JOURNAL OF SOLID STATE CHEMISTRY **116**, 286–289 (1995)

Optical Properties of $BaEu(CO_3)_2F$ and $Na_3La_2(CO_3)_4F:Eu^{3+}$: Correlations to the Crystallographic Structures

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Received July 11, 1994; in revised form October 18, 1994; accepted October 24, 1994

The luminescent properties of trivalent europium are analyzed in $Na_3La_2(CO_3)_4F:Eu^{3+}$ at 77 and 9 K and in $BaEu(CO_3)_2F$ at 77 K. In $BaEu(CO_3)_2F$, the C_{3v} symmetry of the rare earth, deduced from the X ray diffraction study, is confirmed. In $Na_3La_2(CO_3)_4F$, the spectroscopic technique shows that the order which appears at low temperature implies a single site for the rare earth with a C_{3v} or a C_3 symmetry. For both compounds, the energy level scheme of the ^7F_J (J = 0–4) levels is well reproduced (weak RMS standard deviation) from six crystal field (cf) parameters consistent with the C_{3v} site symmetry. © 1995 Academic Press, Inc.

INTRODUCTION

Rare-earth fluorocarbonates were recently synthetized by hydrothermal growth, and their crystal structures were solved from single-crystal X ray diffraction. Both $Na_3Ln_2(CO_3)_4F$ and $BaLn(CO_3)_2F$ (Ln = La, Pr and Ln = Sm, Eu, Gd respectively) (1, 2) exhibit LnO_9F (Ln = La, Eu) polyhedra with a C_{3v} point symmetry for the rare-earth ion. However, in $Na_3La_2(CO_3)_4F$, a splitting of O(1) oxygen atoms on two mirror-related positions occurs (Fig. 1).

The MAS NMR study of ^{23}Na at room temperature (1) reveals a definite motion of Na(2) sodium atoms in $Na_3La_2(CO_3)_4F$, certainly related to the motion of O(1) oxygen atoms. Thus, this technique suggests that the O(1) disorder is probably connected and due to a vibrational movement of carbonate groups. The existence of a broad signal in low frequency Raman spectra supports also this hypothesis (A. Bulou, Le Mans, private communication). As the O(1) oxygen atoms belong to rare-earth polyhedra, the luminescence of trivalent europium in $Na_3La_2(CO_3)_4F:Eu^{3+}$ was investigated in order to characterize the symmetry of rare-earth atoms at low temperature. It was then compared to that of $BaEu(CO_3)_2F$.

CRYSTAL STRUCTURES

The preparation of rare-earth fluorocarbonates, obtained at high temperature (T = 700°C) and under high pressure (P = 220 Mpa) under hydrothermal conditions, and the resolution of the structures are described elsewhere (1, 2). $Na_3La_2(CO_3)_4F$ is hexagonal ($P6_3/mmc$, $Z = 2$, $a = 5.083(1)$ Å, $c = 23.034(5)$ Å), $BaEu(CO_3)_2F$ is rhombohedral ($R\bar{3}m$, $Z = 6$, $a = 5.016(1)$ Å, $c = 37.944(6)$ Å).

In both structures, X ray diffraction study leads to evidence for a 10-fold (3O + 6O + 1F) coordination of the rare-earth atoms with C_{3v} symmetry. The splitting of oxygen atoms O(1) of carbonate groups on two mirror-related positions with a 50% site occupancy can be due to the vibration of carbonate groups. If a freezing of the vibrational disorder occurs at low temperature, one or more rare-earth sites may be expected. Their symmetry must be lowered to C_3, in the best case, or C_2 or C_1 (Fig. 1). This conclusion would be also valid for a microtwinning of the crystals.

In both structures, the LnO_9F polyhedra are linked by vertices with a threefold axis symmetry corresponding to that of the carbonate group and form infinite $LnO_{6/2+3}F$ layers in the (a, b) plane. In $Na_3La_2(CO_3)_4F$, these layers are connected by fluorine atoms in order to form double $(LaO_6)_2F$ layers which insert half of the sodium ions (Fig. 2). On the contrary, the LnO_6F layers are shifted one from each other in $BaEu(CO_3)_2F$ and insert barium ions in 12-fold BaO_6F_6 coordination. It must be noted that a description in terms of $LnCO_3$, CO_3, BaF_2, and NaF planes, which alternate along c, also

