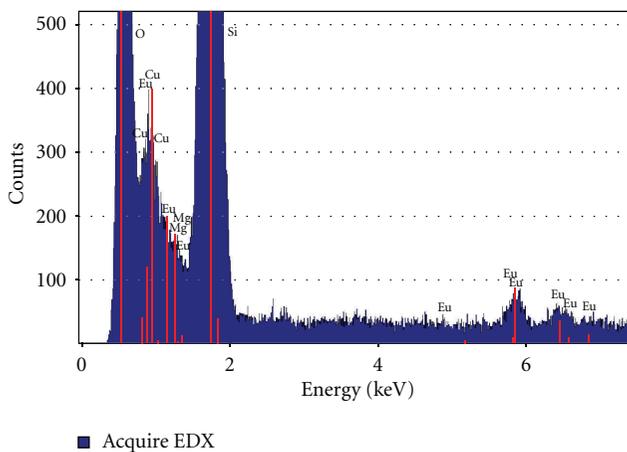
FIGURE 2: EDX spectrum of Mg-codoped xerogels annealed at 600°C for 2 h in air.

by using photoluminescence (PL) spectroscopy of Eu^{3+}-doped and Eu/Mg-codoped SiO_2 glasses made by the sol-gel process. Secondly, the dependence of the PL wavelengths and intensity on the Mg/Eu molar ratios was investigated.

2. Experimental

2.1. Synthesis of Silica Doped with Eu^{3+}. The procedure followed was modified from the literature [11]. Silica glasses were synthesized by sol-gel using tetraethyl orthosilicate ($Si(OC_2H_5)_4$, TEOS), ethanol (ETOH), distilled water, nitric acid (HNO_3, as a catalyst), europium nitrate ($Eu(NO_3)_3 \cdot 6H_2O$), and magnesium nitrate ($Mg(NO_3)_2$) as material sources. In the preparation of pure silica, TEOS (10 mL) dissolved in EtOH (10 mL) was mixed with deionized water (14 mL). In order to catalyze the hydrolysis and polymerization reaction, concentrated nitric acid (5 mL) was added, and the mixture was stirred for 24 h at room temperature. A similar procedure was followed during preparation of a series of europium-doped silica samples. Various masses of europium (iii) nitrate dissolved in ethanol (5 mL) were added to the foregoing mixture immediately after adding

water simultaneously with nitric acid. The solutions were then stirred till gel point. The volume ratio of TEOS, EtOH, water, and HNO_3 used was 1 : 1 : 1.4 : 0.5. The produced gels were dried at room temperature for 2 days. The dried gels were then crushed and later sintered in a furnace at 600°C for 2 h to remove solvent and organic ligands and to obtain full densification. Finally, the powders were recrushed.

2.2. Synthesis of Eu^{3+}- and Mg^{2+}-Codoped Silica. A similar procedure as above was followed during the preparation of these silica glasses, but during the preparation of Eu^{3+}- and Mg^{2+}-codoped silica, a constant mass of europium (iii) nitrate dissolved in ETOH and varying masses of magnesium nitrate also dissolved in ETOH were added simultaneously to the foregoing mixture of silica after adding water with nitric acid, and the solutions were stirred till gel point. The dried gels were then again treated as above.

2.3. Characterization of the Particles. The xerogels were annealed at 600°C before their characterization. The structure was determined by transmission electron microscopy studies using a Tecnai F20 Field Emission TEM coupled with EDAX. The samples for TEM were prepared by sonicating for 15 minutes their methanol suspensions followed by depositing a drop of the suspension on a standard copper grid coated with a holey carbon film. The photoluminescence (PL) emission spectra were taken on a Cary Eclipse fluorescence spectrophotometer equipped with a monochromatic xenon lamp. Each sample in powder form was loaded into a circular holder and excited with 340 nm radiation from a pulsed xenon lamp.

3. Results and Discussion

Figures 1(a) and 1(b) show the prepared nanosized Eu^{3+}-doped and Eu^{3+}- and Mg^{2+}-codoped silica xerogels respectively, under HRTEM. The nanosized silica particles had uniform particle sizes of 1 to 5 nm. The presence of Mg^{2+} causes more particle agglomerations and therefore large particles.

