

Proceedings of the 2nd Winter Workshop S&SRES'96, Polanica Zdrój 1996

SPECTROSCOPIC STUDY OF RARE EARTH CHROMATES: RELATION TO THE STRUCTURE

E. ANTIC-FIDANCEV, M. LEMAITRE-BLAISE

Laboratoire de Chimie Métallurgique et Spectroscopie des Terres Rares
CNRS-UPR209 1, Place A. Briand, 92195 Meudon, France

AND C. PARADA

Dpto de Química Inorganica, Facultad de Químicas
Universidad Complutense, 28040 Madrid, Spain

The luminescence spectra of the trivalent europium ion embedded in various rare earth chromates were analyzed. The spectroscopic data in most of chromates are in agreement with the structural determination but for some others the discrepancy between two methods is underlined. Energy level schemes were deduced from the experimental emission spectra and the crystal field simulation has been performed. The maximum splitting of the 7F_1 manifold of the Eu^{3+} ion as a function of N_o , the so-called crystal field strength parameter, is given. This allows us to classify the compounds according to their crystal field extent.

PACS numbers: 33.50.Dg, 33.50.Hv, 71.70.Ch, 78.50.Ec

1. Introduction

In the course of our study in the research of efficient rare earth phosphors new compounds were synthesized under hydrothermal conditions or by solid state reaction. Therefore, in the ternary system $\text{RE}_2\text{O}_3\text{-CrO}_3\text{-M}_2\text{O}$ (RE = rare earth, M = alkali metal) different chromates studied here by luminescence spectroscopy are the following: double chromates with the potassium, $\text{KRE}(\text{CrO}_4)_2$, [1, 2]; hydroxo-chromates, $\text{RE}(\text{OH})\text{CrO}_4$, [3] and seven hydrated chromates $\text{RE}_2(\text{CrO}_4)_3 \cdot 7\text{H}_2\text{O}$ [4]. They crystallize in the monoclinic or orthorhombic system and the rare earth atom is situated in one point site of very low symmetry in all these chromates except in the last one for which two different environments were found for the lanthanide ion.

It is well known that the compounds in the lanthanide series can show different structures as a consequence of the decrease in the ionic radii. Moreover, the decrease in the ionic radii can lead to a reduction in the coordination number around the lanthanide cation [5]. It is the case of the rare earth chromates.

We report here the optical properties and the simulation of the energy level scheme of trivalent europium ion embedded in the rare earth chromates studied and discuss their relation to the crystal structures previously determined [1-4]. The present work underlines the sensitivity of the spectroscopy for the characterization of new phases.

2. Synthesis and crystallographic background

2.1. $KRE(CrO_4)_2$

The double chromates of rare earth and potassium cation with a general formula $KRE(CrO_4)_2$ were obtained by a hydrothermal synthesis method at low temperature (120-150°C) in sealed glass tubes during one month or by direct reaction in air between the stoichiometric proportions from a finely ground mixture of potassium chromate and rare earth oxides, $K_2Cr_2O_7/RE_2O_3$.

In the lanthanide series three different structural types were found. Compounds with heavy rare earths (La-Eu), constitute the first isostructural series. For that series the monoclinic structural type belongs to the $P2_1/c$ space group (N°14). In that phase the lanthanum ion, nine-fold coordinated, (La-O distances between 2.51 and 2.761 Å) is located in $(La(CrO_4)_2)_n^-$ layer perpendicular to the a crystallographic axis [1]. Each layer is built by double rows of CrO_4^{-2} tetrahedra linked to the lanthanum atom through oxygen atoms. The K^+ ions are situated between these layers. All atoms occupy the general $4e$ position in the crystal lattice. There is only one site of very low symmetry, (C_1) , for the rare earth ion.

In the middle of the rare earth series (RE = Eu, Gd and Tb) another phase with the orthorhombic structure is found, belonging to the $P2_12_12_1$ space group (N°19) [2]. The structure consists of CrO_4 tetrahedra and REO_8 distorted bi-capped trigonal prisms sharing corners and forming channels parallel to the b axis. The rare earth ion is eight-fold coordinated, (Eu-O distances are between 2.25 and 2.74 Å, for example). According to the crystallographic analysis the rare earth ion occupies here also one point site of low symmetry, C_1 .