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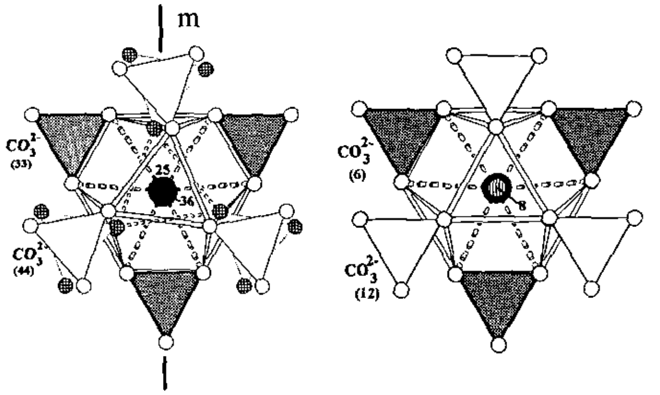

FIG. 1. Projection along *c* of the LnO_9F polyhedra (C_{3v} symmetry) in $Na_3La_2(CO_3)_4F$ (left) and $BaEu(CO_3)_2F$ (right).

emphasizes the analogies between both structures (Fig. 2).

OPTICAL MEASUREMENTS

The luminescence of $Na_3La_2(CO_3)_4F:Eu^{3+}$ and $BaEu(CO_3)_2F$ powder samples was measured under argon ion laser and dye laser excitation at liquid nitrogen temperature. The $Na_3La_2(CO_3)_4F:Eu^{3+}$ spectrum was also recorded at 9 K. The 457.9-nm blue line of a 5-W continuous wave argon ion laser was used to excite the $^5D_2$ level of Eu^{3+} ion, allowing the classical cascade. A rhodamin 6G dye laser pumped by the argon ion laser was used to excite selectively the $^5D_0$ level. The fluorescence emission was detected through a 1-m Jarrell Ash monochromator equipped with a Hamamatsu R374 photomultiplier. The spectral resolution is better than 1 cm^{-1}.

FLUORESCENCE SPECTRA

The emission spectra of both compounds at 9 and 77 K are very similar and consist of narrow lines (1–4 lines) attributed to the $^5D_0 \rightarrow {}^7F_J$ transitions ($J = 0, 1, 2, 4$ respectively) (Fig. 3). $^5D_0$ is the only emitting level: $^5D_2$ and $^5D_1$ are relaxed to $^5D_0$ according to the classical quenching cascade $^5D_2 \rightarrow {}^5D_1 \rightarrow {}^5D_0$. The process is favored by lattice phonons of relatively high frequency (~800 cm^{-1}), which are available in these fluorocarbonates or other compounds such as $La_2O_2CO_3$ (3), and compounds with BO_3 groups (4, 5). It must be also noted that the poor quality of the $Na_3La_2(CO_3)_4F:Eu^{3+}$ spectrum is probably due to low Eu^{3+} ion doping concentration, 2% ($Na_3Eu_2(CO_3)_4F$ does not exist).

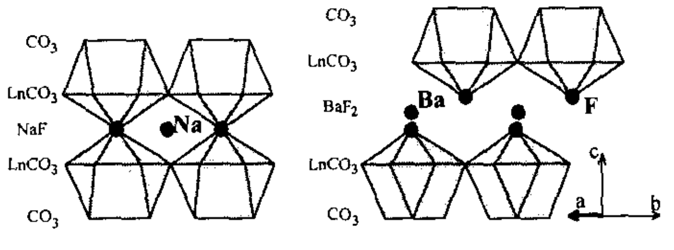

FIG. 2. Part of the $Na_3La_2(CO_3)_4F$ (left) and $BaEu(CO_3)_2F$ (right) structures projected along [21$\bar{3}$0], showing connection of the LnO_9F polyhedra.

For both compounds, the presence of one line for the $^5D_0 \rightarrow {}^7F_0$ transition indicates a single site of C_s, C_n, or C_{nv} symmetry for the rare earth, according to the application of the group theory selection rules for electric dipole transitions (6). A dye laser excitation of the $^5D_0 \rightarrow {}^7F_0$ transition confirms that all lines correspond to a single site.

The $^5D_0 \rightarrow {}^7F_1$ transition is allowed inside the $4f^6$ configuration as a magnetic dipolar transition. As a consequence, the number of observed lines (2 for each compound, Fig. 3) as well as their relative intensity (one to two) indicates that the lowest $^7F_1$ cf level is associated with an E irreducible representation of rank 2. This excludes a C_2 or C_1 symmetry for the rare earth in $Na_3La_2(CO_3)_4F:Eu^{3+}$. Moreover, it implies a positive value for the cf B_0^2 parameter. In that case, the barycenter is equal to 373 cm^{-1}, close to the free ion barycenter position.

