Magnetic properties of nanostructured SiO_2 : Eu^{3+} powders

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Abstract: Eu-doped silica nanoparticles with different concentrations of europium (3 %, 6 % and 15 at. %) were prepared by a hydrothermal procedure. Light scattering measurements of the silica colloids as well as TEM microscopy, revealed a narrow size distribution of the particles, ranging from 5 to 10 nm. X-Ray diffraction showed that all the powders were amorphous. Magnetic susceptibility *vs.* temperature measurements showed a behaviour typical for Eu^{3+} ions, with a plateau below 60 K, and an increase of the mass susceptibility with Eu concentration. The splitting of zero-field cooled (ZFC) and field-coled (FC) susceptibility branches increased with the europium concentration, indicating the presence of interparticle interactions. At temperatures below 40 K, a contribution of paramagnetic impurities obeying the Curie law was observed. Heat treatment of the powders at 823 K and 1073 K increased the magnetic susceptibility. The appearance of a small peak at 70 K indicated the presence of small quantities of ferromagnetic EuO in the powders after heating.

Keywords: magnetic properties, nanoparticles, rare earth, silica, light scattering.

INTRODUCTION

The physical properties of nanosized systems can radically differ from those found in their bulk counterparts, exhibiting some remarkable specific properties. For instance, a decrease of the nanocrystallites size leads to a decrease in the melting point, reduced lattice constants, substantial changes in the conducting, magnetic and optical properties, *etc*.[1]

Among other systems, the physical properties of nanosized materials based on rare earth elements have attracted a great deal of attention during the last decade,[2–4] due the very interesting optical and magnetic properties of these materials, caused by the influence of the crystalline field on the rare earth ions. The crystal field splitting of the $4f$ levels is usually of the order of 10^2 cm^{-1}, which is small compared to the spin-orbit interaction, which is about 10^3–10^4 cm^{-1} in magnitude[5]

and consequently the total angular momentum J is preserved. In addition, all the $4f$ levels are populated at room temperature and the magnetic susceptibility of the lanthanide ions in the crystal surroundings does not differ very much from that of the free ion. However, at low temperatures, only the lowest levels are populated and effect of crystalline field splitting must be taken into consideration.

The wide area of application of rare earth based materials and silica is also one of the reasons for the growing interest which cannot be neglected. For example, the silica matrix combined with rare earths, such as europium, have enormous application in the production of optoelectronic laser diodes, fibers for application in optical telecommunications, laser medical delivery systems, military optical sensors, silica–silica films for wave guide integrated optics, for light conversion from one color to another, the production of fluorescent lamps, TV and computer screen displays, X-rays detection and xerography.[6–8]

The aim of this study was to investigate the magnetic properties of SiO_2:Eu^{3+} nanoparticles, as well as to explain the influence of the europium concentration and sample preparation conditions on the obtained magnetic characteristics.

EXPERIMENTAL

A sol was prepared by leaching water glass, composition $Na_2O \cdot SiO_2$, SiO_2/ Na_2O ratio 3.75 and viscosity 2.2 mPa, using 0.1 M HCl solution. After adding the entire volume of acid needed to fully leach-neutralize the water glass, the mixture was charged into an autoclave and leached at a temperature of 120 ºC and a pressur of 3 bar for 5 h.

Silica acid precipitate was promoted into the sol in the second preparation step in the autoclave under the above given leaching conditions. After hydrothermal treatment, the pH of the silica acid sol was adjusted to pH 9.

Samples of different sol concentrations were then prepared (0.1 M, 1 M and 2 M). To produce Eu^{3+} doped silica sols, europium nitrate was added in amounts corresponding to 3, 6 and 15 at.% of europium

To attain Eu^{3+} doped silica gels, drops of 0.1 M ammonia solution were added to all mixtures of Eu^{3+} doped silica sols. The gel was then dried at 150 °C for a few days and then thermally treated at 550 ºC and 800 ºC for 8 h.

In order to determine the particle size and particle size distribution, all samples were investigated by transmission electron microscopy (TEM JOEL JEM 2000 FX) and light scattering (Brookhaven Instruments light scattering system equipped with a BI-200SM goniometer, a BI-9000AT correlator, a temperature controller and a Coherent INOVA 70C argon-ion laser).

X-Ray diffraction measurements were performed on all thermally treated samples (both at 150 and 550 ºC) using a Brucker D8 Advance diffractometer with Cu Kα radiation.

