#### Journal of Alloys and Compounds 616 (2014) 556-568

Contents lists available at ScienceDirect

### Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom



## Electronic and crystal structure, EPR and magnetic investigations of YF<sub>3</sub>:1%RE (RE = Pr, Ho, Er and Tm) and LaF<sub>3</sub>:1%Pr nanocrystals



E. Talik<sup>a,\*</sup>, P. Zajdel<sup>a</sup>, A. Guzik<sup>a</sup>, D. Skrzypek<sup>a</sup>, L. Lipińska<sup>b</sup>, M. Michalska<sup>b</sup>

<sup>a</sup> Institute of Physics, University of Silesia, ul. Uniwersytecka 4, 40-007 Katowice, Poland <sup>b</sup> Institute of Electronic Materials Technology, ul. Wólczyńska 133, 01-919 Warszawa, Poland

#### ARTICLE INFO

Article history: Received 7 May 2014 Received in revised form 2 July 2014 Accepted 8 July 2014 Available online 16 July 2014

Keywords: Nanomaterials Yttrium compounds Phosphors

#### ABSTRACT

A new chemical synthesis route by a thermal decomposition of nitrates and acetates, preceded by solution displacement reaction, was successfully applied to obtain the YF<sub>3</sub>:1%RE (RE = Pr, Ho, Er and Tm) and LaF<sub>3</sub>:1%Pr nanocrystals. The samples were characterized by the following methods: X-ray diffraction, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), magnetic susceptibility thermal dependence measurements and electron paramagnetic resonance (EPR). The obtained YF<sub>3</sub>:1%RE (RE = Pr, Ho, Er and Tm) materials crystallized with orthorhombic symmetry, whilst LaF<sub>3</sub>:1%Pr exhibits hexagonal structure. Chemical composition determined by EDX, XPS and magnetic measurements was close to nominal formula. SEM images show the nanometric size of the grains. Surface contamination can be suggested to be responsible for the deterioration of the optical properties of the composites.

© 2014 Elsevier B.V. All rights reserved.

#### 1. Introduction

Fluoride materials are useful as crystalline matrices for rare earth ions which are popular activators in optoelectronics [1]. YF<sub>3</sub> belongs to the group of fluoride crystals widely studied for years, as an attractive host for active ions emitting in the UV and visible spectral range. In general, the attractiveness of fluorides results from their low phonon energies, good chemical stability and excellent optical properties [2]. Recently, the set of active oxide and fluoride nanopowders, obtained by a sol-gel method has been characterized by means of laser spectroscopy [3]. In particular – the emission and excitation spectra have been investigated together with fluorescence dynamics profiles, which in turn enabled optimization of developed manufacturing technology. Improved polymer composites, based on Polymethyl methacrylate (PMMA) doped with LaAlO<sub>3</sub>:Pr<sup>3+</sup> and YF<sub>3</sub>:Pr<sup>3+</sup> nanocrystallites, have been obtained and characterized in respect of their luminescent properties in the visible spectral range. The results confirmed that, in general, LaAlO<sub>3</sub>:Pr<sup>3+</sup> nanocrystallites incorporated into a polymer matrix maintained their original optical properties, both with respect of emission characteristics and fluorescence kinetics behavior. This suggests that the active ions were effectively shielded from the interactions with the phonons of PMMA matrix, keeping the luminescent and lasing potential of the crystalline active medium combined with all advantages of the polymer host. In contrast YF<sub>3</sub>:  $Pr^{3+}$  composites exhibited decreased luminescence intensity and significant shortening of the fluorescence lifetime. This may be interpreted in terms of impurities in the polymer matrix (for example the presence of OH<sup>-</sup> groups). However, given the excellent luminescent properties are maintained in the LaAlO<sub>3</sub>:  $Pr^{3+}$  composite materials this argument seems unlikely. In order to fully understand these materials further studies are essential. What is important, unlike in the case of bulk single crystals, the manufacturing of fluoride nanopowders is relatively easy and does not require a fluorinating atmosphere [4].

The aim of this work is characterization of the  $YF_3:1\%RE$  (RE = Pr, Ho, Er and Tm) and LaF<sub>3</sub>:1%Pr nanocrystals obtained by new chemical synthesis – a thermal decomposition of nitrates and acetates, preceded by solution displacement reaction for the above mentioned applications.

#### 2. Experimental

The nanopowders were prepared using new chemical "wet" method as previously reported by us [3]. This simple and cost effective chemical synthesis is a two stage process. The first stage, carried out in solution, relies on a displacement reaction. Owing to good diffusion, the homogenization of compounds proceeds on molecular level. The next step is the thermal decomposition of nitrates and acetates contained within a concentrated solution. Crystallization of the fluoride takes place during the thermal treatment.

 $YF_3$ :1%RE materials were produced as follows. Firstly,  $Y_2O_3$  was dissolved in 0.4 mol/l acetic acid with rare earth oxides dissolved in diluted 0.5 mol/l nitric acid and NH<sub>4</sub>F in deionized water. RE oxides were 4N purity. All other chemicals were

<sup>\*</sup> Corresponding author. Tel.: +48 32 359 1187. *E-mail address: talik@us.edu.pl* (E. Talik).

analytical grade. Next, all solutions were combined together and mixed for 6 h at 70  $^{\circ}$ C using a magnetic stirrer with a stirring speed of 200 rpm resulting in slow evaporation of the mixture. The volume was decreased by approximately 5 times. The concentrated solution was subsequently dried at 150  $^{\circ}$ C for total removal of water. The dry powder was then calcined in air at 400  $^{\circ}$ C for 2 h.

The microstructural observations of the nanopowders as well as the microcompositional analysis were conducted using the JEOL-7600F scanning electron microscope.

Powder diffraction studies were performed on a PW1050 diffractometer in Bragg–Brentano geometry. A nickel filtered Cu K $\alpha_{1,2}$  source was used at 30 kV/ 30 mA. The patterns were collected in step mode in the angular range 10–135° with a step size of 0.02°. The powders were attached to a glass holder using double sided Scotch tape. One of the samples (1% Ho) had bad adhesion to the tape, which resulted in appearance of weak sample holder reflections at 14.1°, 17.0° and 25.6°.

The Rietveld method was applied to refine collected patterns using the Fullprof [5] software. As the width of the diffraction peaks was larger than the machine broadening, size and strain models appropriate for Laue classes mmm (size = 3, strain = 18) for YF<sub>3</sub> and 6/mmm (size = 12, strain = 19) for LaF<sub>3</sub> were added to the refinement. The anisotropic strain broadening was introduced in the quartic form [6] with symmetry constraints and adaptation for the Thompson, Cox and Hastings profile function [7,8]. The anisotropic Lorentzian size broadening was modeled using the spherical harmonic approach developed earlier for preferred orientation Jarvinen [9]. In all cases the ionic form factors of Y<sup>3+</sup>, La<sup>3+</sup> and F<sup>-</sup> were used in the refinement. Visualization of the structures was done using the VESTA software [10].

XPS spectra were obtained using a PHI 5700/660 Physical Electronics Photoelectron Spectrometer with monochromatized Al  $K_{\alpha}$  X-ray radiation (1486.6 eV). A hemi-spherical mirror analyzer measured the energy of electrons with an energy resolution of about 0.3 eV. The photoelectron emission from a surface area of 800 µm × 2000 µm was recorded. All measurements were performed in the conditions of 10<sup>-8</sup> Pa. In every case, a charge neutralizer was used because of the charge effect which occurs for non-conducting samples. The binding energy was determined with reference to the C1s component set at 285 eV. Each peak of the recorded spectrum is characteristic for a certain electron energy level of the measured elements. However, the measured binding energies are not absolutely constant but depend on the chemical environments, where functional groups are located due to modification of the valence electron binding energies are called chemical shifts. The angle between the X-ray source and the sample surface was 45°.

