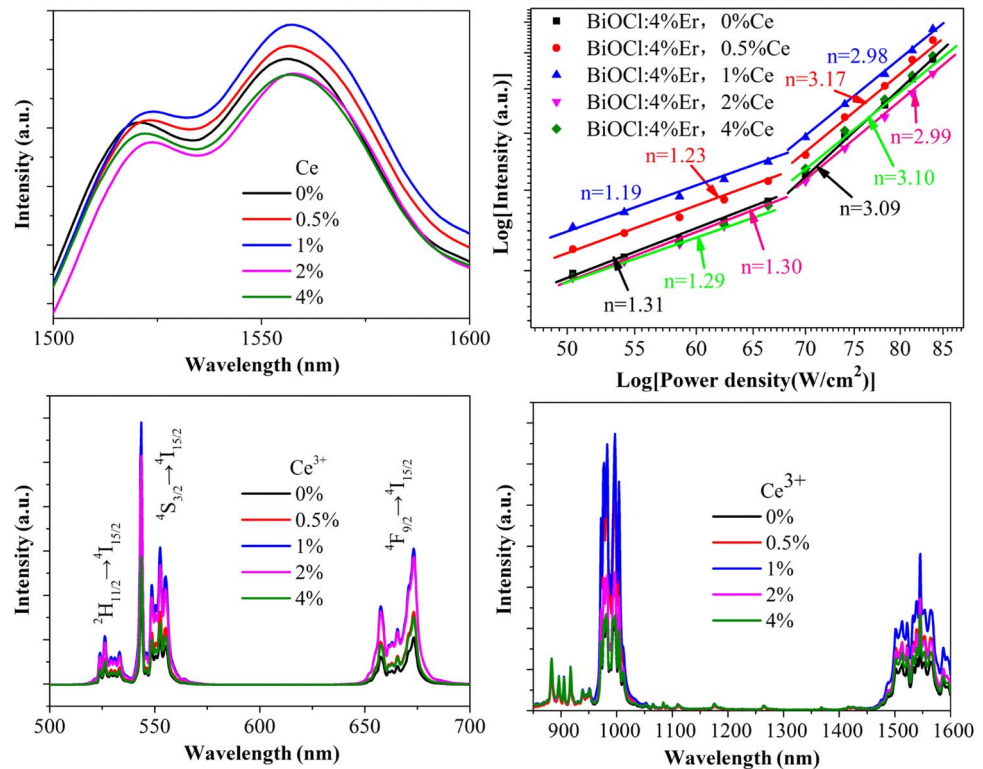


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Abstract: Effect of cerium codoping on Stokes or anti-Stokes luminescence of BiOCl:Er³⁺ crystals, which were controlled by a special photon avalanche (PA) mechanism under 980-nm excitation, was investigated. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis indicate that Ce³⁺ ions were successfully doped into BiOCl lattices. However, in PA photoluminescence behaviors, the doped Ce³⁺ ions did not present efficient resonant energy transfer (ET) processes between the Er³⁺ ions as generally reported. As a result, the intensity of visible PA upconversion emission and 1.54 μm downshifting near-infrared (NIR) emission of Er³⁺ ions shows the same concentration dependence of cerium dopants. This phenomenon can be understood by the influence of cerium dopant content on the magnitude of internal electric field in layered BiOCl crystals, which may play a more important role on the upconversion (UC) and NIR luminescence of Er³⁺ than the traditional ET between rare-earth (RE) ions. The results of our work may offer a different understanding for the method to control the emissions of RE ions.

Index Terms: Ce–Er codoped, BiOCl crystals, photon avalanche, near-infrared (NIR) emission.

1. Introduction

Stokes or anti-Stokes luminescence of trivalent Er³⁺ ions doped in inorganic host have attracted extensive attention for applications such as lasers, biological imaging, infrared detection, and solar cells. [1]–[4] The 1.54 μm near infrared (NIR) emission of Er³⁺ which generally arises from a Stokes downshifted mechanism is particularly interesting as it can be used in eye-safe range-finding and optical fibers telecommunications [5]–[8]. However, the appearance of upconversion (UC) processes that convert the long-wavelength pump sources into short-wavelength emissions are generally believed to be losses for energy conversion into 1.54 μm emission. Therefore, resonant energy transfer processes through codoping Rare earth ions, such as cerium ion, is considered an efficient way to improve the 1.54 μm emission of Er³⁺ ions, because it generally can decrease the visible UC emission via enhancing the population feeding rate from the ⁴I_{11/2} to the ⁴I_{13/2} level of Er³⁺ [9], [10].

