The Effects of Li\textsuperscript{+} Doping on Structure and Upconversion Luminescent Properties for Bi\textsubscript{3.46}Ho\textsubscript{0.04}Yb\textsubscript{0.5}Ti\textsubscript{3}O\textsubscript{12}: xLi Phosphors

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Abstract: A series of novel Li\textsuperscript{+} doped Bi\textsubscript{3.46}Ho\textsubscript{0.04}Yb\textsubscript{0.5}Ti\textsubscript{3}O\textsubscript{12} (BHYTO; xLi, 0 ≤ x ≤ 0.15) upconversion phosphors were prepared through a sol-gel-sintering method. There exist three emission bands centered at 545 nm, 658 nm, and 756 nm in the upconversion emission spectra at 980 nm excitation, corresponding to energy transitions of \( \frac{5}{2}F_4 \rightarrow \frac{5}{2}F_2 \rightarrow \frac{5}{2}I_8 \), \( \frac{5}{2}F_5 \rightarrow \frac{5}{2}I_8 \) and \( \frac{5}{2}F_4 \rightarrow \frac{5}{2}S_2 \rightarrow \frac{1}{2}I_7 \) of Ho\textsuperscript{3+}, and the upconversion emission intensity of BHYTO: 0.05Li is about 2.2 times stronger than that of BHYTO samples. The luminescent lifetime of the strongest emission (545 nm) is in the range of 45.25 to 65.99 ms for the different BHYTO: xLi phosphors. The energy transfers during the upconversion pumping process from Yb\textsuperscript{3+} to Ho\textsuperscript{3+} are mainly responsible for all the emissions, each belonging to a double-photon process. Li\textsuperscript{+} mainly entered into the interspace sites or occupied Bi\textsuperscript{3+} sites in Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12} host during the fabrication process according to its dosage, and the possibility is very low for Li\textsuperscript{+} to take part in the energy transfer process directly due to its lack of matching levels with 4f\textsuperscript{2} of Ho\textsuperscript{3+} and Yb\textsuperscript{3+}. However, Li\textsuperscript{+} doping can not only increase the size of crystal grains to improve crystallinity through XRD analysis, but also reduced oxygen vacancies to decrease the number of quenching centers through XPS analysis. The improved crystallinity and reduced quenching centers are proposed to be the main causes for the enhanced upconversion luminescence of the Li\textsuperscript{+} doped BHYTO phosphor.

Keywords: Li\textsuperscript{+} ion; upconversion luminescence; luminescence enhancement; grain size

1. Introduction

Rare earth (RE) doped upconversion (UC) phosphors played important roles in LED [1], display [2], biological image [3], laser [4], and optical fiber [5], attracting a lot of interests to develop novel optical materials. Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12} (BTO) based materials with an Aurivillius structure have been studied intensively for a long time due to their good electric properties [6], and almost all RE\textsuperscript{3+} doping has positive effects on improving its ferroelectricity of BTO [7]. Following that, the excellent photoluminescence was observed in the BTO based multifunctional materials, such as Er\textsuperscript{3+}, Tm\textsuperscript{3+}, Ho\textsuperscript{3+}, Yb\textsuperscript{3+} single doped, or co-doped BTO phosphors [8]. Recently, an efficient UC phosphor of Ho\textsuperscript{3+}–Yb\textsuperscript{3+} co-doped Bi\textsubscript{3.46}Ho\textsubscript{0.04}Yb\textsubscript{0.5}Ti\textsubscript{3}O\textsubscript{12} (BHYTO) powder was reported [9]. There are three main reasons to contribute BTO to be a good optical host for photoluminescence: (1) RE\textsuperscript{3+} ions have a large solid solubility to substitute Bi\textsuperscript{3+} sites and can disperse evenly in BTO crystal lattice due to similar ionic radius and the same valence state as Bi\textsuperscript{3+} [10], and (2) they can stabilize oxygen in BTO crystal lattice and reduce oxygen vacancy [11], and (3) BTO has a low phonon energy and good physical and chemical stability [12]. Although a lot of RE\textsuperscript{3+} doped phosphors were designed and invented so far, only a few of them obtained practical applications because most of them have a lower luminescence efficiency. So the research on how to improve luminescence efficiency through a simple...
method has a higher value than only to find a novel phosphor. Doping of assistant ions in phosphors has been considered to be an efficient and important way in improving luminescence property [13]. Li⁺ was the most used assistant ion in either down shifting or upconversion RE phosphors. It can enter into the host crystal lattice of these phosphors easily without destroying the original crystal structure since it has a small ion radius and simple electron configuration. However, the enhanced amplitude and initial causes for luminescence improvement in these RE phosphors were usually different, even for the same phosphor fabricated with different methods. For examples, the emission intensities of Li⁺ doped CaMoO₃: Eu³⁺, Yb³⁺ [14], Gd₂O₃: Yb³⁺, Ho³⁺ [15], and Y₂O₃: Eu³⁺ [16] were reported to be 83, 10, and 1.2 times higher than those of phosphors without Li⁺ doping. At present, there are many proposals to illustrate the role of Li⁺ in the process of luminescence enhancement, such as local crystal field distortion [14], charge compensation [17], change in morphology [18], and improved crystallinity and increased grain size [19]. However, some of these proposals were short of data support or not discussed in detail.

