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Magnetic susceptibility and surface properties of $EuAlO_3$ nanocrystals

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ABSTRACT

Nanocrystalline single-phase europium aluminate ($EuAlO_3$) has been synthesized by modified sol-gel method with a new complexing agent – malic acid. The material has been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive analysis (EDS). The nanoparticles have an average size of 50 nm, a density of 7.01 g/cm^3 at T = 293 K, a specific surface area 15.0 m^2/g and form agglomerates. The binding energies of core-level electrons of europium, aluminium, and oxygen in $EuAlO_3$ have been found by means of X-ray photoelectron spectroscopy (XPS) and compared with the values for the respective elements. The temperature dependence between 300 K and 2 K of the experimental AC magnetic susceptibility of $EuAlO_3$ nanocrystals has been determined and compared with the theoretical one for Eu^{3+}. It has been confirmed that the material is paramagnetic in the entire temperature range.

1. Introduction

Complex-oxide nanoparticles are expected to exhibit photocatalytic properties, energy upconversion, self-decontamination and antifungal capacities [1–3]. These materials arouse interest for fundamental research and technological applications. Films produced via the sol–gel-method and activated with lanthanide ions have been used in 2D-optical systems as wave guides and coatings; sol–gel powders and transparent nanomaterials have been applied also in 3D-optical materials [3].

Europium aluminate ($EuAlO_3$) forms in the system europium sesquioxide–aluminium oxide. It melts at T = 2380 K, undergoes a phase transition from an orthorhombic to a rhombohedral structure at a temperature of 1280 K and has a high refractive index; the solid state reaction that results in $EuAlO_3$ should be performed at 1896 K [4,5].

The measurement of anisotropy in the DC magnetic susceptibility of $EuAlO_3$ single crystal has been performed between 1.5 and 300 K. The same experiments have been intended to prove the existence of a broad maximum in χ at T = 60 K predicted theoretically in the temperature dependence of the magnetic susceptibility of the europium aluminium garnet [6].

Single-phase lanthanide orthoaluminates ($LnAlO_3$, Ln = La–Ho, except Ce and Pm) have been prepared by the polymer complex method with citric acid and ethylene glycol [7]. In the same study, orthoaluminates of Er to Lu have been obtained only with by-products.

The aim of this paper is to report for the first time the following results:

(i) a modified sol–gel synthesis of europium monoaluminate using *in situ* polyesterification between malic acid and 1,2-ethanediol.
(ii) XPS studies and temperature dependence of the magnetic susceptibility of nanocrystalline $EuAlO_3$, as obtained by the method above.

2. Materials and methods

2.1. Preparation

The sol–gel syntheses are based on modifications of Pechini's method [8] and yield quality materials provided by the achieved homogeneity during the synthesis.

Europium monoaluminate samples were prepared by an aqueous sol–gel process. The gel was obtained with stoichiometric amounts of analytical-grade Eu_2O_3 ("Fluka", 99.99%), $Al(NO_3)_3{\cdot}9H_2O$ and malic acid (hydroxybutanedioic acid, $HOOCCH_2CH(OH)COOH$). In the sol-gel procedure, 2.9912 g Eu_2O_3 was first dissolved in aqueous solution of malic acid (0.2 mol/dm^3) at 338 K. To this clear solution, 6.3776 g $Al(NO_3)_3$ dissolved in 200 cm^3 bidistilled water was added. The exact molar ratios are as follows: $Eu_2O_3{:}Al(NO_3)_3{\cdot}9H_2O = 1{:}2$, corresponding to $Eu_2O_3{:}Al_2O_3 = 1{:}1$.

The mixture was further stirred at the same temperature for 1.5 h. In a following step, 6 cm^3 1,2-ethanediol was added. The solution was then concentrated (about 5 h) by slow evaporation at 343 K under stirring until a transparent yellowish gel was obtained. The gel was transferred in a Pt crucible and oven-dried (383 K) for 2 h. The gel powder was ground in an agate mortar and preheated for 3 h at 1073 K in air. The gel is very combustible, especially between 373 K and 673 K. A thermal decomposition of the ligands under release of gases takes place between 383 K and 1073 K. After an inter-

