

## THE OPTICAL PROPERTIES OF $\text{Pr}^{3+}$ EMBEDDED IN THE RARE EARTH BOROGERMANATE MATRICES: $\text{REBGeO}_5$

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### Abstract

The luminescent properties of the trivalent praseodymium ion in the trigonal borogermanate matrice  $\text{PrBGeO}_5$  have been analysed. The energy level schemes are deduced from the absorption and emission spectra and reproduced with 14 crystal field parameters (cfps) according to the local point symmetry occupied by the rare earth element in the matrix.

### Introduction

Two crystallographic varieties of  $\text{REBGeO}_5$  system are found. For the larger rare earth ions,  $\text{RE} = \text{La}$ ,  $\text{Pr}$  and  $\text{Nd}$  (Low temperature phase) a trigonal phase having the stillwellite ( $\text{CeBSiO}_5$ ) structural type can be obtained (1- 7). For the smaller ones:  $\text{Nd}$  (high temperature phase)-  $\text{Er}$  and  $\text{Y}$ , a monoclinic phase exists, with the datolite structural type (5, 8). For other rare earths ( $\text{Tm}$ ,  $\text{Yb}$ ,  $\text{Lu}$ ) this stoichiometry doesn't exist, and even  $\text{GdBGeO}_5$  is difficult to obtain free of pyrogermanate  $\text{Gd}_2\text{Ge}_2\text{O}_7$ . The interest of these compounds is their potential use as an effective self-frequency-doubling mini-laser. It is thus important to study their optical properties in order to classify these compounds among the laser matrices and derive the knowledge of the wave-functions, which are necessary to interpret the excited dynamic states in that system.

This work deals with the luminescent properties of the trivalent praseodymium ( $4f^2$  configuration) ion in the trigonal

borogermanate matrices  $\text{PrBGeO}_5$ . The energy level schemes are deduced from the measured absorption and emission spectra at different temperatures. The crystal field calculation can be performed accurately with  $91 \times 91$  matrix taking into account all  $^{2S+1}\text{L}_J$  levels. We have reproduced the energy levels with 14 crystal field parameters according to the local point site symmetry occupied by the rare earth element in the structure.

### Experimental details

Polycrystalline samples of  $\text{REBGeO}_5$  were synthesized by solid state reactions between high purity  $\text{RE}_2\text{O}_3$  (or  $\text{Pr}_6\text{O}_{11}$ ),  $\text{H}_3\text{BO}_3$  and  $\text{GeO}_2$  as starting materials. The stoichiometric mixture is ground and progressively heated in a platinum crucible at  $850^\circ\text{C}$  during 24 hours. The resulting compounds is ground again and heated during 24 hours more at  $1100^\circ\text{C}$ . In order to avoid the formation of the pyrogermanate phase  $\text{RE}_2\text{Ge}_2\text{O}_7$ , some preparations were carried out with small excess of  $\text{H}_3\text{BO}_3$  ( $< 5\%$  mole). The

samples were checked by the X-ray diffraction technique.

The absorption spectra were obtained with 2400 Cary spectrophotometer at 300, 77 and 9 K between 420 and 2500 nm ( 23800 and 4000  $\text{cm}^{-1}$ ).

The luminescence spectra of samples were recorded using 457.9 nm blue line of a 5 W argon ion laser. The emissions observed correspond to  $^3\text{P}_0 \rightarrow ^3\text{H}_J$ ,  $^3\text{F}_J$  and  $^1\text{D}_2 \rightarrow ^3\text{H}_{4,5}$  transitions of  $\text{Pr}^{3+}$  in  $\text{PrBGeO}_5$  matrix. Selectively emission of  $^1\text{D}_2$  level was performed using a continuous rhodamine 6G dye laser pumped by an argon ion laser.

### Crystal structure

The crystal structure of  $\text{REBGeO}_5$  compounds depends on the rare earth size. The borogermanates, which crystallise in the stillwellite structural type, have  $\text{P3}_1$  as space group. In that phase the rare earth ion is in nine-fold coordination and its site point symmetry is very low  $\text{C}_1$ . The second variety of these compounds for the smaller rare earth ions is isomorphous with the datolite  $\text{CaBSiO}_4(\text{OH})$ . The unit cell symmetry is monoclinic and  $\text{P2}_1/a$  as space group (8). The  $\text{RE}^{3+}$  ion is surrounded by eight oxygen atoms forming a distorted cube. Both structure modifications contain  $\text{BO}_4$  and  $\text{GeO}_4$  tetrahedra in an orderly arrangement.

