Synthesis and optical characterization of Er-doped bismuth titanate nanoparticles grown by sol-gel hydrothermal method

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Abstract

The Er^{3+}-doped bismuth titanate ($Bi_4Ti_3O_{12}$, BIT) nanoparticles were synthesized by a combined sol-gel and hydrothermal method under a partial oxygen pressure of 30 bar. The composition and morphology were characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman scattering. They showed pure and homogeneous spherical BIT nanoparticles with a size below the 40 nm. The incorporation of Er ions showed a strong decrease in the lattice parameters, as well as averaged particle size. The reduction of the particle size also led to a stabilization of a pseudo-tetragonal phase with lattice parameter $a = b \approx \sqrt{2}a_T$, where a_T is the lattice parameter of the high-temperature tetragonal phase of BIT. The photoluminescence up-conversion (excitation wavelength = 1480 nm) showed an enhancement of the infrared emission (980 nm) as Er concentration increased, achieving a maximum for 6% mol, while photoluminescence spectra (excitation wavelength = 473 nm) showed a strong green emission (529 and 553 nm) with a maximum at 4% mol.

Keywords: Oxide materials; Sol-gel processes; Hydrothermal; Photoluminescence.

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1. Introduction

Bismuth titanate ($Bi_4Ti_3O_{12}$, BIT) is a member of Aurivillius-type bismuth-layered perovskite oxides, with a general formula (Bi_2O_2) [$A_{m-1}(B)_mO_{3m+1}$]. In this notation A represents a mono-, bi- or trivalent ion, B denotes a tetra-, penta- or hexavalent ion, and m is the number of BO_6 octahedra in each pseudo-perovskite block (m = 1, 2, 3, ...), where m = 3 for BIT compounds. The crystallographic structure consists of a layered arrangement of three perovskite-like cells of ($A_{m-1}(B)_mO_{3m+1}$)$^{2-}$ embedded between two bismuth oxides layers (Bi_2O_2)$^{2+}$ along the c-axis [1,2]. It is widely accepted that the Bi_2O_2 layers have a very important influence on the properties of bismuth layer-structured ferroelectrics (BLSFs), as the Bi_2O_2 layers act as insulating layers and are self-regulated to compensate for space charge due to their net electric charge [3]. This configuration favours outstanding ferroelectric properties, and, as a consequence, it has drawn extensive the attention from the scientific community as one of the most promising candidates to replace the lead-based ceramics.

Due to its low dielectric constant, high Curie temperature and strong anisotropy of the spontaneous polarization, such materials can be used in a broad range of applications, including but not limited to: piezoelectric, dielectric, pyroelectric, electrooptic, antennas, photocatalytic and biosensing fields, as well as potentially optical-electrical integrated and coupling devices [4–8]. However, its high dielectric loss, small remnant polarization and low fatigue-resistance limit its performance in other applications such as ferroelectric random access memory, FRAM, for example [9].

Recent studies have revealed that the rare-earth ion substitution in the A-site of perovskite structures can effectively overcome such drawbacks [10,11]. Park et al. reported fatigue-free, excellent ferroelectrical properties of BIT films doped with La^{3+} ions [12]. Improved results were obtained by Kim et al. through Nd^{+3} doping in BIT films [13]. The fatigue-free behaviour of these films can be attributed to the enhanced stability of oxygen in the Ti–O octahedron layer, which is caused by the substitution of stable rare-earth ions for volatile Bi ions located near the Ti–O octahedron layer. The enhancement of the ferroelectric properties can be explained by the fact that the substitution of Bi atoms by rare-earth ions, with different ionic radius, produces a structural distortion of the perovskite and, consequently, an enhancement of the remnant polarization [11].

On the other hand, the addition of the rare-earth ions with optical activity in the bismuth layer structure opens the possibility for use as a high-performance luminescent material, with a broad field of applications including opto- and microelectronics, as well as photon upconversion (UC) [14,15]. Near-infrared to visible upconversion (UC) is an important approach for the generation of visible luminescence. The interest in UC emission has increased due to the need for all-solid compact laser devices and three-dimensional displays. Trivalent rare earth doping-ions such as Pr^{3+}, Ho^{3+}, Tm^{3+}, Nd^{3+} and Er^{3+} are used as emission centers in UC materials [16–18].