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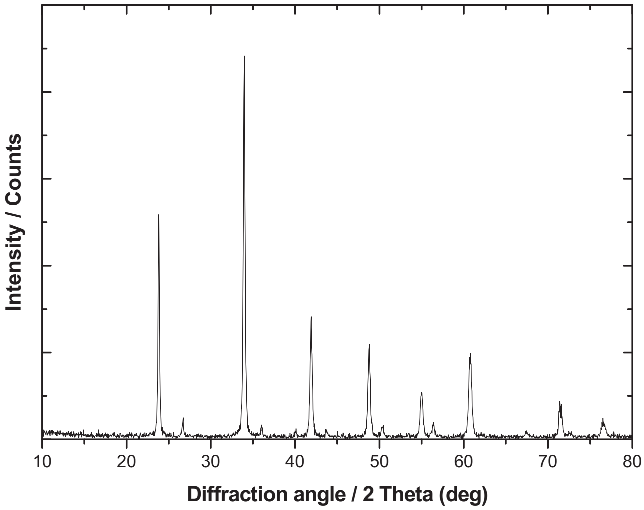

Fig. 1. X-ray diffraction pattern of $EuAlO_3$: (a) sample obtained by the sol–gel method described above; (b) vertical lines: reference sample, file: 00-030-0012 (I).

mediate grinding, the yellow powder was additionally sintered in air for 8 h at 1223 K.

The precursor gel yields perovskite aluminates as end products [9,10]. The temperature of final annealing was chosen to be below the reported orthorhombic to rhombohedral phase-transition temperature.

The partial crystallization of the metal salt was avoided with malic acid, since it contains complex-forming carboxyl and hydroxide groups. Our experimental results on other lanthanide aluminates have supported the use of this complexing agent for a low-temperature synthesis of complex-oxide nanoparticles.

2.2. *Experimental techniques*

Powder X-ray diffractogramme was registered in the angular range from 10° to 80° (2 theta) values of the angle 2θ with a constant step 0.04° and counting time 1 s/step on Bruker D8 Advance diffractometer with Cu Kα radiation and SolX detector. The obtained diagram was evaluated by means of the Diffrac*plus* EVA package [11].

The surface morphology was probed by scanning electron microscope PHILIPS 515 with detection for secondary electron imaging (SEI), backscattered and cathode luminescence microscopy at *max* 30 kV.

Energy-dispersive analysis was performed under the following conditions: accelerating voltage 20.00 kV, uncoated sample, all elements analyzed, standards: EuF_3, for Eu, and SiO_2, for O, optimization element: Ni. The third element, Al, was evaluated by the difference to 100%.

X-ray photoelectron spectra were obtained on a ESCALAB MkII (VG Scientific) spectrometer. C 1s, O 1s, O 2s, Al 2s, Al 2p, Eu 3d, Eu 4d, Eu 5s, and Eu 5p electron core levels were excited with Al Kα and Mg Kα radiation. The pressure was 6.7×10^{-7} Pa in the UHV chamber; all spectra were calibrated with C 1s line reference at 285.0 eV. The total instrumental resolution was ≈1 eV.

The AC magnetic susceptibility was measured in the temperature range 2–300 K with a PPMS – 9 (Physical Properties Measurement System), Quantum Design. The parameters of the AC magnetic field were 1 kHz and 2.387×10^3 Am^{-1} (=30 Oe) [12].

3. Results and discussion

3.1. *Powder X-ray diffraction*

The X-ray diffractogramme of $EuAlO_3$ obtained by the method described above is presented in Fig. 1. The diffraction pattern belongs to the orthorhombic europium monoaluminate; the peaks are sharp and well resolved.

Phase identification was performed with the Diffrac*plus* EVA using ICDD-PDF-2 Database, file 00-030-0012(I). The vertical lines correspond to the positions and the intensities of the reference sample; temperature $T = 298$ K. Phase analysis has confirmed that europium monoaluminate exists as a single-phase.

Mean crystallite size of 50 ± 1 nm was determined with the Topas-4.2 software package using the fundamental parameters peak shape description including appropriate corrections for the instrumental broadening and difractometer geometry.