2. Experiment

In the formula of Bi₃.₄₆Ho₀.₀₄Yb₀.₅Ti₃O₁₂: xLi (x = 0, 0.02, 0.05, 0.10, 0.15), and the mole ratio of Li, Bi, Ho, Yb, and Ti is equal to x: 3.46: 0.04: 0.5: 3, where x denotes nominal Li doped content (Cᵩ) in Bi₃.₄₆Ho₀.₀₄Yb₀.₅Ti₃O₁₂: xLi. During the fabrication of Bi₃.₄₆Ho₀.₀₄Yb₀.₅Ti₃O₁₂: xLi phosphors, LiNO₃ (99%, Macklin, Shanghai, China), Bi(NO₃)₃·5H₂O (99%, SCRC, Shanghai, China), Ho(NO₃)₃·6H₂O (99.99%, Rknerc, Shanghai, China), Yb(NO₃)₃·5H₂O (99.99%, Rknerc, Shanghai, China) and Ti(OC₄H₉)₄ (AR, Macklin, Shanghai, China) were used as the precursors of Li, Bi, Ho, Yb, and Ti ions, respectively. Ho, Yb, and Ti precursors were weighed according to stoichiometry of the formula of Bi₃.₄₆Ho₀.₀₄Yb₀.₅Ti₃O₁₂: xLi, and Bi and Li precursors exceeded 15% and 10% to supplement Bi and Li loss because both of them can partly volatilize during high-temperature treatment [20]. At first, the weighted Li, Bi, Ho, Yb precursors were put into a beaker, and then 15 mL acetic acid (AR, Macklin, Shanghai, China) was added rapidly, followed by heated under 55 °C and stirred for 15 min, and then cooled down to room temperature to obtain solution denoted as A liquid. 1.85 mL tetrabutyl titanate (AR, Macklin, Shanghai, China) was weighted and added into the other beaker containing 15 mL 2-methoxyethanol (AR, Macklin, Shanghai, China), and then stirred for 15 min to form B liquid. Subsequently, the B liquid was dropped into the A liquid gradually and stirred at 550 rpm for 2 h simultaneously under room temperature, and 0.06 Mol/L precursor solution with a golden color was obtained. The solution was dried in an oven at 80 °C until a solid gel was formed, and then sintered at 800 °C for 3 h in a muff furnace followed by cooling to room temperature under air atmosphere. The shape of the sintered product is fluffy, so they were ground in an agate mortar for 5 min to obtain the final BHYTO: xLi phosphor powders.

XRD (Rigaku D/Max 2500V with a Cu Kα target, Rigaku, Tokyo, Japan) was performed to analyze phase structure of the samples, and the operated voltage and current are 40 KV and 100 mA, and the scanning range is from 10° to 60° with 5°/min scanning speed, and the scanning step is 0.020. The lattice parameter and cell volume were calculated automatically through Jade 6.5 software based on the measured XRD data. Inductively coupled plasma emission spectrum (ICPMS Agilent 7700s, Agilent, Santa Clara, CA, USA) was used to assess Li⁺ practical content in the samples. SEM (Gemini Sigma 300/VP, Zeiss, Oberkochen, Germany) was used to analyze the morphology of the samples, operated at 5 kV with a standard beam current, and EDS to analyze elemental compositions of the samples. TEM (Titan G260–300, FEI Company, Hillsboro, OR, USA) was used to observe the morphological characteristics at high magnification. XPS (ESCALAB 250XI, Thermo Fisher Scientific, Waltham, MA, USA) was used to analyze the effects of Li⁺ doping on the structure and valance state of elements, and full spectrum scanning was performed in the range of 0 to 1000 eV with carbon peak correction at 284.6 eV before this analysis. Sample particle size was measured by Zeta potential (NanoBrook Omni, Brookhaven Instruments, Holtsville, NY, USA), and at the beginning of it, an appropriate amount of sample powders
were placed in alcohol for ultrasound for 5 min to obtain a suspension with a concentration of about 0.6 mg/mL for measurement, and each sample was measured three times. An integrated fluorescence spectrometer (FluoroLog-3, Horiba, Kyoto, Japan) was used to measure the PLS and decay lifetime for the phosphors with a low noise 980 nm laser (MDL-III-980-2W, CNI Lasers, Changchun, China) as the pumping source. Note that all the samples had been dried at 120 °C for 2 h in a vacuum drying oven before the tests of the optical properties.