Among the lanthanide ions, Er^{3+} is found to be the most effective dopant for UC emission, and the metastable levels $^4I_{9/2}$ and $^4I_{11/2}$ of Er^{3+} can be conveniently populated using low cost, low power laser diodes operating at 800 and 980 nm [18]. The search for suitable host materials is gaining importance for realizing high UC efficiency in the visible and the mid-IR region. Various host-material dependent factors such as phase purity, particle size, Er doping content, site substitution, and rare earth ion interactions in the host matrix are found to influence the UC emission [19]. Appropriate host materials offering good thermal stability and sensitivity over a wide temperature range (below and above room temperature) are in demand especially for luminescence thermometry applications.

In recent years, different synthesis methods have been reported in the literature for the fabrication of BIT powders. The choice of synthesis process plays a crucial role in obtaining a BIT with specific microstructure control as well as purity and chemical homogeneity. The control of these parameters has a significant effect on dielectric, ferroelectric and optical properties. Among the most popular processes are solid-state reactions [20] and high-energy ball milling processes [21]. However, these methods present some drawbacks, such as: formation of secondary phases, contamination by impurities, high heat treatment temperatures, long processing times and non-uniform particle size distribution.

An effective way to overcome such drawbacks is through wet chemical or soft-chemistry method. These methods not only ensure a homogeneous phase and well-controlled particle size but also more complex architectures and improvement of the dielectrical, structural, morphological and mechanical properties of BIT oxides[18,22,23]. Some of the most popular methods include: sol–gel [19], citrate gel [24], urea precipitation [25], oxalate coprecipitation [26], hydrothermal [27–29], metal organic decomposition [30], polymeric precursor [31], and microwave [32], to name a few. Among these synthetic methods,

hydrothermal or chemical reaction methods are of great interest, because they are safe and eco-friendly. The syntheses are performed at moderate temperatures, T~200 ∘C. To the best of our knowledge, the influence of the atmosphere in the use of hydrothermal methods to prepare BIT and doped-BIT has not been yet reported in the literature.

In this work, we report on structure, surface morphology and UC luminescence properties of BIT materials doped with different Er^{3+} concentrations, synthesized by a combined sol-gel hydrothermal method in an oxygen atmosphere. The effects of Er^{3+} concentration on the UC emissions and their mechanisms are discussed.

2. Experimental

2.1 Synthesis

$Bi_{4-x}Ti_3O_{12}:Er_x$ powders with $x = 0, 2, 4, 6$ and 8 mol%, were synthesised by the sol–gel-hydrothermal process using tetrabutyl titanate (TBT), bismuth (III) chloride ($BiCl_3$, Aldrich) and erbium (III) chloride hexahydrate, 99,9% ($ErCl_3$, Aldrich) as starting materials.

In a procedure, solution A containing 1 mL of TBT (97%) was diluted with 8.5 mL of ethanol for 10 min to form a white solution, which was added dropwise at 60 °C for 3 h with stirring to solution B, which contained 1 mL of HNO_3 in 40 mL of deionised water. An aqueous solution C was prepared by dissolving $BiCl_3 \cdot 6H_2O$ in 1 mL of HCl, and solution D was prepared by dissolving $ErCl_3$ in 2 mL of deionised water.

To prepare the $Bi_{4-x}Ti_3O_{12}:Er_x$ precursor, solutions C and D were added dropwise to solution B. Under stirring and N_2 bubbling, NaOH 10 M was added to the bismuth erbium titanium solution, and a white, homogeneous colloidal bismuth erbium titanium slurry was formed.

The mixed solution was transferred to a 500 mL Teflon-lined stainless steel reactor, sealed and then heated at 180 °C for 48 h under a partial oxygen pressure of 30 bar. At the end of the reaction, the autoclave was cooled down to room temperature. The as-synthesised white powder, attached to the Teflon container, was collected, centrifuged, washed with distilled water and ethanol to remove any remaining ions and dried at 60 °C for 6 h under atmospheric pressure.