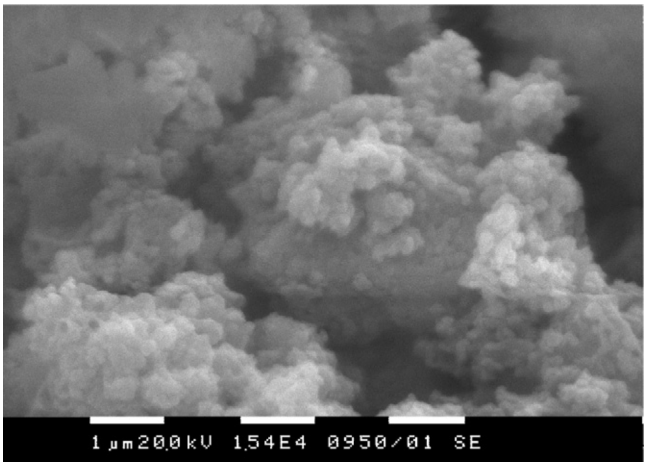

Fig. 2. Scanning electron micrograph of $EuAlO_3$ sample.

The pyknometric density $\rho = 7.01$ g/cm^3 of $EuAlO_3$ was determined at $T = 293$ K; which is in good agreement with that for the bulk crystal ($\rho = 7.04$ g/cm^3 [1]).

The specific surface area of the powder has been determined at liquid–nitrogen temperature and found 15.0 m^2/g, which is a moderate value with respect to the final annealing temperature. Since the latter is relatively high, we should expect that the specific surface area to be low. The specific surface area of the $EuAlO_3$ determines its surface properties and is related to its catalytic capacity.

3.2. *SEM studies*

A typical scanning electron micrograph of $EuAlO_3$ is shown in Fig. 2. The surface morphology reveals small portion of nearly spherical particles, coexisting with clusters of individual particles. All surface concentrations obtained by the EDS measurements correspond to the composition $EuAlO_{2.93}$, with a standard deviation ±0.02 mol%.

3.3. *X-ray photoelectron spectra*

XPS is an appropriate method for probing the atomic environment located close (*ca.* 5–10 nm) to the surface. The information obtained includes binding energies that are related to the magnitude of the chemical bonding [13].

Electron binding energies (BE) for Eu, Al and O atoms have been registered as peaks in the survey spectrum (Fig. 3a), from 0 to 1200 eV. The experimental values were compared with the respective reference values [14].

The depth of penetration in the surface XPS measurements depends on the energy of the core-level electrons and is supposed to reach *ca.* 3–5 nm [15].

Here, we report the BE-values (in increasing order) of Eu 5p, Eu 5s, Al 2p, Al 2s, Eu 4d, O 1s, and Eu 3d. Our measured value of the Al 2p signal was found 73.6 eV (Fig. 3c). The electron core levels of Eu 4d and Al 2s are well resolved. The core-level peak of O 1s is located at 529.6 eV as a single, narrow peak (Fig. 3d). Such a feature is interpreted as an evidence for the existence of one type of oxygen, whereas the numerical value (529.9 eV) is very close to that one for more ionic compounds, including europium oxo-compounds of the type EuX_mO_n [15]. The experimental peaks of Eu 3d core electrons are distinctly found as a pair at 1133.0 eV and 1162.9 eV (Fig. 3b).

The chemical shifts presented in the last column of Table 1 are small and positive in sign, except those for Eu 5p and O 1s. The former is zero within the experimental resolution but the latter

