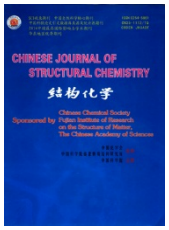

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Influence of Doped Ions on Persistent Luminescence Materials: a Review①

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ABSTRACT　Persistent luminescence materials (PLMs) are potential luminescent materials which can remain emitting light after stopping the excitation. PLMs can avoid the autofluorescence of biological tissues, and play an important role in biosensing, targeted imaging and other fields. However, the applications of PLMs are often restricted by their weak persistent luminescence and short decay time after excitation. Doped ions will directly affect the luminescence centers and trap levels of PLMs, thereby leading to great differences in the optical performance of PLMs. Given this, the selection of doped ions to improve the optical performance of PLMs has become a fascinating research direction in recent years. At present, the published reviews mostly focus on the surface modifications and applications of PLMs. However, the influence of doped ions on the structure and optical performance of PLMs is seldom summarized. In this review, the influence of doped ions on the structure and optical performance of PLMs is introduced from three aspects: the type of doped ions, the number of types of doped ions, and the content of doped ions. Furthermore, we highlight recent achievements and mechanisms in the development of PLMs. Finally, we also propose and discuss the future opportunities and current challenges of ion-doped PLMs.

Keywords: persistent luminescence, doped ions, structure and optical performance;

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1　INTRODUCTION

Persistent luminescence materials (PLMs) can absorb excitation energy and continue to emit light after the excitation is stopped[1-7]. In ancient China, natural minerals with luminous properties were made into luminous cups and night pearls. In 1866, Sidot et al. first prepared the sulfide PLMs ZnS:Cu^{2+}, making PLMs enter the vision of researchers[8]. In 1968, Pailil et al. observed the persistent luminescence of $SrAl_2O_4$:Eu^{2+}, pushing the researches of PLMs into a new stage[9, 10]. Subsequently, Matsuzawa et al. found that the phosphorescence intensity and phosphorescence time of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} phosphors were more than ten times those of early PLMs[11]. Since then, many PLMs have been developed and widely used in transportation, military facilities, biosensing and other fields[12-15].

The persistent luminescence inherence makes PLMs proper candidates in material applications. Given this, many researchers

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are devoted to finding ways to improve the phosphorescence intensity and phosphorescence time of PLMs. The introduction of doped ions provides a possibility to improve the optical performance of PLMs[16-23]. For example, Yamamoto et al. discovered that the phosphorescence intensity and phosphorescence time of the materials were improved after introducing Dy^{3+} ion into $SrAl_2O_4:Eu^{2+}$[11]. Liu et al. enhanced the phosphorescence intensity and prolonged the phosphorescence time exceeding 13 hours by adjusting the contents of Nd^{3+} ion in $Zn_2Ga_{3-x-y}Ge_{0.75}O_8:Cr_x, Nd_y$[24]. Studying the mechanisms of ion doping to enhance the optical performance of PLMs can help design PLMs with stronger phosphorescence intensity and longer phosphorescence time, thereby expanding the applications of PLMs.

Recently, reviews focus on synthesis methods, persistent luminescence mechanisms and applications of PLMs have been published. Li et al. systematically summarized the synthesis techniques, persistent luminescence mechanisms, characterizations and applications of PLMs[9]. Wang et al. summarized the persistent luminescence mechanisms, synthesis methods and biomedical applications of PLMs[25]. Singh et al. outlined the surface modifications, bioimaging applications of PLMs, and future research directions[26]. Doped ions play a vital role in improving the optical performance of PLMs. However, the influence of doped ions on the structure and optical performance of PLMs is seldom summarized. In this review, we mainly focus on how the optical performance of PLMs is affected by the type of doped ions, the number of types of doped ions, and the content of doped ions. Furthermore, the opportunities and challenges of PLMs in ion doping are also presented.

2 INFLUENCE OF DOPED IONS ON THE STRUCTURE AND OPTICAL PERFORMANCE OF PLMs

With the introduction of doped ions, different energy levels are produced in PLMs, resulting in different structures and optical performance. Herein, we classify and discuss how doped ions affect the structure and optical performance of PLMs based on the number of types of doped ions, the type of doped ions and the content of doped ions. To better demonstrate the influence of doped ions on PLMs, a summary of the main influence of doped ions on some common ion-doped PLMs is shown in Table 1.

Table 1. Details of Host, Emitter, Co-dopants, Emission Region and Afterglow Decay of PLMs

Host	Emitter	Co-dopants	Emission region	Afterglow decay	Ref.
$SrAl_2O_4$	Eu^{2+}		450～700 nm	> 2 h	4
$GdAlO_3$	Mn^{2+}	Ge^{4+}	600～840 nm	> 1200 s	64
$Y_3Al_{5-x}Ga_xO_{12}$ (x = 0～4)	Ce^{3+}	Bi^{3+}	505 nm	54～68 min	67
$ZnGa_2O_4$	B^{3+}		502,695 nm	600 s	18
$Zn_{1.25}Ga_{1.5}Ge_{0.25}O_4$	Cr^{3+}	Yb^{3+}, Er^{3+}	650～850 nm	> 480 h	23
Li_2ZnGeO_4	Mn^{2+}		550～800 nm	> 960 h	62
$MgGeO_3$	Mn^{2+}	Bi^{3+}	680 nm	100 min	68
$Y_3Sc_2Ga_3O_{12}$	Ce^{3+}		500 nm	100 min	69
$CaMgSi_2O_6$	Eu^{2+}	Dy^{3+}, Mn^{2+}	468, 600, 670 nm	> 600s	66
$Ca_9Bi(PO_4)_7$	Ce^{3+}	Tb^{3+}, Mn^{2+}	300～500 nm	5 h	70
Ca_2BO_3Cl	Eu^{2+}	Dy^{3+}	580 nm	48 h	71