Alternatively, the generation of NIR emission is different with visible UC luminescence that shows high order power dependence. The population of the emitting level of 1.54 μm mostly depends on the relaxation from higher levels of Er³⁺ ions, such as $^4I_{11/2} \rightarrow ^4I_{13/2}$ [11], which are excited by direct excited state absorption (ESA) or energy transfer (ET) from sensitized ions. Up to date, just few reports presented 1.54 μm emission of Er³⁺ formed through multi-photon process, which is generated by photon avalanche (PA) or similar PA mechanism [12], [13]. As for PA phenomena, it is a strongly non-linear process of population of an emitting high energy level of an active ion, which is considered as one of the relatively efficient one among three basic UC mechanisms but mostly observed in visible UC emissions of RE ions, such as Pr³⁺, Ho³⁺, Tm³⁺, and Er³⁺ ions [14]–[17].

In previous work, we reported a hetero-looping enhanced energy transfer avalanche UC emission as well as synchronous downshifted NIR PA luminescence of Er³⁺ singly-doped BiOCl semiconductor poly-crystals, excited by a 980 nm laser [18]. According to energy level characteristic of Er³⁺ and Ce³⁺ ion and previous work on Ce³⁺-Er³⁺ codoped material systems, it can be supposed that the Ce³⁺ doping may enhance the generation of metastable state reservoir level, $^4I_{11/2}$ levels, corresponding to 1.54 μm emission, which is benefit to get much more efficient NIR emission [5], [9], [10]. As far as we know, there has been no work on the effect of cerium doping on the NIR and visible PA emission of Er³⁺ ion.

In the present work, we reported the effect of CeO₂ dopants on PA Stokes or anti-Stokes luminescence of the special Er³⁺ doped semiconducting BiOCl crystals. However, results show that cerium doping can change the emission intensity of Er³⁺ but have no positive effect on the occurrence and looping property of the PA process. In particular, the visible UC emission and 1.54 μm emissions show the unusual synchronous dependence of cerium concentration, which is contrary to traditional luminescence behavior of Er-Ce codoped systems. The reason was discussed and the result may offer an all different understanding for material factor to control the emissions of RE ions.

2. Experimental

Samples of Bi_(1-x-0.04)Er_{0.04}Ce_xOCl ($x = 0, 0.5, 1, 2, 4$ mol%) were prepared by solid state reaction. NH₄Cl (A.R.), Bi₂O₃ (99.99%), Er₂O₃ (99.99%), and CeO₂ (99.99%) were used as the starting materials. The weighed raw materials were thoroughly mixed in an agate mortar and then placed in a corundum crucible. Then, the powders were sintered at 500 °C for 3 h in air. Some excessive NH₄Cl (20%) is necessary for loss of Cl source at high temperature to obtain the pure phase formation.

The structure of the phosphors was recorded by X-ray diffraction (XRD) using Cu K α radiation on a Bruker D8-Advance Diffractometer. The UV-vis-NIR absorption spectra of the samples were measured on a Hitachi U-4100 spectrophotometer. The valence state of doped Ce ion was detected using X-ray photoelectron spectroscopy (XPS). The UC emission spectra of the samples were measured using the Hitachi F-7000 Fluorescence Spectrophotometer with a 980 nm LD as excitation source. The downshifting NIR luminescence were measured using by a FLS980 fluorescence spectrophotometer (Edinburgh Instrument Ltd, UK) with Xe lamp as excitation as source (excitation wavelength 808 nm). The power dependence of NIR emission intensity were performed by a ZOLIX SBP300 spectrophotometer with InGAs as detector at 800–1800 nm under excitation of 980 nm laser diode (LD). All measurements were made at room temperature.

3. Results and Discussion

Fig. 1 presents the XRD patterns of the BiOCl:4% Er³⁺ powders codoped with Ce ions. As shown in Fig. 1(a), all the detectable peaks could be assigned to the tetragonal structure of BiOCl with space group of P4/nmm, which is in good agreement with the standard values for the BiOCl (JCPDS: No. 06-0249), indicating that pure phase BiOCl crystals have been synthesized successfully. The magnification of a selected region of diffraction peaks exhibits that the

