Crystal structure of ABPO$_5$ and optical study of Pr^{3+} embedded in these compounds

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Abstract
The crystal structure of borophosphates $ABPO_5$ (A = alkaline earth or Pb) was resolved on a polycrystalline sample using the Rietveld method. The x-ray diffraction patterns data show that $ABPO_5$ crystallize in a centrosymmetric space group $P3_121$ and their structure is related to the borogermanates $REBGeO_5$ with a stillwellite-type structure. Pr^{3+} ion was used as a local structural probe to corroborate the structural resolution results. Absorption and fluorescence spectra of $A_{1-x}Pr_xBP_{1-x}Ge_xO_5$ (A = alkaline earth or Pb; $x = 0.05$) have been investigated at different temperatures. At 9 K the $^3H_4 \rightarrow {}^3P_0$ transition of trivalent praseodymium ion ($4f^2$ configuration) is observed as a single line. This indicates a unique crystallographic site for the rare earth ion in these compounds replacing the divalent cation. Energy level schemes were deduced from the low-temperature spectroscopic measurements. Comparing the electronic level splittings of studied compounds with the already reported data on $REBGeO_5$ doped with Pr^{3+} ion, it is possible to dispel the doubt existing about structural determination. Moreover, under 460 nm excitation, intense red emission of trivalent praseodymium is observed corresponding to $^1D_2 \rightarrow {}^3H_4$ transition. The lifetime measurements of $^1D_2$ level have been performed for all the title compounds.

1. Introduction

In the last few years, a great deal of effort has been devoted to investigate the spectroscopic and electrical properties of rare earth borogermanates $REBGeO_5$. This interest is due to their potential use as an effective self-frequency-doubling mini-laser and their ferroelectric character [1–6]. The structure of these phases depends on the RE size. For RE = La, Pr and Nd

(low temperature variety), the $REBGeO_5$ compounds crystallize in a stillwellite-type structure ($CeBSiO_5$) [7–13]. The unit cell is trigonal with $P3_1$ as space group. When the RE ions become smaller in size than Nd, these oxides are isostructural to the datolite ($CaBSiO_4(OH)$) [11,14]. The symmetry is monoclinic with a space group $P2_1/a$.

The spectroscopic study of RE^{3+} ions (RE = Pr, Nd and Eu) has been performed on two borogermanate species (stillwellite and datolite) [1,11,15,16]. It was found that, for Fu^{3+} ion embedded in $LaBGeO_5$ (stillwellite-type), the overall splitting of the $^7F_1$ level was one of the largest observed for the compounds doped with this ion, which induced the large values of second rank crystal field parameters [15,16].

The stillwellite form $REBGeO_5$ offers a greater choice of substitution, the trivalent cation (RE^{3+}) by the divalent cation (A^{2+}) and tetravalent cation (Ge^{IV}) by pentavalent cation (M^V), in order to obtain a large family of oxides with general formula $ABMO_5$ (A = alkaline earth or Pb, M = P, As) [17–19]. These compounds were prepared in polycrystalline form and their crystal structure is related to the stillwellite-type structure, with the proposed space group $P3_121$ [20–23]. Recently, we have studied the luminescence process of Eu^{3+}-ion-doped borophosphates $ABPO_5$ and have found that the size of alkaline earth cation has a great influence on the homogeneity of the materials [24]. Until now, no further optical investigation of Pr^{3+}-ion-doped borophosphates has been reported. Our contribution is to analyse the optical properties of Pr^{3+} ion in relation to structural data. Optical spectroscopy of Pr^{3+} cation is used as a local structural probe. The crystal structure of $PbBPO_5$ as well as absorption, fluorescence and kinetic measurements of $A_{1-x}Pr_xBP_{1-x}Ge_xO_5$ (A = Ca, Sr, Ba and Pb; $x = 0.05$) are presented.

2. Experimental details

Polycrystalline samples of $A_{1-x}Pr_xBP_{1-x}Ge_xO_5$ (A = Ca, Sr, Ba and Pb; $x = 0.05$) have been synthesized by solid-state reaction between high-purity ACO_3, $Pb(NO_3)_2$, H_3BO_3, $(NH_4)_2HPO_4$, GeO_2 and Pr_6O_{11} as starting materials. The stoichiometric mixture was first ground and progressively heated in a platinum crucible at 400 °C for 12 h. The resulting compound was ground again and heated for a further 72 h at 900 °C for A = Ca, 800 °C for Sr, 1000 °C for Ba and 680 °C for Pb. An appropriate excess of H_3BO_3 was then added to compensate the B_2O_3 losses.