Gd_2O_2S	Eu^{3+}	Ti^{4+}, Mg^{2+}	580～720 nm	120 s	20
Lu_2O_3	Tb^{3+}	Ca^{2+}	543 nm	20～30 h	72
KY_3F_{10}	Tb^{3+}		542 nm	108 s	73
AlN	Mn^{2+}		570～700 nm	1 h	74

2. 1 Influence of doped ions type on the structure and optical performance of PLMs

Due to the difference in the atomic structure and energy levels, various doped ions have different effects on the structure and optical performance of PLMs. Thus, the relationship between the type of doped ions and the structure and optical performance of PLMs is introduced in this section.

2. 1. 1 Cr^{3+}-doped PLMs

Cr^{3+} ion is usually introduced into PLMs to obtain red or near-infrared persistent luminescence resulting from its unique electronic transitions. Among them, Cr^{3+}-doped $ZnGa_2O_4$ is one of the research hotspots in PLMs. The $ZnGa_2O_4$ crystal exhibits a cubic spinel structure, in which the Zn^{2+} ion occupies the A-sites of the tetrahedron, and the Ga^{3+} ion the B-sites of the octahedron[27, 28]. Cr^{3+} ion tends to replace Ga^{3+} ion in the distorted octahedral coordination for the reason that Cr^{3+} ion has the same valence electron and ion radius as Ga^{3+} ion, which makes the Cr^{3+}-doped $ZnGa_2O_4$ materials produce strong near-infrared phosphorescence at 696 nm[2, 29, 30]. Hao et al. found that the Cr^{3+}-doped $ZnGa_2O_4$ exhibits excellent optical performance, which can maintain phosphorescence for 10 hours after stopping the ultraviolet light irradiation[31]. Moreover, the author observed that the excitation spectrum of Cr^{3+}-doped $ZnGa_2O_4$ has three excitation bands of 250 ~ 350, 350 ~ 487, and 487 ~ 650 nm, which are caused by the host excitation band of $ZnGa_2O_4$, the charge transfer between $ZnGa_2O_4$ and Cr^{3+} ion, and the electronic transitions of Cr^{3+} ion, respectively. Based on previous researches, Yan et al. further comprehensively studied the persistent luminescence mechanism of $Zn_{2.94}Ga_{1.96}Ge_2O_{10}$:$Cr^{3+}$[19]. As shown in Fig. 1, after the $Zn_{2.94}Ga_{1.96}Ge_2O_{10}$ absorbs incident photons, the electrons of $Zn_{2.94}Ga_{1.96}Ge_2O_{10}$ move to the conduction band and are trapped by native defects by means of nonradiative relaxation. When the ultraviolet light excitation is finished, the combination of holes and electrons released by native defects produces short phosphorescence. Since the absorption spectrum of Cr^{3+} ion fully overlaps with the emission spectrum of $Zn_{2.94}Ga_{1.96}Ge_2O_{10}$, the energy absorbed by $Zn_{2.94}Ga_{1.96}Ge_2O_{10}$ is transferred to Cr^{3+} ion by means of nonradiative energy[32]. The continuous energy transfer causes the electrons of Cr^{3+} ion to transform into three different excited states. Then, the electrons are trapped by the shallow electron traps or deep electron traps by means of nonradiative relaxation[33]. At the same time, the electron (t^2e) fills the energy-matched traps in the form of $^4T_1$ and $^4T_2$ through the tunneling process. When the continuous energy transfer is stopped, the electron traps release the electrons which recombine with Cr^{3+} ion, thereby producing a strong or ultra-long phosphorescence[19].

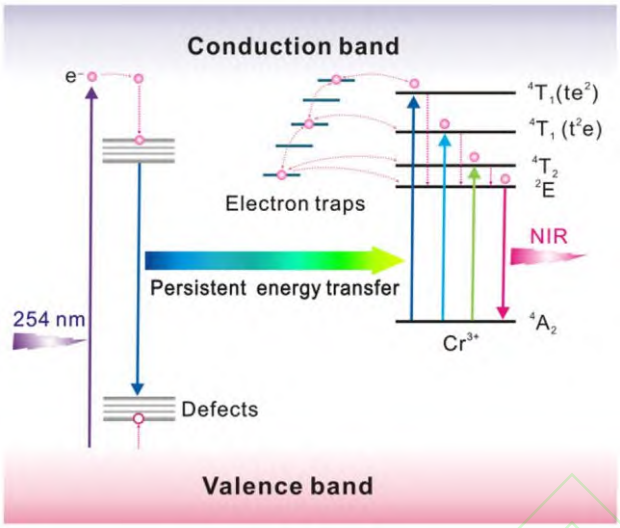


Fig. 1. Persistent energy transfer mechanism of Cr^{3+}-doped $ZnGa_2O_4$ materials