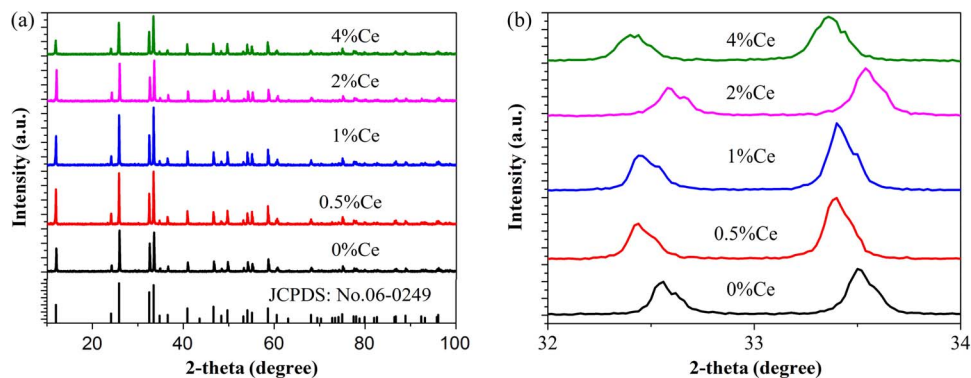


Fig. 1. (a) XRD patterns of BiOCl powders BiOCl:4% Er³⁺ powders codoped with Ce (0, 0.5, 1, 2, 4%). (b) Main diffraction peak near $2\theta = 32^\circ \sim 34^\circ$ with increasing Ce concentration.

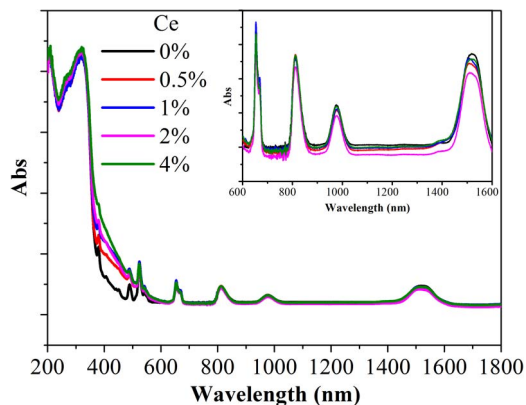


Fig. 2. UV-vis-NIR absorption of Ce doped BiOCl:Er³⁺ crystals.

diffraction peaks move to the small angle direction with increase of the Ce dopant concentration and subsequently move back to large angle direction when the Ce dopant concentration is over 1 mol% [see Fig. 1(b)]. It might be because Ce ion might fill into the interstitial position of BiOCl crystals at low dopant concentration, and consequently the lattice size increase and the diffraction peak move to the small direction. In the case of high dopant level, Ce ions would begin to enter into the lattice of BiOCl crystals via substituting the position of Bi³⁺ ion. As a result, the lattice size decrease and the diffraction peak move to the large direction due to the smaller radius of Ce³⁺ or Ce⁴⁺ than Bi³⁺ [19], [20].

The UV-vis-NIR absorption of Er³⁺-Ce codoped BiOCl is shown in Fig. 2. For semiconductor, changes in the optical properties are observed generally when impurity ions are doped in [21]. In the case of un-doped BiOCl, the intense absorption peak at about 330 nm along with an absorption edge rising steeply at about 378 nm is attributed to charge transfer from valence band (VB) to conduction band (CB) of BiOCl crystals. It shows that the absorption edge of samples Er³⁺-Ce codoped BiOCl red-shifts gradually with the increase of Ce dopant concentration, further indicating effectively doping of Ce ions into BiOCl lattices.

However, the characteristic absorption peak of Ce³⁺ ion was not observed directly in the absorption spectra. To investigate the valence state of doped Ce ions, the representative XPS analysis of the samples doped 1% and 2% Ce was carried out. As shown in Fig. 3, the peaks of 911.45 eV, 899.28 eV, and 887.94 eV correspond to Ce⁴⁺ ions, and the peaks of 902.87 eV and 885.20 eV are ascribed to Ce³⁺ ion [22]. It indicates that Ce³⁺ ions are doped into BiOCl crystals. Therefore, the reason that typical absorption transitions of Ce³⁺ were not observed in the graph might be because the absorption transitions of Ce³⁺ ions in BiOCl is in the

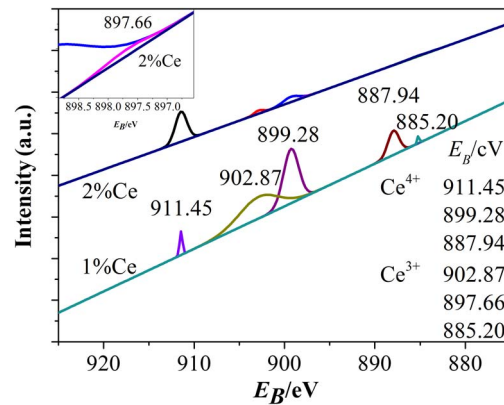


Fig. 3. Representative XPS analysis of the sample doped 1% and 2% Ce.

