THE LUMINESCENT COMPOUND $GdPO_4$:Eu^{3+} INVESTGATED BY MICRO-RAMAN SPECTROSCOPY

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ABSTRACT: *Modes of internal vibration of the phosphate ion* PO_4^{3-} *at a* T_d *symmetry and at a site having* D_{2d} *symmetry are derived from group-theory calculations. The micro-Raman spectra of some orthophosphates activated with* Eu^{3+} *were recorded. The splitting of spectral bands of these orthophosphates shows that the phosphate ion is placed in a crystal on a site of symmetry less than* T_d, *such as* D_{2d}, *the local crystal field may lift some or all of degeneracy of the Raman bands. The results of the current paper show that all of them are lifted totally. The ab initio calculations at level HF with basic set 6-31++G(d) have affirmed above.*

I. INTRODUCTION

The tetrahedral XY_4 molecules and ions have symmetry T_d. However, tetrahedral XY_4 ion in a crystal may not find itself at a site of T_d symmetry. Indeed, it would be located at a site having lower symmetry, often one which is a nontrivial subgroup of T_d [5].

II. THE MODEL OF CALCULATION

In this current work, authors will calculate the fundamental vibrations of free phosphate ion PO_4^{3-} and of that in crystal lattice of phosphate gadolinium, $GdPO_4$. The obtained results will be compared with experimental data which are derived from the micro-Raman spectra of pure $GdPO_4$ and of that activated with rare-earth element Eu. This is one of the luminescent materials which are used to produce the TV screen of new generation – plasma discharge.

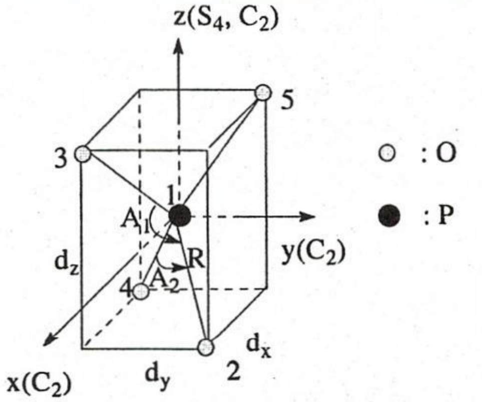


Fig. 1. Model of tetraheral XY_4 molecules

To investigate the geometric structure and symmetric elements of tetrahedral molecule or ion in different conditions, we use a model in which they are inscribed in a cube. If their symmetry is reduced from T_d to D_{2d}, the XY_4 molecule (or ion) being inscribed in the cube which has been deformed by compressing or stretching it along one axis, say the Z axis, as illustrated in Fig. 1. In this model, if the circumscribing cube is compressed or stretched in the direction of Z axis, the XY_4 group will be D_{2d}. If not, it will be T_d.

III. EXPERIMENTAL

III.1. The sample preparation

Gadolinium phosphate, $GdPO_4$ has been prepared by solid phase reaction at temperature of 900 ^0C after dissolution of the constituents in concentrated nitric acid then evaporation to dryness. Details of the syntheses will be published elsewhere [11].

Starting materials are $NH_4H_2PO_4$ (99% minimum) from MERCK; Gd_2O_3 (99,999%) from JOHNSON MATTHEY; Y_2O_3 (99,999%) from RHODIA and Eu_2O_3 (99,99%) from ACROS.

The sample preparation was implemented in the laboratory of chemistry institute of condensed materials, CNRS, 33608 Bordeaux-Pessac, France.

III.2. Micro-Raman spectroscopy

Coupled with an optical microscope, a micro-Raman spectrometer allows for the examination of samples as small as one micrometer in size. Thus, the different components of an heterogeneous sample can be illuminated as pure areas, without the necessity of previous separation [4]. The micro-Raman spectra in the current work all have been recorded on the two Raman micro-spectrometers LABRAM (one in the laboratory of physico-chemystry of molecules, Universite de Bordeaux 1, 351 Cours Liberation, 33405 Bordeaux-Talence, France and another in the center for material science, Nghia do, Tu liem, Hanoi) equipped with a He-Ne laser emitting at 632.8 nm, operating at 15 mW and with a CCD detector. The resolution is 3 cm^{-1} and the recording time is 50s.