2. 1. 2 Mn^{2+}-doped PLMs

Mn^{2+} ion has a typical $3d^5$ electronic configuration. The energy transitions of Mn^{2+} ions are quite sensitive to the ligand/crystal field due to the participation of the *d* shell. Mn^{2+} ions surrounded by anions can have different geometric structures, such as linear, octahedron, spherical, tetrahedron, or square plane. The environment of Mn^{2+} ion at different crystal fields leads to different emission energy distributions and produces an emission band of 450 ~ 750 nm. For example, tetrahedral coordination of Mn^{2+} ion produces green emission[34], while octahedral coordination of Mn^{2+} ion produces orange to red emission[35, 36]. Tan et al. researched the size, crystal structure and optical performance of Mn^{2+}-doped $ZnGa_2O_4$ with a typical rod-shaped structure in different environments[21]. The size of Mn^{2+}-doped $ZnGa_2O_4$ rapidly decreases as the pH increases from 6 to 7.5. In comparison, when the pH further increases to 9.5, the size of the Mn^{2+}-doped $ZnGa_2O_4$ materials slightly increases to 80 nm. The detailed crystal structure of the Mn^{2+}-doped $ZnGa_2O_4$ shows that the materials have lattice fringe (110) parallel to the direction of the crystal rod and lattice fringe (113) at an angle of 66 ° to the direction of the crystal rod[37]. Their interplanar spacing is 0.71 and 0.29 nm, indicating that the Mn^{2+}-doped $ZnGa_2O_4$ grows along the *c* axis[38]. The optical performance of $ZnGa_2O_4$:Mn^{2+} materials was further researched by researchers[39]. The photoluminescence spectrum of Mn^{2+}-doped $ZnGa_2O_4$ materials shows that two emission peaks are detected at 450 and 480 nm, which are resulted from the native defects, for example, interstitial Zn and oxygen vacancies (Fig. 2a). When the pH is below 7.0, the intrinsic luminescence of the materials and the emission of Mn^{2+} ions have a serious overlap. As the pH increases, the intrinsic luminescence intensity gradually decreases, and the emission band intensity of the Mn^{2+} ion increases. The intrinsic luminescence almost disappears and is dominated by the green emission band of Mn^{2+} when the pH increases to 9.5. In this case, the phosphorescence time of Mn^{2+}-doped $ZnGa_2O_4$ materials exhibits more than 100 s (Fig. 2b). According to the above results, a possible persistent luminescence mechanism of Mn^{2+}-doped $ZnGa_2O_4$ materials is proposed (Fig. 2c)[40, 41]. The excited electrons and holes produced under ultraviolet light excitation are trapped by electron traps and hole traps, respectively[42]. Then, some electrons get away from the electron traps under thermal stimulation and transfer to native defects, thereby resulting in the formation of emission peaks from $ZnGa_2O_4$ materials[43]. The other part of the electrons escape and transfer to the excitation level of the Mn^{2+} ion[44]. Subsequently, the recombination of holes and electrons

causes Mn^{2+} ion to emit green light[45].

