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Eu^{3+} as a local probe to characterize the structure of acentric $K_4Eu_2(Co_3)_3F_4$

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Abstract

The optical study of the trivalent europium ion in polycrystalline $K_4Eu_2(CO_3)_3F_4$ is reported. Three main low symmetry sites for Eu^{3+} are deduced from the emission spectra at 4.2 K. Extra lines are also present at low temperature, which may be assigned to a fourth site. When the temperature increases, these extra lines disappear without energy change of other lines. This reversible phenomenon is not yet explained. Above 8 K, site to site energy transfer becomes effective. The electrostatic crystal field effects on the ^7F multiplet are also evaluated on the basis of the phenomenological crystal field theory. © 1998 Elsevier Science S.A.

Keywords: Fluorocarbonate; Europium; Luminescence; Crystal-field

1. Introduction

Rare earth (RE) fluorocarbonates present a large variety of structural types. New phases were recently obtained by using the hydrothermal method [1–4] and we have undertaken the analysis of their optical properties. In previous papers we presented the luminescence of $BaEu(CO_3)_2F$, $Na_3La_2(CO_3)_4F:Eu^{3+}$ [1] and $KGd(CO_3)F_2$: Eu^{3+} [2]. This paper is focused on the optical study of the Eu^{3+} luminescence properties in a new fluorocarbonate family, $K_4RE_2(CO_3)_3F_4$. In the synthesis of $RECO_3F$, (RE=La) or $KRE(CO_3)F_2$, (RE=Gd, Tb), $K_4RE_2(CO_3)_3F_4$ appears as a byproduct [2]. For RE=Pr, Nd, Sm and Eu, $K_4RE_2(CO_3)_3F_4$ is the major product of the crystal growth. According to the X-ray structure determination [3], a disorder of fluor atoms, F(2), engaged in the RE coordination sphere, is assumed. The powder sample of $K_4Eu_2(CO_3)_3F_4$ presents a frequency doubling efficiency similar to that of $KTiOPO_4$.

Both phenomena, F(2) disorder and doubling frequency properties, have motivated the study of the luminescence properties of trivalent europium in these compounds.

2. Experimental details and structural description

The starting materials are K_2CO_3, REF_3 and H_2O and the hydrothermal synthesis is performed at high temperature $T=740°C$ with $P_{max}=220$ MPa during 24 h [3]. The structural characterization of this new structural family $K_4RE_2(CO_3)_3F_4$ (RE=Pr, Sm, Nd, Eu, Gd) was presented in a recent paper [3]. The crystal structure is rhombohedral and belongs to $R32-D_3^7$ acentric space group (No. 155). The rare earth atom is ninefold coordinated and surrounded by 3 fluor atoms at $\langle d_{Gd-F}\rangle=2.27$ Å and by 6 oxygen atoms at $\langle d_{Gd-O}\rangle=2.54$ Å. The rare earth atom occupies C_3 point symmetry site (6c position). The structure (Fig. 1) is described from the stacking of $KRE_2(CO_3)_3$ carbonate planes and K_3F_4 sheets in which atomic disorder appears: F(2) atoms which always belong to rare earth polyhedra are located on a general 18f position with a 1/3 occupancy rate. Such disorder, evidenced by X-ray diffraction, has already been encountered in fluorocarbonates: it can be due either to static distribution (microtwinning) or to vibrational motion.

3. Optical data

The optical investigations, absorption, emission and the

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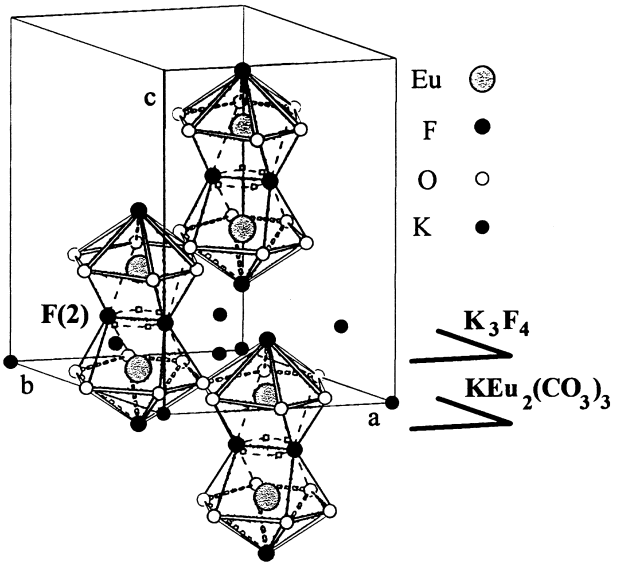