At the end of the rare earth series a third structural modification was found and determined as monoclinic one [6]. The optical analysis were not realized on that series. This class of compounds will not be considered in the following.

2.2. $RE(OH)CrO_4$

The rare earth hydroxo-chromates with a general formula $RE(OH)CrO_4$ were obtained from RE_2O_3 , CrO_3 and $Li(OH)$ in molar ratios 1:4:3, by hydrothermal synthesis for 40 h at 130°C in sealed Pyrex glass tubes. They form one isostructural series for heavy lanthanides (RE = La-Nd) and crystallize in the monoclinic system, space group $P2_1/n$. The rare earth ion occupies one site of low symmetry, (C_1) , in the structure and is nine-fold coordinated (La-O distances: 2.467 to 2.729 Å). The structure $RE(OH)CrO_4$ consists in three-dimensional array in which the tetrahedral CrO_4 groups alternate with REO_9 polyhedra [3].

2.3. $RE_2(CrO_4)_3 \cdot 7H_2O$

Seven hydrated rare earth chromate phases with a general formula $RE_2(CrO_4)_3 \cdot 7H_2O$, exist for $RE = La-Gd$. The single crystals were grown by hydrothermal procedure from an aqueous solution of rare earth oxide, chromium oxide and lithium hydroxide in molar ratios 1:4:3, respectively, for 4 hours at $125^\circ C$ [4]. The compounds exhibit the monoclinic structure, space group $P2_1/n$, with two different crystallographic sites for the rare earth atoms both in nine coordination (Fig. 1a, for $RE = Sm$). The two (REO_9) units will be noted (RE1) and (RE2) in the following. The structure is formed by alternated units of (RE1) and (RE2) bridged by the chromate groups along the b axis (Fig. 1b, for $RE = Sm$). The rare earth oxygen distances $RE-O$ for two samarium atoms are: 2.35 and 2.60 and 2.37 to 2.56 Å for Sm1 and Sm2, respectively.

Lattice parameters for several rare earth chromates are collected in Table I.

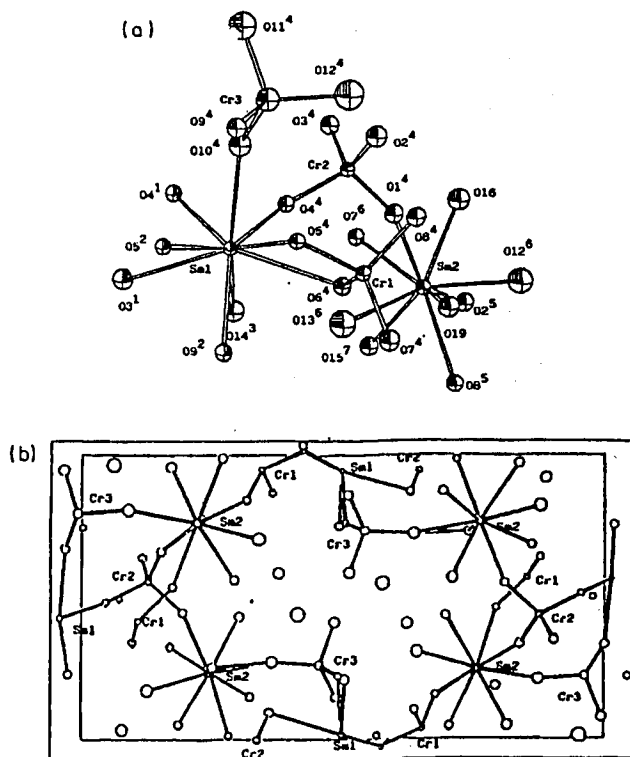


Fig. 1. (a) Coordination polyhedra of two samarium atoms in $Sm_2(CrO_4)_3 \cdot 7H_2O$ (from Ref. [4]). (b) Unit cell of $Sm_2(CrO_4)_3 \cdot 7H_2O$ (from Ref. [4]).

