Effect of Non-stoichiometry on the Luminescence Properties of Lanthanum Oxyfluorides

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The UV and argon-ion laser-excited high-resolution luminescence spectra of the Eu^{3+} ion were used as structural probes to investigate the effect of non-stoichiometry on the structure of the lanthanum oxyfluoride, LaOF, system. The spectra of the two modifications of LaOF:Eu^{3+} are different. For the stoichiometric, rhombohedral LaOF the spectrum is in agreement with the crystallographic C_{3v} point symmetry of the La^{3+} site. The crystal field analysis, based on the $^7F_{0-2}$ levels, revealed only slight distortions from the ordered cubic fluorite phase. In the tetragonal $LaO_{1-x}F_{1+2x}$ phase a symmetry slightly lower than C_{4v} was found for the La^{3+} site, in disagreement with structural data. The Eu^{3+} level scheme in this phase corresponds approximately to those in the tetragonal rare-earth (RE) oxysalts with the $(REO)_n^{n+}$ complex cation. The X-ray powder diffraction patterns of the rhombohedral and the tetragonal phases are similar, resembling the ordered cubic fluorite pattern. In addition to the weak splitting of the major peaks, the position and intensity of secondary reflections differed only slightly.

The non-stoichiometry in the RE_2O_3–REF_3 binary system is one of the most widely studied within all RE (rare-earth) compounds. Recent investigations have shown the existence of several phases (in addition to the strictly stoichiometric REOF one) with the following compositions: $RE_xO_yF_z$; $x=5$, $y=4$ and $z=7$; $x=6$, $y=5$ and $z=8$; $x=17$, $y=14$ and $z=23$ for RE = Y;[1] $x=1$, $y=0.65$ and $z=1.70$ for RE = La,[2] as well as $x=1$, $y=0.70$ and $z=1.60$.[3] Some of these phases can be described by the general formula $RE_nO_{n-1}F_{n+2}$, where n is odd. In addition to the presence of species of well-defined composition in the RE_2O_3–REF_3 phase diagram some non-stoichiometric phases, especially the tetragonal $REO_{1-x}F_{1+2x}$ phase of excess fluorine, show an extended range of solid solubility.

The crystal structure of all RE oxyfluorides, both stoichiometric and non-stoichiometric, can be considered as derived from that of the CaF_2 (fluorite) system. This 'parent' compound crystallizes in the cubic crystal system with $Fm3m$ ($Z=4$) as the space group.[2] In this system the distribution of the different anions is random. With an ordered distribution of the anions a slightly different system is obtained. The crystal system remains cubic, but the space group is now $F\bar{4}3m$ ($Z=4$).[4] In the former case the ideal point symmetry of the RE^{3+} site is O_h, but owing to the irregular distribution of the anions it is much lower. In the latter the point symmetry of the RE site is T_d.

Effect of non-stoichiometry

The structure of the stoichiometric REOF phase has been studied by X-ray diffraction[5] and very recently by neutron powder[6] diffraction. The crystal structure of this phase belongs to the rhombohedral (hexagonal) system with $R\bar{3}m$ ($Z=2$) as the space group. The point symmetry of the RE site is C_{3v}.

The crystal structure of the fluorite-related $LaO_{0.65}F_{1.70}$ phase with excess fluoride has been found to possess tetragonal symmetry (space group $P4/nmm$; $Z=2$) with C_{4v} site symmetry for the RE^{3+} ion.[2] This structure is exactly the same as that of rare-earth oxyhalides, REOX, with X = Cl, Br and I.[7] The stability range of this phase extends very close to the stoichiometric REOF phase, i.e. the value of n is close to 1 in the formula LaO_nF_{3-2n}.[8–11] With decreasing size of the RE^{3+} ion the distortions due to the excess fluorine seem to become more important, and consequently the symmetry of the structure is lowered; $SmO_{0.7}F_{1.6}$ has the orthorhombic (or monoclinic)[12] structure with $Pmmn$ ($Z=2$) as the space group.[3]

Owing to their potential application as solid-state electrolytes, the ionic conductivity of REOF materials has been extensively investigated.[13] The luminescence of several RE^{3+} ions (Eu^{3+},[14–18] Tb^{3+},[19,20] Er^{3+},[19] and Nd^{3+} [21]) has also been observed in both stoichiometric and non-stoichiometric RE oxyfluorides. However, none of these investigations has concentrated on a study of the effect of non-stoichiometry on the luminescence and energy-level scheme of RE^{3+} ions.

