

Tuning Bismuth Activator Valence in Calcium Halophosphate Solid Solution by Controlling Activator Site

ZHANG Qing-Fu¹, LI Chen¹, SONG Zhi-Guo¹, LI Yong-Jin², QIU Jian-Bei¹, YANG Zheng-Wen¹

(1. School of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China;

2. Department of Science Research, Yunnan Technology and Business University, Kunming 651700, China)

Abstract: Effect of halide ions on valence state and luminescence property of Bi ions in calcium halophosphates was investigated. Bi-activated fluorapatite-chlorapatite solid solutions were synthesized by a solid state reaction. The content ratio between Bi^{2+} and Bi^{3+} ions in the crystals could be tuned rationally by the component ratio of F^-/Cl^- , and the absent emission of Bi^{2+} ion occur when halide ions are all occupied by Cl^- ions. The origin of this change is because the Ca_2 site of calcium halophosphate is split into $\text{Ca}(2)\text{a}$ and $\text{Ca}(2)\text{b}$ sites for F^- and Cl^- as the nearest neighbors, and the $\text{Ca}(2)\text{a}$ is adopted to offer activator site that enables Bi^{3+} to be self-reduced. The results in this study can provide a scientific reference for controlling the valence state of Bi ions in crystals.

Key words: calcium halophosphate; bismuth; luminescence properties; control

Recently, besides the excellent potential applications in NIR optical sources^[1-9], bismuth also has received increasing attention due to as an important luminescence active center used in displaying and lighting fields^[7-11], especially divalent Bi. Because of the particular electronic band structure, it has been considered recently to have the application in alternative red or orange emitting phosphors that can be excited by blue or UV light emitting diodes (LEDs)^[2]. However, in stark contrast to the rare-earth and transition-metal ions with relatively simple ionic state, Bi has been identified to be present in various forms, including Bi^{3+} , Bi^{2+} , Bi^+ , Bi atom, Bi cluster and Bi nanocrystal^[12-20]. One important reason is that the activation energy of the chemical transformations of these species is relatively low^[6, 12]. This means both the reducibility of prepared atmosphere and the local chemical condition of crystal structure are anticipated to be sufficient enough to trigger the valence transformation of Bi ion. As a result, stabilizing the divalent bismuth ion in phosphors faces difficulties, and only a handful of matrix materials are known up to now in which efficient stabilization of the Bi^{2+} ion is possible^[15, 21-23].

Very recently, we reported the orange emission and violet emission of Bi ion in $\text{Ca}_5(\text{PO}_4)_3\text{F}$ and $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ prepared in air, and the latter one was considered to be ascribed to Bi^{2+} ion typical emission^[5, 24-25]. It offers the possibility that Bi^{2+} ion may be controlled by the content of halogen in the

apatite crystals. In the present work, we carefully investigated the effect of halide ions on valence state change and luminescence property of Bi ions in calcium halophosphates. The content ratio between Bi^{2+} and Bi^{3+} ions in the crystals could be tuned rationally by the source ratio of F^-/Cl^- , and the absent emission of Bi^{2+} ion will occur when the halide ions are all occupied by Cl^- ions. The reason for this change was discussed according to the fine structure variation of haloapatite solid solutions, which may help to design the composition of Bi^{2+} -activated phosphors and provide a scientific reference for the control of Bi ions valence state in crystals.

1 Experimental details

1.1 Preparations

The bismuth doped $\text{Ca}_{4.99}\text{Bi}_{0.01}(\text{PO}_4)_3\text{F}_{(1-x)}\text{Cl}_x$ ($x=0, 0.4, 0.5, 0.6, 0.7, 0.8$ and 1) samples were synthesized *via* solid state reaction method in air atmosphere. For that, analytical grade reagents CaCO_3 (99.99%), $(\text{NH}_4)_2\text{HPO}_4$ (99%), NH_4F (99%), NH_4Cl (99%) and Bi_2O_3 (99.99%) were used as raw materials. Individual batches of 5 mmol were weighed according to stoichiometric compositions and mixed thoroughly. Both NH_4F and NH_4Cl were added in excess of 10mol% to compensate for volatilization losses. The grinded powder mixtures were then transferred into crucibles for a two-step heating. First, the mixed raw materials

Received date: 2016-08-17; **Modified date:** 2016-10-09

Foundation item: National Natural Science Foundation of China (61465006, 61265007); Reserve Talents Project of Yunnan Province (2015HB013)

Biography: ZHANG Qing-Fu(1993–), male, undergraduate. E-mail: kmlgzqf@hotmail.com

Corresponding author: SONG Zhi-Guo, professor. E-mail: songzg@kmust.edu.cn

were preheated at 400°C for 4 h and grounded together for second time. Subsequently, all products were sintered at elevated temperature about 1100°C for 2 h again in the air. Then, the resulting samples were obtained.