TABLE I
Lattice parameter for the rare earth chromates from
Ref. [1-4].

	a [Å]	b [Å]	c [Å]	β°
$\text{KLa}(\text{CrO}_4)_2$	8.729	7.475	11.049	92.42
$\text{KEu}(\text{CrO}_4)_2$	13.844	5.749	9.048	—
$\text{La}(\text{OH})\text{CrO}_4$	4.723	13.222	7.019	107.28
$\text{Sm}_2(\text{CrO}_4)_3, 7\text{H}_2\text{O}$	7.95	19.02	10.42	90.7

3. Analysis of the luminescence spectra

3.1. Experimental

The luminescence spectra of different rare earth chromates in polycrystalline form were obtained under 457.9 nm excitation of a Spectra Physics 164 Ar-ion laser. A Spectra Physics 375/376 continuous wave dye laser (with rhodamine 6G as the dye) pumped by argon ion laser was used to excite selectively the lowest excited 5D_J level, 5D_0 . The emission of the europium ion, dispersed by 1-m Jarrell Ash monochromator, was detected by a Hamamatsu R 374 photomultiplier in the visible region. All experiments were performed at liquid nitrogen temperature.

3.2. Emission spectra

For all rare earth chromates studied, the emission spectra of the trivalent europium ion embedded in the samples consists of numerous sharp lines. The 5D_0 is the only emitting level. All the observed lines are assigned to the ${}^5D_0 \rightarrow {}^7F_{0-4}$ electronic transitions. The luminescence from other 5D_J levels, $J = 1, 2$, is quenched. It is due to the multiphonon de-excitation process from upper 5D levels to the lowest 5D_0 level, or to the quenching process due to high concentration of the active ion in the pure europium compounds. The overview of the $\text{La}_2(\text{CrO}_4)_3, 7\text{H}_2\text{O} : \text{Eu}^{3+}$ emission spectrum (Fig. 2) recorded from 500 to 750 nm show the ${}^5D_0 \rightarrow {}^7F_2$ transition as the most intense one and it is valid for all rare earth chromates discussed in this work.

3.3. $\text{KLa}(\text{CrO}_4)_2$

The first luminescence study on the chromates has been performed on the lanthanum potassium double chromate, doped with europium as the spectroscopic active ion. As expected from the structural determination, one energy level scheme was deduced from the emission spectrum [7]. The point site symmetry for the rare earth ion is low, (C_1), the degeneracy of levels should be completely lifted in $2J + 1$ components for each J manifold. The optical and the structural data are in agreement in this case since one, three and five Stark components are present for ${}^5D_0 \rightarrow {}^7F_{0-2}$ transitions, respectively, for example.

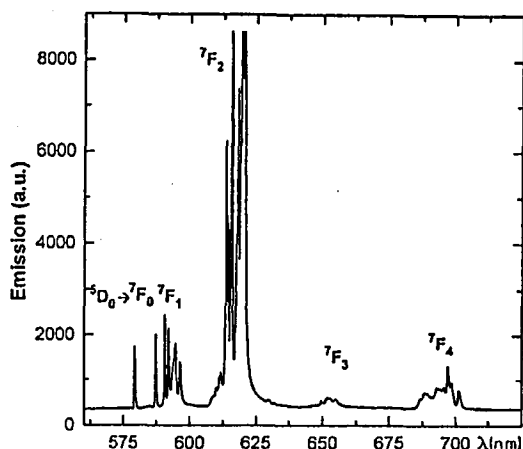


Fig. 2. Emission spectrum of $\text{La}_2(\text{CrO}_4)_3, 7\text{H}_2\text{O}:\text{Eu}^{3+}$ recorded at 77 K under 457.9 nm argon ion laser excitation.