In this paper we report the luminescence spectra and CF (crystal field) analysis of the ^7F_J ($J=0$–2) energy-level scheme of the Eu^{3+} ion in the two different modifications of lanthanum oxyfluoride, the stoichiometric rhombohedral and non-stoichiometric tetragonal forms. The corresponding results of the X-ray powder diffraction studies are also given.

Experimental

Sample preparation. Many investigations have been carried out to characterize the preparation of rare-earth oxyfluorides. The thermal decomposition of fluoride-containing materials often yields products mixed with the corresponding sesquioxide or/and trifluoride. Accordingly, the exact composition of the product is very difficult to control. The two most reliable methods of preparation of stoichiometrically controlled products involve solid-state reactions either between the RE sesquioxide and anhydrous RE trifluoride or between RE_2O_3 and NH_4F. In this study both the stoichiometric rhombohedral and non-stoichiometric tetragonal LaOF forms were prepared by the latter method.

The experimental details are as follows: mixtures of lanthanum sesquioxides with NH_4F were heated in a static N_2 atmosphere at 1050 °C for 1.5 h. When a strictly stoichiometric La_2O_3/NH_4F ratio was used, the rhombohedral LaOF was obtained, but if an excess of NH_4F was present, the tetragonal, non-stoichiometric $LaO_{1-x}F_{1+2x}$ was formed. The products contained only a very small amount of fluoride in excess, corresponding to a value of $x = 0.0375$ at the most, since the initial excess of NH_4F was small, only 7.5 % of the stoichiometric amount.

For luminescence measurements the La^{3+} host cation was in both cases partially replaced by a small amount of Eu^{3+} ion, nominally 2 %. A uniform and random distribution of the Eu^{3+} ion in the host cation site was assumed, owing to the small differences in solubilities between different RE^{3+} ions.

X-Ray powder diffraction. The powder diffraction patterns of lanthanum oxyfluorides were measured at room temperature with a Philips PW 1800 series powder diffractometer system (with Cu K_α radiation) in the 2Θ range between 5 and 60°.

Optical measurements. The luminescence of the powder samples of LaOF:Eu^{3+} was measured under UV, argon-ion and dye-laser excitation at ambient and liquid-nitrogen temperatures (300 and 77 K, respectively). UV radiation from a 200 W mercury lamp restricted with wide-band filters around 300 nm was used to excite the strongly absorbing charge-transfer band of the Eu^{3+} ion. Similarly, the Spectra Physics 2016 argon-ion laser line at 476.5 nm excites the $^5D_2$ level of the Eu^{3+} ion, resulting in emission from the $^5D_{2-0}$ levels. The luminescence was detected by a Hamamatsu R374 photomultiplier through a 1 m Jarrell-Ash Cerny–Turner monochromator. The resolution of the equipment was better than 1.0 cm^{-1}. The emission originating from the $^5D_{0-2} \rightarrow {}^7F_{0-5}$ transitions between 450 and 775 nm was considered in detail.

Results and discussion

X-Ray diffraction. The X-ray powder diffraction patterns reproduced in Fig. 1 are dominated by a few very strong peaks. In spite of a slight descaling of the 2Θ angle the main peaks can be attributed to the cubic LaOF.[4] The close structural relationship of both the tetragonal (pattern A) and rhombohedral (pattern B) forms of LaOF to their cubic precursor is evident.

In addition to the slight splitting of some major peaks, the two reflection patterns differ from each other, and from the cubic form, mainly by the position and intensity of rather weak supplementary peaks. The modification of the cubic pattern can easily be explained by a trigonal and a tetragonal distortion of the cubic cell due to the ordered position of the anions.