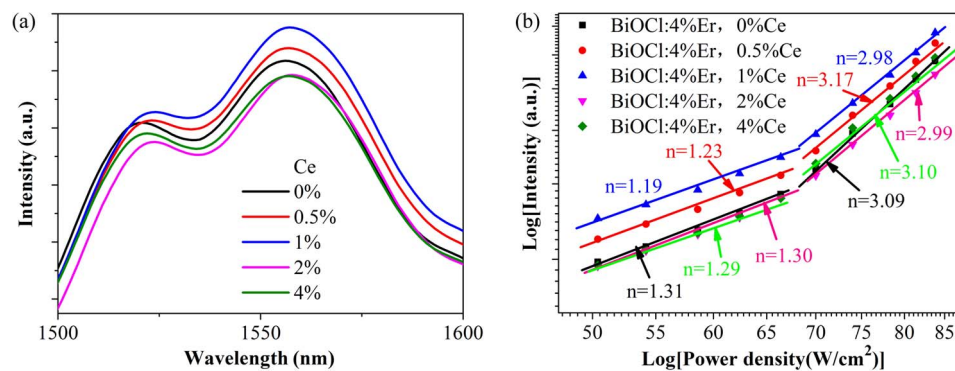


Fig. 4. (a) The 980 nm excited downshifted NIR fluorescence of prepared samples. (b) Plots of its corresponding pump power dependence.

ultraviolet region, which is overlapped with the intense absorption band of BiOCl semiconductor. On the other hand, according to peaks area calculation, the content ration of Ce³⁺/Ce⁴⁺ was estimated to be about 0.73 and 0.108 for the sample doped 1% and 2% Ce, respectively. This indicates that Ce³⁺ ion is formed successfully and doped into BiOCl lattice, which is possibly due to reductive effect of NH₄Cl atmosphere in high temperature solid reaction. It should be noted that the concentration of Ce³⁺ ions in BiOCl doped with 1% Ce is higher than the sample doped with 2% Ce, but the reason has not been understood well up to now.

Fig. 4 gives the downshifted NIR fluorescence of prepared samples excited by 980 nm and the plots of its corresponding pump power dependence. It shows that the intensity of 1.54 μm NIR emissions, ascribed the (⁴I_{13/2} → ⁴I_{15/2}) transition of Er³⁺ ion, was enhanced by Ce doping in low concentration, but was decreased when the Ce dopant concentration is more than 1% mole. Compared with the undoped sample, the luminescence intensity of sample doped with 1% Ce increased by 1.04 times. Interestingly, the pump power density dependence plots of NIR emission bands indicate that the 1.54 μm NIR luminescence present special PA emission behavior when the exaction power is over the threshold point [12]. It is well known that, for online emission processes, taking the UC luminescence as example, the photoluminescence intensity I_{UC} depends on the pumping power IP according to the following equation [23]:

$$I_{UC} \propto I_p^n \quad (1)$$

where n is the number of pumping photons absorbed per UC photon emitted that can be easily calculated from the slope of the linear fit. For the special PA UC phenomena, the photon number

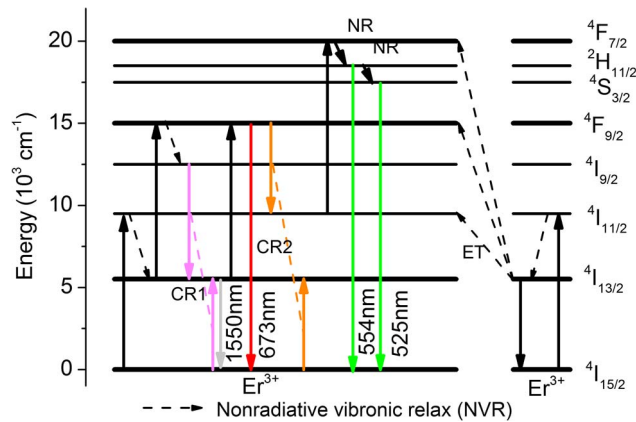


Fig. 5. Energy level diagram of Ce doped BiOCl:Er³⁺ crystals under excitation of 980 nm and the possible PA process.

n will increase sharply over the threshold point due to the occurrence of loping behavior. In this work, the NIR luminescence behaviors of obtained samples exhibit high order nonlinear emission like the UC process, when over power threshold point [see Fig. 4(b)].

