

LASER SELECTIVE EXCITATION OF CaS:Pr *

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C_{2v} and C_{4v} sites have been identified in CaS:Pr,Na by laser selective excitation. Vibronic transition from the sites without charge compensator nearby has also been discussed.

1. INTRODUCTION

CaS has NaCl structure, the local symmetry of Ca is O_h . As trivalent rare earth ion substitutes for divalent calcium, the excessive charge is compensated by codoped monovalent alkali metal ion or by calcium vacancy¹. Moreover, introducing charge compensation distorts the local symmetry of the rare earth ions, thus makes intra-4f configuration electric dipole transition of the rare earth ion possible.

In this paper, Pr^{3+} sites with different local symmetries in CaS:Pr,Na have been studied by laser selective excitation, their properties have been discussed.

2. EXPERIMENTAL RESULTS

Sample was prepared with the method described in². The concentrations of Pr and Na are 0.1 at.% and 0.5at.% respectively. X-ray diffraction shows that only CaS phase exists in the sample.

The sample immersed in liquid nitrogen is excited by a nitrogen laser pumped dye laser. A mixture of coumarin-460 and coumarin-485 dissolved in ethyl alcohol (molar concentration $5 \times 10^{-3} + 5 \times 10^{-3}$) is used as laser dye. Fluorescence of the sample is measured by a Spex-1403 monochromator and processed by a microprocessor. Emission spectrum excited by the nitrogen laser is also measured.

The dye laser is tuned around 20200cm^{-1} , with

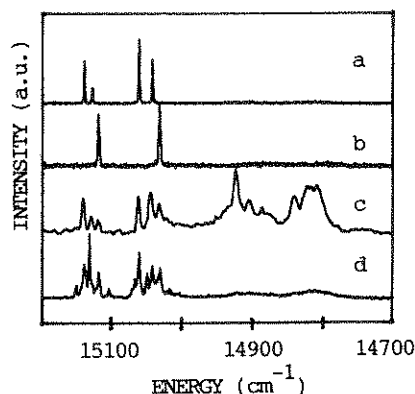


FIGURE 1
 $^3P_0-^3F_2$ emission spectra of Pr^{3+} in CaS: 0.1 at.% Pr, 0.5 at.% Na at 77K, the excitations are a) 20198cm^{-1} ; b) 20182cm^{-1} ; and c) 20291cm^{-1} ; d) 337.1 nm.

which 3P_0 of Pr^{3+} is populated. Spectra of $^3P_0-^3F_2$ emission under various excitation wavenumbers are shown in Fig. 1 a-c. Fig. 1 d is the emission spectrum excited by 337.1nm. In Fig. 2, excitation spectra of the fluorescences corresponding to Fig. 1 a, b and c are shown.

Samples with constant Pr concentration (0.1 at.%) and different concentrations of codopant (0.01 at.% and 0.5 at.% K) were also prepared. Their fluorescence spectra excited by 337.1nm are compared in Fig. 3.

3. DISCUSSION

The emission lines in Fig. 1 a, b and d are

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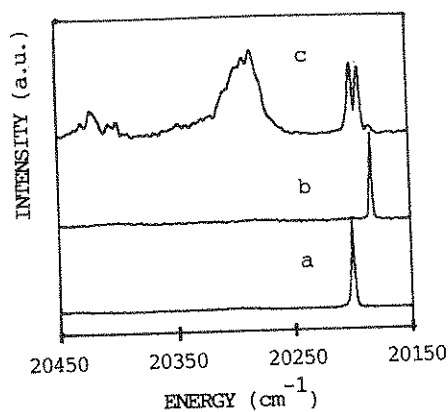


FIGURE 2
Excitation spectra of CaS:Pr,Na, at 77K, monitoring at a) 15062 cm^{-1} (A); b) 15119 cm^{-1} (B); and c) 14927 cm^{-1} (C).

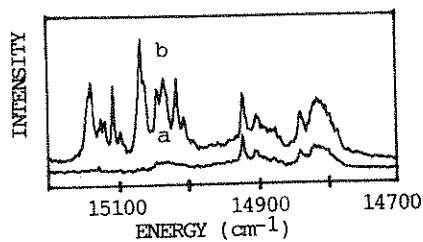


FIGURE 3
 $^3\text{P}_0$ - $^3\text{F}_2$ emission spectra of a) CaS: 0.1 at.% Pr, 0.01 at.% K; b) CaS: 0.1 at.% Pr, 0.5 at.% K, excited with 337.1 nm at 77K.

listed in Table 1. With 337.1nm, many sites can be excited simultaneously. Most of the lines in first row of Table 1 can be selectively excited, site A and site B are the strongest among them. $^3\text{P}_0$ - $^3\text{F}_2$ emissions of A and B are with 4 and 2 lines respectively. Considering possible compensation sites and selection rules, A and B are, most likely, sites with C_{2v} and C_{4v} symmetries, compensations are in (1,1,0) and (0,0,1) directions, which are the directions oriented to the nearest and next nearest calcium sites.

Table 1. $^3\text{P}_0$ - $^3\text{F}_2$ emission lines of various Pr sites in CaS:Pr,Na

Site	Excitation (cm^{-1})	Emission (cm^{-1})
	29665 (337.1nm)	15151.8, 15144.4, 15140.6 15138.4, 15133.0, 15129.0 15123.8, 15119.2, 15105.0 15087.6, 15071.0, 15068.2 15062.0, 15051.2, 15043.4 15037.0, 15032.4, 15022.4 15017.8, 15005.6
A	20198	15140.6, 15129.0, 15062.0, 15043.0
B	20182	15119.4, 15032.4

In the spectrum excited by 337.1nm, besides two groups of narrow lines, there are two broad bands (C) located at about 220 cm^{-1} below the narrow ones, while C is rather weak in the case of selective excitation of A and B. Intensity of C relative to that of the narrow lines increases with reducing the concentration of compensation ions (Fig. 3) or increasing temperature. Excitation peaks of C are at the high energy side of $^3\text{P}_0$. The facts indicate that C is from vibronic transition. Local symmetry of Pr ions without compensation nearby is approximately O_h , intra-4f transition in this case is mainly due to coupling of the electronic states with the vibration modes without inverse symmetry.

REFERENCES

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