(a)

(b)
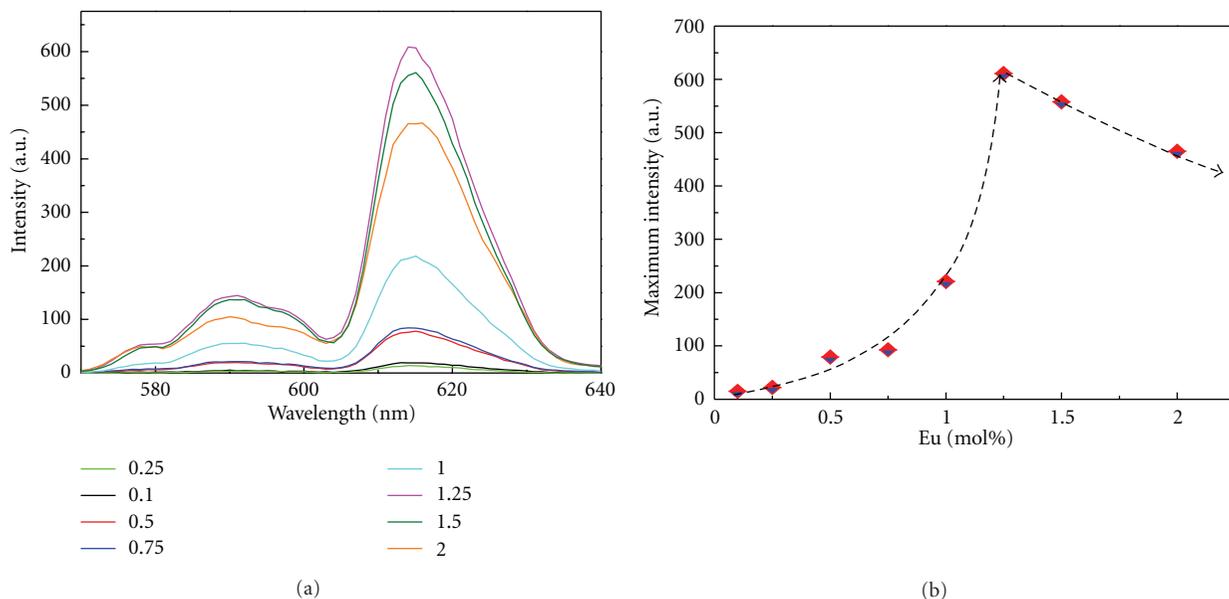
FIGURE 3: (a) Photoluminescence emission spectra of Eu-doped silica nanopowders and (b) variation of PL maximum intensity with an increase in Eu concentrations.


(a)

(b)
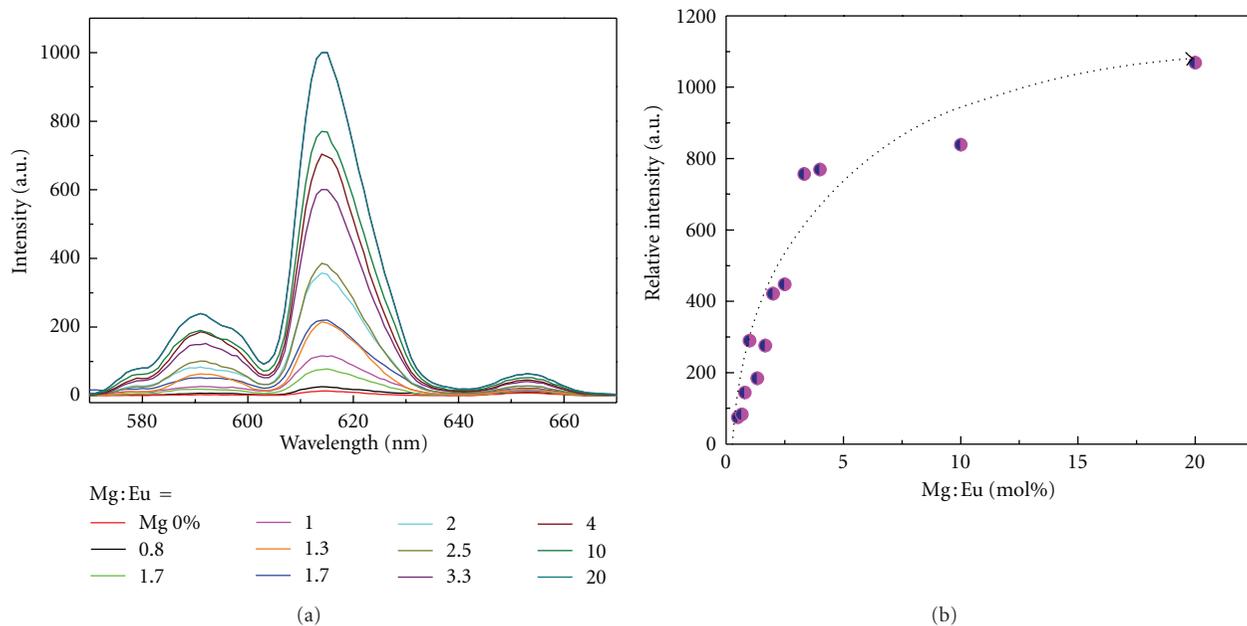
FIGURE 4: (a) Mg-codoped silica (0.5 mol% Eu) xerogels annealed at 600°C for 2 h in air and (b) variation of PL maximum intensity with Mg/Eu molar ratios.