Fig. 1. Perspective view of the structure of $K_4Eu_2(CO_3)_3F_4$.

excitation spectra (laser dye technics), were performed in the 4–300 K temperature range. In the absorption spectrum of $K_4Eu_2(CO_3)_3F_4$ at 4.2 K, a single line exists for the $^7F_0 \rightarrow {}^5D_0$ electronic transition, situated at 17 253 cm^{-1}. One intense line at 19 002 cm^{-1} and a shoulder at 19 025 cm^{-1} (narrow line when temperature increases) are attributed to the next excited level of the ^5D_J manifold, the $^5D_1$ level. Even at higher temperature, no other line is detected for these two levels. The $^5D_0 \rightarrow {}^7F_2$ transition is observed in the absorption spectrum: two intense emission lines are found at 16 393 and 16 313 cm^{-1}.

The absorption study suggests a single point site for the europium ion in $K_4Eu_2(CO_3)_3F_4$ and small values of the second rank crystal-field parameter (cfp) B^2_q. The analysis of the praseodymium and neodymium low temperature absorption spectra (unpublished data), in $K_4Pr_2(CO_3)_3F_4$ and $K_4Nd_2(CO_3)_3F_4$ polycrystalline compounds, suggests also a single site for the rare earth cation.

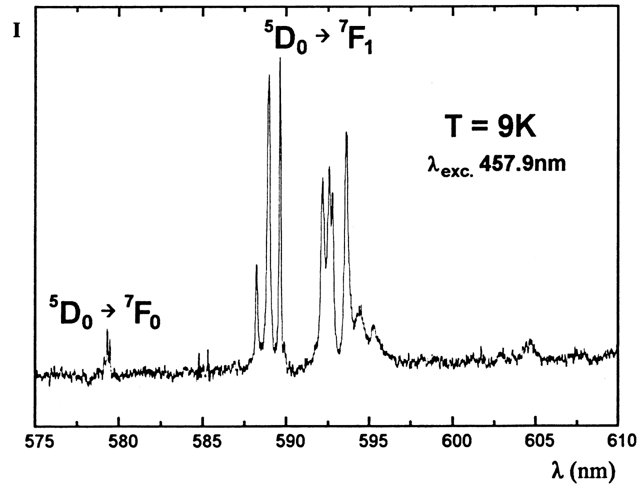

Fig. 2. Luminescence spectrum of $K_4Eu_2(CO_3)_3F_4$ in the $^5D_0 \rightarrow {}^7F_{0,1}$ transition range at $T=9$ K under Ar^+ ion laser excitation.

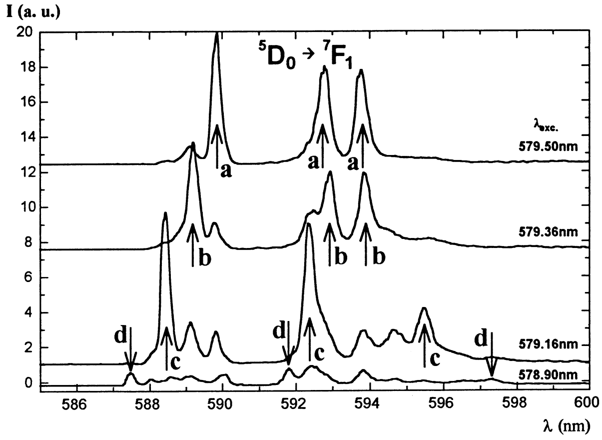

Fig. 3. Dye laser excitation spectra of the $^5D_0 \rightarrow {}^7F_1$ lines in $K_4Eu_2(CO_3)_3F_4$ at $T=4.2$ K.

