Proceedings of the 15th Czech and Slovak Conference on Magnetism, Košice, Slovakia, June 17–21 2013

Ordered Nanoporous Silica Modified with Nanoparticles of Lanthanide Oxides

A. Zeleňáková[a,*], O. Kapusta[b], V. Zeleňák[b]

[a]Institute of Physics, Faculty of Sciences, P.J. Šafárik University, Park Angelinum 9, 041 54 Košice, Slovakia

[b]Institute of Chemistry, Faculty of Sciences, P.J. Šafárik University, Moyzesova 11, 041 54 Košice, Slovakia

Lanthanide oxide nanoparticles were encapsulated inside of pores of highly ordered periodic silica of SBA15 type with hexagonal symmetry. The magnetic properties of such nanoperticles were investigated. The structural characterization using the SAXS, XANES, XRD, and N_2 adsorption measurements showed the presence of lanthanide oxides of Ln_2O_3 type (Ln=La, Pr, Nd, Gd, Eu), with the size of about 5 nm, incorporated in nanoporous channel system. Their magnetic properties, studied by SQUID apparatus, showed the weak antiferromagnetic ordering at 2 K in the nanocomposites Gd_2O_3@SBA15, Pr_2O_3@SBA15 and Nd_2O_3@SBA15. This behaviour of the nanoparticles is caused by blocking process of magnetic moments, which at 300 K exhibit the superparamagnetism, evidenced from ZFC/FC magnetization.

DOI: 10.12693/APhysPolA.126.218

PACS: 75.75.Fk, 81.05.Rm, 75.40.Cx

1. Introduction

Lanthanide metals have attracted much attention as suitable magnetic materials for a wide range of technological and biomedical applications [1]. For example, Gd and its compounds are of current interest as magnetic resonance contrast media, therapeutic agents in tumour treatment and drug delivery [2]. The well-defined shape and size of nanoparticles is necessary for applications. One of the promising methods of packing the magnetic nanoparticles into the ordered structures with the possibility of controlling their size and shape is the nanocasting approach [3].

In our work, we have studied the magnetic properties of Ln_2O_3 nanoparticles (Ln = La, Pr, Nd, Gd, Eu) prepared inside a periodic porous silica matrix SBA-15, which served as a nanosized "mold" with regular hexagonal symmetry.

2. Experimental

Mesoporous material SBA-15 was synthesized according to Zhao, et al. [4]. Nanoparticles were prepared using wet-impregnation method, where the mesoporous silica template was used for the growth of the nanoparticles. The structure of prepared samples was characterized by SAXS (Small angle X-ray scattering), XANES (X-ray Near Edge Spectroscopy), powder X-ray diffraction and by using the method of N_2 adsorption/desorption.

Magnetic properties were investigated using a MPMS-XL5 (Quantum Design) apparatus in the external dc field of up to 5 T and in the temperature range of 2 – 300 K.

3. Results and discussion

N_2 sorption measurements, Fig. 1, show the decrease of the specific surface area S_{BET} from around 720 m^2/g, observed for a blank mesoporous SBA15 matrix, to about 32 – 46 m^2/g for Ln_2O_3@SBA15 nanocomposites, due to the confinement of lanthanide oxide nanoparticles into mesoporous system (Table). This significant decrease of surface area reflects the filling of pores of SBA15 matrix with nanoparticles. Moreover, the filling of pores with nanoparticles was further reflected by the decrease of pore size D_p from around 5.9 nm for blank SBA15 matrix to 5.2 – 5.4 nm for composite Ln_2O_3@SBA15 samples.

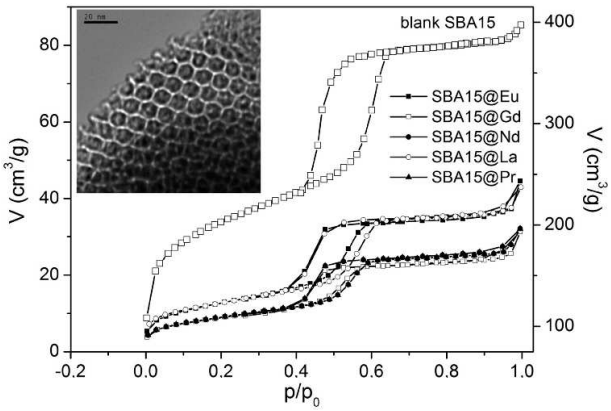

Fig. 1. Nitrogen adsorption/desorption isotherms of blank mesoporous silica (SBA15) and composite samples, containing lanthanide oxide nanoparticles at relative pressure. In the inset is the HRTEM picture of silica matrix.

The method of small angle X-ray scattering (SAXS) confirmed the hexagonal *p6mm* symmetry of the blank mesoporous SBA15 silica matrix as well as of the composites. This showed that during the preparation of Ln_2O_3@SBA15 nanocomposites no destruction or disordering of mesoporous hexagonal structure took place.

*corresponding author; e-mail: adriana.zelenakova@upjs.sk

TABLE

Structural and magnetic parameters.