For XPS investigations, it is important to determine the relative concentrations of the various constituents. The Multipak Physical Electronics program enables quantification of the XPS spectra utilizing peak area and sensitivity factor. The standard atomic concentration calculation provides a ratio of each component to the sum of all elements taken into account in the data. Elemental identification, all elements except H and He are detectable with a detection limit of the order 0.1 at.% for good quality of the spectra. Only those elements are considered for which the specific line is clearly visible in the spectrum. For these lines, the background individually selected in the region limited to the particular line is subtracted and after that integration of the peak area is performed [11]. The Gaussian–Lorentzian functions were used to fit the XPS core level spectra.

Magnetic susceptibility was measured using the Quantum Design MPMS-XL-7AC SQUID magnetometer in the temperature range 2–400 K.

The EPR spectra were collected by the X-band spectrometer with a TE<sub>011</sub> rectangular cavity and 100 kHz field modulation, equipped with an Oxford Instruments ESR 910 helium flow cryostat. The microwave frequency was measured using a Hewlett Packard 534 microwave frequency counter.

#### 3. Results and discussion

#### 3.1. X-ray diffraction

The starting model for the refinement of the  $YF_3$ :RE samples was based on the structure obtained from neutron diffraction by Cheetham and Norman [12], using the *Pnma* space group (SG 62), which was earlier found by Zalkin and Templeton [13].

For the LaF<sub>3</sub>, two different space groups in ambient conditions have been reported: a centrosymmetric *P*-3c1 (SG 165) by Mansmann [14] or non-centrosymmetric *P*6<sub>3</sub>*cm* (SG 185) by De Rango et al. [15]. Both have successfully been applied to a neutron powder diffraction [16] but a later single crystal neutron diffraction study [17] found the latter to be more appropriate. The chosen space group *P*6<sub>3</sub>*cm* has a floating origin along the *c* crystallographic axis and one of the atomic coordinates had to be fixed, so following Gregson et al. [17], the *z* coordinate of La was set at *z*\_La = 0.25.

In the case of the YF<sub>3</sub> series, atoms were refined with individual isotropic atomic displacement parameters (*ADP*). The refinement of

the *ADPs* for the doped LaF<sub>3</sub> material resulted in negative values for fluorine, so in the final model a single isotropic *ADP* was used for all sites. Atomic parameters obtained in the refinement are collected in Tables 1 and 2 and agreement factors in Table 3.

The structures are in a good agreement with those published earlier by Cheetham and Norman [12] for YF<sub>3</sub> materials and by De Rango et al. [15] for LaF<sub>3</sub>. Additional phases were only observed in two samples: YF<sub>3</sub>:1%Pr has a single reflection located at *d*-spacing 3.02 Å and LaF<sub>3</sub>:1%Pr exhibits two broad peaks with inter-planar spacings of *d* = 3.35 Å and *d* = 2.91 Å. In the second one, the *d* = 3.35 Å impurity was overlapping with the 111 reflection, so for the final refinement the angular range (25.8–29.0) was excluded from fit. The single observed impurity line in YF<sub>3</sub>:1%Pr is likely a 200 reflection of trigonal PrF<sub>3</sub> (*P*-3c1, *a* = 7.08 Å, *c* = 7.24 Å) but there are no other peaks available to corroborate this finding. Additionally, the finely powdered samples had bad adhesion to the tape, which resulted in appearance of weak and broad sample holder reflections at 14.1°, 17.0° and 25.6° (see Supplementary Information).

The machine resolution was estimated from a reference pattern of silicon. The profile broadening of diffraction peaks due to size and strain was quantified using general models implemented in the Fullprof suite. The refinement, which included only the size broadening was found to be not sufficient for the YF<sub>3</sub> series, so strain broadening was introduced following the formalism proposed by Stephens [7]. Multiple strain parameters  $S_{HKL}$  quantifying strains and fluctuations of metric parameters had to be included:  $S_{400}$ ,  $S_{040}$ ,  $S_{004}$ ,  $S_{220}$ ,  $S_{202}$ ,  $S_{022}$  for the orthorhombic *Pnma* and  $S_{400}$ ,  $S_{004}$  and  $S_{112}$  for the hexagonal *P*6<sub>3</sub>*cm* refinements. The obtained results are summarized in Tables 4 and 5.

#### 3.1.1. Discussion of strain and size contributions to line profile

The increased surface to bulk ratio in small crystallites, together with the chemical pressure caused by different ionic radii, may lead to the appearance of internal stress in the studied materials. Therefore assessment of the size should be accompanied by the analysis of the strain. The coherent domain sizes (CDS) obtained from the Lorentzian component of the width, primarily varying as  $1/\cos\theta$ , were found to lie between 60 and 85 nm with small anisotropy of shape of less than 1 nm. During the refinement of strain - connected primarily with the Gaussian part varying as  $\tan \theta$  – two different behaviors were observed. No strain (within  $(3\sigma)$  was found in the hexagonal, Pr doped LaF<sub>3</sub>, despite a complete deviation of the refinement towards Lorentzian contribution, which had to be fixed at its maximum allowed value of 1. On the other hand, all samples based on YF<sub>3</sub> revealed a non-zero strain contribution (Table 4), which was mostly confined to the *h\_l* planes as evidenced by significant values of  $S_{400}$ ,  $S_{004}$  and  $S_{202}$  parameters

Atomic parameters of the doped  $\rm YF_3$  compounds. All uncertainties are statistical on  $1\sigma$  level.

Parameter	YF <sub>3</sub> :1%Pr	YF <sub>3</sub> :1%Ho	YF <sub>3</sub> :1%Er	YF <sub>3</sub> :1%Tm
Y position x z B <sub>iso</sub> (Å <sup>2</sup> )	4 <i>c</i> ( <i>x</i> , 1/4, <i>z</i> ) . <i>r</i> 0.36772(7) 0.05922(11) 0.66(2)	n. 0.36760(8) 0.05904(11) 1.06(2)	0.36768(6) 0.05892(8) 0.41(1)	0.36763(8) 0.05909(10) 0.59(2)
F1 position x z B <sub>iso</sub> (Å <sup>2</sup> )	4 <i>c</i> ( <i>x</i> , 1/4, <i>z</i> ) 0.5253(4) 0.5905(6) 0.94(6)	0.5225(4) 0.5914(6) 1.38(6)	0.5231(3) 0.5917(5) 0.70(5)	0.5232(3) 0.5924(6) 0.91(6)
F2 position x y z B <sub>iso</sub> (Å <sup>2</sup> )	8 <i>d</i> ( <i>x</i> , <i>y</i> , <i>z</i> ) 0.1636(3) 0.0628(2) 0.3766(4) 0.93(5)	0.1646(3) 0.0623(2) 0.3758(4) 1.209(5)	0.1648(3) 0.0626(2) 0.3753(4) 0.61(4)	0.1643(3) 0.0633(2) 0.3756(4) 0.80(5)

Atomic parameters of the doped LaF<sub>3</sub>. Single isotropic atomic displacement parameter was used for all atoms  $B_{iso} = 0.05(2)$ . Site symmetries for Wyckoff positions are: (2a) 3.m, (4b) 3.., (6c) ..m.