1.2 Characterization

Crystal structures of the obtained samples were analyzed by X-ray powder diffraction (XRD) with a Rigaku D/max 2200 Diffractometer with Cu K α ($\lambda = 0.1542$ nm) radiation at 36 kV and 30 mA. The emission and excitation spectra were obtained with a HITACHI F-7000 fluorescence spectrophotometer, using a static Xe lamp (150 W). All the measurements were carried out at room temperature.

2 Results and discussion

2.1 Crystal structure

The crystallography of $\text{Ca}_5(\text{PO}_4)_3\text{M}$ ($\text{M} = \text{F}$ and Cl) is well documented in the previous work^[5]. In $\text{Ca}_5(\text{PO}_4)_3\text{M}$ lattice, the position of M^- ion is responsible for the difference in the symmetry, there are two asymmetrical cationic (Ca^{2+}) sites in this system with the first site $\text{Ca}^{2+}(1)$ at the center of a slightly distorted tricapped trigonal prism constituted by six oxygen atoms of the PO_4 network corresponding to C_3 point group symmetry. And the second type of site $\text{Ca}^{2+}(2)$ is coordinated with six oxygen atoms plus two M^- ions, with the local symmetry around the $\text{Ca}^{2+}(2)$ site described by C_s point group. These two cationic sites and crystal structure can be pictorially represented as Fig. 1.

The XRD patterns of Bi doped $\text{Ca}_5(\text{PO}_4)_3\text{F}_{(1-x)}\text{Cl}_x$ samples are given in Fig. 2(a). It shows that the diffraction peaks of the samples with pure F or Cl can be indexed as a pure phase, which coincide well with the reference data of $\text{Ca}_5(\text{PO}_4)_3\text{F}$ (PDF 15-0876) and $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ (PDF 33-0271), respectively^[26]. On the other hand, the representative a-lattice lattice parameter of the prepared samples varies nearly linearly with the change of F/Cl ratio, indicating that apatite solid solutions are formed (Fig. 2(b))^[26].

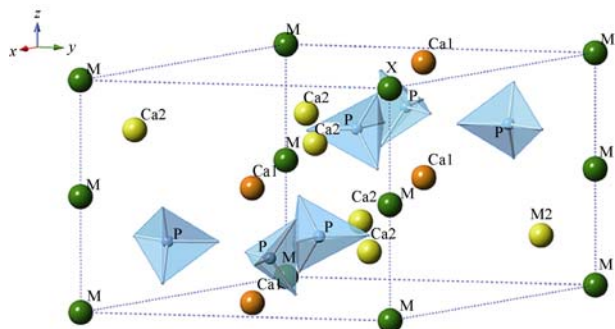


Fig. 1 Two cationic sites and crystal structure of $\text{Ca}_5(\text{PO}_4)_3\text{M}$

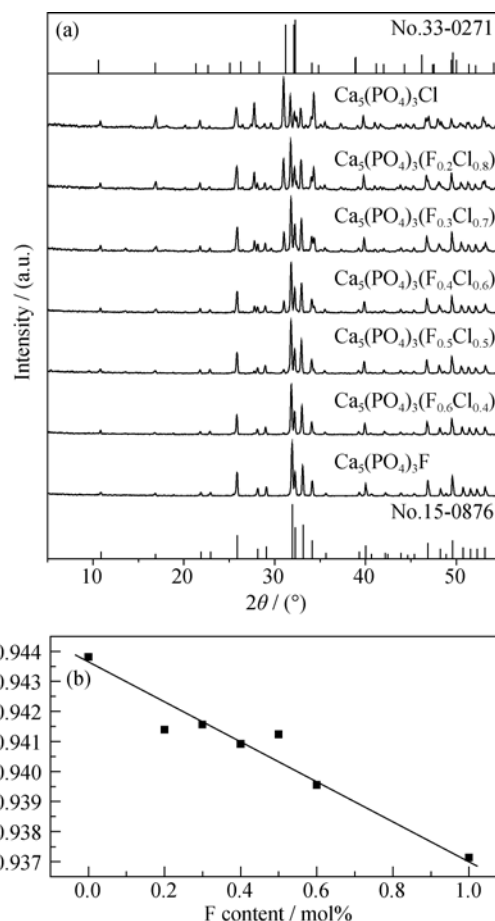


Fig. 2 (a) XRD patterns and (b) A-lattice lattice parameter of the prepared samples varies linearly with the change of F content

It should be clarified that the content ratio between raw material of F and Cl source possibly cannot present the actual ratio of F/Cl in resulted crystals, due to the different reaction and volatilization rate. But the method presented in this study can indicate the variation of ratio of F/Cl in the samples directly.