3.4. $\text{K}(\text{Eu}, \text{Gd})(\text{CrO}_4)_2$

For $\text{K}(\text{Eu}, \text{Gd})(\text{CrO}_4)_2$ compounds synthesized by hydrothermal technique or by solid state reaction, on the contrary, different emission spectra are obtained. In the case of $\text{KEu}(\text{CrO}_4)_2$ prepared by the solid state reaction two relatively intense lines are observed for the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0, {}^7\text{F}_1$ transition, whereas for $\text{KGD}(\text{CrO}_4)_2:\text{Eu}^{3+}$ 1% only one exists. It means two point sites for the stoichiometric europium compound, or an additional impurity phase, and one local symmetry environment in the case of the gadolinium potassium chromate. Moreover, for $\text{KEu}(\text{CrO}_4)_2$ prepared by the hydrothermal method several extra lines are present in the emission spectrum (upper spectrum (a) in Fig. 3). From the crystallographic investigation the same structure was found for both compounds. In fact, the X-ray spectra collected in Fig. 4 are identical for the europium and the gadolinium chromates synthesized using direct solid state reaction. Some new intense diffraction lines (noted by * on the lowest diffraction pattern in Fig. 4) are present for the europium chromate synthesized by the hydrothermal method. The $\text{KEu}(\text{CrO}_4)_2$ synthesized by hydrothermal technique seems to be dimorphic, but this extra phase is not identified yet.

In order to clarify the discrepancy between the structural and optical data for double chromates prepared by direct solid state reaction, $\text{K}(\text{Eu}_x\text{Gd}_{1-x})(\text{CrO}_4)_2$ compounds with various concentrations of the doping ion ($x = 0.01, 0.03, 0.05$ and 1) are studied by luminescence spectroscopy. It is evident from Fig. 5 that at very low concentration of europium, (lower trace d), the extra spectrum disappears, the remaining one corresponds to the rare earth in one local point site in $\text{KGD}(\text{CrO}_4)_2$ chromate as stated by the crystallographic study [2]. The relative intensity of the second spectrum increases with the the doping ion concentration. The extra spectrum does not correspond to the one observed in $\text{KLa}(\text{CrO}_4)_2:\text{Eu}^{3+}$ [7]. This indicates a new phase, whereas no clear difference is seen from X-ray diffrac-

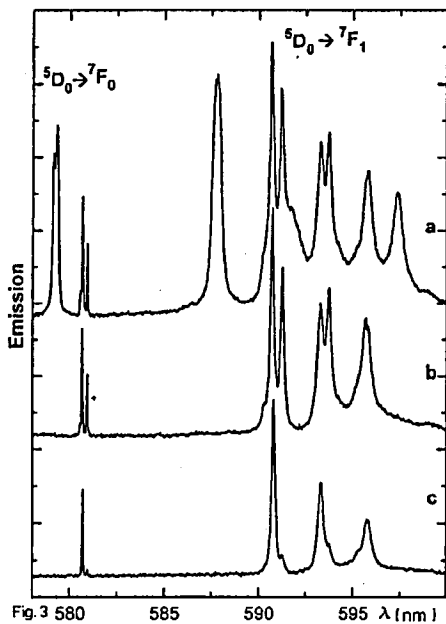
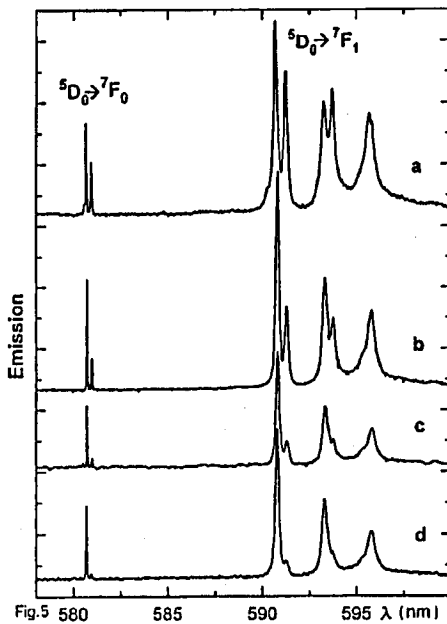
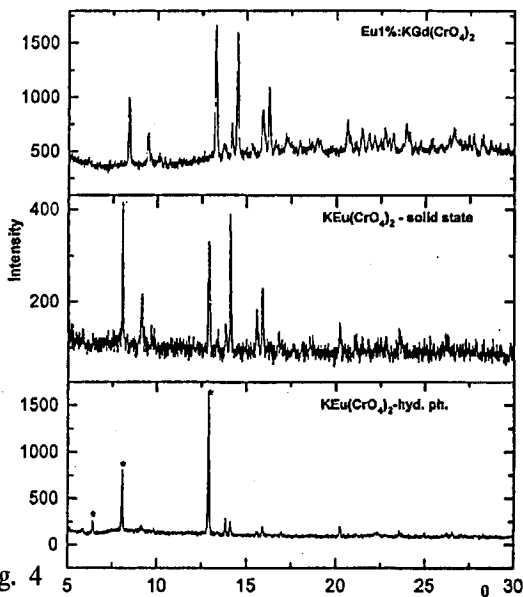
Fig.3 580 585 590 595 λ (nm)Fig.5 580 585 590 595 λ (nm)