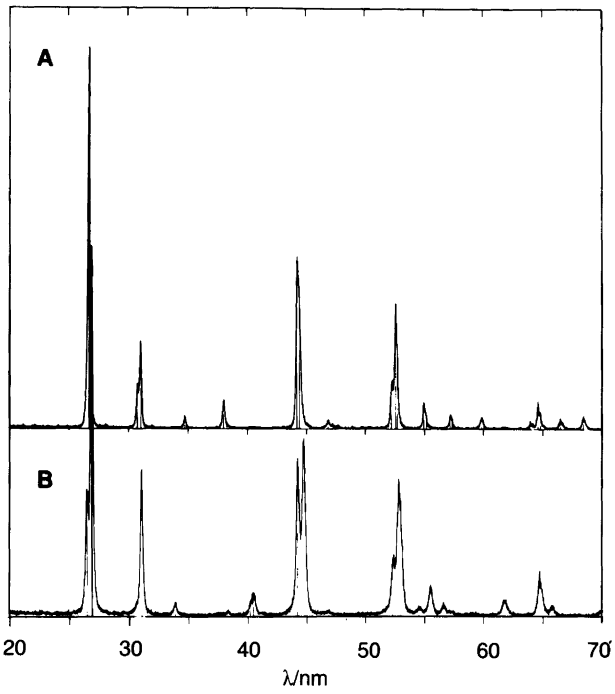

Fig. 1. The X-ray powder diffraction patterns of (A) tetragonal and (B) rhombohedral LaOF.

Luminescence spectra. The reddish emission of the Eu^{3+} ion in both LaOF matrices (Fig. 2) originates mainly from the lowest level of the ^5D manifold, $^5D_0$.[22] An order-of-magnitude weaker emission can be observed from the higher ^5D levels, $^5D_1$ and $^5D_2$, however. The emission from higher excited ^5D levels of the Eu^{3+} ion is usually quenched by multiphonon relaxation of the excitation energy. In LaOF the lattice phonons of highest energy hardly exceed 550 cm^{-1},[23] and at least four phonons are needed to fill the energy gap of 2000 cm^{-1} between the $^5D_1$ and $^5D_0$ (as well as between the $^5D_2$ and $^5D_1$) levels. Such a process, involving a simultaneous absorption of at least four phonons, is unfavourable and improbable, and thus explains the emission from higher ^5D levels.

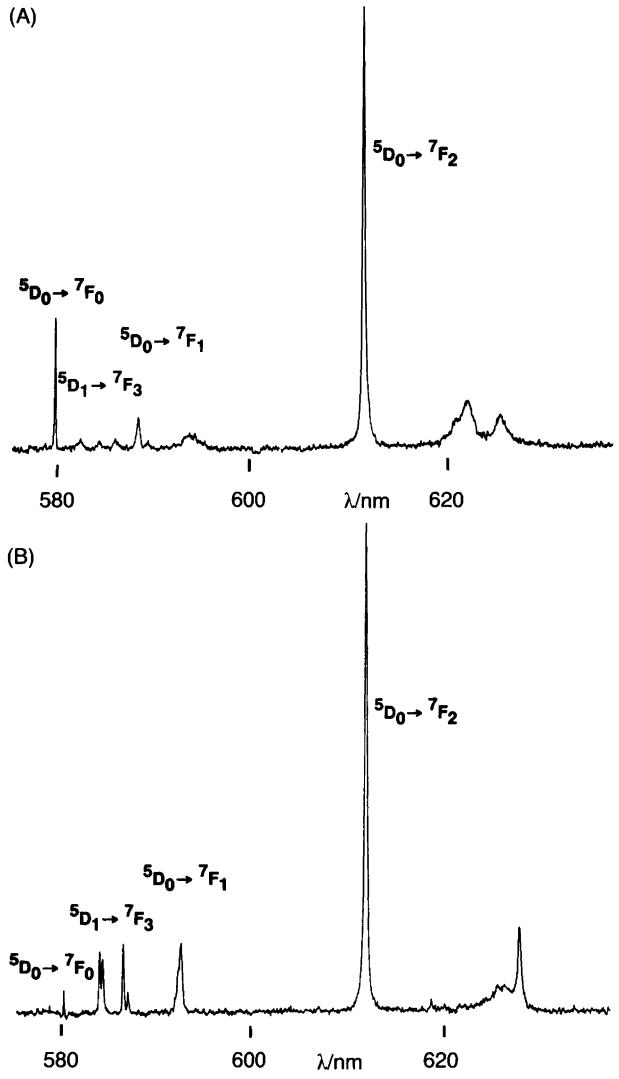

Fig. 2. The UV excited luminescence spectra of Eu^{3+} ion in (A) tetragonal and (B) rhombohedral LaOF at liquid nitrogen temperature.