DC Magnetization measurements were carried out as a function of temperature ($T = 4 – 300$ K) in a magnetic field of 100 Oe using a Quantum Design SQUID magnetometer MPMS XL-5. All measurements were performed in zero field cooling (ZFC) and field cooling (FC) regimes. The ZFC measurements were realized by cooling the sample from room temperature down to 4 K in a zero magnetic field and then the temperature dependence of the magnetic susceptibility was measured in an applied magnetic field of $H = 100$ Oe. The FC procedure was the same as for ZFC, except that the cooling from room temperature down to 4 K was performed under an applied magnetic field of 100 Oe.

RESULTS AND DISCUSSION

In order to correlate the magnetic properties of the investigated system with its morphology and structure, particle sizing was performed. Dynamic light scattering measurements of the samples of SiO$_2$ sol (3×10^{-3} M concentration) were performed at a scattering angle of 90º. The measured particle size distribution is given in Table I. This table shows that the calculated size distribution was highly uniform, *i.e.*, 98 % of the particles had a diameter of 7.7 ± 1.1 nm, while 2 % of them had diameters between 28–33 nm. This result indicates that a slight particle agglomeration had occurred.

TABLE I. Distribution of silica particle sizes in the sol determined by means of dynamic light scattering

d/nm	Share/%	d/nm	Share/%
< 4.5	0	13.7	0
5.0	0	15.8	0
5.8	0	18.3	0
6.6	0	21.1	0
7.7	98	24.4	0
8.9	0	28.2	1
10.3	0	32.6	1
11.8	0	> 33.0	0

A typical transmission electron microscopy microphotograph of the obtained powders is shown in Fig. 1. The powder is composed of small particles loosely condensed together. A comparison with the light scattering results of the sol samples show that a slight agglomeration of the particles of the powder had occurred, accompanied by a minor increase of the average particle size.
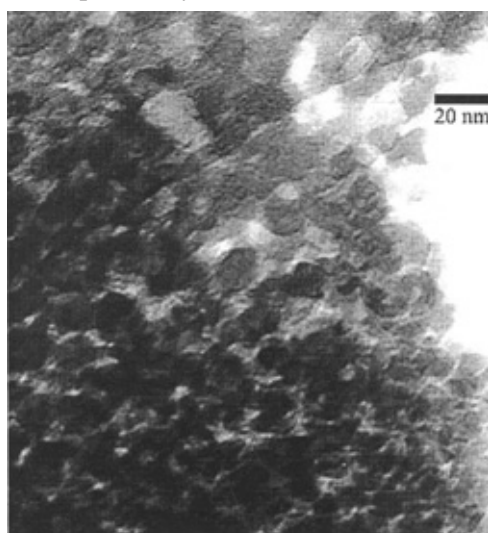

Fig. 1. TEM Photograph of SiO$_2$: Eu^{3+} particles containing 3 at.% Eu^{3+}.

X-Ray measurements showed that all the samples were amorphous, proving that the Eu^{3+} ions were dispersed in an amorphous Si matrix.
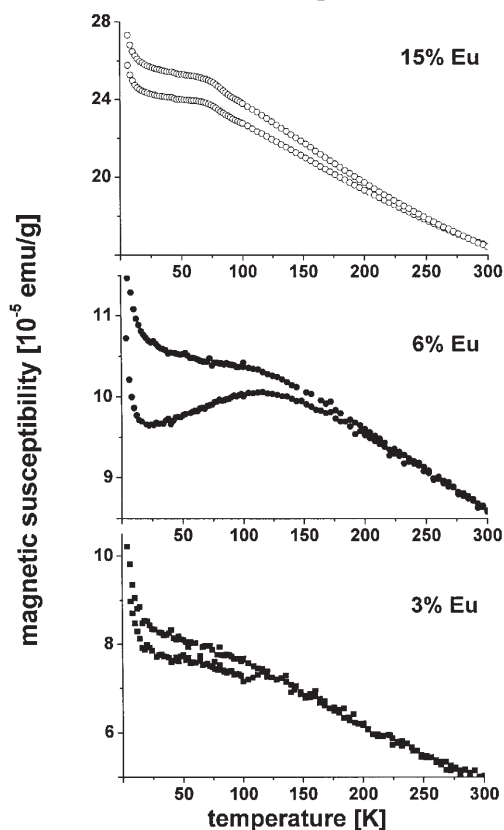

Fig. 2. Temperature dependence of the magnetic susceptibility of SiO_2: Eu^{3+} for different concentrations of europium.