Parameter	La	F1	F2	F3	F4
Wyckoff	6c(x, 0, z)	2a (0, 0, <i>z</i> )	4b (1/3, 2/3, z)	6c(x, 0, z)	6 <i>c</i> ( <i>x</i> , 0, <i>z</i> )
х	0.6710(4)	0	1/3	0.277(2)	0.371(2)
Z	0.25(fix)	0.320(4)	0.212(3)	0.075(4)	0.421(3)

#### Table 3

Background corrected agreement factors of the refinement of all non-excluded points and global  $\chi^2$ . Names of the samples containing a second phase are marked in italics.

Sample	R-factor:	R-factors (%)					
	F	Bragg	р	wp	exp		
LaF <sub>3</sub> :1%Pr YF <sub>3</sub> :1%Pr YF <sub>3</sub> :1%Ho YF <sub>3</sub> :1%Er YF <sub>3</sub> :1%Tm	4.32 0.803 0.883 0.734 0.681	5.01 1.39 1.30 1.28 0.997	15.6 5.86 7.14 5.51 6.14	15.2 8.11 8.33 6.73 7.81	12.23 5.99 7.66 5.29 6.27	1.53 1.83 1.18 1.62 1.55	

(see Table 5). The largest value was found to be generated by the uniaxial strain along *c* axis ( $S_{004}$  factor), being around 10 times larger than the corresponding values along *a* ( $S_{400}$ ) and another order of magnitude higher than along *b* ( $S_{040}$ ). Additionally, it was accompanied by high absolute but negative values of  $S_{202}$ , which indicated anti-correlations of variations along the *a* and *c* axes.

To understand this fact, one must recall that the orthorhombic structure of  $YF_3$  is built of 9-fold coordinated Y atoms (Fig. 1), which are stacked in such a way that yttrium ions form flat layers perpendicular to the *b* axis (Fig. 2). In the *Pnma* space group only the F2 atom is allowed to move along the *c* axis (Table 1) (it is 1 out of 7 positional parameters), therefore any stress will be primarily relaxed by displacements in the *a*-*c* plane. This is in agreement with the result that the distortions are confined in *a*-*c* layers and the Y planes remain flat.

The planar alignment of the cations is also present in the LaF<sub>3</sub> (Table 2) (Fig. 3) but contrary to the YF<sub>3</sub> structure, there are 4 positional fluorine parameters, which can relax in the direction perpendicular to the layer. Therefore, the internal stress can be more easily accommodated by atomic displacements. However, this



**Fig. 1.** The main building blocks of  $YF_3$  structure are edge connected polyhedra. The grey vertices are occupied by F1 and pink by F2. Site symmetry is determined by mirror plane (green) perpendicular to axis *.b* (*m.*). There are 8 Y–F distances close to 2.3 Å with one longer around 2.5 Å. The values given in the picture are calculated for lattice parameters of YF<sub>3</sub>:1%Tm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

comes at a cost of the non-physical values of the atomic displacement parameters (*ADP*) obtained in the refinement of LaF<sub>3</sub>, when each site is treated separately. The physical and stable solution was possible only with single spherical *ADP* for all atoms.

It must be noted that, in a general case, the profile broadening model proposed by Stephens [7] allows for mixing  $1/\cos\theta$  and  $\tan\theta$  contributions to Lorentzian and Gaussian shapes by refining one

#### Table 4

Main profile parameters of the compounds in study. CDS is a coherent domain size estimated from profile broadening with the anisotropy given in curly braces. All reported uncertainties are statistical on  $1\sigma$  level.

Sample	Lattice parameter	r (Å)		$V(Å^3)$	CDS (nm)	Max. strain (%)
	a	b	С			
LaF <sub>3</sub> :1%Pr	7.1868(1)	-	7.3541(1)	328.95(1)	81{1}	3(1)
YF <sub>3</sub> :1%Pr	6.3606(1)	6.8633(1)	4.4035(1)	192.23(1)	63{1}	19(7)
YF3:1%Ho	6.3576(1)	6.8602(1)	4.4019(1)	191.98(1)	70{1}	15(6)
YF <sub>3</sub> :1%Er	6.3554(1)	6.8580(1)	4.4045(1)	191.97(1)	85{1}	16(6)
YF <sub>3</sub> :1%Tm	6.3563(1)	6.8600(1)	4.4025(1)	191.97(1)	62{1}	13(6)

Anisotropic strain and size parameters. *S*<sub>400</sub>, *S*<sub>040</sub> and *S*<sub>004</sub> measure strain along main crystallographic axes, whereas *S*<sub>220</sub>, *S*<sub>202</sub>, *S*<sub>022</sub> and *S*<sub>122</sub> quantify cross-correlations between axial strains. Parameter Lor. is a measure of Lorenztian shape contribution to the strain.

Sample	Strain paramet	Strain parameters								
	S <sub>400</sub>	S <sub>040</sub>	S <sub>004</sub>	S <sub>220</sub>	S <sub>202</sub>	S <sub>022</sub>				
LaF <sub>3</sub> :1%Pr	0.004(2)	-	0.0002(8)	-	S <sub>112</sub> ->	0.04(1)	1(fix)			
YF <sub>3</sub> :1%Pr	0.89(4)	0.07(1)	8.4(3)	0.48(6)	-2.9(2)	1.3(2)	0.49(2)			
YF <sub>3</sub> :1%Ho	0.39(4)	0.033(6)	4.6(4)	0.14(3)	-1.5(2)	0.53(10)	0.69(4)			
YF <sub>3</sub> :1%Er	0.57(2)	0.053(7)	6.7(2)	0.241(3)	-2.4(2)	0.66(9)	0.47(1)			
YF <sub>3</sub> :1%Tm	0.39(2)	0.007(3)	5.2(2)	0.09(2)	-2.0(2)	0.31(8)	0.47(2)			



**Fig. 2.** Anisotropic character of the YF<sub>3</sub> confines the distortion and resulting strain in the *a*-*c* plane. The distance between Y layers is b/2 = 3.4 Å.



**Fig. 3.** Projection of the LaF<sub>3</sub> structure along *c* axis ( $6_3$ ) with different colors used to visualize crystallographically nonequivalent fluorine atoms. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Structural stability analysis obtained by Bond Valence Sum formalism implemented in BondStr program. Two sets of parameters for LaF<sub>3</sub>:Pr were calculated using 10-fold (left) and 11-fold (right) coordination of La.

Sample	LaF <sub>3</sub> :1%Pr	YF <sub>3</sub> :1%Pr	YF <sub>3</sub> :1%Ho	YF <sub>3</sub> :1%Er	YF <sub>3</sub> :1%Tm
Old GII (%)	9.01 7.05	5.45	7.21	7.13	7.00
	8.85 6.23	6 31	6.44	6 39	6.30

# additional parameter reported in Table 5 as *Lor*. Purely Lorenztian shape should give *Lor* = 1 as it was used in the case of LaF<sub>3</sub>. In the refinements of the YF<sub>3</sub> series, its value was close to 0.5 with a 20% larger result observed for Ho doped compound.

In other words, the strain dependence obtained from profile broadening and ADPs indicated that effects of small domain size and doping were relaxed differently in LaF<sub>3</sub> and YF<sub>3</sub>. In LaF<sub>3</sub> the dispersion of lattice parameters was smaller as evidenced by negligible strain parameters  $S_{HKL}$  and a more stable lattice but at a cost of less defined average coordinates and non-physical individual ADPs. In YF<sub>3</sub>, the stress was accommodated mostly by the lattice (high values of  $S_{004}$ ) with more stable atomic parameters within the average cell (well defined individual ADPs). Here, one exception should be raised in the case of holmium doped YF<sub>3</sub>, which has consistently higher ADPs (Table 1) and Lor parameter (Table 5), which would point toward much higher disorder than in the remaining compounds. The YF<sub>3</sub>:1%Ho also stands out as its high ADPs are counter-weighted by the smallest strain parameters  $S_{HKL}$  in the YF<sub>3</sub> series, which puts it in the middle between yttrium and lanthanum compounds.