Figure 2 shows the energy dispersive X-ray spectrum of 2 mol% Mg^{2+}-codoped, annealed silica xerogels. The elemental analysis of the nanoparticles confirms the presence of Si, O, Mg, and Eu in the xerogels (Cu in the EDX spectrum originates from the copper grids). The significantly small counts of Mg^{2+} and Eu^{3+} ions are directly indicative of small concentrations of these ions in the samples.

The effects of europium ion concentration at a constant synthesis temperature of 600°C on the photoluminescence properties of samples are shown in Figures 3(a) and 3(b).

The PL spectra of the samples excited using a wavelength of 325 nm show that the emission intensity is related to the concentration of the Eu^{3+} activator ions. The intensity of the PL peaks was significantly affected by the addition of the europium ions into the sample without any significant change in peak position. The highest luminescence intensity yield of the samples was obtained at a europium concentration of 1.25%, and lower or higher europium contents resulted in a substantial decrease in emission intensity. This decrease in emission intensity indicates the presence of a

stronger cross-relaxation-induced quenching with smaller interion distance [12].

At higher RE concentrations, most ions reside in cluster due to the insolubility of rare-earth ions in glass which are easily affected by the ambient conditions. Under 325 nm excitation, the SiO_2 : Eu samples emit predominantly in the red domain, that is, 570 nm ($^5D_0 \rightarrow {}^7F_0$), 590 nm ($^5D_0 \rightarrow {}^7F_1$), and 614 nm ($^5D_0 \rightarrow {}^7F_2$) [12, 13]. These commonly narrow emissions in red region arise from the f-f transitions of the Eu^{3+} ions. The emission in the vicinity of 590 nm is due to the magnetic dipole transition $^5D_0$-$^7F_1$, which is insensitive to site symmetry, while the emission around $610-630$ nm is due to the electric dipole transition of $^5D_0-{}^7F_2$ that is induced by the lack of inversion symmetry at the Eu^{3+} site [14] and is much stronger than that of the transition to the $^7F_1$ state. The asymmetry ratio of the $^5D_0-{}^7F_2$ to $^5D_0-{}^7F_1$ transitions for the SiO_2 : Eu glasses is about 4 and lies well within the range of values usually found in oxide glasses, indicating that the Eu^{3+} ions occupy low-symmetry sites. The ratio stays approximately constant with an increase in Eu^{3+} ions up to optimum value, suggesting that the Eu^{3+} ions are embedded in the random glass network structure of the amorphous silica matrix. $^5D_0 \rightarrow {}^7F_0$ is a nondegenerate energy which usually shows large values for FWHM indicating the Eu^{3+} are accommodated in a continuous distribution in closely similar local sites within the glass. In principle, electric dipoles are Laporte forbidden. However, provided that the site occupied by the Eu^{3+} does not present a centre of inversion, an odd parity term relaxes the rule in the ligand field Hamiltonian making the transition, $^5D_0 \rightarrow {}^7F_0$, permitted [15, 16].