Sample	S_{BET} (m^2/g)	D_p (nm)	θ (K)	μ (μ_B)	M_S ($A \cdot m^2 kg^{-1}$)
SBA15	719.4	5.9	-	-	-
Gd_2O_3@SBA15	32.3	5.3	-2.24	6.20	60.1
Eu_2O_3@SBA15	46.0	5.3	-252.93	1.74	1.1
Pr_2O_3@SBA15	33.0	5.5	-24.01	1.92	5.8
Nd_2O_3@SBA15	33.0	5.5	-33.96	4.83	16.5
La_2O_3@SBA15	45.2	5.7	-	-	-

Structural characterisation was further made by XANES and XRD measurements. XANES spectra show the presence of lanthanide oxides of Ln_2O_3 type in all modified samples. In Fig. 2 the representative spectra of Gd-based nanocomposite are presented. The XANES peak, measured at Gd L_3 absorption edge, is narrower in the prepared sample than in the reference foil. This effect was observed in all lanthanide samples and could be explained by the nanocrystalline character of composite samples (about 5 nm) in opposite to μm size of reference foil [5].

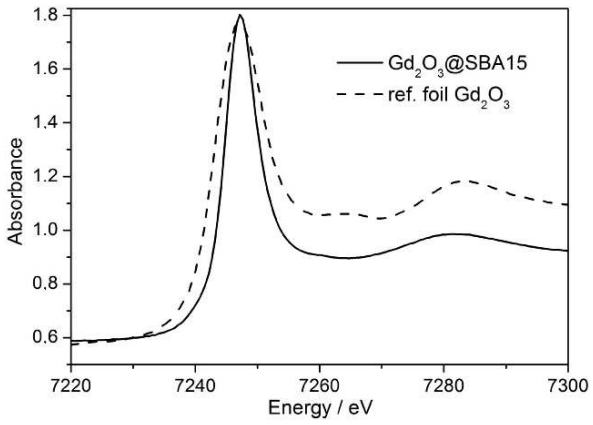

Fig. 2. XANES spectra for nanocomposite sample Gd_2O_3@SBA15 and reference foil.

The magnetic properties of all lanthanide nanocomposite samples were investigated using the measurements of the temperature- and the field-dependences of magnetization. As it is seen from Fig. 3, the samples with Gd, Nd, Pr and Eu exhibit the reversible linear magnetization curve at 300 K, predicting the paramagnetic behaviour, while the La-based nanocomposite is purely diamagnetic, as expected. The shape of the magnetization curves at 2 K, especially in Gd nanocomposite, implies the presence of magnetic interactions at low temperatures. The dc susceptibility studies and their analysis using the Curie-Weiss law show the presence of weak antiferromagnetic interactions (see value of Weiss constant θ in Table). In the samples with Gd_2O_3 and Nd_2O_3 nanoparticles inside the porous silica matrix, the clearly evident superparamagnetic relaxation at high temperatures and blocking process of magnetic moments at low temperatures was observed from ZFC/FC curves and curvature of M vs. H. Therefore we have analysed experimental data using Langevin law and calculated values of magnetic moments, which are given in the Table. The most interesting magnetic properties among all studied Ln_2O_3 nanocomposites exhibited the Gd_2O_3-containing sample, because of the high value of magnetic moment, high saturation magnetization M_S and the presence of superparamagnetism (existence of blocking temperature T_B around of 2.5 K). In the sample with Gd_2O_3 the measured value of magnetic moment μ of 6.20 μ_B is lower than the calculated theoretical value of 7.94 μ_B, which is due to nanosized character of the sample [2].

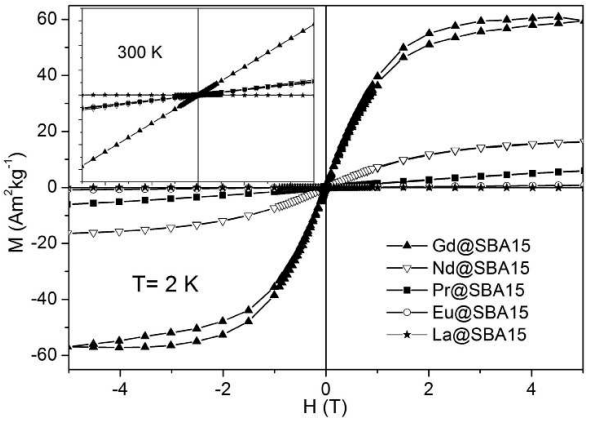

Fig. 3. M vs H of studied samples at 2 K and 300 K (inset).

4. Conclusions

We have prepared lanthanide oxide based nanoparticles, growth of which was controlled by the rigid nanoporous silica template. The encapsulation of nanoparticles inside pores of SBA15 silica and their phase composition was confirmed by structural characterisation. Magnetic study showed the weak antiferromagnetic ordering at low temperature in Ln_2O_3@SBA15 samples. Such long-range ordering at 2 K can be explained by the existence of superparamagnetic particles, which magnetic moments are blocked below critical temperature.

Acknowledgments

This work was supported by the VEGA No. 1/0583/11 project and the grants APVV-0222-10 and APVV-0132-11. The authors (A.Z and V.Z) would like to thank DESY/HASYLAB project under No. I-20110282 EC.

References

[1] S. Wang, *Micr. Mesop. Mat.* **117**, 1 (2009).

[2] Y. Lin, Y. Hung, J. Su, R. Lee, C. Chang, M. Lin, C. Mou, *J. Phys. Chem. B* **108**, 15608 (2004).

[3] M. Ballem, F. Soderlind, P. Nordblad, P.O. Kall, M. Oden, *Micr. Mesop. Mat.* **168**, 221 (2013).

[4] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, *J. Am. Chem. Soc.* **120**, 6024 (1998).

[5] L.X. Chen, T. Liu, M.C. Thurnauer, R. Csencsits, T.J. Rajh, *J. Phys. Chem. B* **106**, 8539 (2002).