Fig. 4 5 10 15 20 25 0 30

Fig. 3. A part of the emission spectrum of pure $\text{KEu}(\text{CrO}_4)_2$; hydrothermal synthesis method (a) and solid state reaction (b) and $\text{KGd}(\text{CrO}_4)_2 : \text{Eu}^{3+}$ 1% solid state reaction (c) recorded at liquid nitrogen temperature.

Fig. 4. X-ray diffraction patterns of $\text{KGd}(\text{CrO}_4)_2 : \text{Eu}^{3+}$ 1% and $\text{KEu}(\text{CrO}_4)_2$.

Fig. 5. Fluorescence spectra for different europium concentrations in $\text{KGd}(\text{CrO}_4)_2$ 1, 3, 5 and 100%, $T = 77$ K, (a) — $\text{KEu}(\text{CrO}_4)_2$, (b) — 5% $\text{Eu}^{3+} : \text{KGd}(\text{CrO}_4)_2$, (c) — 3% $\text{Eu}^{3+} : \text{KGd}(\text{CrO}_4)_2$, (d) — 1% $\text{Eu}^{3+} : \text{KGd}(\text{CrO}_4)_2$.

tion for the compounds synthesized by solid state reaction, or some effects of pair between europium ions, or other interactions. The question is still open. This first approach indicates that the europium ion is situated in all this family chromates in very low symmetry site.

Spectroscopic study performed on $\text{KEu}(\text{CrO}_4)_2$ samples prepared by two techniques, as well as on the doped $\text{KGd}(\text{CrO}_4)_2$ compounds, underlines the difference with the crystallographic analysis. A more detailed study is necessary.

3.5. $\text{RE}(\text{OH})\text{CrO}_4$

For this series we studied the lanthanum hydroxo-chromate doped with the europium trivalent ion. From the emission spectra it is evident that the rare earth ion occupies one point site in that structure and confirms the crystallographic data [3]. As the point site symmetry of the rare earth ion is very low, C_1 , no selection rules exist. In this case, all transitions are allowed and the ${}^7F_{1,2,4}$ levels are split in 3, 5 and 9 Stark sublevels, respectively, see Fig. 6 for ${}^5D_0 \rightarrow {}^7F_{0,1}$ transitions. In the region of the ${}^5D_0 \rightarrow {}^7F_3$ transition some broad vibronics are observed and only four from seven components can be assigned to the 7F_3 level. One energy level scheme for Eu^{3+} can be deduced from the luminescence spectrum. The experimental ${}^7F_{0,1}$ energy levels are only used for determination of the phenomenological crystal field (CF) parameters of rank 2 and the CF strength parameter, N_v (see Sec. 4). The results are gathered in Tables II and III.

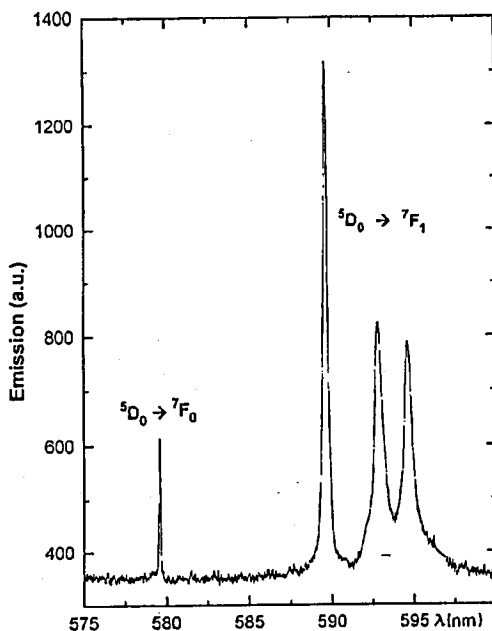


Fig. 6. A part of the emission spectrum of $\text{La}(\text{OH})\text{CrO}_4:\text{Eu}^{3+}$ under 457.9 nm excitations, $T = 77$ K.