The x-ray diffraction (XRD) structural analysis of compounds was performed using a Philips PW 1050 x-ray diffractometer with Cu K_α radiation. The XRD data for structure refinement of $PbBPO_5$ were collected at ambient temperature in 2θ interval of 15–110° with a scanning step of 0.02°.

A CARY 5 E-Varian spectrophotometer was used to record optical absorption spectra of $A_{1-x}Pr_xBP_{1-x}Ge_xO_5$ ($x = 0.05$) compounds at room temperature and 9 K. The low temperature is obtained using a He closed-cycle CTI Cryogenics refrigerator.

The luminescence spectra were recorded on powder samples under laser excitation coming from an OPO (optical parametric oscillator) pumped by the third harmonic of a Q-switched Nd:YAG laser.

3. Results and discussion

3.1. Crystal structure

The structural analysis was performed using the Rietveld method with the computer program FULLPROF [25]. The crystal structure of $PbBPO_5$ has been resolved for the space group

P3$_1$21 (no 152). The initial atomic positions were similar to those already found for the isostructural phase BaBPO$_5$ [23]. The trigonal cell parameters are $a = 6.851(80)$ Å and $c = 6.821(95)$ Å. The thermal parameters (B) were assumed to be isotropic.

The final positions and thermal parameters are reported in table 1. The inter-atomic distances with the corresponding standard deviations are listed in table 2.

Table 1. Atomic parameters and isotropic factors for PbBPO$_5$.

Atom	Position	x	y	z	B_{iso} (Å^2)
Pb	3(a)	0.3917(1)	0.00000	0.33333	0.43
P	3(b)	0.3913(2)	0.00000	0.83333	1.4
B	3(a)	−0.0921(1)	0.00000	0.33333	0.5
O$_1$	6(c)	0.3326(6)	0.1415(9)	−0.0327(7)	1.01
O$_2$	6(c)	0.4192(8)	0.8594(1)	−0.0291(9)	1.22
O$_3$	3(b)	−0.0512(9)	0.00000	0.83333	1.01

Table 2. Interatomic distances (Å) in PbBPO$_5$.

P		B		Pb	
O$_1 \times 2$	1.56529	O$_1 \times 2$	1.47766	O$_1 \times 2$	2.81833
O$_2 \times 2$	1.52064	O$_3 \times 2$	1.43945	O$_1 \times 2$	2.83867
Mean	1.542	Mean	1.458	O$_2 \times 2$	2.55559
				O$_2 \times 2$	2.71286
				O$_3 \times 1$	2.80573
				Mean	2.739

The crystal structure of borophosphates ABPO$_5$ is very similar to the stillwellite-type structure [21]. It can be described as screw chains of distorted tetrahedra BO$_4$ along the c-axis. Each BO$_4$ tetrahedron shares a corner through oxygen atoms with terminal PO$_4$ tetrahedra. The Pb^{2+} ions are located in a polyhedra of nine oxygen atoms. Figure 1 shows a part of PbBPO$_5$ structure projection on the (001) plane.

3.2. Optical properties

In order to complete the structural investigation of these borophosphates we have realized an optical study of Pr^{3+}-ion-doped ABPO$_5$ compounds and used this rare earth ion as a local structural probe. The spectroscopic behaviour is compared with that of the borogermanates which belong to the same family [15,16]. For charge compensation, the divalent and pentavalent ions are simultaneously replaced by the trivalent (Pr^{3+}) and tetravalent ions (Ge^{IV}), respectively.