IV. RESULTS AND DISCUSSION

IV.1. Micro-Raman spectrum of the PO_4^{3-} free ion

Like all orthophosphates, $GdPO_4$ has a tetrahedral ion, PO_4^{3-}. In free state, the symmetry of PO_4^{3-} ion is T_d [2]. In this case, the calculation by using the group theory [1], [10] shows that this ion of symmetry T_d possesses nines modes of normal vibration having the representation

$$\Gamma_{vib}(T_d) = A_1 + E + 2F_2 \qquad (1)$$

It can be seen from Eq.(1) that the free PO_4^{3-} ion has four fundamental bands. The table 1 lists the frequencies and intensities of the observed Raman bands of this free ion [2] and one's *ab initio* Hartree-Fock calculation results using 6-31++G(d) basic set performed with the Gaussian 98. The 6-31++G(d) basic set is very consistent with systems where electrons are relatively far from the nucleus : molecules with alone pairs, anions, systems with significant negative charge, and so on [9]. Fig. 2 illustrates graphically the active vibrations in Raman scattering of a tetrahedron [2].

In case of the free phosphate ion, the band at 938 cm^{-1} (ν_1) is assigned to the P-O stretching vibration which gives rise to the strongest Raman signal. The *ab initio* calculation result shows that the value of the depolarization ratio ρ equals zero. This means that the mode is a totally symmetric vibration, named A_1 [3].

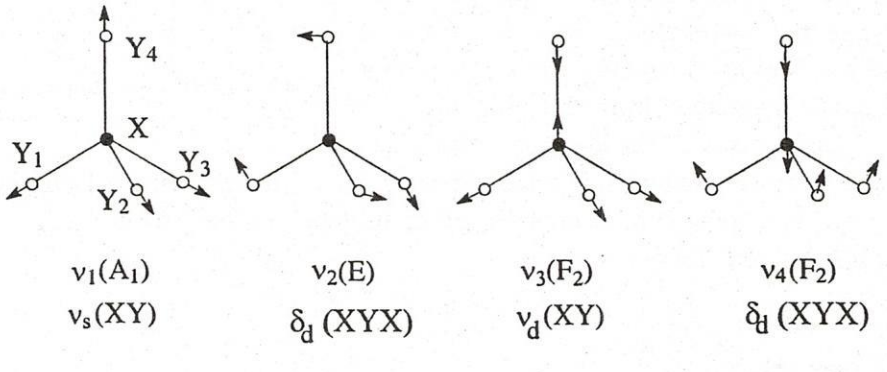


Fig. 2 Normal modes of vibration of tetrahedral ion PO_4^{3-}

The band at 1064 cm^{-1} (ν_3) is due to the antisymmetry PO_4^{3-} stretching vibration whereas the bands observed at 420 cm^{-1} (ν_2) and 567 cm^{-1} (ν_4) arise from the angle bending vibrations. Basing on the *ab initio* calculations, namely normal coordinates, the vibrations ν_2, ν_3, ν_4 can also be assigned easily [9].

Table 1. Raman Frequencies (cm^{-1}) of free phosphate ion

	Observed [6]		Ab initio Calculation		Symmetry of vibration
Designation	Frequency	Intensity	Frequency	Intensity	
ν_1	938	vs	903	17.90	A_1
ν_2	420	w	404	0.90	E
ν_3	1017	medium	987	16.35	F_2
ν_4	567	weak	578	0.32	F_2

vs: very strong; m: medium; w: weak

IV.2. Micro-Raman spectra of ion PO_4^{3-} in the crystal lattice of GdPO4

IV.2.1 The calculation of vibrations by using group theory

When being in the crystal lattice of orthophosphates such as $GdPO_4$, $EuPO_4$,YPO_4,..., the PO_4^{3-} ion has symmetry D_{2d} [2,5,6]. In this case, the calculation of contribution of vibrational modes by using the Herzberg method [10] shows that the PO_4^{3-} ion has nine normal modes with the representation