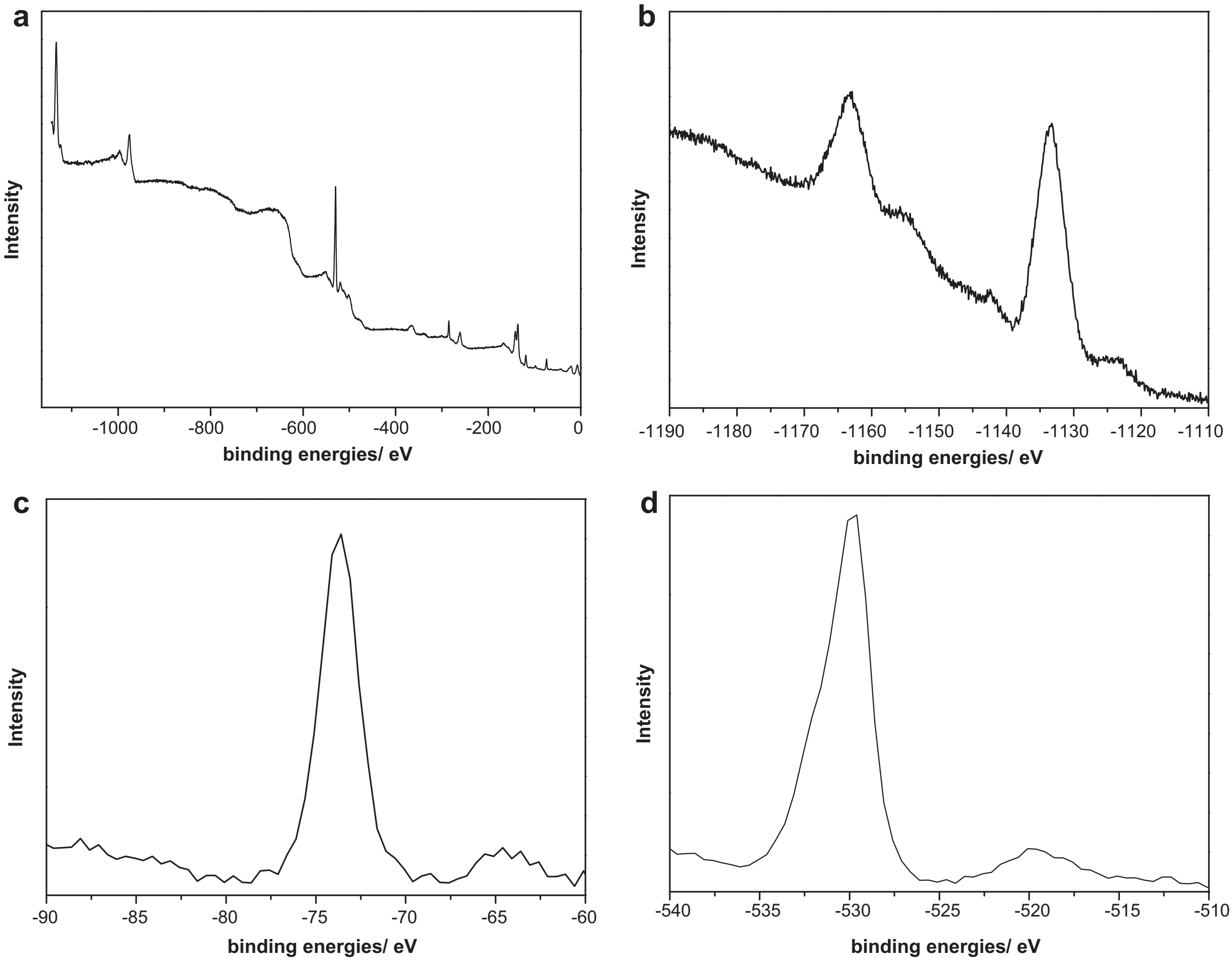

Fig. 3. (a) Survey X-ray photoelectron spectrum of nanocrystalline $EuAlO_3$; (b) Eu 3d XPS band in $EuAlO_3$; (c) Al 2p XPS band in $EuAlO_3$; (d) O 1s XPS band in $EuAlO_3$.

could be explained with a higher kinetic energy (negative shift) of these core electrons with respect to the reference. Unlike oxygen, almost all core-level electrons of Eu and Al are in states of lower kinetic energy, thus producing positive shifts of the BE. This difference reflects certain degree of electron mobility of surface oxygen in the $EuAlO_3$ nanocrystals. Our experimental BE for O 1s in other nanocrystalline lanthanide aluminates also have negative shifts. These facts correspond to almost entirely ionic Eu–O and Al–O bonds.

3.4. Magnetic susceptibility

The ground level of $Eu^{3+} = [Xe]\ 4f^6$ is $^7F_0$. Since $J = 0$, the same level is nonmagnetic, i.e. does not contribute to the magnetic susceptibility x derived within the free-ion approximation for trivalent lanthanides with J being a good quantum number:

$$\chi_m = \left(\frac{NAg^2\beta^2}{kT}\right) J(J+1) \tag{1}$$

where g is Landé factor, β is the Bohr magneton (B.M.), kT is the thermal energy. As a singlet, $^7F_0$ is also not affected by the crystal field. The excited levels of Eu^{3+} above $^7F_0$ are $^7F_1$ and $^7F_2$. For $EuAlO_3$ single crystal they are located at about 370 cm^{-1} and 1000 cm^{-1}, respectively [8]. At $T = 298$ K, $kT = 207\ cm^{-1}$ and the triplet $^7F_1$ is therefore appreciably populated at ordinary temperatures. A magnetic field further admixes states with $J = 1$ and $J = 2$ and induces a magnetic moment in Van Vleck paramagnetism.