The proposed mechanism of PA NIR emissions can be explained as Fig. 5. For the PA process, it is generally based on the existence of an efficient cross-relaxation (CR) process which can populate the intermediate state. We supposed that the $^4I_{13/2}$ level will become a dominant reservoir level through relaxation from $^4I_{11/2}$ level under the effect of intense internal polarized electric field as well as intense nonradiative vibration relaxation that is originated from the vibration of lattice and surface absorbed groups. The great enhancement of electron phonon interaction upon the threshold of excitation power can readily remedy the energy mismatch between the transitions with the intermediate energy level of Er³⁺ ion. Thus, the intermediate population of $^4F_{9/2}$ level (red emission) and $^2H_{11/2}/^4S_{3/2}$ level (green emission) could be greatly enhanced and resulted in the occurrence of remarkable ratio between the population of reservoir level and the excited-state level, which initiated necessary condition for the UC PA processes and lead to the NIR PA behavior synchronously.

However, it should be noted that the Ce doping concentration can change the PA emission intensity but has no obvious either positive or positive effect on the occurrence and looping numbers of PA emission. In previous work, we found that the origin of PA emission was considered to be related to the special polarized internal electric field (IEF) in BiOCl crystals [24], which greatly improve the excitation ability of Er³⁺ ions through the enhancement effect of exciting field. Because the BiOCl crystallize in the tetragonal PbFCl structure (space group: P4/nmm; Z = 2) with alternating (BiO)ⁿ⁺ cation and Cl⁻ anion layers, as showed in [24], which would induce the presence of strong IEF perpendicular to the [Bi₂O₂] slabs and halogen anionic slabs in BiOCl. According to classic electrodynamics theory and our experiment result, the IEF of host will greatly influence the emission behavior of doped RE ions [25]. On the other hand, besides the PA emission behavior, the photon number of 1.54 μ m NIR emission is slightly over 1 below the threshold point. This may be due to saturation effects of excited energy level that is also related to IEF in layered BiOCl crystals. Owing to indirect involvement to the aim of this work, the mechanism for these special phenomena will not be discussed in detail temporarily.

To better understand the effect of Ce dopant on the NIR emission intensity, the visible UC emission of the obtained samples was investigated as compared. Fig. 6 shows the visible UC emission spectral under excitation by 980 nm and the plots of its corresponding pump power dependence. The obtained samples exhibit characteristic sharp emissions, which can be attributed to $^2H_{11/2} \rightarrow ^4I_{15/2}$ (~ 525 nm), $^4S_{3/2} \rightarrow ^4I_{15/2}$ (~ 554 nm), and $^4S_{9/2} \rightarrow ^4I_{15/2}$ (~ 673 nm) transitions of Er³⁺ ions, respectively. Similar to that found in singly doped samples, the codoped crystals exhibit UC PA behavior, in which the number of UC photons (n) for green and red

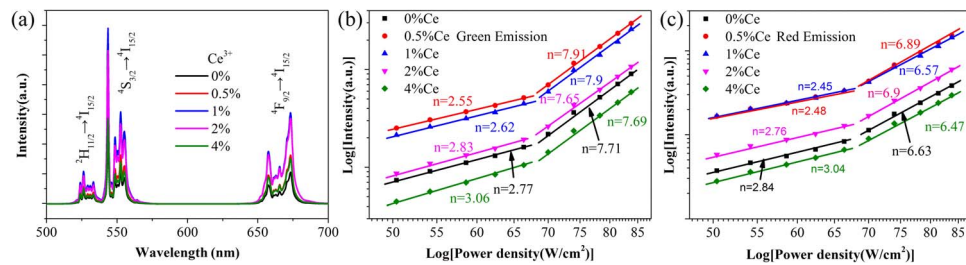


Fig. 6. (a) UC emission spectral of prepared samples under excitation at 980 nm. (b) Pump power dependence of the green emission. (c) Pump power dependence of the red emission.