2.2 Luminescence properties

Before investigating the emission change of Bi doped calcium halophosphate solid solutions, the luminescence properties of Bi doped $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ and $\text{Ca}_5(\text{PO}_4)_3\text{F}$ should be clarified respectively, which have been investigated in our previous research^[5,7,27]. Fig. 3(a) and (b) show the excitation and emission spectra of $\text{Ca}_{4.99}(\text{PO}_4)_3\text{Cl}$ and $\text{Ca}_{4.99}(\text{PO}_4)_3\text{F}$ doped with 1% Bi. For sample of $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$: 1% Bi, it exhibits an asymmetric emission band peaked at 397 nm under UV light excitation, which can be attributed to the fact that Bi^{3+} will replace Ca^{2+} on two different cation sites in $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ lattice. However, for sample of $\text{Ca}_5(\text{PO}_4)_3\text{F}$: Bi, two excitation bands in the excitation spectra monitored at 397 nm are observed, one dominating at 354 nm and another weak shoulder centering at 284 nm. Moreover, an ultra-broadband emission in the longer wavelength order could also be seen

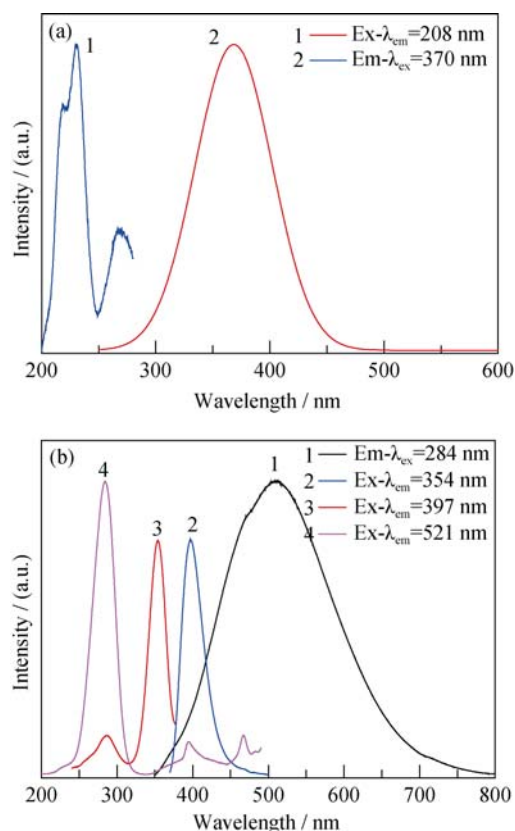


Fig. 3 Excitation and emission spectra of (a) $\text{Ca}_{4.99}(\text{PO}_4)_3\text{Cl}$ and (b) $\text{Ca}_{4.99}(\text{PO}_4)_3\text{F}$ doped with 1% Bi

When excited by 284 nm, which peaks at 521 nm and covers nearly whole visible spectrum to form the orange light emission. According to the traditional charge compensation principle as well as the mechanism for realizing the abnormal reduction of trivalent rare earth (Re^{3+}) ions in solid state compounds^[28-31], we supposed that the Bi^{3+} ions occupied Ca(1) sites could be reduced to Bi^{2+} ions in air, but not for that in Ca(2) sites^[5,30]. However, this cannot well explain the great difference of bismuth activator valence in the two apatite hosts with nearly identical structure.

To better understand the origin of this difference, we investigated the Bi emission dependence on the variation of F/Cl ratio. Fig. 4 shows that with the F^- content decreasing, the emission performance related to Bi^{3+} increases, while that for Bi^{2+} ions reduces gradually. This means that the content ratio between Bi^{2+} and Bi^{3+} ions in the crystals could be tuned rationally by the content ratio of F/Cl, and the absent emission of Bi^{2+} ion will occur when the halide ions are all occupied by Cl⁻ ion. Moreover, this interesting result offers a facile method to obtain the adjustable color of emission from blue to orange in a single-phased haloapatites activated by Bi ions.