Temperature dependences of the magnetic susceptibility per gram of the sample, for all three europium concentrations, are shown in Fig. 2. For each sample, the lower curves correspond to zero field cooled (ZFC) and the higher one to field cooled (FC) measurements. With increasing Eu concentration, the magnetic susceptibility for all the samples increased. At temperature below 80 K, all curves show a plateau which reveals the expected behavior of Eu^{3+} ions.[5,9] On the other hand, each sample showed an inrreversibility effect *i.e.*, separation between the ZFC and FC branches at temperatures T_{irr}. These temperatures also increased with Eu concentration. The separation between the ZFC and FC curves is a measure of the interactions among the Eu ions, and it is obvious from Fig. 2 that it increased with Eu concentration. At lower temperatures, a significant upturn was observed (Figs. 2 and 3), which corresponds to a Curie-like (*i.e.*, paramagnetic) behavior of the susceptibility ($\chi = C/T$). For this temperature region ($T < 40$ K), χ varies linearly with inverse temperature (inset Fig. 3). This effect is caused by a very small presence (≈ 10 ppm) of some residual paramagnetic impurities, the contribution of

which became visible at low temperatures, due to the low value of the susceptibility o the Eu^{3+} ground singlet ($J = 0$) state. The same effect was also reported for europium dispersed in organic–inorganic nanohybrids.[9]

The calculated magnetic susceptibility of the sample with 15 at.% of europium is depicted in Fig. 3 as the full line. It was assumed that the energy spectrum of the Eu^{3+} ion corresponds to the case of a low symmetry crystal field with a singlet ground level ($^7F_0$) and a three-fold splitting of the $^7F_1$ level, as well as a barycentre of the $^7F_2$ level. The contribution of higher energy crystal field levels can be neglected within the measured temperature range 2–300 K. Since the degeneracies of the $^7F_1$ and $^7F_2$ manifolds are completely removed, the first-order Zeeman terms have zero values, and the Van Vleck equation for the Eu^{3+} ion[4] could be written in the form:[10]

$$\chi_M = N \frac{\sum_i \alpha_i e^{-\frac{E_i}{kT}}}{\sum_i e^{-\frac{E_i}{kT}}}$$

The coefficients α_i denote the second order Zeeman contribution of the i-th crystal field level, $i.e.$, they represent temperature independent Van Vleck terms.

In the above equation, the employed values of Eu^{3+} ion crystal field energy levels, which were spectroscopically determined,[4,11] were 310 cm^{-1}, 374.4 cm^{-1}
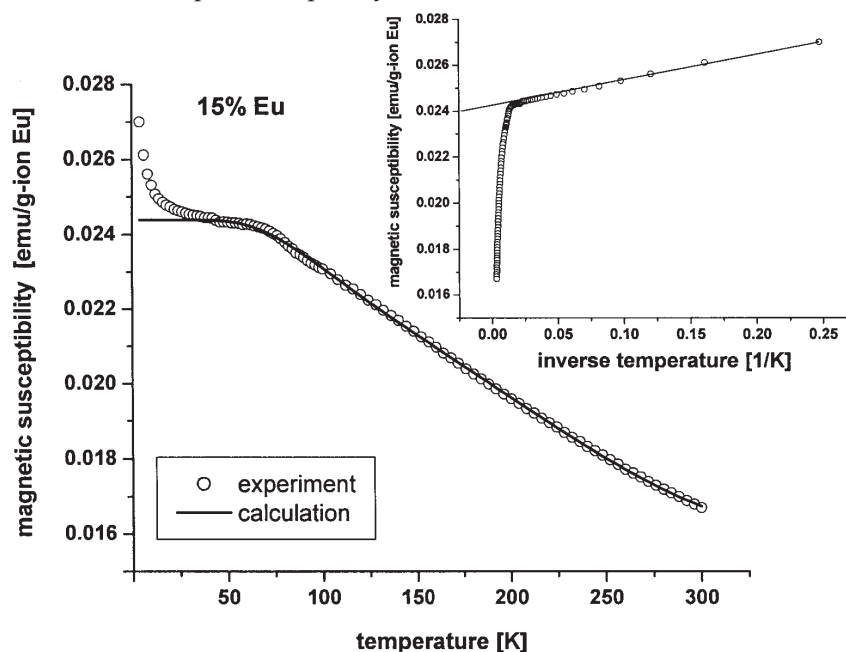