It must be noted that in the case when the refinement of individual isotropic *ADPs* was unsuccessful, an anisotropic approach to *ADP* might have been more appropriate, as reported in previous studies with neutrons [17]. However, refining from powder XRD data *ADPs* of a large (1.3 Å) low-Z (only 8 electrons) ion like fluorine  $F^-$  is difficult due to the weak contribution of fluorine to the total structure factor. Especially, when the compounds contain high-Z ions like Y<sup>3+</sup> or La<sup>3+</sup>.

#### 3.1.2. Discussion of structural details and Bond Valence Sum analysis

The lattice parameters as well as the unit cell volume of yttrium based samples were found to decrease with the increasing atomic number of rare-earth (RE). This is an understandable result of lanthanide contraction as the effective ionic radii of Y and RE elements in the 3+ oxidation state with ninefold coordination are (Å):Y 1.042, Pr 1.179, Ho 1.072, Er 1.062, Tm 1.052, with 10-fold coordinated La<sup>3+</sup> 1.27 Å and fluorine F<sup>-</sup> 1.3 Å [18]. The changes in lattice

#### Table 8

Multiplicity of La–F bond distributions up to 3 Å with bond valence (BV) calculated using BVS for LaF<sub>3</sub>:1%Pr.

_						
	Distance (Å)	BV	Bond	Multi.	Bond	Multi.
	2.421	0.367	La1-F1	1	F1-La1	3
	2.423	0.366	La1–F3	1	F3-La1	1
	2.427	0.361	La1–F2	2	F2-La1	3
	2.437	0.353	La1–F4	1	F4–La1	1
	2.495	0.305	La1–F4	1	F4–La1	1
	2.548	0.267	La1–F3	2	F3-La1	2
	2.826	0.133	La1–F4	2	F4–La1	2
	3.111	0.065	La1–F3	1	F3-La1	1

Bond Valence Sum Parameters for LaF<sub>3</sub>:1%Pr. Coordination number, calculated and predicted distances, polyhedral distortion  $\times$  10<sup>4</sup> [20], nominal valence, Bond Valence Sum, deviation from BVS, deviation from Equal Valence. The upper part is calculated using 10-fold coordination of La, whereas the bottom one contains differences generated by with 11-fold coordination of La.

Atom	Coord.	$d_{\mathrm{avg}}\left(\mathrm{\AA}\right)$	$d_{\rm pred}$ (Å)	Distortion ( <sup>*</sup> )	Nom. Val.	BVS	Dev. BVS (%)	Dev. EqV (%)
10-Fold c	oordination of L	a						
La	10	2.538	2.502	35.7	3+	2.91	2.9	8.7
F1	3	2.420	2.459	0.0	1-	1.10	10.2	0.0
F2	3	2.427	2.459	0.0	1-	1.08	8.4	0.0
F3	3	2.506	2.459	5.6	1-	0.90	10.0	4.6
F4	4	2.646	2.574	46.9	1-	0.92	7.6	9.9
11-Fold c	oordination of L	а						
La	11	2.590	2.540	71.7	3+	2.98	0.7	10.6
F3	4	2.657	2.575	100.9	1-	0.97	3.5	10.9

Bond Valence Sum Parameters for YF<sub>3</sub> series. Coordination number, calculated and predicted distance, polyhedral distortion × 10<sup>4</sup> [20], nominal valence, Bond Valence Sum, deviation from BVS, deviation from Equal Valence.

Atom	Coord.	$d_{\mathrm{avg}}\left(\mathrm{\AA}\right)$	$d_{\rm pred}$ (Å)	Distortion ( <sup>*</sup> )	Nom. Val.	BVS	Dev. BVS (%)	Dev. EqV (%)
YF <sub>3</sub> :1%Pr								
Y	9	2.323	2.310	11.5	3+	2.96	1.5	5.4
F1	3	2.372	2.310	26.8	1-	0.89	10.9	8.5
F2	3	2.299	2.310	0.03	1-	1.03	3.2	0.4
YF₃:1%Ho								
Y	9	2.323	2.310	11.1	3+	2.95	1.6	5.3
F1	3	2.372	2.310	25.7	1-	0.89	11.1	8.4
F2	3	2.299	2.310	0.02	1-	1.03	3.2	0.3
YF₃:1%Er								
Y	9	2.323	2.310	11.6	3+	2.96	1.5	5.4
F1	3	2.372	2.310	26.8	1-	0.89	11.0	8.5
F2	3	2.299	2.310	0.03	1-	1.03	3.2	0.4
YF₃:1%Tm								
Y	9	2.323	2.310	11.8	3+	2.96	1.4	5.5
F1	3	2.372	2.310	27.3	1-	0.89	10.9	8.6
F2	3	2.298	2.310	0.06	1-	1.03	3.4	0.5

parameters are followed by the behavior of the unit cell volume, which is consistent with earlier results by Zalkin and Templeton obtained for binary REF<sub>3</sub> [13].

In order to estimate the stability of the structure, a Bond Valence Sum (*BVS*) analysis of the refinement was done using the BondStr program within the Fullprof suite. The Bond Valence Parameters for La, Y and F were taken from Zachariesen [19] and the polyhedral distortion index was calculated on the basis of Balic, Zunic and Vickowic [20]. The results are presented in Tables 6–10. Table 6 presents Global Instability Indexes (*GII*) for all refined structures. Old *GII* measures the root mean square deviation of *BVS* calculated for all non-equivalent sites, whereas *GII*(*c*) includes site multiplicities. In all cases, they were found to lie below 10% indicating stable structures. The worst agreement (largest instability) was found in cases of YF<sub>3</sub>:1%Ho and LaF<sub>3</sub>:1%Pr, which is in agreement with the high *ADPs* and the lowest strain broadening observed in these materials.

The 9-fold coordination of yttrium in YF<sub>3</sub> is an established fact (Fig. 1) [12,13,21]. Eight out of 9 Y–F bonds are around 2.3 Å with one being over 2.5 Å (see Table 10). The most distant Y–F1 bond is over 10% longer than the expected Y–F distance of 2.3 Å [19]. It is however necessary to obtain the balanced structure as its formal charge transfer of 0.17 electrons is around 50% of the 0.34 charge provided by each of the other bonds (see Table 10).

A less clear situation is encountered in the LaF<sub>3</sub> structure, where lanthanum is usually reported to be 10 or 11 coordinated [17] (Fig. 4). The *BVS* analysis was therefore performed using both coordinations, which differed by inclusion of a distant (3.11 Å) F3 site. The addition of the 11th fluorine resulted in a slight improvement of the *GIIs* (Table 6) but increased distortion index [20] of the La polyhedron from 35 to 71. Additionally, the stability of the surroundings of the F3 ion worsened by a factor of over 20 times (Table 7).



**Fig. 4.** 11-Fold coordination of La atom is formed by 4 crystallographically nonequivalent fluorine sites. Green surface marks ... *m* mirror plane. All distances are given in Ångströms. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Comparison of the effective bond valences in the LaF<sub>3</sub> structure (Table 8) indicated that the most distant bond had minimal (0.07) contribution to bond valence (*BV*), which was over 50% smaller than the 9th and 10th La-F4 2.8 Å bonds (*BV* 0.13). The remaining 8 La-F connections had formal *BVs* between 0.27 and 0.36.