3. Results and Discussion

ICPMS measurement was performed to grasp whether Li⁺ was successfully doped into the fabricated BHYTO: xLi samples, and the results were shown in Table 1. The detected Li⁺ content (C_D) in the final sintered products is less than that of the doped Li⁺ content (C_P) in all the samples before sintering due to the volatilization of Li⁺. The detected Li⁺ content (C_D) can be considered as Li⁺ practical content in the final compound of the phosphors ignoring measurement error. C_D values are 1.70%, 4.88%, 9.92%, and 14.93% for the BHYTO: xLi phosphors with x equal to 0.02, 0.05, 0.10, and 0.15, respectively, and corresponding Li doping efficiencies (η_D) are 77.27%, 88.73%, 90.18%, and 90.48%. The values of C_P and η_D increased with the increase in absolute mass for excessive Li⁺ dosage. Note that η_D was defined as the ratio of C_D to doped Li⁺ content (C_P). The results suggest that excessive dosage of 10% Li⁺ for the raw materials during the fabrication process is available. For the convenience of description, the nominal Li doped content was used to express Li⁺ content in all the BHYTO: xLi phosphors.

Table 1. The results of ICPMS measurement for Li content in BHYTO: xLi samples (x = 0.02, 0.05, 0.10, and 0.15).

| Sample No. | Sample Names | C_N (mol%) | C_P (mol%) | C_D (mol%) | η_D (%) |
|------------|--------------|------------|------------|------------|---------|
| 1          | BHYTO: 0.02Li | 2          | 2.2        | 1.70       | 77.27   |
| 2          | BHYTO: 0.05Li | 5          | 5.5        | 4.88       | 88.73   |
| 3          | BHYTO: 0.10Li | 10         | 11         | 9.92       | 90.18   |
| 4          | BHYTO: 0.15Li | 15         | 16.5       | 14.93      | 90.48   |

Notes: Nominal Li⁺ content (C_N), doped Li⁺ content (C_P) in the samples before sintering, detected Li⁺ content (C_D) in the sintered products and Li⁺ doping efficiency (η_D) during the whole fabrication process.

In order to obtain the structural information about phase, crystallinity, and crystal distortion of BHYTO: xLi phosphors, XRD was performed and the results were shown in Figure 1a. It can be seen that the phosphors consisted of dominant orthorhombic perovskite Bi₄Ti₃O₁₂ phase and a small amount of pyrochlore Bi₅Ti₃O₁₂ phases, and no other phase, such as Li₂O or Li₂TiO₃, detected, suggesting that Li⁺ entered into the crystal lattice of bismuth titanates. It was reported that the radius of Bi³⁺, Ho³⁺, Yb³⁺, and Li⁺ was 0.103 nm, 0.090 nm, 0.087 nm, and 0.076 nm, respectively [21]. The diffraction peaks of pristine BHYTO without Li⁺ doping shifted toward larger angle in comparison with pure Bi₄Ti₃O₁₂ phase (Card no. 35–0795), as shown in Figure 1b. Ho³⁺ and Yb³⁺ are inclined to substitute Bi³⁺ site in Bi₄Ti₃O₁₂ [22] because of the same valence and close ion radius, and the substitution by smaller ion radius can result in crystal shrink. However, the diffraction peaks shifted towards smaller angle for BHYTO: 0.02Li sample compared to BHYTO samples, and then shifted towards larger angle gradually with further increase in Li⁺ content. The possible reason is that Li⁺ ions first entered into the interspaces of crystal lattice when its dosage was low and induced the expansion of the crystal cell, resulting in the shifts of diffraction peaks towards smaller angle. However, with the increase in Li⁺ dosage, the amounts of available interspaces in BHYTO crystal were reduced little by little, and Li⁺ began to occupy Bi³⁺ sites, causing volumetric shrinkage of the crystal cell and resulting in the shifts of diffraction peak towards a larger angle. Figure 1c shows the volume (V_C) of crystal cell and grain sizes (D_C) of crystal grains for the BHYTO: xLi phosphors with various Li⁺ content based on the XRD data of Figure 1a. The V_C values first increased and then decreased while the D_C increased monotonously with the increase
in Li⁺ content in the BHYTO: xLi phosphors, and the $D_C$ values were calculated to be about 34.59 nm, 37.36 nm, 38.33 nm, 45.74 nm, and 48.17 nm for the BHYTO: xLi samples with $x$ equal to 0, 0.02, 0.05, 0.1, and 0.15, respectively, according to famous Scherrer formula.