2.3 Solid solutions

Generally, due to polarization and electronegativity difference between F^- and Cl^- ions^[32-33], the increasing

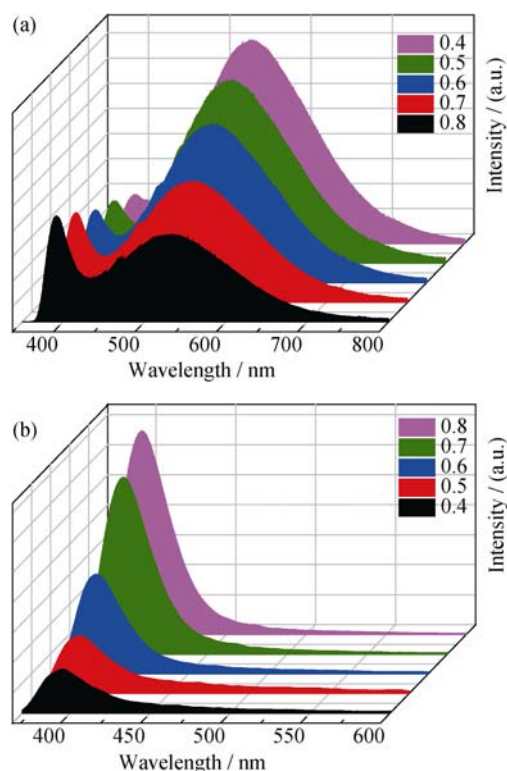


Fig. 4 The emission of (a) Bi^{2+} and (b) Bi^{3+} -doped $\text{Ca}_{4.99}\text{Bi}_{0.01}(\text{PO}_4)_3\text{F}_{(1-x)}\text{Cl}_x$ ($x=0.4, 0.5, 0.6, 0.7$ and 0.8)

content of F^- may have influence on reduction of doped activators. For example, it has been reported that Eu^{3+} can be easily reduced to Eu^{2+} in fluorite glass^[28,34-35]. However, in the haloapatite crystals, we considered that the content of F^- , namely the reduction ability difference between F^- and Cl^- ions should not be the direct reason for reducing Bi^{2+} ions. Because in previous work, we observed that the Bi^{3+} ions doped in the $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ crystals could not be reduced in reduction air at high temperature^[5]. Therefore, we proposed that the fine structure difference for the two kinds of apatite may be responsible for the valence tuning of Bi ions.

Previously, it has been found that the lattice parameters of the apatite solid solutions vary systematically with halogen composition^[26]. As shown in Fig. 5(a), F^- at the unit-cell position of $(0, 0, 1/4)$ is coordinated in a triangular-planar fashion by Ca at $(x, y, 1/4)$ on the Ca(2) site. In contrast to F^- , which occupies a special position at $(0, 0, 1/4)$ in the unit cell, Cl^- occupies split positions ranging from 0.346(4) to 0.4428(2) in the z-coordinate because of the larger ionic radius of Cl^- (Fig. 5(b)). Moreover, as shown in Fig. 5(c), it has been confirmed that the Ca(2) site is also split into Ca(2)a and Ca(2)b sites for F^- and Cl^- as nearest neighbors, respectively. In comparison to the Ca(2)a- F^- arrangements, the larger Cl^- ion presses the triangular arrangement of Ca-ions outward to facilitate an energetic more favorable constellation resulting in the formation of Ca(2)b- Cl^- arrangements, which leads to

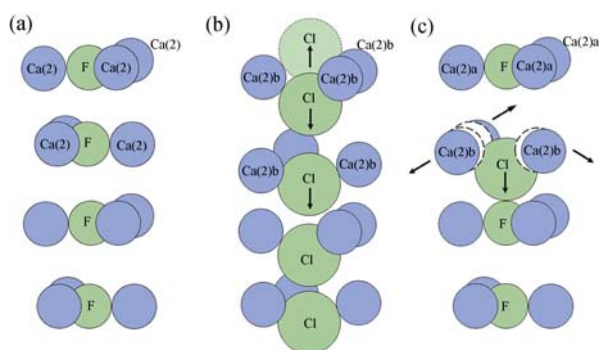


Fig. 5 Triangular-planar arrangement of Ca_3M in haloapatite along the z -axis of (a) fluorapatite, (b) chlorapatite, and (c) haloapatite solid solution. Substitution of Cl^- for F^- into the triangular arrangement and splitting of the $\text{Ca}(2)$ site into $\text{Ca}(2)\text{a}$ and $\text{Ca}(2)\text{b}$

symmetry reduction. Importantly, the occupancies of the $\text{Ca}(2)\text{a}$ and $\text{Ca}(2)\text{b}$ sites have been confirmed to correlate strictly with the $\text{F}-\text{Cl}$ content^[26]. This means the dependence of relative luminescence intensity of $\text{Bi}^{2+}/\text{Bi}^{3+}$ on the halogen composition is highly consistent with the ratio of $\text{Ca}(2)\text{a}/\text{Ca}(2)\text{b}$ sites. Herein, according to comprehensive survey of the performances of Bi doped calcium halophosphate solid solutions, an attempt was made to relate Bi^{2+} with its incorporation into the $\text{Ca}(2)\text{a}$ sites, which causes the activation of self-reduction for Bi^{3+} ions.