In the present study, the AC magnetic susceptibility of nanocrystalline europium aluminate has been measured between 2 and 300 K. Fig. 4 contains the results of the temperature dependence of both the real, χ'_m, and the imaginary, χ''_m, parts of the magnetic susceptibility; the subscript "m" designates "molar". It is seen that χ''_m is approximately zero without any hysteresis effect. It is noteworthy that the experimental data do not reveal any distinct, though flat, maximum in the vicinity of $T = 60$ K as found in the single-crystal $EuAlO_3$ [6].

The theoretical curve displayed in Fig. 4 has been calculated using Van Vleck's equation for molar magnetic susceptibility of

Table 1
Positions of core-level binding energies in nanocrystalline $EuAlO_3$.

Electron core level	Reference BE/eV [14]	Experim. BE/eV	Chemical shift/eV
Eu 5p	22	21.1	−0.9
Eu 5s	32	43.1	11.1
Al $2p_{1/2}$	72.9	73.6	0.7
Al $2p_{3/2}$	72.5		
Al 2s	118	118.6	0.6
Eu $4d_{3/2}$	133	135.6	2.6
O 1s	543.1	529.6	−13.5
Eu $3d_{5/2}$	1127.5	1133.0	5.5
Eu $3d_{3/2}$	1158.6	1162.9	4.3

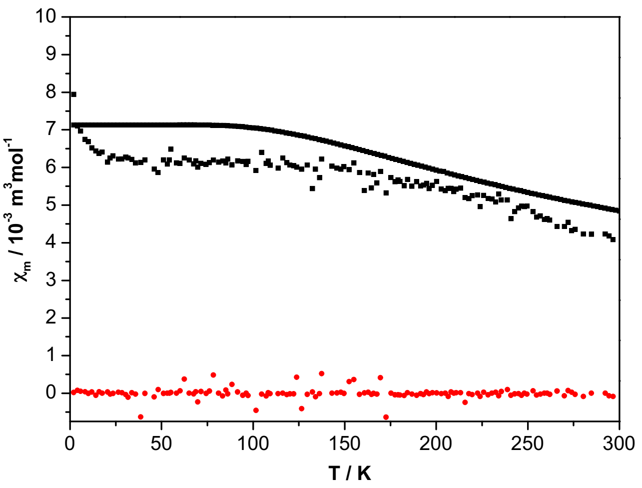

Fig. 4. Temperature dependence of the AC molar magnetic susceptibility of nanocrystalline $EuAlO_3$ (lower dotted curve-imaginary part χ''_m, upper dotted curve-real part χ'_m) and theoretical temperature dependence of the molar magnetic susceptibility of Eu^{3+} (top curve).

trivalent europium:

$$\chi_m = \frac{(0.1241/xT)[24 + (13.5x - 1.5)e^{-x} + (67.5x - 2.5)e^{-3x} + (189x - 3.5)e^{-6x}]}{(1 + 3e^{-x} + 5e^{-3x} + 7e^{-6x})}, \tag{2}$$

where $x = 418/T$, with screening constant $\sigma = 33$ and T designating temperature [16,17]. The experimental χ_m vs. T curve is lower than the theoretical χ_m vs. T but both change in the same manner within the interval 300–20 K. Below 20 K, however, there is a sharp increase of the real part χ'_m while the theoretical values remain constant. Similar temperature dependencies (both experimental and theoretical) have been observed with EuF_3 [18]. Since our complex-oxide nanomaterial has been synthesized under oxidizing conditions, we do not suggest that the increase of χ'_m below 20 K is due to the presence of Eu^{2+} ions. The latter are isoelectronic with Gd^{3+} ions, both with $[Xe]4f^7$ electron configuration for the ground state, the ground level being $^8S_{7/2}$; spin-only formula is applicable to these $4f^7$ ions [13]. Obviously, the real part of the AC magnetic susceptibility follows a Curie-type behaviour in the range 2–10 K; the temperature of magnetic transition "paramagnetic–antiferromagnetic" should be expected below 2 K.