2.2 Characterization

Er-doped BIT powders were structurally characterised by X-ray diffraction (XRD). Data were acquired using a Siemens Advanced D-8 diffractometer with CuK_α radiation at 40 kV and 30 mA. Raman spectra were recorded on a WITEC model CRC200, using a 5.5 mW laser with a wavelength of 514.5 nm with a grating of 1200 groove/mm. Surface morphological analysis of BIT nanoparticles were carried out by scanning electron microscopy (FEI Quanta 650F Environmental SEM). The UC spectra were obtained by exciting with a 980 nm and 1480 nm laser (Alcatel 1933 SMG) with a maximum power of 50 mW. The laser was focused on the samples using a lens with a focal length of 30 mm. The emitted light was collected using a lens with focal length 50 mm and focused on the entrance slit of a CCD spectrograph (Andor Shamrock 303i).

The luminescence decay curves were obtained by exciting with a 10 ns pulsed optical parametric oscillator laser (EKSPLA/NT342/3/UVE) and the emission was focused in the entrance of the spectrograph coupled to a photomultiplier (R928 Hamamatsu in the Vis range or 5509-73 Hamamatsu for the NIR range) and recorded using a digital storage oscilloscope (Tektronix 2430).

3. Results and discussion

3.1 XRD patterns

Fig. 1 shows the XRD patterns of the BIT and Er-doped BIT samples. As shown in Fig. 1 the sharp and well-defined peaks reveal high crystallinity for all of the as-prepared Er-doped BIT powders, which were not submitted to any heat treatment.

The XRD Bragg reflection was assigned by using an orthorhombic perovskite structure (space group *Fmmm*, JCPDS card no 56-0814) of BIT at room temperature. The peak associated with the (117) plane of BIT and Er-doped BIT shows the highest intensity, indicating that all sample compositions conform to the bismuth layered structure with $m = 3$. The results are in agreement with earlier observations reporting that the strongest diffraction corresponds to the (11_{2m+1}) reflection in the Aurivillius phase for bismuth layered structured ferroelectrics compositions [33].

Fig. 2 displays the XRD patterns of BIT and Er-doped BIT in the 28–30° 2Θ range for all of the samples.

The effect of Er-substitution on the BIT structure can be seen in the clear shifting of the (1 1 7) reflection. Fig. 2 shows the X-ray diffraction patterns of BIT and the BIT-doped phases. The shift of the strongest diffraction peak (*hkl*) is closely related to the ionic radii of Er^{3+}, Bi^{3+} and Ti^{4+}. According to Shannon et *al*. [34], the ionic radii are 1.03 Å for Bi^{3+}; 0.88 Å for Er^{3+} and 0.605 Å for Ti^{4+}. When Er^{3+} replaces Bi^{3+} in the structure, the difference in the ionic radii leads to a decrease in the lattice parameters and the cell volume (Table 1), this is observed by shift of the XRD peak (117) to higher angles as shown in Fig. 2. To further evaluate the variation of the crystal structure the lattice parameters were calculated and shown in Table 1. The Rietveld refinement showed that all the crystal structures converged to the tetragonal phase, i.e. *a* = *b* (see Table 1). While it is well-known that BIT shows the tetragonal phase at temperatures above 675°C, Hirata et al. found that there is no obvious changing in XRD pattern for tetragonal and orthorhombic phases [35]. This is because the ratio of *a*- and *b*-axis varies very close to 1 with *a*/*b* = 0.993 [1], 0.9835 [35], 0.985 [36], 1.008 [37], 1.011 [38], 1.006 [39] and 0.993 [40].

In addition, Du et al. reported the presence of a stable tetragonal phase at room temperature in nanoparticles [40,41]. The origin of this stabilization was attributed to the surface energy mechanism. Due to the very high specific surface area of the nanoparticles, an excess surface energy per unit volume is created. Then, this excess of surface energy contributes differentially to the relative free energies of the tetragonal and orthorhombic phases, leading to the stabilization of the tetragonal phase at room temperature [41]. Their observations suggested that the critical particle size to stabilize this phase is below 40 nm [40,41].