TABLE II

5D_0 and 7F_1 energy positions, 7F_1 barycenters and overall splittings (all values in cm^{-1}).

	KLa(CrO_4) ₂	KEu(CrO_4) ₂	KEu(CrO_4) ₂ hyd.ph.	KGd(CrO_4) ₂	La(OH)CrO ₄	La ₂ (CrO ₄) ₃ , 7H ₂ O Site 1	La ₂ (CrO ₄) ₃ , 7H ₂ O Site 2
5D_0	17259	17208	17259	17218	17248	17260	17248
7F_1	261	295	247	289	293	233	319
	366	367	364	363	385	434	365
	503	425	520	433	436	498	437
$bc\ ^7F_1$	376.6	362.3	377	361.66	371.3	388.3	373.6
$\Delta E\ ^7F_1$	242	130	273	144	143	265	118

TABLE III

Crystal field parameter values of rank 2 and CF strength parameter, N_v , for the rare earth chromates studied in this work (all values in cm^{-1}).

B_q^k	KLa(CrO_4) ₂	KEu(CrO_4) ₂	KEu(CrO_4) ₂ hyp.ph.	KGd(CrO_4) ₂	La(OH)CrO ₄	La ₂ (CrO ₄) ₃ , 7H ₂ O Site 1	La ₂ (CrO ₄) ₃ , 7H ₂ O Site 2
B_0^2	-630	315	-713	359	306	-867	318
B_2^2	282	150	322	154	191	133	96
N_v	1182	602	1341	665	647	1406	548

3.6. $RE_2(\text{CrO}_4)_3, 7\text{H}_2\text{O}$

We also analysed the luminescence of the europium embedded in the first chromate of that isostructural series, $\text{La}_2(\text{CrO}_4)_3, 7\text{H}_2\text{O}:\text{Eu}^{3+}$. Two different local environments are present for the rare earth ion in that crystallographic phase as it is shown in Fig. 7. This confirms the structural determination given in Ref. [4].

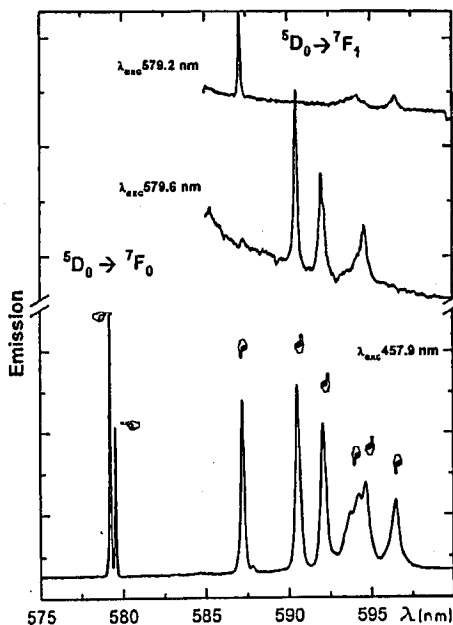


Fig. 7. A part of the emission spectrum of $\text{La}_2(\text{CrO}_4)_3, 7\text{H}_2\text{O}:\text{Eu}^{3+}$ under various excitations, $T = 77\text{ K}$.

The selective excitation in the two 0-0 lines observed for $\text{La}_2(\text{CrO}_4)_3, 7\text{H}_2\text{O}:\text{Eu}^{3+}$ allows us to separate two different energy level schemes. They are associated to sites with quite different crystal field strengths. According to the structural determination both sites correspond to rare earth atoms in low symmetry environment, C_1 . Then, $2J+1$ Stark sublevels are expected for 7F_J manifolds, as explained in sections 3.3. and 3.5. In fact, numerous extra lines observed in the emission spectrum are identified as vibronics associated to ${}^5D_0 \rightarrow {}^7F_2$ and ${}^5D_0 \rightarrow {}^7F_3$ transitions. The appearance of these vibronics complicates the assignment of the electronic lines and for some J levels some components are missing. All M_J sublevels are found for the 7F_1 level for both sites, whereas for the 7F_2 level we observed all components only for site 2. From the overall splittings of 7F_1 levels, 265 and 118 cm^{-1} for site 1 and site 2, respectively, it is obvious that the crystal field strengths are different for two rare earth ions. It is discussed more in detail in Sec. 4 treating the CF simulation.