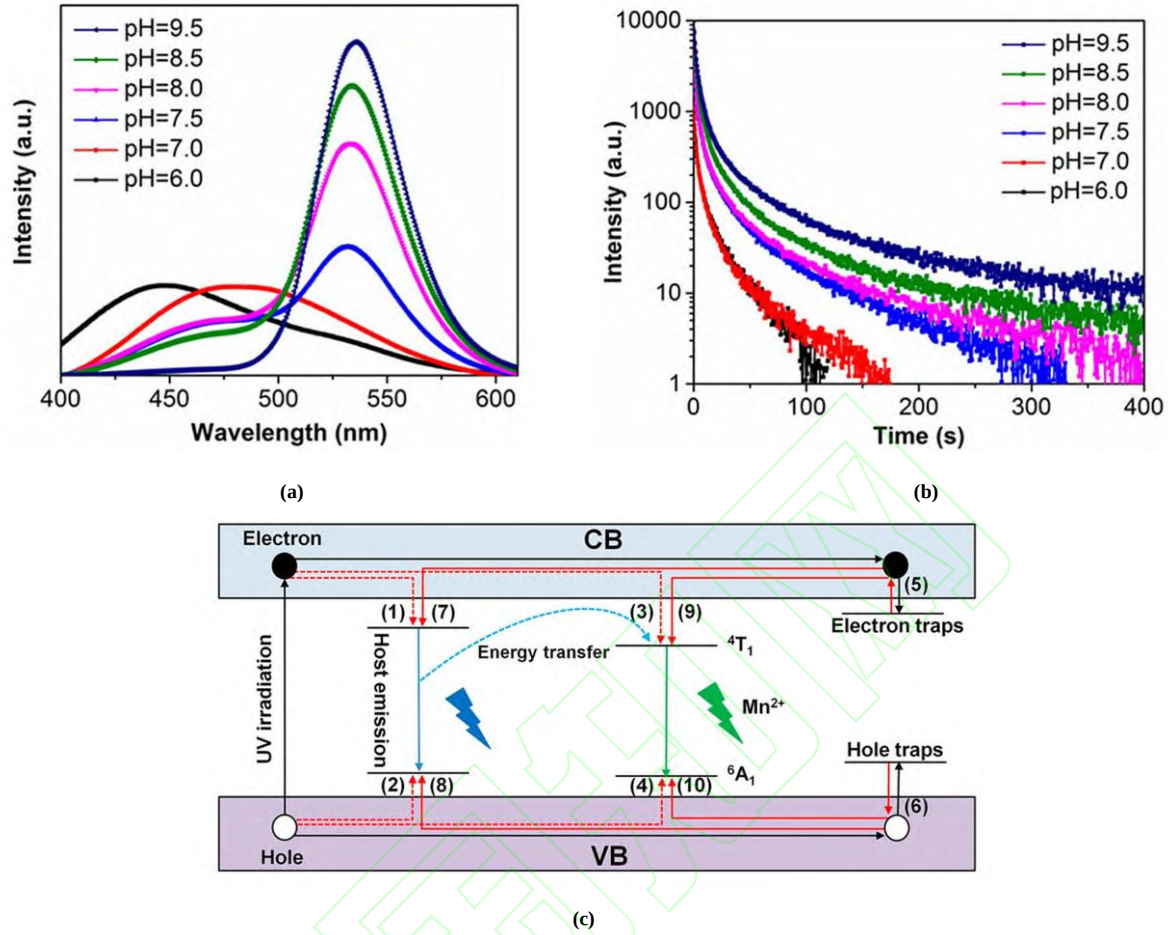


Fig. 2. (a) Photoluminescence spectrum, (b) phosphorescence decay curve, (c) persistent energy transfer mechanism of $ZnGa_2O_4$:Mn^{2+} materials

2. 1. 3 Eu^{2+}-doped PLMs

Eu^{2+} ion is a common doped ion in PLMs. The introduction of Eu^{2+} ion usually produces yellow, orange and red emissions for the reason that the crystal field reduces the emission energy of $4f^6 5d^1$ electron configuration of Eu^{2+} ion[46]. Yang et al. researched the structure and optical performance of Eu^{2+}-doped $SrAl_2O_4$ materials[4]. It is found that the crystal phase of the Eu^{2+}-doped $SrAl_2O_4$ materials corresponds to the standard pattern, indicating that the structure of the $SrAl_2O_4$ materials has not obviously changed after the introduction of Eu^{2+} ion. Moreover, Eu^{2+}-doped $SrAl_2O_4$ shows a strong emission band of 450 ~ 700 nm and exhibits a phosphorescence time that exceeds 2 hours. Considering the structure and characteristics of $SrAl_2O_4$:Eu^{2+}, a possible persistent luminescence mechanism of $SrAl_2O_4$:Eu^{2+} is deduced. The $SrAl_2O_4$ material as the host lattice absorbs the soft X-ray photon energy and stores it in electron traps. Then, the energy gets away from the electron traps and transfers to the $4f^6 5d^1$ energy level in the Eu^{2+} ion, which causes the Eu^{2+} ion to produce radioactive transition luminescence.

2. 1. 4 B^{3+}-doped PLMs

B^{3+} ion can replace Ga^{3+} ion in $ZnGa_2O_4$ materials to improve the optical performance of $ZnGa_2O_4$ materials because of the

similarity of valence and chemical properties between Ga^{3+} and B^{3+} ions. Wang et al. researched the changes in the optical performance of $ZnGa_2O_4$ materials after B^{3+}-doping[18]. Both $ZnGa_2O_4$ and $ZnGa_2O_4$:B^{3+} can detect phosphorescence signal peaks at 502 and 695 nm. However, the phosphorescence decay curves indicate that the phosphorescence intensity and the phosphorescence time of $ZnGa_2O_4$:B^{3+} have been significantly improved compared with $ZnGa_2O_4$. According to previous reports, the proper trap depth is essential to achieve a better optical performance of PLMs[1, 47, 48]. There is a bold inference that the introduction of B^{3+} ion can also increase the content of electron traps Ga'_{Zn}, thus leading to the enhancement of optical performance of $ZnGa_2O_4$ after B^{3+}-doping.

2. 2 Influence of the number of types of doped ions on the structure and optical performance of PLMs

As above mentioned, the structure and optical performance of PLMs are closely related to the type of doped ions. Most PLMs used in practical applications need to be doped with multiple ions to enhance optical performance. The simultaneous introduction of multiple ions will affect not only the host of PLMs, but also the interaction among different ions. Therefore, we introduce the influence of the number of types of doped ions on the structure and optical performance of PLMs in this section.

2. 2. 1 Ge^{4+} and Cr^{3+} co-doped PLMs

The introduction of Ge^{4+} ion will change the width of the material bandgap due to its unique electronic structure. Thus, the change of structure and optical performance of Ge^{4+}, Cr^{3+} co-doped PLMs is discussed[5]. Wang et al. found that the crystal phases of the Cr^{3+}-doped $ZnGa_{1.995}O_4$ and Ge^{4+}, Cr^{3+} co-doped $ZnGa_{1.995}O_4$ materials are corresponding to the standard pattern, indicating that the structure of the materials has not obviously changed after Ge^{4+}, Cr^{3+} co-doping. In addition, the emission spectra of $ZnGa_{1.995}O_4$:Cr^{3+} and $Zn_{1.25}Ga_{1.5}Ge_{0.25}O_4$:$Cr^{3+}$ both present a near-infrared emission band of 650 ~ 900 nm[49, 50]. The phosphorescence decay curves show that the optical performance of $Zn_{1.25}Ga_{1.5}Ge_{0.25}O_4$:$Cr^{3+}$ is better than that of $ZnGa_{1.995}O_4$:Cr^{3+}[5]. Based on the above results, the introduction of Ge^{4+} improves the filling efficiency of electron traps, thus increasing the phosphorescence time of the materials[23].

