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Crystal Field Effects in Lutetium Disilicates Doped with Eu^{3+} *

JORMA HÖLSÄ†, PIERRE PORCHER**

Department of Chemistry, Helsinki University of Technology, SF-02150 Espoo, Finland

and CHRISTIAN CHATEAU

E.R. 211 du C.N.R.S., 1 Pl. A. Briand, F-92190 Meudon, France

The rare earth (RE) silicates yield a disilicate phase with the composition of the RE_2O_3:SiO_2 ratio 1:2 throughout the whole RE series [1]. The $RE_2Si_2O_7$ phase, however, shows structural polymorphism depending on the temperature and pressure used in preparation [1–3]. To date, as many as seven different polymorphic forms have been found. In most cases the crystal structures of the RE disilicates have been determined [1, 3–7] but only a few investigations of the luminescence properties of these silicates have been carried out [8–10].

In this paper we report the comparative study of the optical luminescence of the Eu^{3+} ion for two forms of the lutetium disilicate, the ambient pressure form C-$Lu_2Si_2O_7$ and one of the high pressure forms, D-$Lu_2Si_2O_7$. In addition, we have carried out the parametric simulation of the crystal field (c.f.) splittings of the $^7F_{0-5}$ energy levels.

Experimental

Preparation of $Lu_2Si_2O_7$

The ambient pressure C form of the lutetium disilicate was prepared from a mixture of coprecipitated lutetium and europium hydroxides and silicic acid heated at 1620 K for 60 h. The D form of lutetium disilicate was obtained through the high pressure and temperature transformation of the C form treated for 1 h at 1470 K and 2 GPa and rapidly quenched. The nominal concentration of the Eu^{3+} dopant was 5 mol per cent.

Optical Measurements

The luminescence of $Lu_2Si_2O_7$:Eu^{3+} powder samples was excited by radiation from either a conventional UV lamp or a rhodamine dye laser. A 200 W mercury lamp with wide-band filters provided a global excitation source passing radiation of around 250 nm. This wavelength corresponds to the higher wavelength limit of the strong charge-transfer absorption band (maximum at 220 nm) of the Eu^{3+} ion in both forms of $Lu_2Si_2O_7$.

A Spectra Physics 375/376 continuous wave dye laser (with rhodamine 6G as the dye) pumped by a Spectra Physics 164 argon ion laser was used to excite selectively on the lowest excited ^5D level of the Eu^{3+} ion, $^5D_0$, near 580 nm.

The luminescence was recorded at ambient and liquid nitrogen temperatures. The emission was dispersed by a 1-m Jarrell–Ash monochromator and detected by a Hamamatsu R374 photomultiplier. The wavelength range between 400 and 750 nm was scanned.

Crystal Structure of $RE_2Si_2O_7$

The ambient pressure form of RE disilicates, C-$RE_2Si_2O_7$ (RE = Tm–Lu and also In and Sc), crystallizes in the monoclinic crystal system with the space group $C2/m$ ($Z = 2$) [6]. The crystal structure consists of Si_2O_7 double tetrahedra as well as REO_6 octahedra. The two SiO_4 tetrahedra within the $Si_2O_7^{6-}$ group are linked with the Si–O–Si angle of 180°. The rare earth ions occupy one site with C_2 symmetry.

Under high pressure and temperature the thortveitite type C disilicate transforms to the D-$RE_2Si_2O_7$ [3] which crystallizes in the monoclinic crystal system with the space group $P2_1/a$ ($Z = 2$) [7]. The orientation of the $Si_2O_7^{6-}$ groups as well as their connection to the REO_6 polyhedra in D-$RE_2Si_2O_7$ differ slightly from those in the C form. The RE atoms occupy a single site with C_1 symmetry.

Results and Discussion

Energy Level Schemes

The $^7F_{0-5}$ energy level schemes of the Eu^{3+} ion in the high and low pressure forms of lutetium disilicate reveal only minor differences in the c.f. splittings and in the barycenters of the individual $^{2S+1}L_J$ levels (Fig. 1). The close resemblance of the energy level schemes is due to the similar coordination of the lutetium atoms in the two disilicate forms. The effect of the phase transitions induced by the external pressure seems to have only minor effects both on the crystal structure and on the energy level scheme of the Eu^{3+} ion. In the REOOH case both the structural modifications [11, 12] and the energy level schemes of the Eu^{3+} ion [13] were significantly affected by the external pressure.

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†Author to whom correspondence should be addressed. Present address: Chemistry Department, University of Dar es Salaam, P.O. Box 35061, Dar es Salaam, Tanzania.