Multiplicity of Y-F bond distributions up to 2.6 Å with bond valence (BV) calculated using BVS for YF<sub>3</sub> series.

Bond type and multiplicity	YF <sub>3</sub> :1%Pr		YF <sub>3</sub> :1%Ho		YF <sub>3</sub> :1%Er		YF <sub>3</sub> :1%Tm	
	Distance	BV	Distance	BV	Distance	BV	Distance	BV
Y1-F1 F1-Y11 1	2.276	0.366	2.282	0.360	2.283	0.359	2.280	0.362
Y1-F1 F1-Y11 1	2.294	0.348	2.292	0.351	2.288	0.354	2.289	0.354
Y1-F2 F2-Y12 1	2.294	0.348	2.295	0.347	2.293	0.350	2.292	0.351
Y1-F2 F2-Y12 1	2.298	0.345	2.298	0.345	2.300	0.343	2.297	0.345
Y1-F2 F2-Y12 1	2.304	0.339	2.304	0.340	2.303	0.340	2.305	0.338
Y1-F1 F1-Y11 1	2.545	0.177	2.542	0.178	2.546	0.176	2.548	0.176

561



LaF<sub>3</sub>:1%Pr

Fig. 5. SEM images of the nanopowder YF<sub>3</sub>:Er. The nano-sized grains forming agglomerates are visible.

Altogether, the 10-fold coordination of lanthanum was sufficient to provide good charge stability of the structure and did not require to accept significant distortions of local polyhedra.

#### 3.2. SEM/EDX

SEM images show the morphologies of grains in the examined compounds at magnifications  $\times$ 50,000 (Fig. 5). The crystalline particles YF<sub>3</sub>:1%RE and LaF<sub>3</sub>:1%Pr show the distribution of the grain size. The obtained powders can be said to be included to nanocrystalline materials since a large number of the grains are below/close to 100 nm. The observed bigger grains probably came as a result of localized region subjected to higher calcination temperatures. Moreover, in some areas this has lead to heterogeneity in the

particles, as was found for microarea of LaF<sub>3</sub>:1%Pr. These grains were enriched in oxygen and depleted of lanthanum (Fig. 6a). The microanalysis of the chosen areas are shown in Fig. 6b and their composition in Table 11. The differences between grain sizes suggest that during short calcination times (2 h), the temperature distribution in the sample was not homogeneous.

As reported previously for LaAlO<sub>3</sub>:Pr<sup>3+</sup> [3], nanocrystallites incorporated into a polymer matrix keep their original optical properties, while  $YF_3$ :Pr<sup>3+</sup> composites showed decreased intensity of luminescence and significant shortening of the fluorescence lifetime. This might be explained by some surface contribution. For LaF<sub>3</sub>:1%Pr the ratio La/F is 2.9 while for YF<sub>3</sub>:1%Pr the ratio Y/F is only 2.2. For the rest of the compounds Y/F is 2.5. The ratio C/O is the highest for YF<sub>3</sub>:1%Pr and 1%Tm and is about 4.5; for the compounds doped with Er, Ho and for LaF<sub>3</sub>:1%Pr it is about 2. The



Fig. 6. (a) EDX element maps for LaF<sub>3</sub>:1%Pr. Contamination enriched with oxygen and depleted with lanthanum is visible. Local elemental analysis was performed in areas shown in part (b). Results of analysis are given in Table 11.

Elemental microanal	ysis of LaF <sub>3</sub> :1%Pr.	Areas are shown	in Fig.	6b.
---------------------	---------------------------------	-----------------	---------	-----

Areas	С	0	F	La
Whole area	10.12	8.55	60.41	19.43
Spectrum 2	10.90	24.25	54.00	10.21
Spectrum 3	11.43	6.81	59.89	20.43
Spectrum 4	12.07	6.64	59.54	20.41

All results in atomic %.

chemical composition of the surface can be significant for the coupling with the polymer matrix.

#### 3.3. XPS

The XPS spectra in the wide energy range 0–1400 eV of LaF<sub>3</sub>: 1%Pr and YF<sub>3</sub>:1%Ho are shown as examples in Fig. 7. Besides the lines related to the yttrium or lanthanum and fluorine i.e., the elements forming the compounds, the additional lines of carbon and oxygen were observed in all investigated compounds. They are connected with the contamination of the surface.

Fig. 8 shows the Y3d spin–orbit split doublets for  $YF_3$ :1%RE. The binding energies for each compound are collected in Table 12. These Y3d lines were fitted with synthetic peaks. Besides the main



Fig. 7. Overview example XPS spectra in the wide energy range 0-1400 eV of  $YF_3$ :1%Ho and LaF<sub>3</sub>:1%Pr. Additional lines of C and O are related to the surface contamination.



Fig. 8. XPS core lines of Y3d.

lines, additional lines at lower biding energy are also observed. Their intensities are close to 10% of the intensity of the main doublet line.

F1s lines are shown in Fig. 9. The measured lines positions of the main line are comparable with the data published by Wang et al. Kirikova et al. and Chong et al. [22–24]. Moreover, the additional low binding energy lines are visible.

The positions of core levels and the valence band are collected in the Table 12. Some distribution of the binding energies can be related to the complexity of the carbon line C1s. The most intensive C1s line was assumed for calibration of the spectra.

The additional low intensity lines (A) at lower binding energies, can be related to surface contribution. A similar effect was visible for LaF<sub>3</sub> spectra measured by Chong et al. [24]. The additional line of La3d at 834.4 eV, present also in this work, was ascribed to La<sub>2</sub>O<sub>3</sub>. Such oxide is not present in these XRD measurements. Some extra phase observed for the samples doped with praseodymium is related to the presence of  $PrF_3$  detected in the magnetic measurements.

Another reason for the presence of the low intensity lines may be considered to be due to a difference in the binding energy of the longest bonds between the fluorine and the rare earth ion (see Figs. 1 and 4). Such kind of bonds can be weaker giving a lower binding energy with the intensities around 10%. The indication of such contribution is asymmetry of the  $\text{REF}_3$  XPS lines, observed towards low binding energy but mostly publish without deconvolution.

Fig. 10a and b shows valence bands consisting fluorine F2p and Y4d or La5d states. The width of energy gap estimated from this measurement is  $\sim$ 10 eV, taking the Fermi level location about the center of the energy gap. Similar values of the energy gap were estimated in the literature for YF<sub>3</sub> (10.3 eV) [25] and for LaF<sub>3</sub> (9.7 eV) [26].

The observed chemical shifts are positive and equal about +3 eV for Y4p<sub>3/2</sub>, in relation to the elemental position 24 eV; +1 eV for F2s (30 eV elemental position) and about +3 eV for La5p<sub>3/2</sub> (17 eV for elemental position)(Table 12) [27]. It indicates the covalent contribution to the bonds in these compounds.

Fig. 11 presents the La3d spin–orbit doublet of LaF<sub>3</sub>:1%Pr. Each of La3d line has a double peak structure corresponding to the La3d<sup>9</sup>4f<sup>0</sup> (M) and the satellite lines S attributed to La3d<sup>9</sup>4f<sup>1</sup>L (L is a hole in valence band) states which are visible at higher binding energy (Table 12). Moreover, additional lines (A), similarly to those earlier described for the F1s and Y3d, are observed. A change of a shape of the La3d line in fluoride in relation to the oxide material was observed. For comparison similar line measured in SrLaAlO<sub>4</sub> was added [28]. The change of the ratios of intensities  $I_S/I_M$  show the same tendency as the theoretical calculations for oxide and fluorine materials [29] which is shown in Fig. 11.