2. 2. 2 Pr^{3+}, Cr^{3+} co-doped PLMs

The number and depth of the trap energy levels of PLMs are changed after the introduction of Pr^{3+} ion because of the special 4*f*5*d* electronic structure and abundant electronic transition types of Pr^{3+} ion. Therefore, the changes in structure and optical performance of $Zn_{2.94}Ga_{1.96}Ge_2O_{10}$ after the introduction of Pr^{3+} and Cr^{3+} ions are discussed[19]. By analyzing the XRD pattern, the structure of $Zn_{2.94}Ga_{1.96}Ge_2O_{10}$:$Cr^{3+}$, Pr^{3+} has not obviously changed, and the pure spinel phase is still maintained. Later, the author does in-depth studies on the optical performance of $Zn_{2.94}Ga_{1.96}Ge_2O_{10}$:$Pr^{3+}$, Cr^{3+}. The electrons recombine with holes in the natural defects, thereby leading to a wide emission band of 350 ~ 660 nm. In addition, the Cr^{3+} ion provides a near-infrared emission band of 695 nm through the $^2E \rightarrow {}^4A_2$ transition[27], while the Pr^{3+} ion increases the phosphorescence time by adjusting the depth and density of traps based on the energy levels of 4*f* electron configurations[51-55]. Similarly, Yu et al. did further research on the persistent luminescence mechanisms of $Zn_3Ga_2GeO_8$:Cr^{3+}, Pr^{3+} to clarify the function of Pr^{3+} ion[56]. The introduction of Pr^{3+} ion deepens the trap energy level and increases the number of traps. Given this, a possible persistent luminescence mechanism of $Zn_3Ga_2GeO_8$:Cr^{3+}, Pr^{3+} is proposed (Fig. 3). Trap *A* forms more traps than trap *A′* by introducing Pr^{3+} ion, thereby improving the phosphorescence intensity and the phosphorescence time of $Zn_3Ga_2GeO_8$:Cr^{3+}, Pr^{3+} materials.

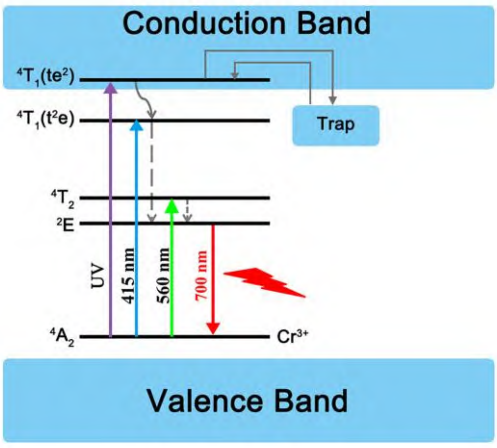
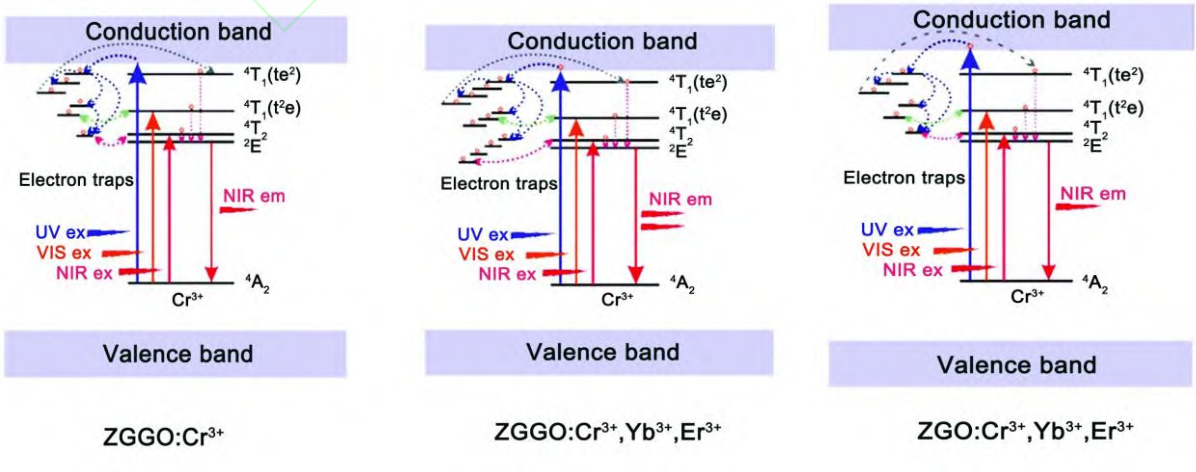


Fig. 3. Persistent luminescence mechanism of $Zn_{2.94}Ga_{1.96}Ge_2O_{10}:Pr^{3+}$, Cr^{3+} materials

2. 2. 3 Yb^{3+}, Er^{3+}, Cr^{3+} co-doped PLMs

Yb^{3+} ion and Er^{3+} ion are rare earth element ions used as luminescence centers, which are usually introduced into PLMs to change the density and depth of the trap levels resulting from their unique electronic structure. Consequently, the structure and optical performance of $Zn_{1.25}Ga_{1.5}Ge_{0.25}O_4$:$Yb^{3+}$, Er^{3+}, Cr^{3+} (ZGGO:Cr^{3+}, Yb^{3+}, Er^{3+}) with a pure spinel phase is discussed[23]. Yan et al. found that the structure of $Zn_{1.25}Ga_{1.5}Ge_{0.25}O_4$ has not obviously changed after doping with Yb^{3+}, Er^{3+} and Cr^{3+} ion. Moreover, ZGGO:Cr^{3+}, Yb^{3+}, Er^3 presents an excellent optical performance, and the phosphorescence time exceeds 20 days. Later, the author studied the persistent luminescence mechanism of ZGGO:Yb^{3+}, Er^{3+}, Cr^{3+} (Fig. 4). The excited electrons are captured by electron traps under ultraviolet light irradiation, and then moves to deep traps by means of nonradiative relaxation. Subsequently, the combination of the excited electrons and the Cr^{3+} ion leads to the formation of a persistent phosphorescence signal after the ultraviolet radiation is stopped. The introduction of Yb^{3+} and Er^{3+} ions can not only provide the materials with additional electrons and energy levels, but also adjust the density and depth of traps[51, 57, 58]. The excited electrons are trapped in the deepest 4*f* energy levels of Yb^{3+} and Er^{3+} ions, thereby extending the time for the trapped electrons to return to the ^2E energy level of Cr^{3+} ion (Fig. 4a, b)[58], which also obviously prolongs the phosphorescence time of materials.