Some consideration can be done on the energy position of the ${}^5D_0 \rightarrow {}^7F_0$ transition and the rare earth coordination in the chromates. For example, two in-

tense lines observed for the ${}^5D_0 \rightarrow {}^7F_0$ transition in $\text{La}_2(\text{CrO}_4)_3, 7\text{H}_2\text{O}:\text{Eu}^{3+}$ are situated at 17260 and 17248 cm^{-1} for site 1 and site 2, respectively. In the case of $\text{KEu}(\text{CrO}_4)_2$ double chromate (discussed in Sec. 3.4.) the positions of two lines detected for the ${}^5D_0 \rightarrow {}^7F_0$ transition lie at lower energy: 17218 and 17208 cm^{-1} . The rare earth coordination is different in these chromates. In the seven hydrated chromates both lanthanide ions are nine-fold coordinated and in the potassium double chromate the rare earth is eight-fold coordinated. In hydroxo-chromate (Sec. 3.5.), for which the rare earth is also surrounded by nine oxygen atoms, this transition is found at the same energy position as in the $\text{La}_2(\text{CrO}_4)_3, 7\text{H}_2\text{O}$, as well as for the impurity phase present in the $\text{KEu}(\text{CrO}_4)_2$ compound (Sec. 3.4.) prepared by the hydrothermal synthesis method (see Table II). For this impurity phase the coordination of the rare earth is then supposed to be nine also. Moreover, from emission (upper spectrum, Fig. 3), it can be deduced that the local environment of the rare earth ion is very low, like in other chromates, but with greater crystal field strength.

4. Crystal field simulation

The trivalent europium ion, $4f^6$ configuration, possesses a total of 3003 $[SLMJ]$ Stark levels for low symmetry sites. The particularity of this configuration is that the lowest level, 5D_0 , of the first excited 5D_J multiplet is situated at 12000 cm^{-1} far from the highest J level of the ground 7F_J multiplet. So, the phenomenological CF simulation can be performed on the ground multiplet only, taking into account its 49 components. The wave functions are relatively pure, there is only a small admixture with the 5D and 5G states.

According to Wybourne's formalism, the crystal field Hamiltonian can be expressed as

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

with B_q^k and S_q^k being the real and imaginary CF parameters and C_q^k the spherical harmonics [8].

In the case of C_1 local symmetry for the rare earth ion, there are 15 CF parameters, 9 real and 6 imaginary ones. This large number of fitting parameters necessitates a great number of experimental levels [9]. For CF simulation in chromates an approaching symmetry, for example C_{2v} symmetry, can be used giving good results [7]. Here, instead of 15 we deal with only 9 real CF parameters

$$H_{\text{cf}}(C_{2v}) = B_0^2 + B_0^4 + B_0^6 + B_2^2(C_2^2 + C_{-2}^2) + B_2^4(C_2^4 + C_{-2}^4) \\ + B_2^6(C_2^6 + C_{-2}^6) + B_4^4(C_4^4 + C_{-4}^4) + B_4^6(C_4^6 + C_{-4}^6) + B_6^6(C_6^6 + C_{-6}^6).$$

To evaluate the strength of the crystal field about the rare earth ion surrounded by its ligand cortege in various compounds, the crystal field strength parameter, N_v , is used, given by [10]

$$N_v = \left[\sum_{kq} \frac{4\pi}{2\kappa + 1} |B_q^k|^2 \right]^{1/2}.$$

From the emission spectra of chromates studied, the only observed level assigned with no doubt for all of them, is the 7F_1 level. Therefore, we are interested in the 7F_1 manifold and the phenomenological CF calculation is performed taking into account only the B_0^2 and B_2^2 parameters. For the $J = 1$ value, the CF strength parameter N_v is then

$$N_v = \left[\frac{4\pi}{5} \sum_q |B_q^k|^2 \right]^{1/2}$$

In Table III one can find the CF parameter values of rank 2 deduced from the experimental optical data and the CF strength parameter N_v . The evolution of the overall 7F_1 splitting in function of N_v is presented in Fig. 8. This parameter classifies the compounds according to their crystal field extent. In chromate family, two groups are constituted, with small or medium N_v values and the largest N_v values as it is explicit from Fig. 8. The N_v values calculated for various chro-