Table 1. The experimental $^7F_{0-4}$ and calculated $^7F_{0-2}$ energy-level schemes of the Eu^{3+} ion in tetragonal and rhombohedral LaOF (all values in cm^{-1} units).

Level	Rhombohedral LaOF		Tetragonal LaOF	
	E_{exp}	E_{calc} [a]	E_{exp}	E_{calc} [b]
$^7F_0$	0	0	0	0
$^7F_1$	344	346	247	247
	348	346	396	395
	350	350	416	415
$^7F_2$	855	856	870	870
	880	880	895	895
				942
			1179	1178
	1302	1302	1264	1264
$^7F_3$	1867		1852	
	1875			
	1937		1908	
	1952		1950	
	2104		2052	
$^7F_4$	2506			
	2822		2878	
	2860		2896	
	3015			
	3064			
	3073		3093	
	3087		3132	

[a] According to C_{3v} symmetry. [b] According to C_{2v} symmetry.

The intensities of the $^5D_{0-2} \rightarrow {}^7F_{0-5}$ transitions indicate the induced electric dipole interaction as the major origin of the emission. The $^5D_0 \rightarrow {}^7F_{2,4}$ transitions have the highest intensity in both matrices, while the magnetic dipole transitions (e.g. $^5D_0 \rightarrow {}^7F_1$) allowed alone in the presence of inversion symmetry for the Eu^{3+} site are of moderate intensity. The most striking difference can be observed in the intensity of the $^5D_0 \rightarrow {}^7F_0$ transition, which is, to a first approximation, allowed only for C_s, C_n or C_{nv} symmetries.[24] A $^5D_0 \rightarrow {}^7F_0$ transition of high intensity is in accordance with the C_{4v} site symmetry in tetragonal LaOF:Eu^{3+}. In general, the Eu^{3+} emission spectrum for tetragonal LaOF has striking similarities to the spectra of typical RE oxysalts.[25-29] This will be treated in detail later.

The $^5D_0 \rightarrow {}^7F_0$ transition in rhombohedral LaOF:Eu^{3+} is rather weak, despite the low C_{3v} site symmetry. The proximity of a higher pseudo-symmetry for the Eu^{3+} site offers a plausible explanation for this discrepancy. The structure of the rhombohedral REOF is close to that of the ordered fluorite, with slight trigonal distortions.[6] Since the $^5D_0 \rightarrow {}^7F_0$ transition is forbidden for T_d site symmetry, the low intensity of this transition in rhombohedral LaOF can be taken as the effect of the T_d pseudo-symmetry.

Analysis of the Eu^{3+} energy-level schemes. The CF energy-level schemes of the ^7F_J ($J = 1$–4) levels of the Eu^{3+} ion in both LaOF matrices (Table 1) were deduced from the analyses of the corresponding luminescence spectra according to the group-theoretical rules for C_{3v} and C_{4v} site symmetries (Table 2).[30] The comparison between the number of theoretically allowed and experimentally observed levels confirms the C_{3v} site symmetry in rhombohedral LaOF. However, a careful scrutiny of the Eu^{3+} energy-level scheme reveals several pairs (or even triplets as for the $^7F_1$ level) of CF sublevels, with very small energy differences of the order of 10–15 cm^{-1}. For the rhombohedral LaOF the structural data, as well as the intensity of the $^5D_0 \rightarrow {}^7F_0$ transition, have suggested the T_d symmetry as a higher pseudo-symmetry for the Eu^{3+} site. Indeed, when the pseudo-doublet or triplet levels are taken into account, one obtains for most ^7F_J levels an energy-level scheme consistent with T_d symmetry.

According to a superficial examination, the Eu^{3+} energy-level schemes for the two LaOF seem to be rather dissimilar. The tetragonal LaOF presents a much more com-

Table 2. The splitting of the ^7F_J (J = 0–4) levels under a crystal field potential of T_d, C_{3v}, C_{4v} and C_{2v} symmetry.