### Results and discussion

In the low temperature absorption spectra of studied compounds, the  $^3\text{H}_4 \rightarrow ^3\text{P}_0$  transition is observed as a single line which confirms the crystallographic data one the rare earth local environment.

The praseodymium doped and pure compounds fluoresce reasonably well. Under 457.9 nm argon ion laser excitation at 77 and 9K, the radiative desexcitation between  $^3\text{P}_2$ ,  $^3\text{P}_1$  and  $^3\text{P}_0$  levels occurs and almost all emission observed arises from  $^3\text{P}_0$  level (figure 1). In the doped sample  $^1\text{D}_2$  is also an emitting level. By using the selective dye laser excitation accorded on  $^1\text{D}_2$ , only the fluorescence from this level is recorded, permitting the construction of the partial energy level scheme

for  $^3\text{H}_J$  ( $J=4-6$ ) ground multiplet and the first excited  $^3\text{F}_J$  ( $J=2-4$ ) multiplet.

The analysis of all transition recorded by absorption or emission technique shows that the degeneracy of the J levels is completely lifted for the trigonal phase which doesn't permit a point site symmetry higher than  $\text{C}_2$ . In fact, the real symmetry is  $\text{C}_1$  in agreement with the crystallographic data.

Our optical study on praseodymium permits to underline some discrepancy with the previous work reported by Kaminskii et al. (7). In their work the attribution of the  $^3\text{H}_6$  level in  $\text{LaBGeO}_5$ :  $\text{Pr}^{3+}$  compound is wrong. They assigned some electronic lines of  $^1\text{D}_2 \rightarrow ^3\text{H}_4$  transition to  $^3\text{P}_0 \rightarrow ^3\text{H}_6$ . The lowest  $^3\text{H}_6$  level is situated at 4220  $\text{cm}^{-1}$  instead at 4368  $\text{cm}^{-1}$  as is given in ref. 8. The other observed electronic levels are in rather good agreement.

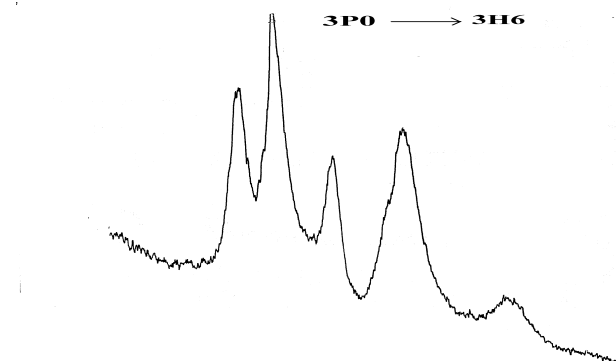


Figure 1: Part of emission spectrum of  $\text{Pr}^{3+}$  at 77 K in stillwellite type structure.

The crystal field splitting of the  $^3\text{P}_1$  level is one of the largest (532 $\text{cm}^{-1}$  for  $\text{PrBGeO}_5$ ) splitting obtained for that level among all studied praseodymium compounds. This indicates a large absolute value for the crystal field parameter of rank 2. The high  $^3\text{P}_0$  energy level position (20852 and 20838  $\text{cm}^{-1}$  for  $\text{LaBGeO}_5$ : $\text{Pr}^{3+}$  and  $\text{PrBGeO}_5$  respectively) confirms nine-fold coordination around the rare earth ion in the trigonal phase. The rather complete energy level scheme permits a simulation in a  $\text{C}_2$  symmetry, considered as an approximation of the  $\text{C}_1$  real symmetry.

### Simulation of the energy level schemes

The praseodymium trivalent ion (4f<sup>2</sup> configuration) is very convenient for the crystal field calculation. The crystal field calculation can be performed accurately with 91x91 matrix taking in account all <sup>2s+1</sup>L<sub>J</sub> levels.