Oppositely, the emission spectrum excited by the 457.9 nm line of an argon Ar^+ ion laser as well as by a doubled-, or tripled-YAG:Nd^{3+} laser, exhibits a complex feature. In Fig. 2, a part of the luminescence spectrum, relative to the $^5D_0 \rightarrow {}^7F_{0-1}$ transitions recorded at 9 K, is presented. It is clear that the $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1$ transitions are manifold, the $^5D_0 \rightarrow {}^7F_0$ transition consists of three major lines. At 4.2 K, dye laser excitation at 17 250, 17 260 and

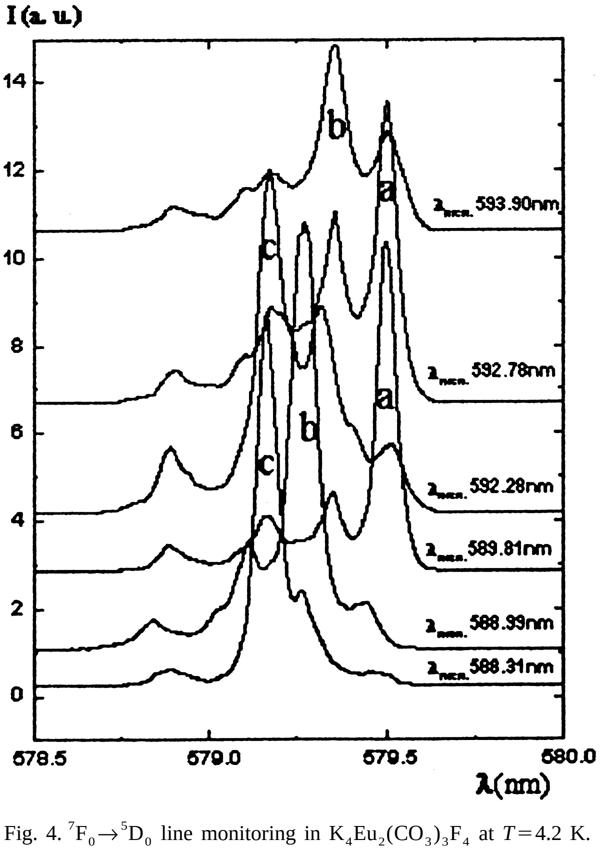

Fig. 4. $^7F_0 \rightarrow {}^5D_0$ line monitoring in $K_4Eu_2(CO_3)_3F_4$ at $T=4.2$ K.

Table 1
Experimental, calculated energy level schemes, second rank crystal field parameters for the $^7F_1$ manifold of Eu^{3+} and crystal field strength parameter, N_v, in $K_4Eu_2(CO_3)_3F_4$ (all values in cm^{-1})

$^{2S+1}L_J$ level	Site a		Site b		Site c		Site d	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
$^7F_0$	0	0	0	0	0	0	0	0
$^7F_1$	303	303	288	288	272	272	252	252
	386	386	395	395	385	385	377	377
	415	415	421	421	473	473	531	531
B_0^2		252		285		519		784
B_2^2		174		225		242		273
N_v		558		677		985		1385

17 266 cm^{-1} allows us to distinguish three main low symmetry sites (a, b, c) for Eu^{3+} (Fig. 3). However, all the lines in the $^5D_0 \rightarrow {}^7F_1$ transition range are not explained and a fourth low symmetry site is evidenced by monitoring the $^7F_0 \rightarrow {}^5D_0$ area (Fig. 4). This new $^5D_0 \rightarrow {}^7F_0$ transition is found at 17 274 cm^{-1}. The corresponding excitation spectrum of this line appears at the bottom of Fig. 3. This minor component (d site) disappears above 20 K and, at 50 K, the overall spectrum is similar to the emission spectrum of Fig. 2. This phenomenom is reversible and cannot be explained by a structural transition of $K_4Eu_2(CO_3)_3F_4$. It must be noted that no energy variation of the other lines is observed when the temperature increases. However, site to site energy transfer appears and depends strongly on the temperature: energy transfer from d site to a, b, c sites occurs at $T > 20$ K while energy transfer between the main a, b, c components is effective at $T > 8$ K.

$^5D_0 \rightarrow {}^7F_1$ transitions are almost identical for a, b, c, d sites (Fig. 5). Moreover, a broad band is recorded at 571 nm (17 513 cm^{-1}) at 250–260 cm^{-1} from $^5D_0$ level and can be attributed to the presence of low frequency vibronics.