Taking into account this effect, we estimated an average particle size using the (117) diffraction peak and the Scherrer equation given by:

$$d = k\lambda/(\beta\cos(\theta)) \tag{1}$$

where *d* is particle size, *k* ~ 1 is the shape factor, $\lambda = 0.1540$ nm is the wavelength of the CuK_α radiation, β is the full-width at half-maximum (FWHM) and θ is the diffraction angle [42]. The averaged particle size, the peak position and the FWHM are displayed in the Table 1.

As shown in Table 1, the lattice parameters, *a*, *b* and *c*, decrease with increasing Er^{3+} content. The variations of lattice parameters and cell volume can be ascribed to the substitution of large-ion-radius Bi^{3+} ions by smaller Er^{3+} ions in the BIT lattice.

The lattices parameter obtained from XRD are in very close agreement with a pseudo-tetragonal phase found by Hirata et al with $a = b \approx \sqrt{2}a_T$ with a_T = 3.85 Å being the lattice parameter of the high-temperature tetragonal phase [35].

Lattices parameters (Å)	Erbium content in $Bi_{4-x} Er_xTi_3O_{12}$ mol%				
	0 %	2 %	4 %	6 %	8 %
a	5.42707	5.42164	5.41723	5.41849	5.41895
b	5.42707	5.42164	5.41723	5.41849	5.41895
c	32.64568	32.62741	32.53729	32.71974	32.36215
Volume ($Å^3$)	961.5161	959.056	954.7196	960.6527	950.3152
Particle size (nm)	32.7	21.5	29.4	17.2	21.9

Table 1. Lattice parameters and crystallite sizes of BIT and Er-doped BIT.

3.2 Raman spectra

As mentioned previously, the BIT structure is composed of $(Bi_2Ti_3O_{10})^{2-}$ perovskites units embedded between two bismuth oxides layers $(Bi_2O_2)^{2+}$ along the c-axis. In the perovskite units, Ti atoms are surrounded by oxygen octahedrons, and Bi atoms occupy the outside of TiO_6 octahedrons[43]. In our case, this behaviour can be explained by the existence of three types of substitution of Er ions for Bi ions in BIT. Er ions can substitute for Bi ions (*i*) in the perovskite units only (A sites of the pseudo-perovskite blocks), (*ii*) in the Bi_2O_2 layers only, or (*iii*) in both. A Raman spectroscopic study was done to determine the substitution sites of Er atoms in BIT and structural changes of TiO_6 octahedrons.

The room temperature Raman spectra the BIT and Er-doped BIT samples are shown in Fig. 3. Raman selection rules for pseudo-orthorhombic BIT with space group *Fmmm* allow 24 active optical modes of different symmetries $(6_{Ag}+2B_{1g}+8B_{2g}+8B_{3g})$[44,45]. However, as shown in Fig. 3*a*, only 11 Raman modes were observed, which is partially due to the possible overlap of vibrations and the broadening or weak features of some bands.

It has been reported that different ferroelectric orderings can be derived from the orthorhombic structure in BIT [44]. Thus, BIT prepared by diverse methods and chemical routes show variation on the local structures relating to ferroelectric orderings, which results in the differences in the Raman spectra of BIT. The Raman spectrum of the BIT sample (Fig. 3*a*) is similar to those obtained for nanoparticles of pure BIT in previous studies [46]. The spectra exhibit intense phonon modes at about 285, 470 and 490 cm^{-1}, together with some weak modes. The characteristic modes can be labelled according to the

assignments of Graves et al. [47]. The Raman modes in the range 200-400 cm^{-1} (B_{2g} + B_{3g} modes) have been ascribed to O–Ti–O. A major mode at 470-490 cm^{-1} has been assigned to the split between B_{2g} and B_{3g} modes and described as a Ti–O torsional mode. A band feature at 651 cm^{-1} exhibits Ag character and has been associated with the Ti–O symmetric stretch. According to the symmetry of TiO_6, the mode at 258 cm^{-1} is Raman inactive and can be observed when distortion occurs into octahedron. The mode at 336 cm^{-1} arises from a combination of stretching and bending vibrations. Some phonon modes, e.g., at 322 cm^{-1}, 542 cm^{-1}, 651 cm^{-1} and 859 cm^{-1}, appear wide and weak because of the considerable distortion in the TiO_6 octahedral and hence these phonon modes may induce stresses in crystalline BIT. The appearance of modes at 285, 542 and 859 cm^{-1} suggests the presence of perovskite structure[18]. In general, our results in the formation of BIT are in agreement with previously published results, even although some differences exist in relation to the mode counting in the polycrystalline material, due to possible symmetry breaking, low peak intensity and overlap of vibration modes [18,28].