(a) **(b)** **(c)**

Fig. 4. Persistent luminescence mechanism of (a) ZGGO:Cr^{3+},

(b) ZGGO:Cr^{3+},Yb^{3+},Er^{3+}, (c) ZGO:Cr^{3+},Yb^{3+},Er^{3+}. ZGO refers to a zinc gallate matrix

2. 2. 4 Eu^{3+}, Ti^{4+} and Mg^{2+} co-doped PLMs

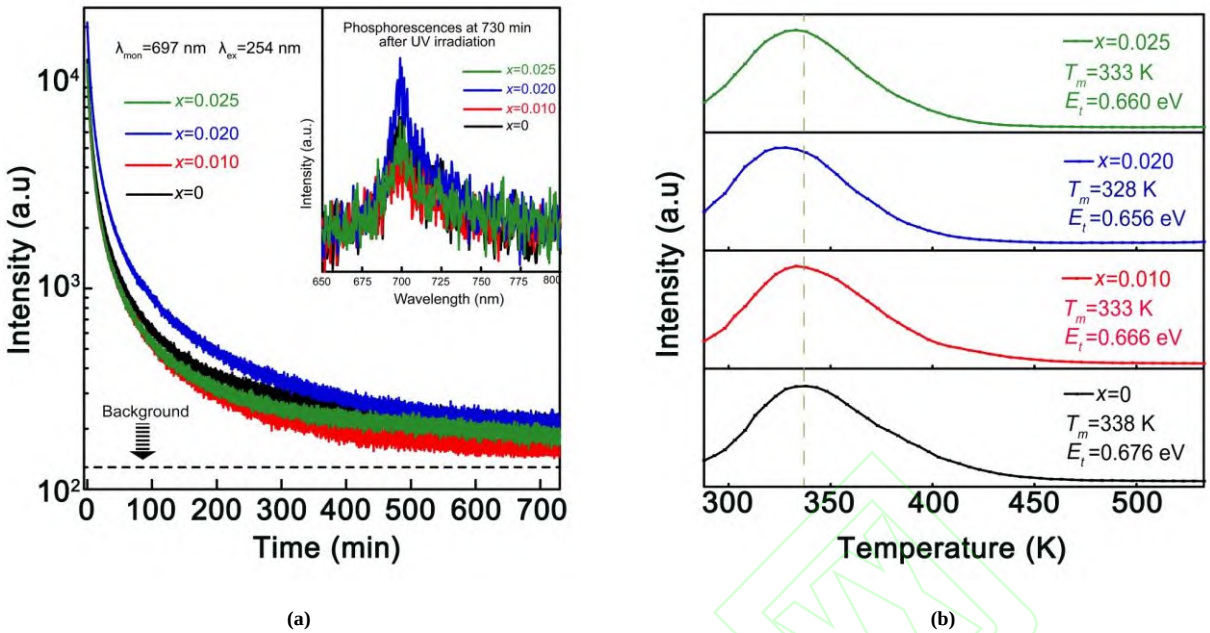
Viana et al. researched the structure and optical performance of Eu^{3+}, Ti^{4+}, Mg^{2+} co-doped Gd_2O_2S materials with a pure hexagonal Gd_2O_2S phase[20]. The study found that Ti^{4+} and Mg^{2+} ions are trapping centers, and Eu^{3+} ions are the emission centers. The Gd_2O_2S:Eu^{3+}, Ti^{4+}, Mg^{2+} has an emission band of 580 ~ 720 nm due to the electronic transitions of Eu^{3+} ion. Therefore, it can be inferred that the Eu^{3+} ion plays the role of the luminescence center in the materials. Moreover, Gd_2O_2S: Eu^{3+}, Ti^{4+}, Mg^{2+} has a longer phosphorescence time compared with Gd_2O_2S: Eu^{3+} for the reason that Ti^{4+} and Mg^{2+} ions play an important in improving the density of trap energy levels. However, the particle size and crystal structure of Gd_2O_2S materials have not obviously changed after the introduction of Eu^{3+}, Ti^{4+} and Mg^{2+} ions.

2. 3 Influence of the content of doped ions on the structure and optical performance of PLMs

As mentioned above, some doped ions play the role of the emission center of PLMs, while other doped ions will affect the number and depth of trap levels. Therefore, it is of great necessity to understand how the content of doped ions influences the structure and optical performance of PLMs. This section will discuss how the content of doped ions affects the structure and optical performance of PLMs.