Therefore, our experimental results point out the absence of magnetic cooperative effects within the studied temperature range. The magnetic behaviour of nanocrystalline $EuAlO_3$ corresponds effectively to a magnetically dilute system.

4. Conclusions

Malic acid facilitates a modified sol–gel preparation of nanocrystalline europium aluminate ($EuAlO_3$) as the calcination at 1223 K is below the phase-transition temperature, >1280 K [4] and that of 1896 K needed for the solid-state reaction to complete [2]. The XRD confirms single phase and the surface SEM micrographs reveal certain degree of agglomeration. The binding energies of Eu 5p, Eu 5s, O 2s, Al 2p, Al 2s, Eu 4d, O 1s, and Eu 3d electrons are chemically shifted in $EuAlO_3$ compared with the reference and correspond to ionic metal–oxygen bonds. The AC magnetic susceptibility measurements reveal that this nanomaterial is paramagnetic between 2 and 300 K with nearly Curie-type paramagnetism below 20 K.

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References

[1] T. Ghosh, S. Chhaparwal, in: W.A. Goddard III, D.W. Brenner, S.E. Lyshevski, G.J. Iafrate (Eds.), Handbook of Nanoscience, Engineering and Technology, CRC Press, Boca Raton, 2007, pp. 21–45.
[2] C.N.R. Rao, A.K. Cheetham, J. Mater. Chem. 11 (2001) 2887–2894.
[3] M. Bredol, M. Schem, Structured Sol–gel-films Doped with Lanthanides, Annual Report, 2006.
[4] P.A. Arsenev, L.M. Kovba, Kh.S. Bagdasarov, B.F. Dzhurinskii, A.V. Potemkin, B.I. Pokrovskii, F.M. Spiridonov, V.A. Antonov, V.V. Ilyukhin, Compounds of Rare Earth Elements. Systems with the Oxides of I–III Group Elements, Nauka, Moscow, 1983.
[5] L. Vasylechko, A. Senyshyn, U. Bismayer, Perovskite-Type Aluminates and Gallates, in: K.A. Gschneidner Jr, J.-C.G. Bünzli, V.K. Pecharsky (Eds.), Handbook on the Physics and Chemistry of Rare Earths, Elsevier, Amsterdam, 2009, pp. 113–295 (Muenster University of Applied Sciences, 2006).
[6] L. Holmes, R. Sherwood, L.G. Van Uitert, Phys. Rev. 178 (1969) 178–576.
[7] H. Takata, M. Iiduka, Y. Notsu, M. Harada, J. Alloys. Compd. 408 (2006) 1190–1192.
[8] M.P. Pechini, Method of Preparing Lead and Alkaline Earth Titanates and Niobates and Coating Method Using the Same to Form a Capacitor, US Patent 3,330,697, 1967, 6 pp.
[9] S. Mathur, M. Veith, H. Shen, S. Hüfner, M.H. Jilavi, Chem. Mater. 14 (2002) 568–582.
[10] M. Chroma, J. Pinkas, I. Pakutinskiene, A. Beganskiene, A. Kareiva, Ceram. Int. 31 (2005) 1123–1130.
[11] International Centre of Diffraction Data, ICDD: PDF-2, Record Number 00-030-0012.(I), 2009.
[12] S. Hatscher, H. Schilder, H. Lueken, W. Urland, Pure Appl. Chem. 77 (2005) 497–511.
[13] B. Glorieux, R. Berjoan, M. Matecki, A. Kammouni, D. Perarnau, Appl. Surf. Sci. 253 (2007) 3349–3359.
[14] G.P. Williams, Electron binding energies of the elements, in: D. Lide (Ed.), Handbook of Chemistry and Physics, CRC Press, Boca Raton, 2004–2005, pp. 10–209.
[15] F. Mercier, C. Alliot, L. Bion, N. Thromat, P. Toulhoat, J. Electron Spectrosc. Relat. Phenom. 150 (2006) 21–26.
[16] A.T. Casey, S. Mitra, in: E.A. Boudreaux, L.N. Mulay (Eds.), Theory and Applications of Molecular Paramagnetism, Wiley-Interscience, New York, 1976, pp. 278–316.
[17] J.H. Van Vleck, The Theory of Electric and Magnetic Susceptibilities, Oxford University Press, London, 1932.
[18] S. Kern, P.M. Raccah, A. Tveten, J. Phys. Chem. Solids 31 (1970) 2639–2642.