![Figure 1](image-url)

**Figure 1.** (a) XRD pattern, (b) an enlarged XRD graph in the range of $2\theta = 29.8°–30.5°$, and (c) the volume of crystal cell and grain sizes of BHYTO: xLi phosphors.

For an Aurivillius structured material, the lattice distortion and strain are usually expressed by the ratios of crystal parameters, that is, $b/a$ and $c/a$, respectively, and the ratios increased with the increase in crystal distortion and strain increases [23]. Compared to Li⁺ undoped BHYTO, the degree of crystal distortion and strain were relieved significantly in Li⁺ doped BHYTO: xLi phosphors, because the ratio of $b/a$ and $c/a$ decreases gradually. However, the reduced full width at half maxima (FWHM), shown as Table 2, and increased grain sizes imply an enhanced crystallization in the Li⁺ doped samples. It was reported that Li₂O can not only act as a flux to lower sintering temperature and promote the elemental diffusion so as to increase density and grain size of glass [24] and ceramics [25], but also act as catalyst to facilitate the synthesis of composite oxide [26], which could improve crystallization of products.

**Table 2.** The crystal parameters and FWHM for the BHYTO: xLi phosphors.

| Sample Names      | a (Å)   | b (Å)   | c (Å)   | FWHM (°/rad) |
|-------------------|---------|---------|---------|--------------|
| BHYTO:0.0Li       | 5.3930  | 5.4229  | 32.7941 | 0.263/0.00459|
| BHYTO:0.02Li      | 5.4081  | 5.4367  | 32.8188 | 0.243/0.00424|
| BHYTO:0.05Li      | 5.4011  | 5.4298  | 32.8278 | 0.237/0.00414|
| BHYTO:0.1Li       | 5.4035  | 5.4266  | 32.8016 | 0.199/0.00347|
| BHYTO:0.15Li      | 5.3993  | 5.4251  | 32.8219 | 0.189/0.00330|

Figure 2 shows the SEM results for the BHYTO: xLi phosphors. It can be observed that all the BHYTO: xLi phosphors mainly consisted of micro-sized particles with irregular shape and most of the particles in weight had size in the range of 1 to 2 μm. There are some tiny particles on the surface of the micro-sized ones. EDS results show that the samples were composed of Bi, Yb, Ho, Ti, and O elements and no impurity element detected in the samples. The detected C element came from a graphite conductive adhesive tape used to adhere the sample powders during SEM measurement. Li⁺ was not detected by EDS due to its low atomic number. Figure 2g shows the content and average content of each element at 1 and 2 spot. It can be seen that the proportion of each element has little difference and is relatively consistent with the proportion of elements in Bi₁₄Ti₁₂O₃₃₂. Figure 2h shows histogram of particle size for the samples, the particle size of all the samples changed little and was above 1 μm, which was consistent with the results in SEM.
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Figure 2. SEM of the BHYTO: xLi samples with x values equal to (a) 0, (b) 0.05, (c) 0.10, (d) 0.15, respectively, and (e), (f) EDS of 1st and 2nd spots in Figure 2b, (g) the elemental content in the samples of the BHYTO: 0.05Li samples, and (h) histogram of particle size for the samples.

Figure 3a shows TEM micrograph of BHYTO: 0.05Li sample with the optimal UC luminescence among all the BHYTO: xLi phosphors, and the micro-sized particles have a shape of small compact blocks. Figure 3b shows the selected area electron diffraction (SAED) pattern observed from c-axis direction, which presents a rectangle shape (in blue), and the length for the two intersecting edges of the rectangle is very close but not exactly the same, which is the structural feature of a typical orthorhombic crystal system. Figure 3c shows high-resolution transmission electron microscopy (HRTEM) image obtained by focus to a spot on the thin edge of a grain, where a fine and delicate crystal structure with regular atomic arrangement can be observed, and the distance between two neighboring parallel crystal planes in mutually perpendicular directions are 0.271 nm and 0.273 nm, corresponding to (200) and (020) crystal planes of Bi$_4$Ti$_3$O$_{12}$, respectively [27]. Figure 3d shows (020) lattice fringe obtained from a filtering method through DM software (Digital Micrograph 3.7), where more regular structure of atomic array can be observed, and the vague areas in this image denoted as 1, 2, and 3 implies some defects of dislocations existed.
Figure 3e shows high-angle-annular-dark-field scanning transmission electron microscopy (HAADF-STEM) diagram and elemental distribution. The color of the object image is very bright, suggesting the phosphor contained some elements with large atomic number (i.e., Bi). The insert graphs in Figure 3 show the element compositions and distributions, and all the elements of Bi, Ho, Yb, Ti, O in the samples were detected except for Li elements due to its low atomic number, and the distributions of Bi, Ho, Ti, and O are uniform and dispersed more evenly than Yb element.