3.3. Absorption measurements

In the Pr^{3+} absorption spectra at 9 K in A$_{1-x}$Pr$_x$BP$_{1-x}$Ge$_x$O$_5$ (A = Ca, Sr, Ba and Pb; $x = 0.05$), the ^{3}H$_4 \rightarrow {}^3$P$_0$ transition is observed as a single line which confirms the presence of only one site for the rare earth ion substituting the alkaline earth in the structure. On the basis of a comparison of the present spectra with the work already reported on the borogermanates with a related structure [26], all absorption peaks could be easily attributed to different ^{3}H$_4 \rightarrow {}^3$P$_J$, ^{1}D$_2$ transitions. However, small variations occur in the energy level
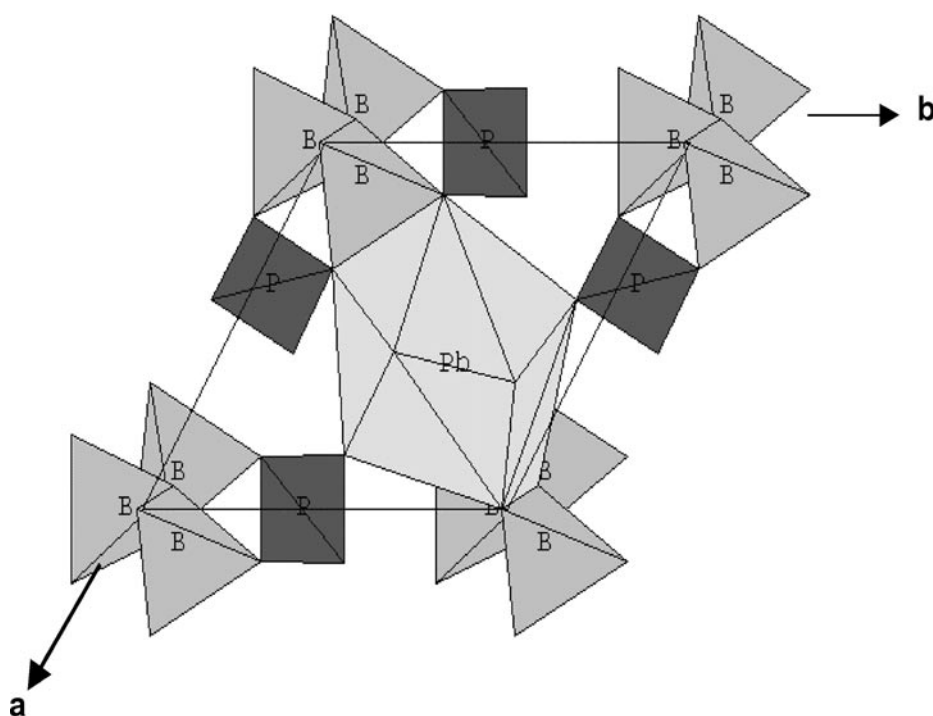
Figure 1. Projection of PbBPO$_5$ structure on (001) plane.

positions for Pr^{3+}-doped different borophosphate compounds. This is due to the 4f orbit which lies well inside the ion and is protected by outer 5s^2 and 5p^6 shells. Therefore, the splittings are only weakly affected by the local environment [27].

One can observe that the $^3P_0$ energy level position (20 695 cm^{-1} for A = Pb) is situated between the datolite (20 605 cm^{-1} for GdBGeO$_5$:Pr^{3+}) and stillwellite (20 838 cm^{-1} for PrBGeO$_5$) energy level positions [26]. This energy level position suggests that the rare earth cation can be ninefold coordinated, as found by the crystal structure resolution, but there is no obvious indication that the structure of the borophosphate compounds is related to the stillwellite-type structure.

The visible part of the energy level schemes for Pr^{3+} in ABPO$_5$ (A = Ca, Sr, Ba and Pb) is listed in table 3. Figures 2 and 3 report the visible range of the absorption spectra of Pr^{3+}-doped calcium borophosphate. One can notice that at 9 K, the second Stark component of the ground $^3H_4$ manifold is also populated and the energy difference between the fundamental and the second Stark level is 29 cm^{-1}.

3.4. Luminescence and lifetime measurements

The luminescence spectra (figure 4) were recorded on powder samples of A$_{1-x}$Pr$_x$BP$_{1-x}$Ge$_x$O$_5$ ($x = 0.05$) under laser excitation coming from an OPO pumped by the third harmonic of a Q-switched Nd:YAG laser. The excitation wavelength 470 nm corresponds to the $^3H_4 \rightarrow {}^3P_1$ transition. All the emissions coming from the $^3P_0$ and $^1D_2$ emitting levels are similar for the various A cations (A = Ca, Sr, Ba and Pb). One can observe that the $^1D_2$ emission is much more intense than the $^3P_0$ emission. An intensified optical multi-channel analyser (OMA)

Table 3. Experimental energy values of Pr^{3+} in $A_{1-x}Pr_xBP_{1-x}Ge_xO_5$ ($x = 0.05$) at 9 K.