$$\Gamma_{vib}(D_{2d}) = 2A_1 + B_1 + 2B_2 + 2E \qquad (1)$$

Therefore, combinating Eq. (2) with the character table of the group D_{2d}, it would be predicted that in the Raman spectrum, the seven fundamental bands of ion PO_4^{3-} of orthophosphate crystal will be observed (2 bands A_1, 1 band B_1, 2 bands B_2 and 2 doubly degenerated bands E) instead of four bands as above. This is resulted by the splitting of spectral bands due to the symmetry reduction from group T_d to group D_{2d} [5]. Basing on the correlation between the group T_d and the D_{2d}, it is able to determine the procedure of splitting spectral bands caused by symmetry low. The table of the symmetry correlation $T_d - D_{2d}$ [3] shows that the species A_1 of T_d is unchanged when the symmetry lowers from T_d down to D_{2d}; species E of T_d is split into $A_1 + B_1$; species F_2 of T_d is split into $B_2 + E$.

Considering IR spectrum, four fundamental bands of ion PO_4^{3-} including two bands B_2 and two bands E will be observed.

IV.2.2 The calculations based on the model

The above-mentioned splitting of spectral bands due to the symmetry reduced from group T_d down to D_{2d} may be identified by the *ab initio* calculations on the basic of the above suggested model.

To utilize the above model, outhors assume that ion phosphate is only compressed or stretched along the direction of axis Z when being in the crystal lattice. This means that only side d_z is changed, another sides d_x and d_y remain.

Firstly, the ab initio calculation will be performed to find out the parameters coresponding to the case of free phosphate ion. The results are stated in the highlighted row in the table 2. In this case, it can be seen that $d_z = d_y = d_z = 1.81$ Å .

The combination the results of *ab initio* calculation with Fig. 1 gives

$R = R(1,2) = R(1,3) = R(1,4) = R(1,5)$

$A_1 = A(2,1,3) = A_3 = A(2,1,5)$

$A_2 = A(2,1,4) = A_5 = A(3,1,5)$

Now, the bond lengths and bond angels will be determined corresponding with every value d_z around of 1.81 Å from 1.00 to 2.50 Å provided that the structure must be always assured as D_{2d}. The calculation results of the structural parameters correspond with different values d_z have been reported in the table 2.

The second step is to implement the *ab initio* calculation for the phosphate ion respectively with the different value d_z, the bond lengths and the bond angels as listed in the table 2. The ab initio calculation results of the frequencies are reported in the table 3.

Table 2. The calculation results of the structural parameters for the phosphate ion.

d_z(Å)	R (Å)	A_1 (degree)	A_5(degree)	Notes
2.50	1.7910	119.15	91.48	$\neq D_{2d}$
2.00	1.6265	112.21	104.12	
1.95	1.6112	111.48	105.52	
1.90	1.5962	110.75	106.95	
1.81	1.5717	109.47	109.47	
1.70	1.5388	107.76	112.94	
1.65	1.5150	107.02	114.51	
1.50	1.4859	104.76	119.37	
1.00	1.3767	97.58	137.41	$\nu_1 < 0$ (virtual)

Table 3. The calculation results of the vibrational frequency (cm^{-1}) for phosphate ion with different structural parameters.

Modes	d_z (Å)						
	1.5	1.65	1.70	1.81	1.90	1.95	2.0
1	300	359	378	404	392	385	379
2	460	429	421	404	417	423	427
3	537	562	570	578	568	560	548
4	586	584	584	578	568	560	548
5	586	584	584	578	580	580	578
6	1158	1065	994	903	837	799	761
7	1215	1144	1073	987	910	868	828
8	1309	1186	1099	987	910	868	828
9	1309	1186	1099	987	922	884	845

From the above calculated results, a few comments can be given as follows :

+ When d_z = 1.81 Å, ion PO_4^{3-} has the symmetry T_d. Two models 1 and 2 are of the doubly degenerate E species. The models 3, 4, 5 are of the triply degenerate F_2 species. The mode 6 is of non-degenerate A_1 species; The model 7, 8, 9 are of the triply degenerate F_2 species. Thus, it could be obviously that the comparision the observed frequencies and calculated frequencies allows to assign the spectral bands of the free phosphate ion (Table 1).

+ When ion is compressed (d_z shortend), the splitting of the spectral bands takes place. The E species (404 cm^{-1}) is split into two including A_1 (mode 1) and B_1 (mode 2); the first F_2 species (578cm^{-1}) is split into two including B_2 (mode 3) and E (mode 4 & mode 5); the A_1 species (mode 6) remains. The second F_2 species (987 cm^{-1}) is split into two including B_2 (mode 7) and E (mode 8 and mode 9).