Fig. 3b shows that with an increasing Er content (2 mol %), the Raman scattering peaks exhibit a strong decrease in intensity and become broader. A marked shift to higher frequencies and a broadening of the linewidth (FWHM) were observed as the Er concentration increased. This behaviour increases for samples with 4, 6 and 8 mol %, as shown in Fig. 3c, d and e.

The vibrational modes of Er-doped BIT can be classified as the internal modes of TiO_6 octahedra and the lattice transition involved in the motion of the cations in the pseudo-perovskite slabs and the Bi_2O_2 layers. For the Er-doped BIT, it was reported that the mode at about 60 cm^{-1} is due to the displacement of Bi^{3+} ions in Bi_2O_2 layers, and that those at 77 and 120 cm^{-1} are related to the vibration of the ions in the A sites of the pseudo-perovskite blocks [48]. In general, these modes become increasingly diffuse and broad with increasing Er content, implying the active participation of the A-site in the substitution process[18]. In our case, the reduction of the intensity of these modes with increasing Er content, suggests that the incorporation of Er^{3+} does not occur mainly at the A-site in the pseudo-perovskite blocks.

In metal oxides with MO_6 octahedral symmetry (M=Ti, Ta, Nd, Zr, Cu, etc.), the intra-group energy binding is large compared with the inter-group or crystal binding energy. Therefore, to a first approximation, the internal mode description is suitable for the interpretation of the Raman modes

originating from the Ti–O bond. A perfect 'isolate' TiO_6 octahedron has six vibrational modes: A_{1g}, E_g, F_{1u}, F_{1u}, F_{2g} and F_{2u} [49], where, A_{1g}, E_g and F_{2g} are Raman active, F_{1u} and F_{1u} are infrared active, and F_{2u} is silent. With the lowering of the symmetry of TiO_6 octahedron inside the BIT nanocrystal, all of selection rules are broken, and all these vibrational modes can become Raman active with various intensities. The modes observed at 589 and 869 cm^{-1} clearly have A_{1g} character due to the pure stretching mode of TiO_6 octahedra. This mode remains unchanged with Er substitution, so the Er does not substitute for Ti, only for Bi. The 518 and 544 cm^{-1} modes can be assigned to B_{2g} and B_{3g}, which come from the splitting of an E_g mode. This E_g mode, involving opposing excursions of the external apical oxygen atoms of the octahedral, is two-fold degenerate for a tetragonal-like cell [24]. It splits into two components, $B_{2g} + B_{3g}$, with pseudo-orthorhombic distortion. All of these changes show that the substitution of Er for Bi in perovskite layer causes an increase in the symmetry of TiO_6 octahedron and a decrease in pseudo-orthorhombic distortion.

On the other hand, Zhu et al. have reported the dependence between the crystal structure, phase transition and grain sizes of 23, 42 and 53 nm for $Bi_{4x}La_xTi_3O_{12}$ nanocrystals [49]. The results showed that La substitution for Bi strengthens the short-range interaction between the atoms, decreases orthorhombic distortion and leads to a ferroelectric–paraelectric phase transition at the critical La content for the BIT nanocrystals. This effect is increased with decreasing grain size (23 nm). Our result shows similar behaviour to those reported by the authors, considering the particle size of our samples.

Fig. 4 shows the SEM micrographs of the BIT and Er-doped BIT samples. It is clearly seen that the nanoparticles in Fig. 4a, c and e, (x = 0, 4 and 8 mol %) are nearly spherical with a diameter range of 0.5, 0.2 and 0.25 µm respectively. As shown in Fig. 4b and d (x = 2 and 6 mol %), the plate-like primary powders have agglomerate size bigger than 5 µm. When the micro-plates are overlapped on top of each other, the bottom plate could be clearly seen through the upper plate, indicating that the plate-like primary particles are considerably small. The agglomeration process was attributed to Van der Waals forces. Particles have a tendency to form agglomerates, in order to reduce surface free energy in BIT nanocrystals. In Fig. 4f the EDX result shows that the sample only contains the elements Bi, Ti, O and Er.