#### 3.4. Magnetic susceptibility

In order to estimate the concentration of the  $RE^{3+}$  ions, magnetic measurements were done. The magnetic susceptibility temperature dependence of YF<sub>3</sub>:1%RE and LaF<sub>3</sub>:1%Pr were measured in a magnetic field of 0.5 T and over temperature range 1.9–400 K (Fig. 12). The obtained curves were fitted to the Curie–Weiss law in the temperature range 200–400 K. The range of the fit depends on the sample due to crystal field effect.

$$\frac{1}{x} = \frac{1}{x_0 + \frac{C}{T - \theta}} \tag{1}$$

Using Eq. (1), the Curie constant *C*, the Curie–Weiss temperature  $\theta$  and the temperature-independent diamagnetic susceptibility  $\chi_o$  were obtained. The Curie constant value was used for the calculation of the effective magnetic moment of the nanocrystals.

Parameters of XPS lines of investigated compounds.

Compound band	YF <sub>3</sub> :1%Pr		YF <sub>3</sub> :1%Ho		YF <sub>3</sub> :1%Er		YF₃:1%Tm		LaF <sub>3</sub> :1%Pr	
	$E_B$ (eV)	$\Gamma_{\rm HMFW}({\rm eV})$	$E_B$ (eV)	$\Gamma_{\rm HMFW}({\rm eV})$	$E_B$ (eV)	$\Gamma_{\rm HMFW}({\rm eV})$	$E_B$ (eV)	$\Gamma_{\rm HMFW}({\rm eV})$	$E_B$ (eV)	$\Gamma_{\rm HMFW}  ({\rm eV})$
F <sup>-</sup> 2p (VB)	9.5	2.9	9.4	3.3	9.4	2.5	9.0	2.9	9.9	2.7
Y <sup>3+</sup> 4p <sub>3/2</sub>	27.2	2.9	27.0	3.3	26.7	2.5	26.6	2.9		
$Y^{3+} 4p_{1/2}$	28.2	2.9	28.1	3.3	27.7	2.5	27.7	2.9		
F <sup>-</sup> 2s	31.4	2.9	31.1	3.3	31.0	2.5	30.8	2.9	30.9	3.5
Y <sup>3+</sup> 3d <sub>5/2</sub>	160.4	2	160.3	2.4	160.5	2.3	159.6	2.3		
	159.0 (A)		158.4 (A)		158.4 (A)		157.2 (A)			
	12%		16%		7%		9%			
Y <sup>3+</sup> 3d <sub>3/2</sub>	162.4	2	162.4	2.4	162.6	2.3	161.6	2.3		
	161.0 (A)		160.4 (A)		160.4 (A)		159.2 (A)			
$F^{-1}$ 1s	686.0	2.2	685.8	2.3	686.5	2.5	685.2	2.5	686.0	2.3
	684.6 (A)		683.9 (A)		684.4 (A)		683.3 (A)		684.0 (A)	
	13%		14%		7%		9%		16%	
La <sup>3+</sup> 5p <sub>3/2</sub>									19.9	2.3
									21.0 (S)	
									14%	
									17.6 (A)	
									15%	
La <sup>3+</sup> 5p <sub>1/2</sub>									22.5	2.3
									23.5 (S)	
									19.7 (A)	
La <sup>3+</sup> 3d <sub>5/2</sub>									837.8 (M)	3.3
									841.6 (S)	
									16%	
									834.4 (A)	
									16%	
La <sup>3+</sup> 3d <sub>3/2</sub>									854.5 (M)	3.3
									858.7 (S)	
									851.1 (A)	

Binding energy for elements: F2s - 30 eV; F1s - 685 eV; La5p - 17 eV; La3d<sub>5/2</sub> - 835.8 eV; La3d<sub>3/2</sub> - 853 eV; La M<sub>4</sub>N<sub>45</sub>N<sub>45</sub> - 854 eV; Y4p - 24 eV; Y3d<sub>5/2</sub> - 156 eV; Y3d<sub>3/2</sub> - 158 eV [27].







**Fig. 10.** (a) XPS valence band of LaF<sub>3</sub>:1%Pr together with La5p and F2s states with deconvolution and (b) comparison of valence bands all measured compounds and deconvolution of the Tm doped sample as example.



**Fig. 11.** XPS core lines of La3d<sub>5/2</sub> and La3d<sub>3/2</sub> of LaF<sub>3</sub>:1%Pr compared with La3d lines of SrLaAlO<sub>4</sub>. A decrease of S lines intensity for fluorine compounds is visible.

Using the calculated effective magnetic moment and assuming the theoretical value of the effective magnetic moment for the free  $RE^{3+}$  ion, the concentration of Ho, Er and Tm ions was found as close to 1% (Table 13). A discrepancy is observed for the samples doped with Pr ions. Additionally for these samples the magnetic upturn is observed at about 54 K which suggests the presence of the PrF<sub>3</sub> phase ascribed to the Van Vleck paramagnetism [30]. This additional phase is visible in the XRD pattern.

A comparison of the experimental  $\chi_o$  values and the total of the  $\chi_o$  obtained as a sum of the Slater diamagnetic susceptibilities of

YF<sub>3</sub> and LaF<sub>3</sub> elements was done. The total diamagnetic contribution was  $-3.8 \times 10^{-5}$  emu/mole for YF<sub>3</sub> and  $-4.8 \times 10^{-5}$  emu/mole for LaF<sub>3</sub>. These values are close to the fitted values.

#### 3.5. EPR

Because of the high spin-lattice rate, the EPR spectra of the trivalent rare earth ions are observed at a low temperatures. In addition, no EPR signal from the non-Kramers ions: Ho, Pr and Tm was observed [31]. However, the EPR measurements exhibit the presence of impurity phases in all studied systems.

#### 3.5.1. EPR study of $YF_3$ nanopowder doped with Er

The low temperature EPR spectrum of  $YF_3$ :1%Er shown in Fig. 13, reveals the presence of three broad signals in the range 10–500 mT.

It is known that in trivalent erbium ions with the configuration  $4f^{11}$  (L = 6, S = 3/2) the spin–orbit coupling produces an array of states, of which the lowest is  ${}^{4}I_{15/2}$ . This is split by the cubic crystal field into two doublets,  $\Gamma_{6}$  and  $\Gamma_{7}$ , with an effective spin S = 1/2 and three  $\Gamma_{8}$  quartets with an effective spin S = 3/2. In crystal fields with symmetries lower than cubic, the  $Er^{3+}$  ion ground term splits into the eight Kramers doublets [31].

The spin Hamiltonian characterizing the EPR spectra of the rare earth Kramers ions (when the quadrupole coupling and nuclear Zeeman interactions are negligible) can be expressed as [32]:

$$H = \mu_{\rm R} \mathbf{SgB} + \mathbf{SAI} \tag{2}$$

where  $\mu_{\rm B}$  is the Bohr magneton; *S* and *I* are the electron and nuclear spins, respectively; **B** is the external Zeeman field; **g** and **A** are tensors characterizing Zeeman and hyperfine interactions, respectively. Erbium has one stable odd isotope, of mass number 167, with 22.94% abundance and I = 7/2. As a result, the EPR spectrum of  ${\rm Er}^{3+}$  should show a central signal corresponding to the fine-structure transition  $M = +1/2 \leftrightarrow M = -1/2$  Kramers doublet transition for the <sup>166</sup>Er isotope with no nuclear magnetic moments



**Fig. 12.** Magnetic susceptibility and inverse of magnetic susceptibility vs temperature. Solid line presents the Curie–Weiss fit for the inverse of susceptibility. The magnetic susceptibilities of LaF<sub>3</sub>:1%Pr and YF<sub>3</sub>:1%Pr are negative near room temperature. In order to draw the inverse susceptibilities, their values were corrected of  $+5 \times 10^{-5}$  emu/mol.