+ When the ion is so much compressed ($d_z \leq 1.0$ Å), the calculation results for mode 1 gives a negative frequency, or namely as a virtual frequency. This proves that it is a transition, unstable structure, and an intermediate structure of some equilibrium structures.[9]. Thus, when the ion is compressed to some limited values, the structure which has the symmetry D_{2d} will not exist, but become an another one.

+ When the ion is stretched (d_z lengthened), the splitting of the spectral bands also takes place similarly to the case of compression. However, here there will be some differences. Namely, mode 1 is the E species (404 cm^{-1}) that is split into two including B_1 (mode 1) and A_2 (mode 2); the first F_2 species (578 cm^{-1}) is split into two including E (mode 3, and mode 4) and B_2 (mode 5); the A_1 species (mode 6) still remains; the second F_2 species (987 cm^{-1}) is split into two including E (mode 7, mode 8) and B_2 (mode 9). Althogh there are some differences, the case still obeys the $T_d - D_{2d}$ correlation. But when the stretch is too much ($d_z >> 2.0$ Å), the symmetry D_{2d} is broken by the evidence that the splitting of the spectral bands will not take place in accordance with the above rule.

+ Mode 6 (equivalent with ν_1 in the table 1) is of the A_1 species and remains when the ion symmetry is reduced from T_d down to D_{2d}. It is the symmetry P-O stretching vibration that gives rise to a strongest intensity. Fig. 3 depicts the dependence of Raman frequency of the mode 6 (ν_1) on the values of d_z.

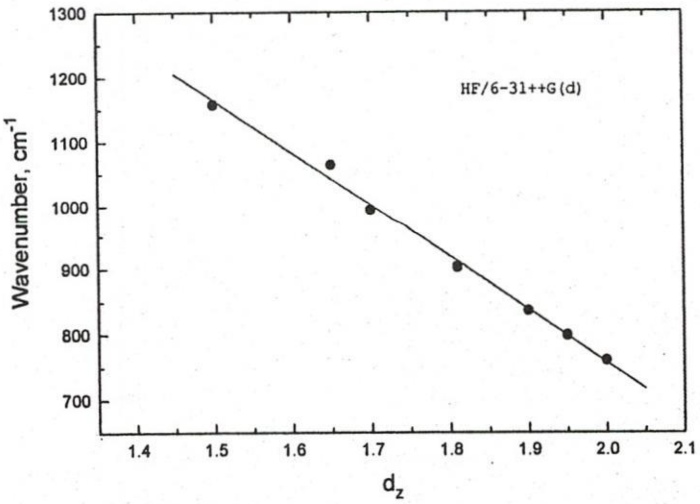


Fig. 3. Dependence of Raman frequency of mode 6 (ν_1) on d_z

It can be seen from Fig. 3 that the more ion is compressed the more Raman frequencies increase.

Fig. 4 gives the Raman frequency of A_1 vibration, $\nu_1 = 979$ cm^{-1}. The curve in Fig. 3 allows to detemine the value $d_z = 1.6933$ Å in accordance with $\nu_1 = 979$ cm^{-1}. Now, it is possiple to calculate the length of P-O bond ($R_{P\text{-}O}$) by combinating the determined value of d_z with fig.1. The calculation gives $R_{P\text{-}O} = 1.5369$ Å . This result is very good agreement with Mooney's work, namely $R_{P\text{-}O} =$ 1.5400 Å [5].

Obviously, from value of $R_{P\text{-}O}$, the other quantities, such as the bond angles, can be deduced easily as follows

$$A_1 = A(2,1,3) = A_3 = A(2,1,5) = 107.67 \text{ (degree)}$$

$$A_2 = A(2,1,4) = A_5 = A(3,1,5) = 113.15 \text{ (degree)}$$

IV. 2.3. Micro-Raman spectrum of $GdPO_4$

Fig. 4 gives the Raman spectrum of $GdPO_4$ in the 150 – 1200 cm^{-1} region. Generally, the spectral bands observed mainly in the range under 1100 cm^{-1}. Using the calculation results of above model, the symmetry of spectral bands of phosphate ion PO_4^{3-} can be assigned.