3.3 Up-conversion photoluminescence spectra

The up-conversion photoluminescence (UC) emission spectrum of Er-doped BIT nanoparticles as a function of the wavelength is shown in the Fig. 5a. The UC spectrum was measured at an exciting wavelength of 1480 nm. The synthesized samples show a strong emission in the near infrared around ~ 980 nm and a weak band of red emission at ~ 666 nm, which are assigned to the $^4I_{11/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ ion Er^{3+} transitions, respectively [18,50]. As displayed in Fig. 5a, the intensity of UC emission processes increases as the Er^{3+} ion concentration increases, reaching a maximum at 6 mol%. After that, the luminescence intensity decreases rapidly due to the greater amount of Er^{3+} ions and the shorter distance among them, thus favouring energy transfer through non-radiative processes between the ions. The photoluminescence spectrum (Fig. 5b) was measured at an exciting wavelength of 473 nm. The nanoparticles exhibit a strong green emission between 529 and 553 nm and a weak emission at 666 nm red corresponding to the transitions $^2H_{11/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$, respectively. The maximum intensity is reached for the sample doped at 4 mol%.

There are several mechanisms to describe the UC process. The easiest way to populate the upper levels is through successive absorption of two or more photons by the ground state absorption (GSA), followed by excited-state absorption (ESA) processes. Another way to populate these levels is by energy transfer between neighbour activator ions [51].

To better understand the mechanism involved in this process, the decay curve of the emission $^4I_{11/2} \rightarrow {}^4I_{15/2}$was measured. A quick rise of the intensity with a lifetime (τ) around $\tau \sim 0.11\text{-}0.22$ ms is observed followed by a rapid decrease with a longer lifetime of $\tau \sim 1$ ms, as displayed in Fig. 7. This means that two photons of 1480 nm are successively absorbed by the material and the $^4I_{9/2}$ level is populated immediately. Then, because of the small energy difference, the $^4I_{9/2}$ level decays nonradiatively to $^4I_{11/2}$ level. After that, the emission is generated and decays to the ground state $^4I_{15/2}$. This process is consistent with the GSA/ESA mechanism explained above. The diagram of the mechanism of the up-conversion processes for the emission is shown in Fig. 8.

4. Summary and conclusions

Different samples of Er-doped $Bi_4Ti_3O_{12}$ (BIT) were prepared by a combined sol-gel hydrothermal method. The hydrothermal reactions were carried out under a partial oxygen pressure of 30 bar.

XRD patterns confirm that Er^{3+} replaces Bi^{3+} in the structure at all concentrations investigated. The increasing mol% of Er leads to a decrease in the lattice parameters and the cell volume, and shows an average of the grain size of approx. 25 nm. We found that the small size of the nanoparticles stabilized a tetragonal phase at room temperature with lattice parameter $a = b \approx \sqrt{2}a_T$.

Raman spectra showed that the Er substitution by Bi (4, 6 and 8 % mol) does not occur mainly at the A-site in the pseudo- perovskite blocks because the characteristic modes disappear with increasing Er concentration. Instead, the substitution occurs mainly in the Bi_2O_2 layers.

The UC photoluminescence of Er-doped BIT nanoparticles showed a strong emission in the near infrared (980 nm) and a weak band of red emission (666 nm). The maximum emission is obtained at 6 mol%. The decay curve of the infrared emission indicated two interaction zones: (*i*) a quick rise of the intensity with a lifetime ranging $\tau \sim 0.11$-0.22 ms and, then, (*ii*) a decrease with a longer lifetime of $\tau \sim 1$ ms. This means that two photons of 1480 nm are successively absorbed by the material and the $^4I_{9/2}$ level is populated immediately, then, because of the small energy difference, the $^4I_{9/2}$ level decays nonradiatively to $^4I_{11/2}$ level. The photoluminescence spectrum showed that nanoparticles exhibit a strong green emission between 529 and 553 nm and a weak emission red at 666 nm. In this case, the maximum emission was obtained for 4 mol%.

5. Acknowledgments

6. References

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