Figure 3. (a) TEM image, (b) SAED pattern, (c) HRTEM image, (d) fringes of (200) obtained by filtering, and (e) HAADF-STEM diagram and elemental distribution for BHYTO: 0.05Li samples.

Figure 4a shows a full scan of XPS in the range of 0 to 1000 eV to analyze the chemical compositions and electron binding energy of BHYTO: 0.05 Li samples, and as a comparison, XPS of pristine BHYTO samples was also shown to illustrate Li$^+$ doping effects. All the elements of Bi, Ti, O, Ho, Yb, and Li in the phosphors were detected though the peak of Li$^+$ is very weak (see Figure A1 in Appendix A). Figure 4b shows high revolution XPS of Bi 4f, and there are two main peaks centered at 158.3 eV and 163.6 eV, very close to those of Bi 4f in Bi$_2$O$_3$ and BTO, corresponding to a pair of spin-orbit splitting energy of Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$ [29]. Additionally, there is the other pair of smaller peaks with higher energy on the right, and both of the energy difference between these two pairs of peaks are equal to 5.3 eV, implying that they are both originated from electron transition of
During high-temperature heat treatment process to produce Bi$_4$Ti$_3$O$_{12}$ based materials, oxygen vacancies were easily formed on the surface of the samples, which created a crystal field environment around Bi$^{3+}$ ions different from that of Bi$^{3+}$ ions internal the body. In this work, Bi$_4$ 4f and Bi$_C$ 4f denote as Bi$^{3+}$ ions near the surface and internal crystal lattice, respectively, and Bi$_S$ 4f has a higher binding energy than Bi$_C$ 4f. For BHYTO: 0.05Li phosphors, the peaks of Bi$_S$ 4f shifted close to Bi$_C$ 4f peaks and the area surrounded by Bi$_S$ 4f curve and based line became smaller, which suggests Li$^+$ doping had an effect on stabilizing oxygen in crystal lattice to make the environment around Bi$^{3+}$ ions near the surface more similar to that in the body. As shown in Figure 4c, the peaks of 457.6 eV and 463.3 eV correspond to the characteristic binding energy of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ [30], and the peak of Ti 2p$_{1/2}$ overlaps with Bi 4d$_{3/2}$ to form a wide energy peak. Note that nearly no change for the Ti 2p spectra indicates that Li$^+$ did not substitute Ti$^{4+}$ for the perovskite layer in BTO host. Figure 4d shows two symmetrical peaks at 529.1 eV and 530.9 eV, corresponding to the binding energy of O 1s [31]. They were denoted as lattice oxygen (O$_L$) and absorbed oxygen (O$_A$), respectively, and can be usually used as the probe for material oxygen vacancies. Compared to the XPS of BHYTO samples [22], O 1s peaks for BHYTO: 0.05Li sample have the same positions, but have a wider full width at half maximum (FWHM) and larger integrated curve area surrounded by XPS fitting curve and based line, suggesting that Li$^+$ doping can stabilize oxygen in crystal lattice. This result is consistent with the previous analysis about Bi 4f spectra because of existing interaction between Bi and O elements. The XPS of Yb 4d and Ho 3p are shown in Figure 4e,f, where the values of FWHM and integrated curve area increased with Li$^+$ doping for the same reason as Bi$^{3+}$ 4f orbits, and Ho 3p peak shifted towards higher binding energy due to the charge repulsion effect of Li$^+$ to the electrons in Ho 3p orbits. The reduced oxygen vacancies are consistent with the improvement of crystallinity for Li$^+$ doped BHYTO phosphors. The results of XPS prove that the UC luminescence enhancement of BHYTO: xLi phosphors is not caused from increased oxygen vacancies.