Magnetic properties of investigated compounds. Diamagnetic susceptibility, effective magnetic moment, Curie–Weiss temperature, effective magnetic moment calculated from the Hund's rules and computed concentration of the rare earth ions is given.

	$\chi_0^* 10^5$ (emu/mol)	$\mu_{\mathrm{eff}}\left(\mu_{\mathrm{B}} ight)$	$\Theta$ (K)	$\mu_{\text{theor}}$ ( $\mu_{\text{B}}$ )	Concentration (%)
YF <sub>3</sub> :1%Er	-3.78	0.92	3	9.58	0.93
YF <sub>3</sub> :1%Ho	-0.74	1.07	-10	10.61	1.02
YF₃:1%Tm	-1.72	0.73	9	7.56	0.93
YF <sub>3</sub> :1%Pr	-8.05	0.33	0	3.58	0.85
LaF <sub>3</sub> :1%Pr	-6.50	0.32	-3.4	3.58	0.80



**Fig. 13.** X-band EPR spectrum of YF<sub>3</sub>:Er at T = 4.2 K (gain:  $1 \times 10^2$ ).

.aF<sub>s</sub>:Pr

YF<sub>\_</sub>:Pr

(abundance 77.06%) and eight hyperfine transitions distributed about the central signal. It can be seen (Fig. 14) that the hyperfine structure is not resolved in the EPR spectrum of the  $YF_3:1\%$ Er compound.

Taking into account the crystal structure of YF<sub>3</sub> we assume that trivalent erbium substitutes for Y<sup>3+</sup> in YF<sub>3</sub> preserving the monoclinic (*.m.*) local site symmetry of Y-ion. The EPR spectrum was fitted to the effective Hamiltonian  $H = \mu_B SgB$  with S = 1/2 and **g**-tensor exhibiting monoclinic symmetry. The g values are:  $g_1 = 14.60$ ;  $g_2 = 2.99$  and  $g_3 = 1.71$ .

According to Ref. [31] the *g*-values associated with transitions within the  $\Gamma_6$  and  $\Gamma_7$  states in cubic symmetry are 6.00 and 6.8, respectively. If the overall crystal field symmetry is lower than cubic, the principal components of the *g*-tensor can be related to the *g*-value calculated for cubic symmetry  $g_c$  by:

$$g_{c} = g_{av} = (1/3)(g_{1} + g_{2} + g_{3})$$
(3)

This approach is only valid if the lower symmetry crystal field is small when compared to cubic crystal field [33] and has been used successfully in the analysis of rare earth EPR spectra [34,35]. However, if the difference between the value of  $g_c$  and  $g_{av}$  is large (>0.1), the assumption that the low symmetry components of the crystal field are small compared to those when the cubic crystal field is present, breaks down [35]. In our case, the  $g_{av}$  value is 6.43 and is significantly distant from the value predicted for cubic symmetry. It would indicate that the low-symmetry crystal field around the erbium ion may be strong.

The low temperature EPR spectrum for YF<sub>3</sub>:1%Er compound revealed only broad resonance signals with the linewidth in the range: 8–25 mT and the absence of any hyperfine components. This means the formation of clusters (i.e., aggregation) of erbium ions. The broadening of resonance lines is the result of both

Fig. 14. X-band EPR spectra of LaF\_3:Pr, YF\_3:Pr, Tm, Ho, Er at a room temperature (gain:  $1\times 10^4).$ 

variations present: the crystalline field in the clusters [36] and magnetic interactions.

#### 3.5.2. Identification of Mn<sup>2+</sup> impurity

YF<sub>3</sub>:Er

The EPR measurements exhibit the presence of  $Mn^{2+}$  ions in the all investigated compounds. Figs. 14 and 15 show the X-band EPR spectra collected at a room and liquid helium temperatures, respectively. There can be seen the sextet centered at  $g \approx 2.0$  (marked as S1) and the single line resonance near  $g \approx 4.3$  (marked as S2), which are the signature of isolated  $Mn^{2+}$  in sites with different local symmetry.

As the Mn<sup>2+</sup> ions belong to d<sup>5</sup> configuration, in the axial distortion of octahedral symmetry of crystal field, it gives rise to three Kramers doublets. Therefore, five fine structure transitions are possible. Each fine structure transition will be split into six hyperfine components due to <sup>55</sup>Mn hyperfine coupling (I = 5/2; 100% abundance). For powder and polycrystalline samples, all components of the fine structure except that with  $M_S = +1/2 \leftrightarrow M_S = -1/2$  are broadened to such an extent that they cannot be observed. Thus, only one six line pattern is recorded in the experimental spectrum [31].

The spin Hamiltonian for Mn<sup>2+</sup> in low symmetric crystal field is given by:

$$H = \mu_{B}gBS + ASI + D(S_{z}^{2} - 35/12) + (1/2)(E(S_{+}^{2} + S_{-}^{2}))$$
(4)

where *D* and *E* are the axial and rhombic fine structure parameters. As  $Mn^{2+}$  is the S-state ion, the *g*- and A-tensors are isotropic. The inset in Fig. 14 shows the spectrum calculated with *g* = 2.00 and  $A = 84 \times 10^{-4} \text{ cm}^{-1}$ . As the ionic radius of  $Mn^{2+}$  is 0.96 Å and from



Fig. 15. X-band EPR spectra of LaF<sub>3</sub>:Pr, YF<sub>3</sub>:Ho,Pr,Tm at T = 4.2 K (gain:  $1 \times 10^4$ ).

the magnitude of spin-Hamiltonian parameters [37], it is reasonable to assume that manganese occupy yttrium site and the valence of manganese remains as Mn<sup>2+</sup>. Simultaneously, a complete smearing of the hyperfine forbidden lines and significant broadening of hyperfine allowed lines (linewidth of each component is  $\Delta B = 5 \text{ mT}$ ) become visible (see Figs. 14 and 15). These are the characteristic features of Mn<sup>2+</sup> EPR spectra in disordered systems [38]. They are due to effects of distribution of zero field splitting (D, E) parameters around their average values.

The investigations of the EPR spectra of Mn<sup>2+</sup> in a variety of disordered materials (glasses and polycrystalline powders) show that the spectra have been characterized in addition hyperfine sextet, the absorption around  $g \approx 4.3$  [39]. These resonances arise from the isotropic transitions within the lowest or middle Kramers doublets. In our case, the intensity ratio  $I_{2,0}/I_{4,3}$  decreases with decreasing temperature, therefore the resonance near g = 4.3 arises from the transition within the lowest Kramers doublet. An isotropic gfactor of 30/7 from a high-spin d<sup>5</sup> ion in a site of rhombic symmetry can only appear if the symmetry is completely rhombic ( $\lambda = E/$ D = 1/3). Such interpretation was supported also by successful simulation of the EPR spectra for d<sup>5</sup> ions by Yahiaoui and Kliava [40,41].