**Permanent address: E.R. 210 du C.N.R.S., 1 Pl. A. Briand, F-92190 Meudon, France.

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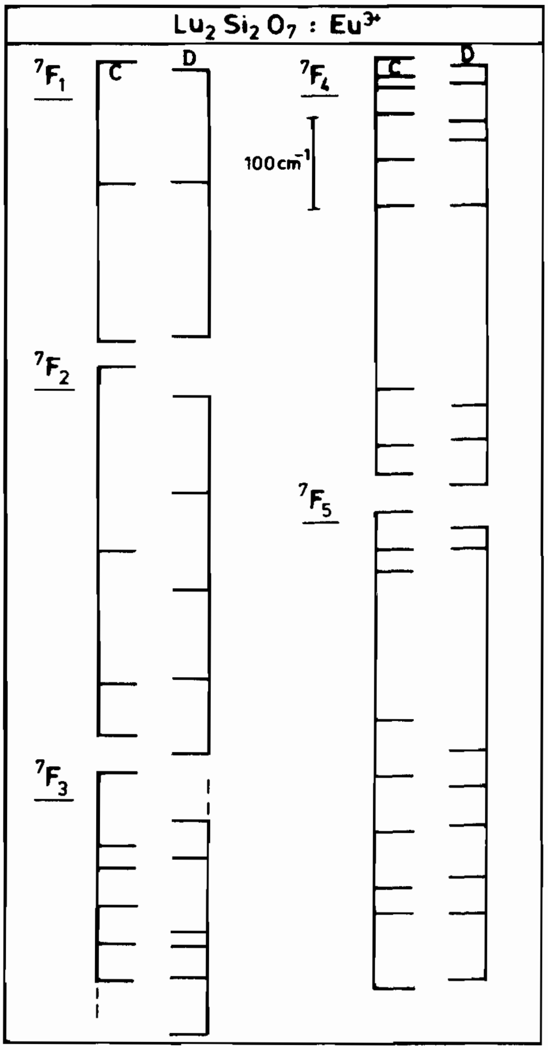

Fig. 1. Comparison between the experimental c.f. splittings of the $^7F_{0-5}$ levels of the Eu^{3+} ion in the low ($C\text{-}Lu_2Si_2O_7$) and the high pressure modification ($D\text{-}Lu_2Si_2O_7$).

Crystal Field Analysis

Using Wybourne's formalism [14] the c.f. Hamiltonian can be expressed as a sum of the products between the real and imaginary even rank c.f. parameters (B_q^k and S_q^k) and spherical harmonics (C_q^k).

$$\mathcal{H}_{cf} = \sum_{kq} (B_q^k(C_q^k + (-1)^q C_{-q}^k) + iS_q^k(C_q^k - (-1)^q C_{-q}^k))$$

In the C_2 symmetry case the c.f. Hamiltonian $\mathcal{H}_{cf}(C_2)$ contains 14 parameters including 5 imaginary ones (Table I).

The phenomenological simulation of the c.f splittings between the 32(33) Stark sublevels of the $^7F_{0-5}$ energy levels yielded excellent results. The overall r.m.s. deviation between the calculated and experimental energy levels equals to 6 cm^{-1} in both disilicates (Table I). Furthermore, no large individual discrepancies within the energy level schemes can be observed.

TABLE I. The Values of the Even Rank Crystal Field B_q^k and S_q^k Parameters for $C\text{-}Lu_2Si_2O_7:Eu^{3+}$ and $D\text{-}Lu_2Si_2O_7:Eu^{3+}$ [a]

	$C\text{-}Lu_2Si_2O_7$	$D\text{-}Lu_2Si_2O_7$
B_0^2	40(21)	122(22)
B_0^2	−755(12)	−705(13)
B_2^2	−1092(51)	−863(41)
B_2^4	−318(23)	59(25)
S_2^4	−1541(29)	−1512(27)
B_4^4	−567(21)	−444(27)
S_4^4	154(23)	−236(24)
B_0^6	−994(55)	−513(56)
B_2^6	−13(28)	109(37)
S_2^6	198(39)	64(47)
B_4^6	−91(29)	−312(33)
S_4^6	488(29)	214(37)
B_6^6	54(28)	685(30)
S_6^6	−425(28)	−200(31)
S	615	569
r.m.s. deviation	5.8	5.5

[a] The numbers in parentheses refer to the standard deviations of the parameters. All values are in cm^{-1} units.

The best fit sets of the B_q^k and S_q^k parameters are characterized by weak B_0^2 and strong B_2^2 parameter values. The high values of the B_2^2 parameter indicate important deviation from higher than the C_{2v} symmetry for the Lu site. A significant distortion even from the C_{2v} symmetry is revealed by the unusually strong S_2^4 parameter. When these results are compared to the slight differences in RE–oxygen distances given by the structural data, it is evident that even slight distortions induce significant effects to the crystal field experienced by the Eu^{3+} ion.

The results of the c.f. analysis obtained for the high pressure and temperature form of the lutetium disilicates are rather similar to those obtained for the low pressure form. The lowering of the site symmetry from C_2 in the form C to C_1 in the form D seems to have no effect either on the quality of the simulation or on the magnitude of the c.f. parameters. The individual parameter values differ significantly only in a few cases, the B_2^4 and B_6^6 differing the most between the two sets (*cf.* Table I). The B_2^4 parameter values are rather small and the lack of experimental data for the $^7F_6$ energy level renders the sixth rank parameters less well defined than the second and the fourth rank parameters. The c.f. strength parameter is slightly weaker in the D-$Lu_2Si_2O_7$:Eu^{3+} but the two values lie close to the experimental uncertainty.

The comparison of the best fit c.f. parameter sets of $Lu_2Si_2O_7$:Eu^{3+} to those obtained for the RE oxy salts, *i.e.* oxyhalides, oxysulfates and oxymolybdates/oxytungstates [15–18], shows no resemblance between these results. Consequently, the existence of the $(REO)_n^{n+}$ complex cation as the basic structural unit in RE disilicates is highly improbable despite the apparent similarities in empirical formulae.

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