$^{2S+1}L_J$	E (cm^{-1})			
	A = Ca	A = Sr	A = Ba	A = Pb
$^1D_2$	16 616[a]	16 618[a]	16 619[a]	16 628[a]
	16 645	16 648	16 650	16 655
	16 809	16 813	16 806	16 815
	16 922	16 926	16 924	16 933
	16 960	16 958	16 957	17 181
	17 174	17 176	17 179	
$^3P_0$	20 660[a]	20 662[a]	20 664[a]	20 665[a]
	20 688	20 691	20 693	20 695
$^3P_1, {}^1I_6$	21 141[a]	21 147[a]	21 143[a]	21 149[a]
	21 171	21 177	21 174	21 176
	21 253	21 260	21 258	21 318
	21 317	21 319	21 319	21 356
	21 358	21 360	21 360	21 498
	21 506	21 522	21 522	21 714
	21 684	21 818	21 595	21 795
	21 810		21 666	
	21 930		21 811	
$^3P_2$	22 151	22 130	22 144	22 114
	22 346	22 345	22 352	22 340
	22 562	22 568	22 562	22 564
	22 623	22 630	22 625	22 605

[a]Temperature component.
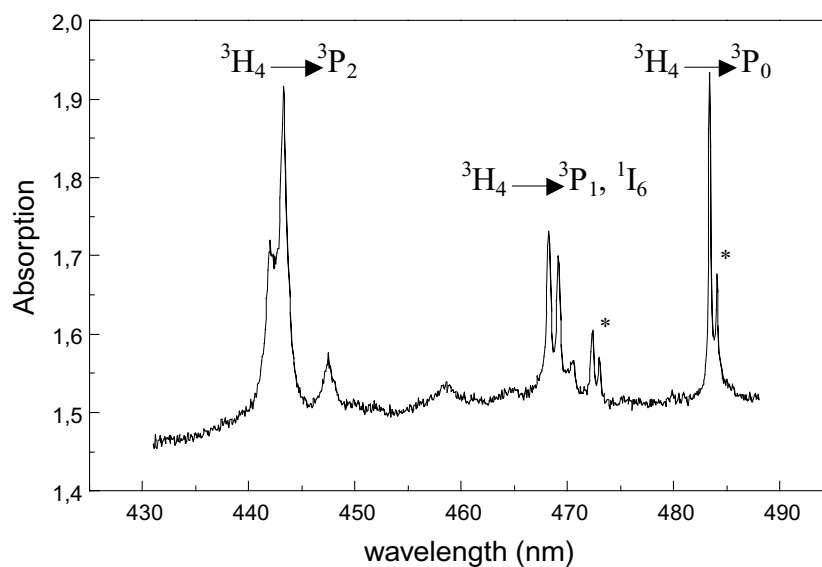
Figure 2. Absorption spectrum of $Ca_{0.95}Pr_{0.05}BP_{0.95}Ge_{0.05}O_5$ at 9 K.
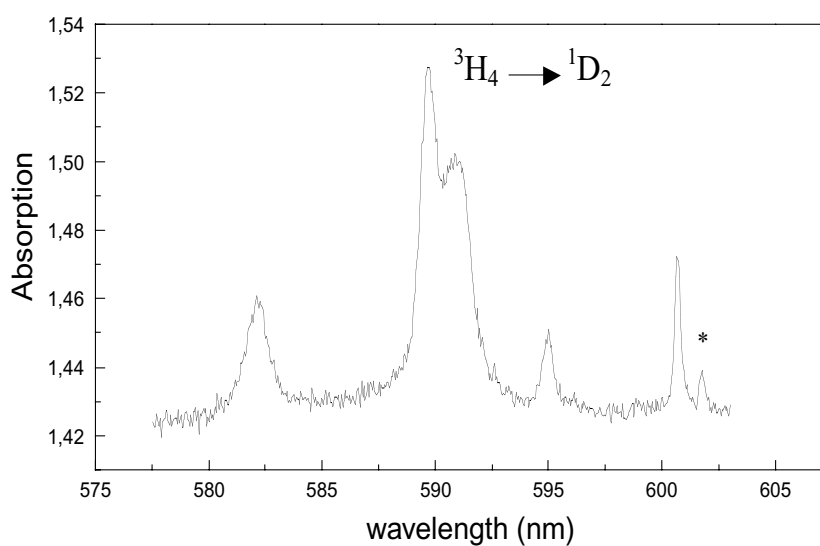
Figure 3. Absorption spectrum of $Ca_{0.95}Pr_{0.05}BP_{0.95}Ge_{0.05}O_5$ at 9 K.