#### 4. Concluding remarks

The thermal decomposition method was successfully applied for the first time in order to obtain the good quality YF<sub>3</sub>:1%RE materials. The SEM investigations showed that the particles are nanometric in size as also confirmed by XRD measurements. The synthesized samples have a stoichiometry close to the nominal what composition as confirmed by XRD and magnetic measurements. For the samples doped with praseodymium, PrF<sub>3</sub> was also observed. Surface contamination can be suggested to be responsible for the deterioration of the optical properties of the composites. Positions of XPS lines are in agreement with the literature data. The energy gap is about 10 eV. The chemical shift of the XPS lines indicate covalent type of bonds. To the best of our knowledge, no EPR measurements have been done on YF3:1%Er material. We conclude that trivalent erbium preserves the local site symmetry of the Y-site in the investigated fluoride material. The absence of any hyperfine structure and broad resonance signals which are observed in the EPR spectrum of YF<sub>3</sub>:1%Er indicate the formation of clusters of activator ions. No rare earth related EPR signal was observed for samples: YF<sub>3</sub>:1%RE (RE = Ho, Pr, Tm). Contrary to the erbium doped sample, XRD results indicate absence of holmium clustering. EPR measurements exhibit the presence of Mn<sup>2+</sup> ions in the all investigated compounds. We suppose that these uncontrolled impurities originate from the chemical ingredients during the technology procedure. From EPR it is observed that the Mn<sup>2+</sup> ions in the all investigated compounds occupy more than one sites: the first one is characterized by weakly deformed cubic sites with distribution spin Hamiltonian parameters around their average values and the other has completely rhombic symmetry sites.

#### Acknowledgments

We express our thanks to the Director of Institute of Electronic Materials Technology, Dr Z. Łuczyński for support of this work. SQUID magnetometer was financed by European Regional Development Fund whereas SEM/EDX Jeol was financed by Regional Fund for Environmental Protection in Katowice.

#### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jallcom.2014. 07.074.

#### References

- [1] B.P. Sobolew, The Rare Earth Trifluorides, Institut d'Estudis Catalans, Barcelona, Spain, 2000.
- [2]
- A. Kaminskii, Laser Crystals, Springer, Berlin, 1990. A. Jusza, L. Lipinska, M. Baran, P. Mergo, A. Millan, F. Dieleman, R. [3] Piramidowicz, Proc. SPIE 8435, Organic Photonics V, 84351T, June 1, 2012, doi:10.1117/12.922143.
- [4] B.P. Sobolev, Crystallogr. Rep. 47 (1) (2002) S63-S75.
- [5] J. Rodriguez-Carvajal, Recent developments of the program FULLPROF, in commission on powder diffraction (IUCr) Newsletter, vol. 26, 2001, pp. 12-19 <http://journals.iucr.org/iucr-top/comm/cpd/Newsletters/>.
- [6] J. Rodriguez-Carvajal, M.T. Fernández-Díaz, J.L. Martínez, J. Phys, Condens. Matter 3 (1991) 3215-3234.
- [7] P.W. Stephens, J. Appl. Cryst. 32 (1999) 281-289.
- [8] P. Thompson, D.E. Cox, J.B. Hastings, J. Appl. Cryst. 20 (1987) 79-83.
- [9] M. Jarvinen, J. Appl. Cryst. 26 (1993) 527-531.
- [10] K. Momma, F. Izumi, J. Appl. Crystallogr. 44 (2011) 1272-1276.
- [11] Multipak Software Version 6, edited by Physical Electronics, Minnesota, 1998.
- [12] A.K. Cheetham, N. Norman, Acta Chem. Scand. Ser. A 28 (1974) 55-60.
- [13] A. Zalkin, D.H. Templeton, J. Am. Chem. Soc 75 (1953) 2453.
- [14] M. Mansmann, Zeit. Anorg. und Allgem. Chem. 331 (1964) 98–101.
- [15] C. de Rango, G. Tsoucaris, C. Zelwer, Compt. Rend. Hebd. Seances Acad. Sci., Ser. C, Sci. Chim. 263 (1966) 64-66.
- [16] T.J. Udovic, Q. Huang, A. Santoro, J.J. Rush, Z. Krist. 223 (1979) 697-705.
- [17] D. Gregson, C.R.A. Catlow, A.V. Chadwick, G.H. Lander, A.N. Cormack, B.E.F. Fender, Acta Cryst. B 39 (1983) 687-691.
- [18] R.D. Shannon, Acta Cryst. A32 (1976) 751-767.
- [19] F.W.H. Zachariesen, J. Less Common Metals 62 (1978) 1-7.
- [20] T. Balic Zunic, I. Vickovic, J. Appl. Cryst. 29 (1996) 305-306.
- [21] B.E.G. Lucier, K.E. Johnston, D.C. Arnold, J.-L. Lemyre, A. Beaupre, M. Blanchette, A.M. Ritcey, R.W. Schurko, J. Phys. Chem. C 118 (2014) 1213-1228.
- [22] M. Wang, Q. Huang, J. Hong, X. Chen, Mater. Lett. 61 (2007) 1960-1963.
- [23] N.Yu. Kirikova, J.C. Krupa, N.V. Makhov, C. Severac, J. Elect, J. Electron Spectrosc. Relat. Phenom. 122 (2002) 85-89.
- [24] L. Chong, J. Zou, X. Zeng, W. Ding, J. Mat. Chem. A 1 (2013) 3983-3991.
- [25] E. Sarantopoulou, Z. Kollia, A.C. Cefalas, Opt. Mater. 18 (2001) 23-26.
- [26] H.D. Wiemhöfer, W. Göpel, Frasenius, J. Anal. Chem. 341 (1991) 106–111.
- [27] J. Moulder, W. Stickle, P. Sobol, K. Bomben, Handbook of X-ray photoelectron spectroscopy, Phys. Electron. (1995)
- [28] E. Talik, A. Pajączkowska, A. Guzik, P. Zajdel, J. Kusz, A. Kłos, A. Szysiak, Mater. Sci. Eng. B 182 (2014) 74-80.
- [29] C. Suzuki, T. Mukoyama, J. Kawai, H. Adachi, Phys. Rev. B 51 (1998) 9507-9514. [30] C. Leycuras, H. Le Gall, M. Guillot, A. Marchand, J. Appl. Phys. 55 (1984) 2161-
- 2163.
- [31] A. Abragam, B. Bleaney, Electron Paramagnetic Resonance of Transition Ions, Clarendon Press, Oxford, 1970.
- [32] S.K. Misra, Physica B 253 (1998) 111.
- [33] J.D. Carey, R.C. Barklie, J.F. Donegan, F. Priolo, G. Franzo, S. Coffa, Phys. Rev. B 59 (1999-II) 2773.

- [34] J. Dziesiaty, St. Muller, R. Boyn, Th. Buhrow, A. Klimakow, J. Kreissl, J. Phys. :Condens. Matter 7 (1995) 4271.
  [35] R.K. Watts, W.C. Holton, Phys. Rev. 173 (1968) 417.
  [36] S.A. Kazanskii, Sov. Phys. JETP 62 (1985) 727.
  [37] V.K. Jain, G. Lehman, Phys. Status Solidi B 159 (1990) 495. and references

- therein.
- [38] S.K. Misra, Physica B 203 (1994) 193.
  [39] V. Cerny, B. Frumarova-Petrova, J. Rosa, I.L. Licholit, M. Frumar, J. Non-Cryst. Solids 192&193 (1995) 165.
- [40] E.M. Yahiaoui, R. Berger, Y. Servant, J. Kliava, L. Cugunov, A. Mednis, J. Phys.: Condens. Matter 6 (1994) 9415.
   [41] J. Kliava, R. Berger, Mol. Phys. Rep. 39 (2004) 130.