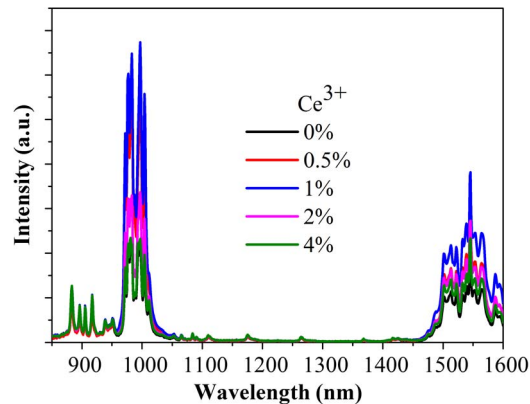


Fig. 7. Downshifted NIR luminescence of prepared samples excited by 808 nm.

emissions increase dramatically over the threshold of power density. It indicated that the possible number change of incident photons involved in the UC process caused by Ce doping was not obvious as that observed in downshifting NIR emission behaviors. However, the addition of Ce ions did not directly decrease the visible UC emission as previous reports [9], [22], [26]. In particular, the UC emissions show the synchronous concentration dependence of cerium dopant to that of 1.54 μm NIR emissions. This means that the enhancement of NIR emission caused by Ce doping is possibly not due to the traditional resonant energy transfer processes between Ce³⁺ and Er³⁺ ions.

Generally, the phonon-assisted energy transfer between Er³⁺ and Ce³⁺ would facilitate the population of the ⁴I_{13/2} level and simultaneously reduces the UC process [9], [10]. To clarify the reason for unusual effect of cerium codoping on the Stokes or anti-Stokes luminescence of BiOCl:Er³⁺ crystals, the population state of ⁴I_{11/2} energy level were studied by excitation at 808 nm. Fig. 7 gives the 808 nm excited downshifted NIR luminescence of prepared samples. It indicates that Er³⁺ ion emit special dominant 1 μm NIR emissions, meaning that the ⁴I_{11/2} energy level of Er³⁺ ions doped in BiOCl may have greater emission cross area than in other crystals. This property of Er³⁺ doped BiOCl crystals may offer a new candidate for RE doped luminescent materials to getting efficient 1 μm NIR emission. However, result of NIR luminescence spectral clearly indicates that the concentration dependency of the NIR emission at 1 μm band on the Ce dopant is the same as that of visible UC emissions, as well as 1.54 μm NIR emissions. Namely, without luminescence lifetime analysis, the above results clearly indicate that the doping of Ce³⁺ ions do not improve the relaxation of ⁴I_{11/2} \rightarrow ⁴I_{13/2}, or the resonant energy transfer processes between Er³⁺ and Ce³⁺ ions is not the crucial factor that determined UC and 1.54 μm NIR emission process in BiOCl crystals.

It is worth noting that with the increase of Ce addition, the change trend of PA luminescence of BiOCl:Er³⁺ crystals is closely related to that of the XRD results. That is, considering the effect of Ce dopant concentration, the turning point for the two kinds of properties is synchronous.

This means that the luminescence intensity of Er³⁺ ions in BiOCl crystals is more possibly determined by material structure rather than by energy transfer between RE ions. In previous work, we found that the magnitude of IEF in BiOCl play a crucial role on occurrence of the PA emission mechanism and luminescence intensity of Er³⁺ ion because according to classic electrodynamics theory [27], the intensity of photoluminescence, especially the high order nonlinear photoluminescence, is greatly involved with the IEF of the host. Therefore, the unusual effect of Ce doping on the Stokes or anti-Stokes PA luminescence of BiOCl:Er³⁺ crystals might be explained as follows. Ce⁴⁺ ion has smaller a radius and can enter into the interstitial sites when doped into BiOCl crystals, which may form cation vacancy and charge disequilibrium in lattice. This would decrease the magnitude of IEF, which play a more important role on the PA emission intensity than the Ce³⁺ ion. Therefore, the samples containing more Ce⁴⁺ ions may present relatively lower emission intensity, such as the BiOCl:Er³⁺ doped with 1 and 2% Ce. Although it has no effective method to quantitatively analyze the variation of IEF in BiOCl crystals up to date, this work may offer a different insight into the material structure factor that determines and controls the photoluminescence of doped RE ions.

4. Conclusion

Ce ion can be doped into BiOCl:Er³⁺ semiconducting crystals, but Ce³⁺ did not act as efficient resonant ions to change the visible UC emission and 1.54 μm NIR luminescence of Er³⁺ ion as it did previously. The unusual effect of cerium codoping on Stokes and anti-Stokes PA luminescence of BiOCl:Er³⁺ crystals may be understood by cerium dopant content on the magnitude of IEF in layered BiOCl crystals, which play a more important role on the Er³⁺ activated luminescence.

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