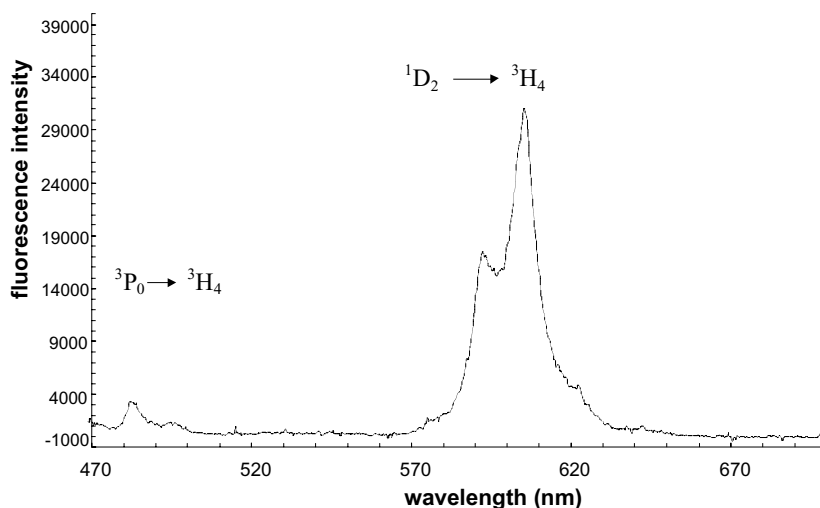**Figure 4.** Room temperature luminescence spectrum for the $Pb_{0.95}Pr_{0.05}BP_{0.95}Ge_{0.05}O_5$ material under 470 nm excitation.

is used for the detection of luminescence. With this apparatus, it is possible to record the emission with different time delays after the laser pulse excitation and therefore to obtain the lifetime decay profiles (figure 6).

From figure 5, it is obvious that the luminescence intensity of the $^3P_0$ level decreases very quickly. The $^3P_0$ lifetime is estimated to be around 0.1 μs, which represents a very small value. This could indicate either very strong non-radiative relaxation from the $^3P_0$ level towards the $^1D_2$ level as the phonon energy of the material is quite high, but this also could be related to the excited state absorption into the 5d bands from the ^3P_J level, under laser excitation. This was already observed in other Pr^{3+}-doped hosts.
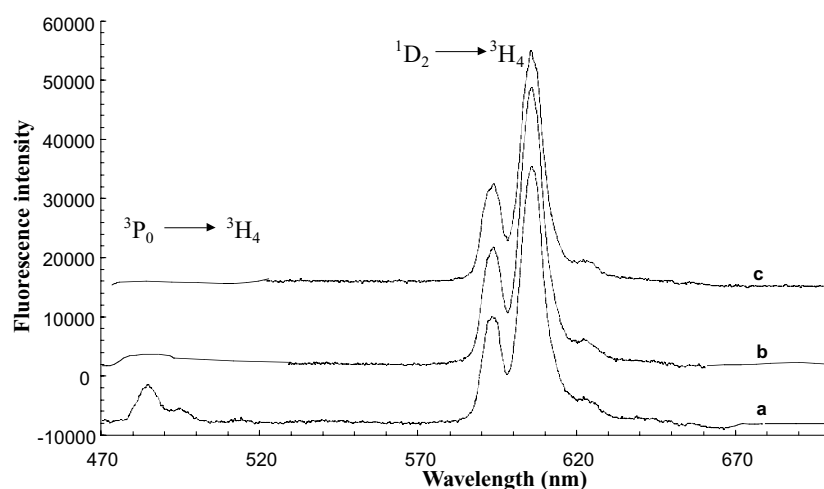
Figure 5. Emission spectrum of the Sr$_{0.95}$Pr$_{0.05}$BP$_{0.95}$Ge$_{0.05}$O$_5$ compound for different pulse delays after laser excitation: (a) pulse delay = 0, (b) pulse delay = 100 ns and (c) pulse delay = 200 ns at 77 K.
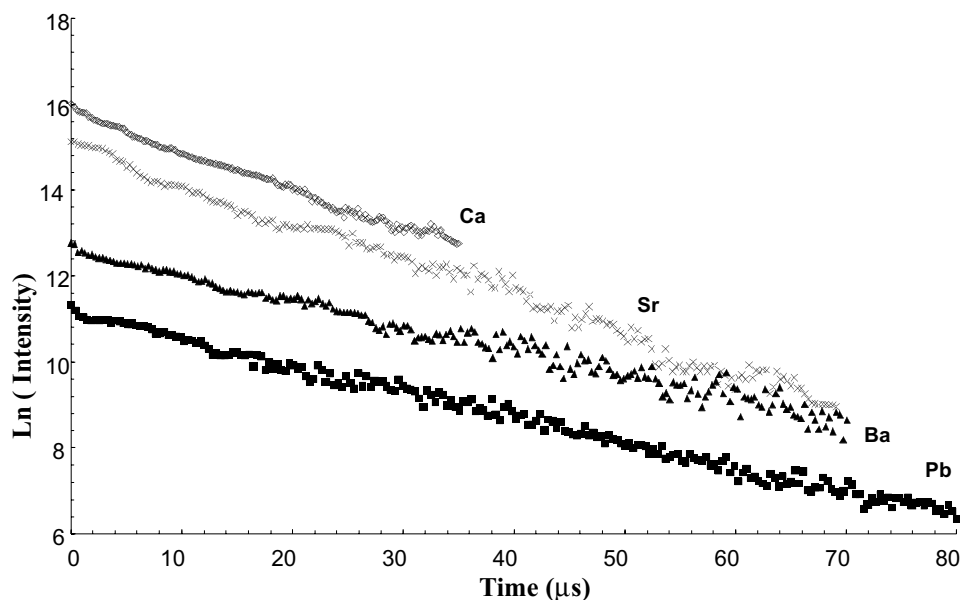
Figure 6. Room temperature ^{1}D$_2$ fluorescent decay profiles for Pr^{3+} ion in different borophosphate compounds.