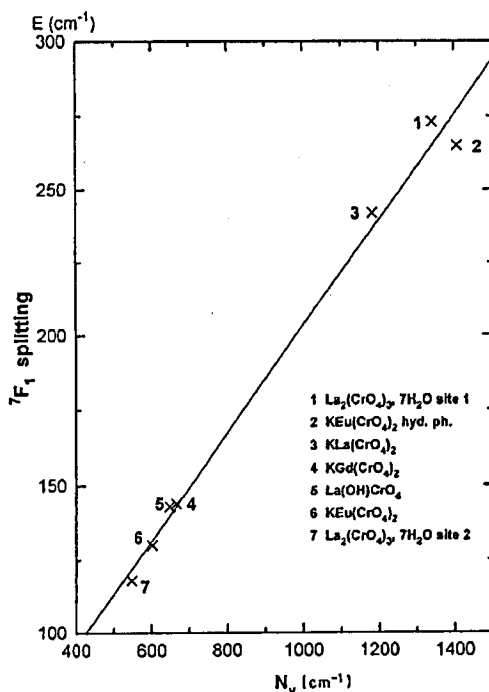


Fig. 8. The CF strength parameter N_v in function of the overall 7F_1 splitting.

mates are small in comparison with those found in the C-type rare earth oxide series, for example, for which N_v is going from 1491 cm^{-1} (Gd_2O_3) to 2158 cm^{-1} (Sc_2O_3) [11]. In fact, the maximum splitting of the 7F_1 level is 273 cm^{-1} for the unknown phase in $\text{KEu}(\text{CrO}_4)_2$ synthesized by hydrothermal method (or 265 cm^{-1}

for $\text{KLa}(\text{CrO}_4)_2$) instead of 461 cm^{-1} in Sc_2O_3 . Therefore, the CF parameters of rank 2 in chromates are not high and it seems to be alike for other CF parameter values. This indicates the low potential of those compounds as efficient phosphors or for laser application.

Acknowledgments

The authors wish to thank Dr. P. Porcher for providing CF calculation program.

References

- [1] I. Bueno, C. Parada, O. Garcia, E. Gutiérrez Puebla, A. Monge, C. Ruiz Valero, *J. Chem. Soc. Dalton Trans.*, 1911 (1988).
- [2] I. Bueno, C. Parada, J.A. Hermoso, A. Vegas, A. Martinez Ripoll, *J. Solid State Chem.* **85**, 83 (1990).
- [3] I. Bueno, C. Parada, E. Gutiérrez Puebla, A. Monge, C. Ruiz Valero, *J. Solid State Chem.* **78**, 78 (1989).
- [4] I. Bueno, C. Parada, A. Monge, C. Ruiz Valero, *An. Quim.* **87**, 1050 (1991).
- [5] C.K. Jorgensen, *Chimica* **38**, 74 (1984).
- [6] I. Bueno, C. Parada, A. Monge, C. Ruiz Valero, in: *Proc. Latin-American Inorg. Chem. Meeting, Santiago de Compostela, Spain, Sept. 1993*, p. 392.
- [7] E. Antic-Fidancev, M. Lemaitre-Blaise, P. Porcher, I. Bueno, C. Parada, R. Saez Puche, *Inorg. Chim. Acta* **182**, 5 (1991).
- [8] B.G. Wybourne, *Spectroscopic Properties of Ions in Crystals*, Interscience, New York 1965.
- [9] E. Antic-Fidancev, M. Lemaitre-Blaise, J.P. Chaminade, P. Porcher, *J. Alloys Comp.* **180**, 223 (1992).
- [10] F. Auzel, O.L. Malta, *J. Phys. (France)* **44**, 201 (1983).
- [11] O.L. Malta, E. Antic-Fidancev, M. Lemaitre-Blaise, A. Milicic-Tang, M. Taibi, *J. Alloys Comp.* **228**, 41 (1995).