Figure 5a shows the UC emission spectra of BHYTO: xLi phosphors under the excitation of 980 nm laser, there are three UC emission bands including a green band centered at 545 nm, a red one centered at 658 nm, and a near-infrared one at 756 nm for all the BHYTO: xLi phosphors. According to energy level analysis, these emission bands are assigned to the characteristic transitions of $^5$F$_4$/S$_2$ → $^5$I$_8$, $^5$F$_5$ → $^5$I$_8$, and $^5$F$_4$/S$_2$ → $^5$I$_7$ of Ho$^{3+}$, respectively [32,33]. With the increase in Li$^+$ content in BHYTO: xLi phosphors, the emission intensity increased gradually and reached an optimal value in BHYTO: 0.05 Li samples, which is about 2.2 times stronger than that of pristine BHYTO samples. However, the luminescence intensity decreased gradually with Li$^+$ further doping though they are much stronger than that of BHYTO and BHYTO: 0.02Li samples. Figure 5b shows the decay time of carriers for the BHYTO: xLi phosphors monitored the dominant green emission (545 nm). Each curve in the graph represents the decay process with time for the carriers populated on Ho: $^5$F$_4$/S$_2$ level. The decay data were well fitted by Equation (1) [34] with bi-exponent items,

$$I_t = I_0 + A_1 e^{-t/\tau_f} + A_2 e^{-t/\tau_s}$$  \hspace{1cm} (1)

where, $I_t$ denotes luminescence intensity at decay time $t$, and $I_0$ denotes luminescence intensity at beginning decay time, $A_1$ and $A_2$ are constants, and $\tau_f$ and $\tau_s$ represent two different decay lifetime for the bi-exponent items. Mean lifetime ($\tau_m$) was expressed as Equation (2) [35].

$$\tau_m = \int_0^{\infty} \frac{I(t)}{I_0} dt$$  \hspace{1cm} (2)
Figure 4. (a) XPS survey scan spectrum of pristine BHYTO and BHYTO: 0.05Li samples, and high resolution XPS spectra of (b) Bi 4f, (c) Ti 2p and Bi 4d, (d) O 1s, (e) Yb 4d, and (f) Ho 3p.
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Figure 5. (a) UC PLS pumped by a 980 nm laser and the pumping power and its density were set to be 245 mW and 613 mW/cm², respectively (b) decay time of carriers on 5F4/5S2 level of Ho3+ for BHYTO: xLi (x = 0, 0.02, 0.05, 0.10, 0.15) phosphors monitored at 545 nm emission.

Based on the data in Figure 5b and Equation (2), the mean lifetime of Ho: 5F4/5S2 was calculated to be 55.28 μs, 65.99 μs, 57.51 μs, 46.22 μs and 45.25 μs for BHYTO: xLi samples with x equal to 0, 0.02, 0.05, 0.10, and 0.15, respectively. Compared to BHYTO: 0.02Li samples, the lifetime of BHYTO: xLi (x = 0.05, 0.10, 0.15) is shorter while the UC emission intensity is stronger.