In both spectra, two strong lines and a third weak one are present for the electric dipolar $^5D_0 \rightarrow {}^7F_2$ transition. This is in good accordance with a C_{3v} or C_3 point symmetry for the rare earth. If the barycenter is supposed to be close to the free ion barycenter, the lowest cf level must be associated to an E irreducible representation, which gives more constraints to the values of B_0^4 and B_3^4.

$^5D_0 \rightarrow {}^7F_3$ is not observed. Usually, the intensity of that transition is low, but always detected. That transition, forbidden at the first order by the electric/magnetic dipole selection rules, is observed only as a consequence of the *J* mixing, which mixes the $^7F_3$ wavefunctions with other ^7F_J, especially $^7F_1$, $^7F_2$, and $^7F_4$, through the second–fourth-order cf parameters (7). The lack of that transition is consistent with the relatively small values of the second- and fourth-order cf parameters (Table 1).

Four lines are observed for $^5D_0 \rightarrow {}^7F_4$ transition. If the symmetry of the rare-earth point site is C_{3v} or C_3, five and six lines can be respectively expected. Then it is not possible to decide by the spectroscopic tool if the rare-earth symmetry has been really lowered to C_3 for $Na_3La_2(CO_3)_4F$.

In addition, some weak extra lines are present at the feet of $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions in $BaEu(CO_3)_2F$ spectrum. These satellites, indicated by arrows in Fig. 3, correspond to extra levels due to phonon coupling. The

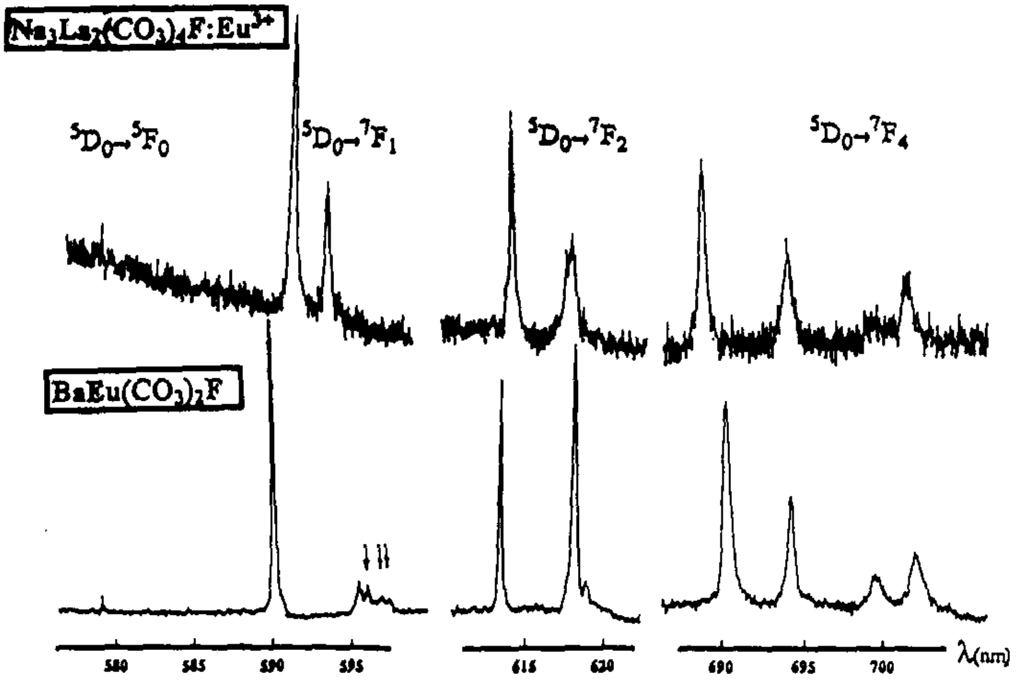

FIG. 3. Luminescence spectra of Eu^{3+} in $Na_3La_2(CO_3)_4F:Eu^{3+}$ and $BaEu(CO_3)_2F$ at nitrogen temperature.

same feature was observed for $LaBO_3$ (4) and $NdBO_3$ (8) around the hypersensitive transitions.

A partial energy level scheme for ^7F_J levels can be deduced from these spectra (Table 1).