	T_d					C_{3v}			C_{4v}					C_{2v}			
	A_1	A_2	E	T_1	T_2	A_1	A_2	E	A_1	A_2	B_1	B_2	E	A_1	A_2	B_1	B_2
$^7F_0$	1					1			1					1			
$^7F_1$				1			1	1		1			1		1	1	1
$^7F_2$			1		1	1		2	1		1	1	1	2	1	1	1
$^7F_3$		1		1	1	1	2	2		1	1	1	2	1	2	2	2
$^7F_4$	1		1	1	1	2	1	3	2	1	1	1	2	3	2	2	2

plicated scheme which, of course, is primarily due to the presence of a higher number of CF levels for the C_{4v} symmetry. However, a few lines with no theoretical explanation were also observed experimentally. Two obvious explanations for this observation are available; first, the point symmetry of the Eu^{3+} site is lower than the C_{4v} given by the structural data,[2] or, secondly, there exist several different sites for the Eu^{3+} ion. However, the latter explanation must be ruled out, since only one $^5D_0 \rightarrow {}^7F_0$ transition can be observed. Furthermore, the scanning of the $^5D_0 \rightarrow {}^7F_0$ transition region with dye-laser excitation did not produce any significant changes in the emission spectrum. The local symmetry of the Eu^{3+} ion must thus be distorted from C_{4v}. In order to facilitate interpretation of the emission spectrum, the selection rules[30] for electric as well as for magnetic dipole transitions are preserved rather well.

The observation of extra lines in the emission spectrum can be understood on the grounds of structural data that give three main ways in which the $LaO_{1-x}F_{1+2x}$ structure can accommodate the excess fluoride:[2] (i) replacement of O^{2-} by F^-, (ii) F^- residing in interstitial positions and (iii) vacancies (V_F) created at F^- positions.

Owing to these different possibilities, it is not surprising to find the lowering of the Eu^{3+} site symmetry from C_{4v} (maybe to C_{2v}). This interpretation is also supported by information on SmOF,[12] which previously had been assigned to a monoclinic system where the RE site symmetry must be lower than C_{nv}; $n < 3$. However, the extra splitting of several CF sublevels is very small; e.g. for the $^7F_3$ level the splitting is effectively hidden by the width of the emission lines. This fact indicates only modest distortions from the C_{4v} symmetry. The CF analysis of the $^7F_{1,2}$ energy-level scheme to be carried out in the next section will give an estimate of the amount of the distortions by the magnitude of the B_2^k ($k = 2$ and 4) parameters not allowed for the C_{4v} symmetry.

Crystal-field analysis. In this section the following two effects are to be estimated by CF analysis: (i) the amount of trigonal distortion from T_d symmetry in rhombohedral $LaOF:Eu^{3+}$ (i.e. C_{3v} vs. T_d symmetry) and (ii) the magnitude of distortions from C_{4v} in tetragonal $LaO_{1-x}F_{1+2x}:Eu^{3+}$ (i.e. C_{2v} vs. C_{4v} symmetry). The CF analysis is carried out on the $^7F_{0-2}$ level basis only, since the $^7F_{3-6}$ level sets are badly incomplete. However, even this restricted basis set will give a sufficient description of the magnitudes of the effects studied.

By following Wybourne's formalism[32] the CF Hamiltonian can be expressed as a sum of the products between the real and imaginary even-rank CF parameters (B_q^k and S_q^k) and spherical harmonics (C_q^k) [eqn. (1)].

$$H_{CF} = \sum_{kq} [B_q^k(C_q^k + C_{-q}^k) + iS_q^k(C_q^k - C_{-q}^k)] \quad (1)$$

For T_d symmetry (as well as for other symmetries considered in the present study) the CF Hamiltonian contains no imaginary parameters.[30] Furthermore, the allowed T_d