As is well known, many factors might have effects on the emission efficiency of RE3+. In this article, the effects of charge compensation should be excluded because that charge compensation was used to apply in a charge imbalanced system, such as CaSrAl2SiO7: Ce3+ with the substitution of bivalent Sr2+ by trivalent Ce3+ [36], Ca₃(PO₄)₂: Tb3+ with the substitution of bivalent Ca2+ by trivalent Tb3+ [17], and ZnO: Eu3+ with the substitution of bivalent Zn2+ by trivalent Eu3+ [37]. Codoping monovalent alkali element such as Li+, Na+, and K+ with the trivalent RE3+ can realize charge compensation. However, the situation is distinctly different. For the Bi₃.₄₆Ho₀.₅₄Yb₀.₅₃Ti₃O₁₂ samples without Li+ doping, it is a charge balanced system, and charge compensation is not necessary and the substitution of Bi3+ by Li+ can even lead to the imbalance of charge in the whole sample. So the luminescence enhancement by Li+ in this work seems not to be relevant with charge compensation. There is no obvious difference in particle size was observed for the samples with various Li+ contents. The results of SEM and Zeta potential suggest that the change of UC luminescence for BHYTO: xLi phosphors with different Li+ contents is not originated from particle size. The luminescence enhancement through Li+ doping in this study is also not caused by crystal distortion or increased strain. In order to further prove this viewpoint, Eu3+ doped BTO: xLi (BETO: xLi) samples were also fabricated in the same method as BHYTO: xLi phosphors. The PLS of Bi₃.₄₆Eu₀.₅₄Ti₃O₁₂: xLi (BETO: xLi, x = 0, 0.05, 0.1, 0.15) are shown in Figure A2a (in Appendix A) since Eu3+ is a famous luminescent probe to examine structural symmetry around a certain ion in lattice based on the ratio of emission intensity of 5D0 → 7F2 (electric-dipole-allowed transition) to 5D0 → 7F1 (magnetic-dipole-allowed one) of Eu3+ [16]. Eu3+ can be used as luminescent probe for BHYTO: xLi phosphors because it can substitute the same Bi3+ sites as Ho3+, Yb3+, and Li+ in BTO lattice through above XRD analysis. There are two strong red emission bands positioned at about 615 nm and 594 nm in PLS of BETO: xLi samples, corresponding to 5D0 → 7F2 and 5D0 → 7F1 transitions of Eu3+, respectively. As shown in Figure A2b (in Appendix A), the ratios decreased with the increase in Li+ doping content (0 ≤ x ≤ 0.15) in the BETO: xLi samples. This result reflected an increased structural symmetry and a decreased crystal distortion with the increase in Li+ content in the phosphors. Obviously, the luminescence enhancement was not originated from crystal distortion for BHYTO: xLi and BETO: xLi phosphors. For
BHYTO: x Li phosphors, XRD results showed that the increase in Li$^+$ doping content led to the gradual increase in grain size and promoted the improvement of crystallinity. XPS results showed that the oxygen vacancy defects gradually decrease and Li$^+$ can act as a flux, which further confirmed that Li$^+$ doping would improve the crystallinity of the sample. Furthermore, improved crystallinity of Li$^+$ doped samples can increase oscillating strength for optical transitions, reduce quenching centers, such as density of grain boundary and oxygen vacancies [38], which is a main positive factor to improve emissions of RE phosphors. However, the UC luminescence is not only determined by crystallization since excessive Li$^+$ doping ($x \geq 0.10$) can make some RE ions squeezed out or deviated from their original sites in BHYTO lattice, leading to increased aggregation of RE ions, so, thus, decreasing the dispersibility of RE ions to produce local concentration quenching, so thus resulting in a weak degradation of UC emission intensity for BHYTO: xLi phosphors ($x \geq 0.10$).

For a UC luminescent process, integral emission intensity ($I$) is usually proportional to the power ($n$) of pumping laser power ($P$), and the relationship formula is shown as Equation (3) [39],