First of all, it can be asserted that the band at 979 cm^{-1} is a totally symmetric vibration A_1 which is equivalent to ν_1 in the table 1 and to mode 6 in the table 3.

Six remaining bands due to the double splitting of the three spectral bands (E and $2F_2$) caused by the reduction of symmetry. The result of the spectral splitting has been reported in the table 4.

Comparing the Raman spectrum of $GdPO_4$ recorded by the authors and IR spectrum of that by Agrawal [6], obviously it can be seen that the two bands at 418 cm^{-1} (ν_2) and at 397 cm^{-1} (ν_3) present in Raman spectrum, but not in the IR spectrum. Thus, it can be concluded that the two bands (ν_2 and ν_3) belong to the A_1 and B_1 species, respectively. This conclusion is in good agreement with the results of the group theory calculation that both A_1 and B_1 species are forbidden in IR spectrum.

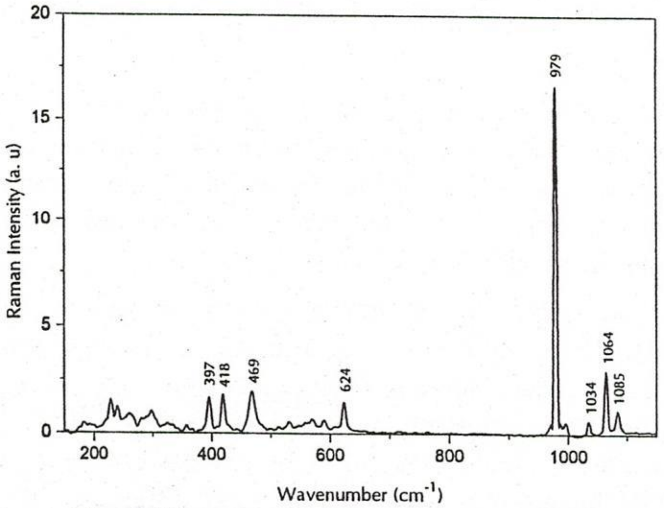
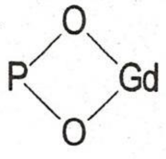


Fig. 4. The micro-Raman spectrum of $GdPO_4$

Table 4. The spectrum splitting according to T_d –D_{2d} correlation

free PO_4^{3-} [6]	PO_4^{3-} in the lattice of $GdPO_4$	PO_4^{3-} in the lattice of YPO_4
$\nu_1(A_1) = 938$	$\nu_1(A_1) = 979$	$\nu_1(A_1) = 998$
$\nu_2(E) = 420$	$\nu_2(A_1) = 418$	$\nu_2(A_1) = 484$
	$\nu_3(B_1) = 397$	$\nu_3(B_1) = 340$
$\nu_3(F_2) = 1017$	$\nu_5(B_2) = 1064$	$\nu_5(B_2) = 1058$
	$\nu_7(E) = 1034$	$\nu_7(E) = 1025$
$\nu_4(F_2) = 567$	$\nu_4(B_2) = 624$	$\nu_4(B_2) = 660$
	$\nu_6(E) = 469$	$\nu_6(E) = 580$

The bands in the 200 – 350 cm^{-1} region are associated with bridging phenomena Gd –O in the following manner [5]



The band at 1084 cm^{-1} can be due to the overtone or the combination of the vibrations with low frequency.

The same procedure is performed for Raman spectrum of YPO_4 (Fig. 5).