2. 3. 1 Pr^{3+}, Cr^{3+} co-doped PLMs

Normally, Cr^{3+} ion serves as the luminescence center of PLMs, while Pr^{3+} ion affects the number and depth of trap levels. Yan et al. studied how the contents of Pr^{3+} and Cr^{3+} ions influence the structure and optical performance of PLMs. It is found that the increase of Cr^{3+} content promotes the energy release of $Zn_{2.94}Ga_{1.96}Ge_2O_{10}$:$Cr^{3+}$, Pr^{3+}. Therefore, as the amount of Cr^{3+} ion doping increases, the phosphorescence intensity and phosphorescence time of the material decrease[19, 27, 59]. Similarly, Zhang et al. studied the changes in particle size of Pr^{3+}, Cr^{3+} co-doped $Zn_2Ga_{2.98-x}Ge_{0.75}O_8$ materials with different Pr^{3+} contents[22]. It is found that the average size of the materials decreases with the increase of Pr^{3+} contents. Considering that the doped ions can strongly affect the crystal growth rate through surface charge modification[60], the size reduction of $Zn_2Ga_{2.98-x}Ge_{0.75}O_8$:$Cr^{3+}$, Pr^{3+} may be related to the influence of Pr^{3+} ion on the surface charge of the material. Specifically, the surface charge distribution of the materials will be changed when the Pr^{3+} ion is introduced into the materials, thereby reducing the growth rate. Subsequently, the optical performance of Pr^{3+}, Cr^{3+} co-doped $Zn_2Ga_{2.98-x}Ge_{0.75}O_8$ materials is researched. As shown in Fig. 5a, the phosphorescence intensity and the phosphorescence time of the materials increase as the increase of Pr^{3+} doping contents due to the changes in the trap levels of the materials caused by the introduction of Pr^{3+} ion (Fig. 5b). When the content of Pr^{3+} ion is too high, the luminescence performance will decrease due to the concentration quenching effect.

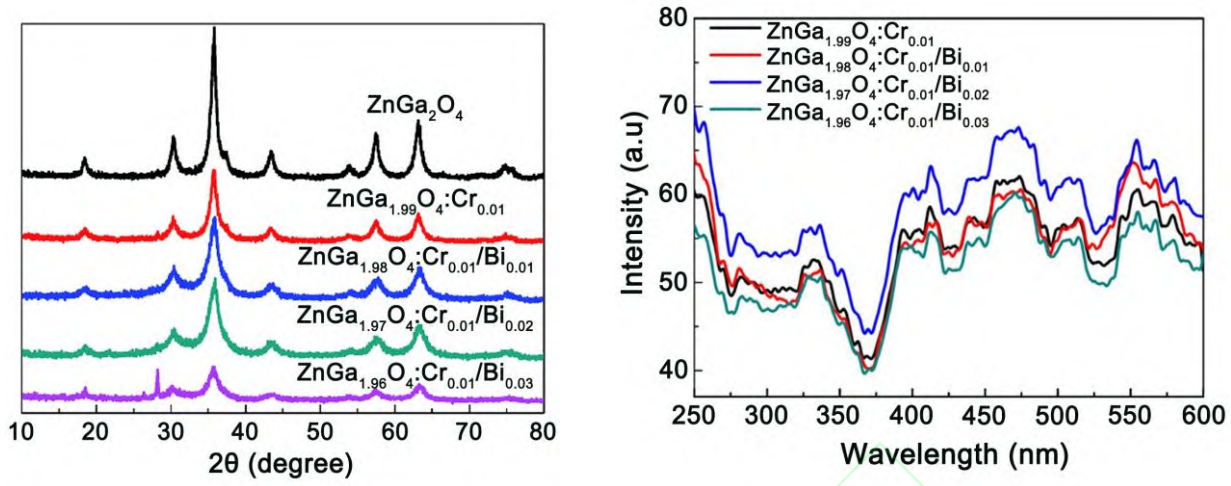


(a) (b)

Fig. 5. (a) Phosphorescence decay curves of Pr^{3+}, Cr^{3+} co-doped $Zn_2Ga_{2.98-x}Ge_{0.75}O_8$ materials with different Pr^{3+} doping contents. The inset presents the phosphorescence intensity of the materials after the ultraviolet light irradiation is stopped, (b) Thermo-luminescence spectra of Pr^{3+}, Cr^{3+} co-doped $Zn_2Ga_{2.98-x}Ge_{0.75}O_8$ materials with different Pr^{3+} doping contents

2. 3. 2 Bi^{3+}, Cr^{3+} co-doped PLMs

Bi^{3+} ion can significantly reduce the bandgap energy of PLMs and improve the efficiency of electron trap filling resulting from its unique 6*s* orbital. Tuerdi et al. researched the influence of crystalline structure, emission peak wavelength and phosphorescence time of $ZnGa_2O_4$:Bi^{3+}, Cr^{3+} materials with different Bi^{3+} doping contents[16]. The Bi^{3+} ion tends to replace Ga^{3+} ion in $ZnGa_2O_4$ with a similar ion radius, which makes the material produce higher periodic lattice distortion, thereby making the materials exhibit a longer phosphorescence time. When the doped ratio of Bi^{3+} ion is low, the crystal phase of Cr^{3+}, Bi^{3+} co-doped $ZnGa_2O_4$ materials corresponds to its standard spectrum, indicating that the structure of $ZnGa_2O_4$ materials has not obviously changed after the introduction of Bi^{3+} ion. However, when the doped ratio of Bi^{3+} ion increases to 0.03, a strong peak related to the rhombohedral Bi^{3+} structure at 28.01 ° is observed in the XRD pattern (Fig. 6a), illustrating that the original crystal structure of the materials is destroyed. Correspondingly, its optical performance is also reduced. The phosphorescence emission spectrum of $ZnGa_2O_4$:Bi^{3+}, Cr^{3+} materials with different Bi^{3+} doping contents shows a red-shift of emission peak wavelength, which indicates that Bi^{3+} ion reduces the crystal field intensity of the Cr^{3+} ion (Fig. 6b).