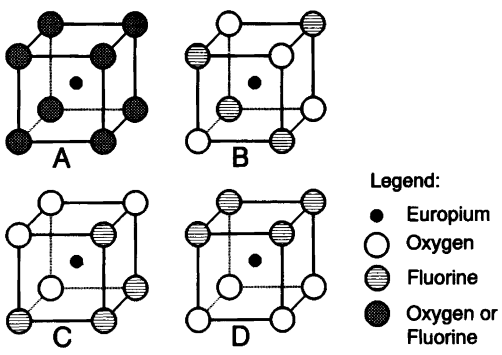

Fig. 3. The schematic representation of possible Eu sites in LaOF: (A) fluorite (O_h), (B) ordered fluorite (T_d), (C) LaOF (C_{3v}) and (D) $LaO_{1-x}F_{1+2x}$ (C_{4v}).[31]

Table 3. The second- and fourth-rank crystal field parameter values (in cm^{-1} units) for the rhombohedral (T_d and C_{3v} site symmetries) and tetragonal (C_{4v} and C_{2v} site symmetries) $LaOF:Eu^{3+}$.

	B_0^2	B_2^2	B_0^4	B_2^4	B_3^4	B_4^4
T_d	–	–	1410	–	−1689	–
C_{3v}	10	–	1810	–	−1534	–
C_{4v}	−710	–	−1810	–	–	−865
C_{2v}	−706	45	−1814	−105	–	−867

parameter values are restricted for symmetry reasons to the following: $B_0^4/B_3^4 = -1.1832$ and $B_0^2 = 0$. For the other symmetries no restrictions are imposed on the B_q^k parameter values. The form of the CF Hamiltonian for the T_d, C_{3v}, C_{4v} and C_{2v} symmetries can be found in Table 3.

The results of fitting the B_q^k parameter sets to the experimental $^7F_{0-2}$ levels in rhombohedral LaOF:Eu^{3+} show that the theoretical B_0^4/B_3^4 ratio (−1.1832) is not accurately followed for T_d symmetry (Table 3). On the contrary, the C_{3v} simulation gave the exact theoretical value for the parameter ratio, together with a negligible B_0^2 value. This is the final confirmation of the insignificant nature of the trigonal distortion from the cubic precursor in rhombohedral LaOF. The present results are rather surprising, since the spectroscopic methods are usually very sensitive to even very small changes in crystal structure.

The simulation of the $^7F_{0-2}$ energy-level scheme of the Eu^{3+} ion in tetragonal $LaO_{1-x}F_{1+2x}$ was carried out without difficulties even for the higher C_{4v} symmetry (Table 3). As far as the B_0^2 parameter is concerned, the values differ significantly from those for rhombohedral LaOF. However, if the fourth-rank parameters are scrutinized with care one observes the striking similarity in the B_0^4 parameter values. Further, despite the incompleteness of the $^7F_{3-4}$ level sets a rather similar general appearance of the CF splittings is observed. It seems that in spite of the drastic differences in the close-range coordination of the Eu^{3+} ion, which is mainly responsible for the magnitude of the B_q^2 parameters, the long-range ordering of anions in both compounds is rather similar.

In contrast to the structural data,[2] the energy-level scheme of the tetragonal LaOF:Eu^{3+} suggested a RE site symmetry lower than C_{4v}. A CF simulation according to C_{2v} symmetry shows quantitatively that these distortions are of minor importance. The parameters involved, B_2^2 and B_2^4, assumed very low values, and there were no changes in the parameters allowed only for C_{4v} symmetry.

Finally, the CF simulation of the $^7F_{0-2}$ energy-level scheme of the Eu^{3+} ion in the tetragonal LaOF yielded a set of B_q^k parameters which resemble those of the typical RE oxysalts possessing the tetragonal $(REO)_n^{n+}$ complex cation.[22,25–29] However, the very high value of the B_0^4 parameter does not fit this scheme perfectly, and thus additional studies of the effect of the $^7F_{3-4}$ levels to the B_q^k set must be carried out to clarify this problem.

Conclusions

In this study it was shown by using X-ray powder diffraction as well as high-resolution luminescence spectroscopy, together with crystal-field analysis, that the structural distortions from the ordered cubic fluorite phase in rhombohedral LaOF are of minor importance. In the case of the fluorite-related tetragonal $LaO_{1-x}F_{1+2x}$ phase with a small excess of fluoride, the point symmetry of the La site has been lowered from that of C_{4v} indicated by structural data. The magnitudes of the distortions were found by CF analysis to be very small, however. The relationship of the tetragonal LaOF phase to other tetragonal RE oxysalts is left in doubt.

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