Fig. 3. Temperature dependence of the magnetic susceptibility of SiO$_2$: Eu^{3+} with 15 at.% of Eu (open points), calculation using Eq. (1) (solid line). Inset: Magnetic susceptibility $v.s.$ inverse temperature shows the paramagnetic contribution of impurities at lower temperatures.
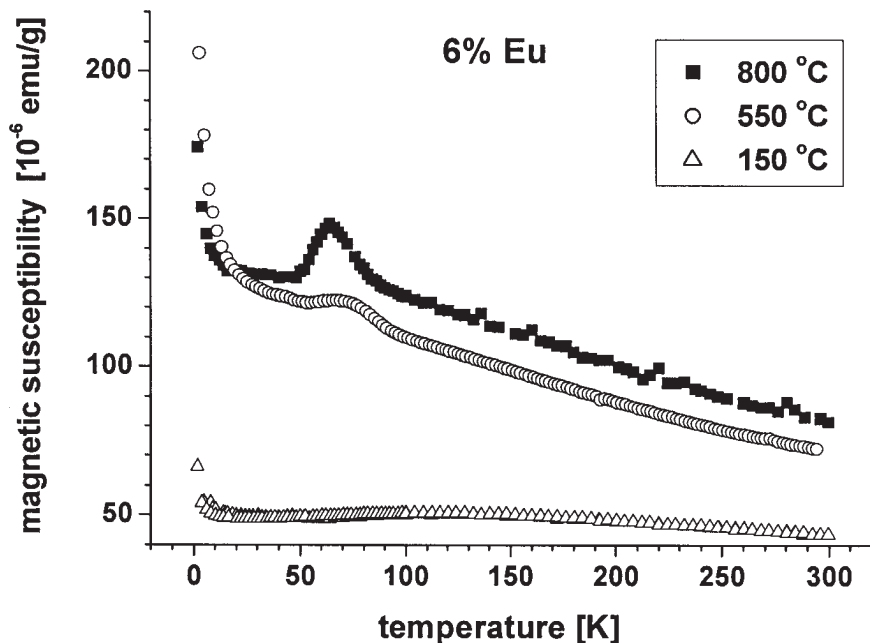
Fig. 4. Temperature dependence of the magnetic susceptibility of SiO_2: Eu^{3+} with 6 at.% of Eu after heat treatment at several temperatures.

and 452.4 cm^{-1} for $^7F_1$, and 1033.2 cm^{-1} for the barycentre of $^7F_2$. The calculation is depicted in Fig. 3, where a good agreement with the experimental data can be observed, except at the lower temperatures, where the contribution of paramagnetic impurities was significant. The inset of Fig. 3 shows the linearity of the magnetic susceptibility with the inverse temperature below 40 K, which supports the proposition concerning the contribution of paramagnetic impurities. Similar results were obtained for the samples with 3 at. % and 6 at.% Eu concentrations.

The effect of sample heating (for the 6 at.% Eu sample) on the magnetic susceptibility behavior is shown in Fig. 4. There is a visible peak in the susceptibility, appearing at about 70 K, for the samples treated at 823 and 1073 K for a period of 8 h. It should be noticed that the peak became more pronounced for higher heating temperatures and that the gram susceptibility was also increased. The position of the peak could indicate the presence of ferromagnetic EuO, which was possibly formed during sample heating in air. The Curie point for bulk EuO was reported to be T_C = 77 K.[12] The somewhat lower values of the EuO phase transition temperature obtained with the present samples can be explained as being the consequence of their nanoparticle form. In the same way, the increased susceptibility values for the heated samples can also be explained, as the heating procedure leads to an increase of the overall particle size.