(a) **(b)**

Fig. 6. (a) XRD patterns of $ZnGa_2O_4$, $ZnGa_2O_4:Cr^{3+}$ and $ZnGa_2O_4:Cr^{3+}$, Bi^{3+}, (b) Phosphorescence spectra of $ZnGa_2O_4$, $ZnGa_2O_4:Cr^{3+}$ and $ZnGa_2O_4:Cr^{3+}$, Bi^{3+}

2. 3. 3 B^{3+}, Cr^{3+} co-doped PLMs

As mentioned above, the introduction of B^{3+} ion can improve the optical performance of $ZnGa_2O_4$. On this basis, the researchers studied the influence of doped ion content on PLMs. For example, Yan et al. synthesized $ZnGa_2O_4:B^{3+}$, Cr^{3+} materials by hydrothermal method, and studied the optical performance of $ZnGa_2O_4:Cr^{3+}$ with different B^{3+} doping contents[17]. The XRD pattern presents that the structure of the material has not obviously changed after doping with the B^{3+} and Cr^{3+} ions. Besides, the emission wavelength of the materials has not obviously changed when the B^{3+} ion is introduced into the materials, which indicates that the B^{3+} ion does not play the role of luminescence center in the materials. At the same time, the improvement of the optical performance of materials shows that the introduction of B^{3+} ion injects new electron traps into the materials and increases the content of electron traps.

2. 3. 4 Eu^{3+}, Ti^{4+} and Mg^{2+} co-doped PLMs

Eu^{3+}, Ti^{4+} and Mg^{2+} ions will act as luminescence centers or trap levels to affect the optical performance of the material. Therefore, studying the optical performance of $Gd_2O_2S:Eu^{3+}$, Ti^{4+} and Mg^{2+} materials with different doping contents will help us better understand the role of these ions in the material[20]. The study found that Eu^{3+} ion provides trap levels for electron-hole recombination, and Ti^{4+} ion provides electron traps to achieve the formation of the phosphorescence signal. Since Ti^{4+} ion replaces Gd^{3+} ion and destroys the charge conservation of the materials, it is necessary to introduce Mg^{2+} ion to maintain charge balance. In addition, as the doping contents of Mg^{2+} ion increase, the phosphorescence intensity of the material increases. This indicates that the introduction of Mg^{2+} ion can induce the formation of intermediate trap levels in the material, which prolongs the storage time of the carriers in the material, thus realizing the improvement of the persistent performance of the materials[61].

Apart from the ion-doped PLMs mentioned above, other doped ions also have an impact on the structure and optical performance. For example, $Li_2ZnGeO_4:Mn^{2+}$[62], $SrAl_2O_4:Eu^{2+}$, Dy^{3+}[63], $GdAlO_3:Mn^{4+}$, Ge^{4+}[64], $LaAlO_3:Mn^{4+}$, Ge^{4+}[65], $CaMgSi_2O_6:Eu^{2+}$, Dy^{3+}, Mn^{2+}[66], $Y_3Al_{5-x}Ga_xO_{12}:Ce^{3+}$, Bi^{3+} ($x = 0 \sim 4$)[67], $MgGeO_3:Mn^{2+}$, Bi^{3+}[68], $Y_3Sc_2Ga_3O_{12}:Ce^{3+}$[69],

$Ca_9Bi(PO_4)_7$:Ce^{3+}, Tb^{3+}, Mn^{2+}[70], Ca_2BO_3Cl:Eu^{2+}, Dy^{3+}[71], Lu_2O_3:Tb^{3+}, Ca^{2+}[72], KY_3F_{10}:Tb^{3+}[73] and AlN:Mn^{2+}[74].

3 CONCLUSION

In this review, we mainly focus on the impact of the type of doped ions, the number of types of doped ions, and the content of doped ions on the structure and optical performance of PLMs. In the past decade, although various doped ions have been widely used to improve the optical performance of PLMs, there is still much work to do in the future. First, in the actual preparation process, the optical performance of PLMs will be affected by the symmetry of matrix lattice, the radius of activated ions, and the electronegativity and distribution of external electron cloud. This should be paid more attention to by researchers. Second, exploring the relationship between doped ions and the host lattice and investigating the influence of the defects caused by doped ions on the storage time of the carriers. At present, these issues still have no exact quantitative relationship, and further researches are needed. Third, understanding the role of trap types, trap contents and probability of trapping electrons in the researches of the persistent luminescence mechanisms. Forth, exploring new doped ions and substrates. For example, most current PLMs are based on aluminates, gallates and silicates matrices. It is necessary to find new matrices with excellent properties. Collectively, with the deepening research of PLMs, ion-doped PLMs with higher luminescence intensity and phosphorescence lifetime will have a broad development prospect.

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Influence of Doped Ions on Persistent Luminescence Materials: a Review

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Doped ions will directly affect the luminescence centers and trap levels of persistent luminescence materials (PLMs), thereby leading to great differences in the optical performance. Herein, we discuss how doped ions affect the structure and optical performance of PLMs based on the types of doped ions, the number of the types of doped ions and the content of doped ions.