Figure 4(a) contains the emission spectra of sol-gel glasses containing 0.5 mol% Eu^{3+} and varying Mg : Eu mole ratios annealed for 2 h at 600°C. The presence of Mg codopant significantly increases the luminescence intensity. The Mg^{2+} ions disperse the Eu^{3+} clusters, enhancing 590 nm ($^5D_0 \rightarrow {}^7F_1$) and 614 nm ($^5D_0 \rightarrow {}^7F_2$) emissions due to increased ion-ion distances and decreased cross-relation. The introduction of Mg^{2+} codopants with different valence from Eu^{3+} also produces defects, because of charge compensation requirements, resulting in change of energy transfer with the presence of Mg^{2+} ions. The ratio of increase in intensities of both the 590 and 614 nm peaks of Eu^{3+} at higher concentrations of Mg^{2+} is different from that at lower concentration of Mg^{2+} ions which indicates a change of surrounding of the Eu^{3+} ions in the SiO_2 lattice at lower concentration of codopant.

An approximately parabolic relation (Figure 4(b)) was observed between the intensity of emission peaks and the molar ratio of Mg : Eu, which increases significantly as Mg^{2+} ion concentration increases with a critical value of codopant/RE ratio of 20 : 1. Previously aluminium [17] has been shown to be more efficient in enhancing luminescence of dopants in materials such as Tb^{3+} [18] and thus became the standard codopant used by different research groups [19] in the phosphor field. Now, we see other elements such as Eu and Mg showing similar properties.

4. Conclusions

Eu^{3+}-doped and Eu^{3+}- and Mg^{2+}-codoped silica phosphor powders were successfully synthesized by the sol-gel process. The PL results of the doped and codoped silica glasses showed predominantly red emission peaks at 570, 590, and 614 nm. The origin of these three peaks is ascribed to the crystal field splitting of the 4 f levels of Eu^{3+} ion. While an increase in luminescence intensity was observed as the Mg^{2+}-to-Eu^{3+} ratio increased for the range investigated, significant luminescence enhancement was observed for codopant : Eu ratio of 20 : 1. This enhanced photoluminescence was attributed to two possible factors, the first being an energy transfer from the SiO_2 : Mg nanostructures resulting in enhanced emission from Eu^{3+}. The second factor was that the Mg^{2+} ion disperses the Eu^{3+} clusters, enhancing the 590 nm ($^5D_0 \rightarrow {}^7F_1$) and 614 nm ($^5D_0 \rightarrow {}^7F_2$) emissions as a result of the increased ion-ion distances and decreased cross-relation.

Acknowledgments

References

[1] L. L. Hench and J. K. West, "The sol-gel process," *Chemical Reviews*, vol. 90, no. 1, pp. 33–72, 1990.

[2] A. P. Golovina, V. K. Runov, and N. B. Zorov, "Chemical luminescence analysis of inorganic substances," in *Ferrites. Transitions Elements Luminescence*, vol. 47 of *Structure & Bonding*, pp. 53–119, 1981.

[3] H. Eilers and B. M. Tissue, "Laser spectroscopy of nanocrystalline Eu_2O_3 and Eu^{3+}:Y_2O_3," *Chemical Physics Letters*, vol. 251, no. 1-2, pp. 74–78, 1996.

[4] R. S. Meltzer, S. P. Feofilov, B. Tissue, and H. B. Yuan, "Dependence of fluorescence lifetimes of Y_2O_3:Eu^{3+} nanoparticles on the surrounding medium," *Physical Review B*, vol. 60, no. 20, pp. R14012–R14015, 1999.

[5] T. Igarashi, M. Ihara, T. Kusunoki, K. Ohno, T. Isobe, and M. Senna, "Relationship between optical properties and crystallinity of nanometer Y_2O_3: Eu phosphor," *Applied Physics Letters*, vol. 76, no. 12, pp. 1549–1551, 2000.

[6] G. Wakefield, E. Holland, P. J. Dobson, and J. L. Hutchison, "Luminescence properties of nanocrystalline Y_2O_3:Eu," *Advanced Materials*, vol. 13, no. 20, pp. 1557–1560, 2001.

[7] H. Peng, H. Song, B. Chen et al., "Temperature dependence of luminescent spectra and dynamics in nanocrystalline Y_2O_3:Eu^{3+}," *Journal of Chemical Physics*, vol. 118, no. 7, pp. 3277–3282, 2003.