CONCLUSION

SiO$_2$: Eu^{3+} nanopowders with different concentration of europium (3 at. %, 6 at %, 15 at.%) were syhtesized by a hydrothermal method. Details of the procedure are given in brief as well as the results of TEM and light scattering characterization concerning the size of the particles. Both methods confirmed that the size of the particles was between 5–10 nm with a very narrow size distribution and an average size of 7.5 nm. DC Magnetic measurements, conducted in zero field cooled (ZFC) and field cooled (FC) regimes, showed bifurcation between the ZFC and FC branches for all the samples. The magnitude of the bifurcation between the ZFC and FC branches for all the samples. The magnitude of the bifurcation and irreversibility temperature (T_{irr}) increased with increasing Eu^{3+} concentration, indicating a strengthening of the interparticle interactions. The magnetic susceptibility increased with increasing europium concentration. At temperatures below 80 K, all the curves showed a plateau, which revealed the expected behavior of Eu^{3+} ions. At temperatures below 40 K, contributions of paramagnetic impurities (about 10 pmm) obeying Curie law was detected. The magnetic susceptibility was calculated using the Van Vleck equation for Eu^{3+}. For the calculations, spectroscopically determined energy levels for the triplet $^7F_1$ and the barycentre of $^7F_2$ were used. All higher levels could be neglected within the experimentally employed temperature range $4\,K \leq T \leq 300$ K. After heat treatment, the susceptibility showed a peak at about 70 K, corresponding to ferromagnetic EuO which appeared due to a very small degree of oxidation of europium. The Curie temperature for bulk EuO is $T_C = 77$ K and the somewhat lower value is a consequence of the nanosize of the particles.

И З В О Д

МАГНЕТНЕ ОСОБИНЕ НАНОСТРУКТУРНИХ SiO$_2$: Eu^{3+} ПРАХОВА

ВОЈИСЛАВ СПАСОЈЕВИЋ, МИРОСЛАВ ДРАМИЋАНИН, ВУКОМАН ЈОКАНОВИЋ[1], ЖЕЉКА АНДРИЋ, ЈОВАН БЛАНУША, ВЛАДАН КУСИГЕРСКИ, МИОДРАГ МИТРИЋ, МАРИН ТАДИЋ и АНА КАПИЧИЋ

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Наночестице SiO$_2$: Eu^{3+} са неколико концентрација еуропијума (3 ат. %, 6 ат. % и 15 ат. %) су добијене хидротермалном методом. Помоћу ТЕМ микроскопије и методе расејања светлости нађено је да величине честица чине уску дистрибуцију од 5 – 10 nm, док дифракција зрачења показује да су узорци аморфни. Температурска зависност магнетне сусцептибилности показује типично понашање за Eu^{3+} јон са платоом испод 60 K и порастом магнетне сусцептибилности са концентрацијом еуропијума. Раздвајање ZFC и FC грана се повећава са порастом концентрације еуропијума што указује на постојање интеракције између честица. На температурама испод 40 K примећује се допринос парамагнетних примеса који се може описати Curie-овим законом. Термичко третирање узорака на 823 и 1073 K доводи до повећавања магнетне сусцептибилности. После термичког третмана примећује се мали максимум у сусцептибилности на температуре 70 K што индицира присуство мале количине феромагнетног EuO.

REFERENCES

1. G. Cao, *Nanostructures & Nanomaterials: Synthesis, Properties & Applications*, Imperial Colege Press, London, 2004
2. *Nanoscale Materials in Chemistry*, K. J. Klabunde, Ed., Wiley, New York, 2001, p. 292
3. *Characterization of Nanophase Materials*, Z. L. Wang, Ed., Wiley, New York, 2000, p. 406
4. S. Hazarika, S. Rai, *Opt. mater.* **27** (2004) 173
5. A. S. Borovik-Romanov, N. M. Kreines, *Z. Teor. Eksp. Fiz.* **6** (12) 790
6. A. Lempicki, A. J. Wojtowich, C. Brecher, in *Wide-gap limunescent Materials: Theory and Applications*, S. R. Rotman, Ed., Kluwer, MA, 1996
7. D. Hreniak, E. Zych, L. Kepinski, W. Strek, *J. Phys. Chem. Solids* **64** (2003) 111
8. M. Cannas, R. Boscaino, F. M. Geraldi, M. Leone, *J. Non-Cryst. Solids.* **216** (1997) 99
9. A. V. S. Amaral, L. D. Carlos, V. de Zea Barmudes, *IEEE Transaction on Magnetics* **37** (2001) 2935
10. J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities*, Oxford University Press, Oxford, 1932
11. C. K. Dahmouche, L. D. Carlos, V. de Zea Bermudez, R. A. Sà Ferreira, A. Passos de Almeida, C. V. Santilli, A. F. Craevich, *Phys. Rv. B* (submitted for publication)
12. M. M. Schieber in *Selected Topics in Solid State Physics (Experimental Magnetochemistry)*, E. P. Wohlfarth, Ed., North Holland Publishing Company, Amsterdam, 1967, p. 298.