The lifetime values of ^{3}P$_0$ and ^{1}D$_2$ manifolds have been measured at 485 and 606 nm respectively. Figure 6 presents the fluorescence decay profiles for the ^{1}D$_2$ emitting level at 300 K. In table 4 are reported the ionic radii (coordination 9) of A cations and the lifetime values obtained for the different Pr^{3+} materials at 300 and 77 K. Different behaviours are observed in correlation with the cation size: faster decays are observed for the smallest cations. The ionic radii of the praseodymium ions are respectively 1.179 and 1.126 Å [28] for the eight (datolite)

and nine (stillwellite) coordinances. The kinetic values can therefore be controlled by the distortions around the rare earth cations depending on the cation sizes. The kinetic of the $^1D_2$ emitting level can be affected either by ion–ion interaction (cross-relaxation mechanisms) or by interactions between the host and the rare earth ions (non-radiative relaxation). The non-radiative relaxation is very important when the energy difference between the emitting state and the level situated just below is 3500 cm^{-1}, e.g. ΔE ($^3P_0/^1D_2$), while the non-radiative relaxation is negligible for $\Delta E > 6500$ cm^{-1} (ΔE ($^1D_2/^1G_4$)). The cross-relaxation effect could be considered as constant for the same dopant concentration when the energy level position is not strongly modified in the borophosphate matrices (see energy level positions in table 3). Further experiments with different rare earth contents are required to give clear conclusions on the kinetic analysis. Narrow lines are observed in the absorption and emission spectra of the calcium compounds in addition to shorter lifetimes associated with a higher intensity signal. This indicates that the calcium borophosphate compound is the most suitable host for the praseodymium ion.

Table 4. $^1D_2$ lifetime values of Pr^{3+} in different borophosphates and ionic radii of A cations (A = Ca, Sr, Pb and Ba).

Materials	$^1D_2$ level lifetime (μs) 300 K	$^1D_2$ level lifetime (μs) 77 K	Ionic radius (A)
$Ca_{0.95}Pr_{0.05}BP_{0.95}Ge_{0.05}O_5$	123	163	1.12
$Sr_{0.95}Pr_{0.05}BP_{0.95}Ge_{0.05}O_5$	127	185	1.26
$Pb_{0.95}Pr_{0.05}BP_{0.95}Ge_{0.05}O_5$	177	195	1.29
$Ba_{0.95}Pr_{0.05}BP_{0.95}Ge_{0.05}O_5$	181	208	1.42

4. Conclusion

The crystal structure of $PbBPO_5$ has been solved on polycrystalline samples. The compound seems isostructural to the stillwellite with a centrosymmetric space group $P3_121$. The absorption and emission spectra of trivalent praseodymium ion in new rare earth–alkaline earth borophosphates compounds, $A_{1-x}Pr_xBP_{1-x}Ge_xO_5$, have been analysed. Optical measurements suggest that the datolite structure cannot be excluded for the local surrounding around the rare earth cations. Further analysis with the neodymium cation is in progress for a better understanding of this family of compounds.

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