$$I = P^n$$

where index $n$ denoted the number of absorbed photons in the UC process. Figure 6a,b show the dependence of UC intensities of green, red and near-infrared emissions on pumping power of 980 nm laser for BHYTO and BHYTO: 0.05Li samples, and the monitored emission wavelengths are 545 nm, 658 nm, and 756 nm, respectively. There appeared good linear fitting relationships between UC emission intensity and pumping power for all the emissions of each sample. The fitting index $R^2$ values for each emission are all above 0.996 for BHYTO samples and above 0.992 for BHYTO: 0.05Li ones. The measured slope value is indicative of an upconversion process, which involves at least $n$ photons, where $n$ is the smallest integer greater than slope value (or equal to slope value if slope value is an integer) [40]. The slope values of all fitting lines are from 1.19 to 1.42, which lie in the range of 1 to 2, proving that the UC mechanism for BHYTO: xLi phosphors belong to a double-photon process for each of green, red and near-infrared emissions. The slope values of the fitting line deviate from the up limit of 2 and approaches close to the low limit value of 1. The deviation is caused from the competition between linear decay and UC processes for the depletion of the intermediate excited states. For a typical upconversion process mainly composed of three levels, if linear decay of the intermediate level is the dominant depletion, upconversion can be neglected, and, consequently, excited-state population densities ($N_2$) in emission level has a relationship with excited-state population densities ($N_1$) in intermediate level and pumping power ($P$): $N_2 \propto N_1^2 \propto P^2$, corresponding to up limit of 2. In contrast, if upconversion is dominant, the linear decay term can be neglected, resulting in: $N_2 \propto N_1^2 \propto P$, corresponding to the lower limit of 1 [41]. The slope values are closer to the low limit, suggesting that upconversion is more obvious than decay for the depletion of the intermediate level. From another point of view, the low slope values reflect that BHYTO: xLi phosphors have relatively high upconversion efficiency. The phenomenon of low $n$ value for double-photon upconversion process also occurs in Yb$^{3+}$–Er$^{3+}$ doped BaTiO$_3$ and Ho$^{3+}$ / Er$^{3+}$–Yb$^{3+}$ co-doped NaLaMgWO$_6$ [42,43].
The energy transfer process for the UC luminescence of BHYTO: xLi (x = 0, 0.02, 0.05, 0.10, 0.15) is shown in the Figure 7. Under 980 nm excitation, some Yb$^{3+}$ ions absorbed the first photon energy and were pumped to exciting state from ground state (i.e., Yb: $^2F_{7/2} + h\nu_0 \rightarrow$ Yb: $^2F_{5/2}$), then transferred the energy to neighboring Ho$^{3+}$ ions and excited them to intermediate $^5I_8$ level (i.e., Yb: $^2F_{5/2} + $ Ho: $^5I_8 \rightarrow$ Yb: $^2F_{7/2} + $ Ho: $^5I_6$). Some Ho$^{3+}$ ions populated in this level absorb the second photon energy transferred from Yb$^{3+}$ and pumped to $^5F_{7/5}/^5S_2$ levels (i.e., Yb: $^2F_{5/2} + $ Ho: $^5I_6 \rightarrow$ Yb: $^2F_{7/2} + $ Ho: $^5F_4/^5S_2$). When these Ho$^{3+}$ ions in $^5F_4/^5S_2$ transited to $^5I_7$ and $^5I_8$, a near-infrared emission centered at 756 nm and a green emission centered at 545 nm were produced (i.e., Ho: $^5F_4/^5S_2 \rightarrow$ Ho: $^5I_7 + h\nu_1$, Ho: $^5F_4/^5S_2 \rightarrow$ Ho: $^5I_6 + h\nu_2$), respectively. Some Ho$^{3+}$ populated in $^5I_6$ level decayed to the next $^5I_7$ level through non-radiative relaxation, and then absorbed the second photon energy and pumped to $^5F_5$ emission level (i.e., Yb: $^2F_{5/2} + $ Ho: $^5I_7 \rightarrow$ Yb: $^2F_{7/2} + $ Ho: $^5F_5$), finally producing a 658 nm red emission when they came back to ground level directly (i.e., Ho: $^5F_5 \rightarrow$ Ho: $^5I_6 + h\nu_3$). The above emission process is a typical ET (energy transfer) process from Yb$^{3+}$ to Ho$^{3+}$. Which existed other energy transfer processes to produce the above emissions, such as GAT (energy transfer through absorption energy by ground state) [44] or EAT (excitation state absorption) [45], but ET process was mainly responsible for the energy transfer in Ho$^{3+}$–Yb$^{3+}$ co-doped phosphors because Yb$^{3+}$ has much larger absorption section than Ho$^{3+}$ for 980 nm exciting light. It is well agreement with the fact that the UC emission intensity is relatively weak for Ho$^{3+}$ single-doped BTO phosphors [9].

Figure 6. Log-log diagram of the dependence of UC emission intensities for green, red and near-infrared emissions on pumping power ($P$) of 980 nm excitation for (a) BHYTO and (b) BHYTO: 0.05Li samples.

Figure 7. Schematic diagram of energy transfers during the UC process for BHYTO: xLi phosphors.
4. Conclusions

In this study, a series of novel efficient Li+ doped BHYTO phosphors were fabricated successfully. The detected Li+ content (C) is very close to the nominal doped one (CN) in the samples BHYTO: xLi samples with x ≥ 0.05 through ICPMS measurement. Li+ entered into the interspace of BHYTO crystal lattice when its dosage was low, and substitute Bi3+ sites with further increase in Li+ dosage. The crystallinity and grain sizes increase monotonously with the increase in Li+ content in BHYTO: xLi samples. Compared to BHYTO samples, the UC emission intensity of BHYTO: xLi increased obviously when x ≥ 0.05. UC emission mechanism of the BHYTO: xLi phosphors belong to a double-photon energy transfer process mainly through ET from Yb3+ to Ho3+ without Li+ direct participation. The causes of luminescence enhancement were discussed in details based on the results of XRD, SEM, TEM, EDS, XPS, and PLS measurements of Eu3+ doped BETO: xLi. The improved crystallization and reduced quenching centers such as oxygen vacancies promote light absorption from pumping source and increase oscillating strength for optical transitions, which have primary responsibility for the improved UC luminescence of BHYTO: xLi phosphors. It can be inferred that the method of luminescence enhancement in this study can probably be extended for the other RE phosphors with similar structure.

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Appendix A

![High resolution XPS spectra of Li 1s.](image)
Figure A2. (a) The PLS and (b) the ratios of 615 nm/594 nm emission for Bi$_{1,9}$Eu$_{0.1}$Ti$_3$O$_{12}$: xLi (BETO: xLi, x = 0, 0.05, 0.1, 0.15).

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