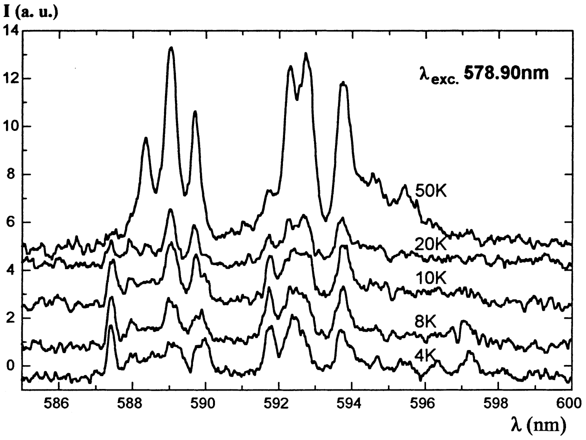

Fig. 5. Selective excitation spectra at $\lambda_{exc.} = 578.90$ nm, ($^5D_0 \rightarrow {}^7F_1$ transition of site d in $K_4Eu_2(CO_3)_3F_4$), as a function of the temperature.

4. Crystal-field simulation

Three and five lines exist for the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions, respectively, for the a, b, c, d sites in $K_4Eu_2(CO_3)_3F_4$. Five lines are unambiguously assigned to the $^5D_0 \rightarrow {}^7F_3$ transition and nine lines are observed for the $^5D_0 \rightarrow {}^7F_4$ transition. This situation indicates that Eu^{3+} site symmetry is lower than C_3, deduced from the X-ray structure determination.

Table 2
Experimental and calculated energy level scheme for Eu^{3+} in site b in $K_4Eu_2(CO_3)_3F_4$ (all values in cm^{-1})

$^{2S+1}L_J$ level	Site b	
	Exp.	Calc.
$^7F_0$	0	0
$^7F_1$	288	288
	395	399
	421	417
$^7F_2$	890	891
	951	937
	1048	1053
	1088	1092
	1179	1184
$^7F_3$	1833	1837
	1854	1860
	1910	1912
	–	1917
	1966	1963
	1977	1968
	–	2079
$^7F_4$	2560	2548
	2606	2623
	2775	2768
	2868	2867
	2937	2934
	2968	2974
	3049	3051
	3049	3056
	3166	3154

Table 3
Crystal field parameters for Eu^{3+} ion located in site b in $K_4Eu_2(CO_3)_3F_4$

Parameter	Values (cm^{-1})
B^2_0	238
B^2_2	141
B^4_0	−288
B^4_2	1281
B^4_4	476
B^6_0	207
B^6_2	−1073
B^6_4	896
B^6_6	126
Residue	1162
σ	9
N_v	3070

The experimental and calculated energy levels for the $^5D_0 \rightarrow {}^7F_1$ transitions are given in Table 1 for the a, b, c, d sites, together with the calculated second rank crystal field parameters (cfp). Rank 4 and 6 cfp are calculated for site b and the corresponding energy level scheme appears in Table 2. For this site, the full set of phenomenological cfp is collected in Table 3. Second rank B^k_q parameters are weak, due to small $^7F_1$ splitting. Other parameters display higher values, in agreement with larger $^7F_{2-4}$ splittings. Due to the relatively high cfp of rank 4 and 6, there is an important J mixing which permits the observation of the $^7F_3$ level.

5. Conclusion

The optical study of luminescence in $K_4Eu_2(CO_3)_3F_4$ shows that Eu^{3+} site symmetry is low (lower than C_3) and is not consistent with the X-ray study.

In the first approach, the splitting of the $^5D_0 \rightarrow {}^7F_0$ or $^5D_0 \rightarrow {}^7F_1$ lines is explained by the presence of four Eu^{3+} sites. Consequently, a high resolution structural study must be performed in order to determine accurately the order which must occur at the F(2) fluorine site. Synchrotron diffraction experiments are scheduled, together with neutron diffraction at low temperature. However, low frequency vibronics probably influence the energy levels and this route must be explored.

References

[1] E. Antic-Fidancev, M. Lemaître-Blaise, P. Porcher, N. Mercier, M. Leblanc, J. Solid State Chem. 116 (1995) 286.
[2] N. Mercier, M. Leblanc, E. Antic-Fidancev, M. Lemaître-Blaise, P. Porcher, J. Alloys Comp. 225 (1995) 198.
[3] N. Mercier, J. Durand, M. Leblanc, Eur. J. Solid State Inorg. Chem. 34 (1997) 241.
[4] N. Mercier, M. Leblanc, Eur. J. Solid State Inorg. Chem. 28 (1991) 727.