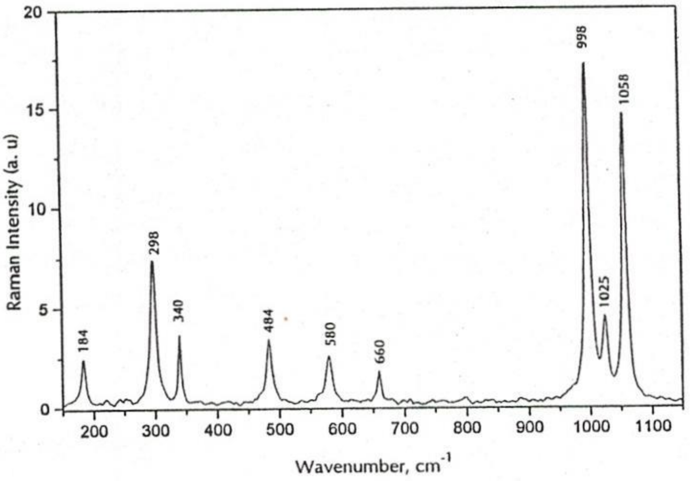


Fig. 5. The micro-Raman spectrum of YPO_4

IV.2.4. Micro-Raman spectra of $GdPO_4$ activated with Eu^{3+}

Fig. 6 gives the spectrum of $GdPO_4$ activated with 5% Eu^{3+}. Observing this spectrum with the one of the non-activated $GdPO_4$ (Fig.4), evidently these two spectra are the same in the position as well as in relative intensity in 150- 1100 cm^{-1} region.

The same results will be obtained even $GdPO_4$ is activated with1% or 10% Eu^{3+}. Because when being activated, a number of ion Eu^{3+} will replace Gd^{3+} in the lattice, but the dimensions of Eu^{3+} and Gd^{3+} are just a little bit different from each other, respectively 1,066 $\overset{0}{A}$ and 1,053 $\overset{0}{A}$ [8], so there almost is no difference between the spectra of the activated $GdPO_4$ and of the non-activated $GdPO_4$.

V. CONCLUSIONS

The assignment and interpretation of spectral bands of gadolinium phosphate $GdPO_4$ has been carried out perfectly by basing on the combination between the group theory and the *ab initio* calculation.The results arisen from the ab initio calculation allows to understand clearly the mechanism of spectral band splitting.

It could be seen that the structural model used for the calculation is consistent with the experimental data obtained from observed micro-Raman spectra. The model can also be used for the other molecules having the same symmetry.

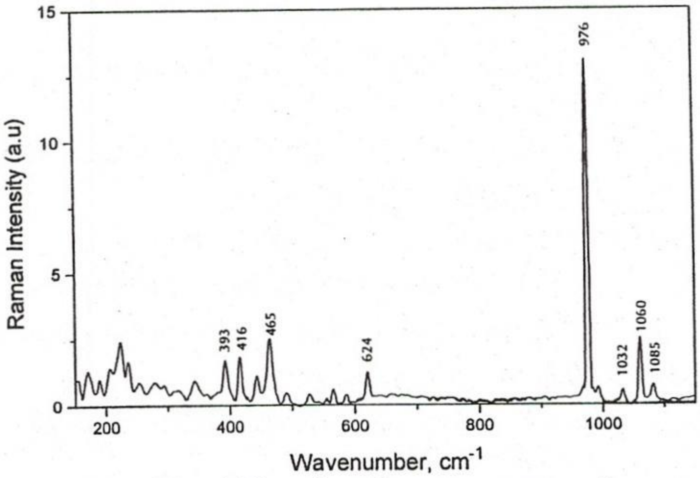


Fig. 6. The micro-Raman spectrum of $Gd_{0,95}Eu_{0,05}PO_4$

Thus, the procedure in which the group theory calculation and the *ab initio* calculation can be opened up a new path in the research on the vibrational spectra.

KHẢO SÁT HỢP CHẤT PHÁT QUANG $GdPO_4:Eu^{3+}$ BẰNG QUANG PHỔ MICRO-RAMAN

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TÓM TẮT: *Các mode dao động nội của ion phosphate* PO_4^{3-} *theo nhóm đối xứng điểm* T_d *và theo nhóm đối xứng vị trí* D_{2d} *được tính toán bằng lý thuyết nhóm. Chúng tôi đã ghi phổ micro-Raman của một số orthophosphate tăng hoạt bằng ion đất hiếm* Eu^{3+}*. Sự tách các đỉnh phổ của các orthophosphate chứng tỏ rằng ion phosphate trong tinh thể ở vị trí có đối xứng thấp hơn* T_d *như* D_{2d} *và trường tinh thể dịa phương có thể làm giảm một phần hoặc toàn bộ sự suy biến của các đỉnh phổ Raman. Kết quả của bài báo này cho thấy sự suy biến đã hoàn toàn biến mất. Kết quả tính toán ab initio ở mức HF với hệ hàm cơ sở 6-31++G(d) đã xác nhận điều này.*

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