The crystal field potential is written as follows:

$$H_{cf} = \sum_{k,q} B_q^k [C_q^k + (-1)^q C_{-q}^k] + i S_q^k [C_q^k - (-1)^q C_{-q}^k]$$

Where  $C_q^k$  are the tensors depending on the spherical harmonics and  $B_q^k$ ,  $S_q^k$  represent the real and imaginary parts of the phenomenological crystal field parameters (cfps) adjustable to the experiment data. The number of the cfps is limited according to the symmetry of the rare earth point site.

**Table I:** Experimental and calculated energy values of Pr <sup>3+</sup> in PrBGeO<sub>5</sub>

<sup>2S+1</sup> L <sub>J</sub> Level	E (exp.) cm <sup>-1</sup>	E (cal.) cm <sup>-1</sup>	<sup>2S+1</sup> L <sub>J</sub> Level	E (exp.) cm <sup>-1</sup>	E (cal.) cm <sup>-1</sup>	<sup>2S+1</sup> L <sub>J</sub> Level	E (exp.) cm <sup>-1</sup>	E (cal.) cm <sup>-1</sup>
<sup>3</sup> H <sub>4</sub>	0	12	<sup>3</sup> F <sub>2</sub>	5230	5230	<sup>1</sup> I <sub>6</sub>	17294	17324
	8	31		5312	5309		17489	17508
	324	328		5350	5337		-	20753
	373	392		5480	5485		-	20759
	410	432		5537	5515	<sup>3</sup> P <sub>0</sub>	20838	20801
	508	505	<sup>3</sup> F <sub>3</sub>	6604	6620		-	21123
		655		6625	6652	<sup>1</sup> I <sub>6</sub>	21133	21133
	803	777		6698	6693		21238	21247
	922	895		6769	6755	<sup>3</sup> P <sub>1</sub>	21297	21307
				6791	6769		-	21524
<sup>3</sup> H <sub>5</sub>	2092	2109	<sup>3</sup> F <sub>4</sub>	6830	6841	<sup>1</sup> I <sub>6</sub>	-	21548
	2115	2119		6902	6900		-	21548
		2409		7047	7037	<sup>3</sup> P <sub>1</sub>	21770	21784
	2442	2411		7081	7109		21848	21848
		2528		7095	7113	<sup>1</sup> I <sub>6</sub>	-	21910
		2545		7107	7138		-	22026
	2594	2588		7117	7155		-	22226
		2701		7117	7155		22259	22267
		2785		7231	7222		-	22347
		2892		7323	7319		22354	22364
<sup>3</sup> H <sub>6</sub>	2956	2943	<sup>1</sup> G <sub>4</sub>	7349	7328	<sup>3</sup> P <sub>2</sub>	22584	22567
	4206	4213		7396	7383		22625	22620
	4228	4228		9821	9814		22794	22825
	4459	4457		-	9878		-	23017
	4490	4501		9986	9952		23068	23060
	4647	4653	<sup>1</sup> D <sub>2</sub>	10066	10039	<sup>1</sup> S <sub>0</sub>	-	46262
	4716	4714		10123	10109			
	4743	4730		10175	10159			
	4765	4756		10191	10198			
	4827	4817		10294	10323			
	4962	4980		10383	10411			
	-	5012		16790	16770			
	-	5160		16872	16854			
	-	5161		17176	17165			

In the present case and according to the crystallographic data, the point symmetry is assumed to be approximated by  $C_2$ . Fifteen cfps are then included in the simulation (14 when  $S_2^{2k}$  is set to zero by an appropriate choice of the reference axis system).

The refinement is carried out by taking into account the 69 experimental levels. The procedure is conducted by minimizing the r.m.s standard deviation. The results of the simulation are presented in Table I with the crystal field parameters values listed in Table II. The agreement between the experimental and calculated energies are satisfactory considering the relatively great number of phenomenological parameters and the large region of explored spectra.

**Table II:** Crystal-field parameters of  $\text{Pr}^{3+}$  in  $\text{PrBGeO}_5$

Bkq	Value in cm-1
$B_0^2$	-388
$B_2^2$	963
$B_0^4$	1130
$B_2^4$	-141
$S_2^4$	378
$B_4^4$	312
$S_4^4$	-239
$B_0^6$	-214
$B_2^6$	648
$S_2^6$	27
$B_4^6$	366
$S_4^6$	-225
$B_6^6$	-243
$S_6^6$	-447
Nbre levels	69
$\sigma$	21.3
Residue	21717

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