SIMULATION

The $4f^6$ configuration of the europium ion is very convenient for crystal field calculations. This is due to a ground term ^7F_J ($J = 0 - 6$), well isolated from the rest of the configuration (about 12000 cm^{-1} between $^7F_6$ and $^5D_0$). Furthermore, this term is the only one of this multiplicity and, consequently, is not mixed by the crystal field with terms of other multiplicities. Thus, instead of considering the complete $4f^6$ configuration, involving a very large secular determinant (3003 × 3003), the crystal field calculation can be performed accurately on a reduced $|^7F_{JM}>$ basis involving only 49 determinantal states (9). In Wybourne's formalism (10) the crystal field potential is writ-

TABLE 1

Experimental and Calculated Crystal Field Energy Levels (cm^{-1}) of Eu^{3+} Ion in $Na_3La_2(CO_3)_4F:Eu^{3+}$ and $BaEu(CO_3)_2F$

	$Na_3La_2(CO_3)_4F:Eu^{3+}$			$BaEu(CO_3)_2F$		
	Experimental	Calculated	Irreducible representation	Experimental	Calculated	Irreducible representation
$^7F_0$	0	0	A_1	0	0	A_1
$^7F_1$	352	352	E	320	319	E
	413	413	A_2	479	482	A_2
$^7F_2$	994	995	E	964	968	E
	1080	1080	A_1	1093	1093	E
	1092	1093	E	1110	1107	A_1
$^7F_4$	2763	2763	A_1	2784	2783	A_1
	2871	2871	E	2864	2862	E
	2977	2977	E	2977	2981	E
	3018	3018	A_1	3024	3024	A_1
$^5D_0$	17271			17266		

TABLE 2

Crystal Field Parameters of Eu^{3+} in $Na_3La_2(CO_3)_4F : Eu^{3+}$ and $BaEu(CO_3)_2F$ (Values Are in cm^{-1}), Number N of Levels, RMS, and Residue (in cm^{-2})

	B^2_0	B^4_0	B^4_3	B^6_0	B^6_3	B^6_6	Levels	Residue	σ
$Na_3La_2(CO_3)_4F : Eu^{3+}$	277	−208	−465	245	342	1210	10	1.5	0.7
$BaEu(CO_3)_2F$	585	123	−435	19	219	1088	10	49.5	3.5

ten as a sum of products of spherical harmonics and cf parameters as

$$H_c = \sum_{k,q} B^k_q[C^k_q + (-1)^q C^k_{-q}] + iS^k_q[C^k_q - (-1)^q C^k_{-q}].$$

In that expression B^k_q and S^k_q are the real and imaginary part of the cf Hamiltonian. The number P of nonzero cf parameters depends on the symmetry. For C_{3v} symmetry, only six B^k_q are nonvanishing.

The experimental data are relatively poor for both compounds, 10 transitions are observed, and the simulations of the energy level schemes must be performed carefully. The refining procedure minimizes the RMS deviation $\sigma = \sum_i (\sigma_i^2/N - P)^{1/2}$ considered as the figure of merit. It consists of a four-step calculation, which takes into account the considerations mentioned above from the observed spectra. The first step finds B^2_0 from the $^7F_1$ splitting. The second step keeps B^2_0 fixed and includes the experimental $^7F_2$ level in order to test possible values of fourth order cf parameters B^4_0 and B^4_3. In the third step, the B^6_2 parameters are freely varied on $^7F_4$ experimental level. In the last step, all cf parameters vary simultaneously. The reproduction of the experimental energy level schemes (Table 1) can be considered as satisfactory when good RMS deviations and small residues ($R = \Sigma(\sigma_i^2)$, 1.5 and 49.5 cm^{-2} in our case, Table 2) are obtained. The sets of cf parameters of $Na_3La_2(CO_3)_4F : Eu^{3+}$ and $BaEu(CO_3)_2F$ are close together (Table 2), which is another confirmation of the structural analogies.

CONCLUSION

Luminescence spectroscopy of Eu^{3+} confirms the structural analogies between $Na_3La_2(CO_3)_4F : Eu^{3+}$ and $BaEu(CO_3)_2F$. The crystal field is weak and does not seem to be strongly influenced by the connection of LaO_9F polyhedra through fluorine atoms in $Na_3La_2(CO_3)_4F$. Six cf parameters, consistent with the C_{3v} symmetry, are sufficient to reproduce the energy level schemes.

The number of the observed emission lines in $Na_3La_2(CO_3)_4F$ at nitrogen temperature (9 K also) is compatible with a C_{3v} or C_3 symmetry: C_2 and C_1 symmetries are excluded. The freezing of the motional disorder of carbonate groups at low temperature implies that the rare-earth C_{3v} symmetry observed at room temperature must be lower. The C_3 symmetry satisfies these requirements only. The order–disorder transition must be characterized.

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