[8] M. Yu, J. Lin, J. Fu, and Y. C. Han, "Sol–gel fabrication, patterning and photoluminescent properties of $LaPO_4$:Ce^{3+}, Tb^{3+} nanocrystalline thin films," *Chemical Physics Letters*, vol. 371, no. 1-2, pp. 178–183, 2003.

[9] K. A. Gschneidner Jr., J.-C. Bünzli, and V. K. Pecharsky, "Preface," *Handbook on the Physics and Chemistry of Rare Earths*, vol. 39, pp. 5–8, 2009.

[10] A. J. Silversmith, D. M. Boye, R. E. Anderman, and K. S. Brewer, "Fluorescence line narrowing and decay dynamics in sol-gel glasses containing Eu^{3+}," *Journal of Luminescence*, vol. 94-95, pp. 275–278, 2001.

[11] L. F. Koao, H. C. Swart, E. Coetsee, M.-M. Biggs, and F. B. Dejene, "The effect of Mg^{2+} ions on the photoluminescence of Ce^{3+}-doped silica," *Physica B*, vol. 404, no. 22, pp. 4499–4503, 2009.

[12] X.-C. Jiang, C.-H. Yan, L.-D. Sun, Z.-G. Wei, and C.-S. Liao, "Hydrothermal homogeneous urea precipitation of hexagonal $YBO_3:Eu^{3+}$ nanocrystals with improved luminescent properties," *Journal of Solid State Chemistry*, vol. 175, no. 2, pp. 245–251, 2003.

[13] R. Reisfeld, A. Patra, G. Panczer, and M. Gaft, "Spectroscopic properties of cerium in sol-gel glasses," *Optical Materials*, vol. 13, no. 1, pp. 81–88, 1999.

[14] C. Guo, F. Gao, Y. Xu, L. Liang, F.G. Shi, and B. Yan, "Efficient red phosphors $Na_5Ln(MoO_4)_4:Eu^{3+}$ (Ln =La, Gd and Y) for white LEDs ," *Journal of Physics D*, vol. 42, Article ID 095407, 2009.

[15] L. D. Carlos, R. A. Sá Ferreira, V. de Zea Bermudez, C. Molina, L. A. Bueno, and S. J. L. Ribeiro, "White light emission of Eu^{3+}-based hybrid xerogels," *Physical Review B*, vol. 60, no. 14, pp. 10042–10053, 1999.

[16] O. L. Malta and L. D. Carlos, "Intensities of 4f-4f transitions in glass materials," *Quimica Nova*, vol. 26, no. 6, pp. 889–895, 2003.

[17] A. J. Silversmith, N. T. T. Nguyen, B. W. Sullivan, D. M. Boye, C. Ortiz, and K. R. Hoffman, "Rare-earth ion distribution in sol-gel glasses co-doped with Al^{3+}," *Journal of Luminescence*, vol. 128, no. 5-6, pp. 931–933, 2008.

[18] D. M. Boye, A. J. Silversmith, T. N. Nguyen, and K. R. Hoffman, "Effects of rehydration on Tb^{3+} spectroscopy in sol-gel glasses," *Journal of Non-Crystalline Solids*, vol. 353, no. 24-25, pp. 2350–2354, 2007.

[19] A. Monteil, S. Chaussedent, G. Alombert-Goget et al., "Clustering of rare earth in glasses, aluminum effect: experiments and modeling," *Journal of Non-Crystalline Solids*, vol. 348, pp. 44–50, 2004.

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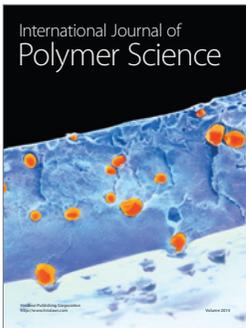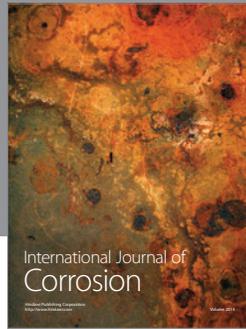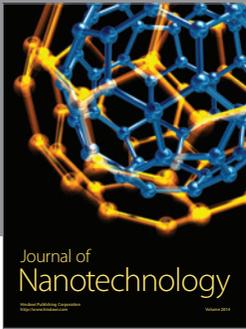
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