In order to confirm above assumption, we compared the emission peak position of Bi^{2+} ions in different samples, which have just one kind of sites in the apatite host. It is because the transition of Bi^{2+} is the $6s \rightarrow 6p$ internal electronic configuration transition, which is very sensitive to its local structure^[36-39]. This means if the self-reduction behavior of Bi^{3+} to Bi^{2+} is mainly related to the reduction effect of F^- content rather than the occupancies of $\text{Ca}(2)\text{a}$ sites, its emission center position will change significantly with composition variation, just as observed in other hosts^[14-15,39]. Conversely, when the self-reduction of Bi^{2+} centers just occurs at $\text{Ca}(2)\text{a}$ sites, it means the nearest local environments of Bi^{2+} ions are nearly analogous and it will give an almost identical emission. Interestingly, as showed in Fig. 6, the center position of the orange broadband emission keeps nearly unchangeable when the content ration of F/Cl varies. This could offer direct evidence for confirming the formation of Bi^{2+} at $\text{Ca}(2)\text{a}$ sites of $\text{Ca}_5(\text{PO}_4)_3\text{F}_{(1-x)}\text{Cl}_x$ solid solutions. It means that in calcium halophosphate solid solutions, the site and valence of Bi activator can be controlled and tuned facilely by the ration of F/Cl .

It should be noted that on the basis of the above conclusion, the Bi^{3+} ions that occupied $\text{Ca}(2)$ sites could be reduced to Bi^{2+} ions in air, but not for that in $\text{Ca}(1)$ sites as we proposed previously. In other word, that self-reduction behavior of Bi ion in the haloapatite crystals is partially

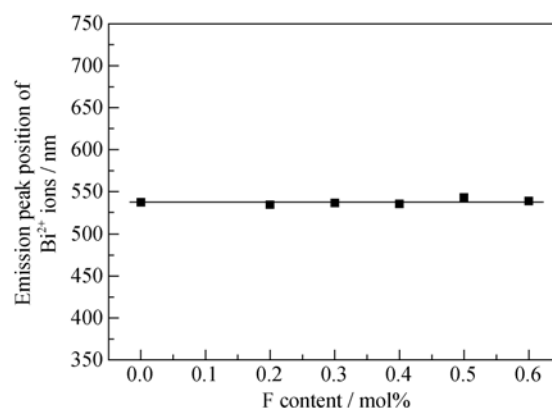


Fig. 6 The emission peak position of Bi^{2+} ions in samples with different F contents

different to the well-adopted conditions for realizing the abnormal reduction of Re^{3+} ^[28-31,34], which might enrich understanding mechanism of structure self-reduction and provide a scientific reference for the control of valence state of Bi ion in crystals. We think it might be related to the relatively lower activation energy of the chemical transformations of Bi ions. But the detailed mechanism for the surroundings of $\text{Ca}^{2+}(2)\text{a}$ site that is beneficial for the formation and stabilization of Bi^{2+} have not been understood well, and further investigations will be done.

3 Conclusion

Bi doped $\text{Ca}_5(\text{PO}_4)_3\text{F}_{(1-x)}\text{Cl}_x$ phosphors were prepared by solid state reaction method in air. The content ratio between Bi^{2+} and Bi^{3+} ions in the crystals could be tuned rationally by the content ratio of F/Cl , and the absent emission of Bi^{2+} ion will occur when the halide ions are all occupied by Cl^- ion. The reason for this change can be described to the splitting Ca_2 site of calcium halophosphate into $\text{Ca}2\text{a}$ and $\text{Ca}2\text{b}$ sites for F^- and Cl^- as nearest neighbors, the latter of which is be beneficial for the stabilization of Bi^{2+} ions. The results in this study can help to the design of the composition of Bi^{2+} -activated phosphor and provide a scientific reference for the control of valence state of Bi ion in crystals.

References:

- [1] XU BEI-BEI, CHEN PING, ZHOU SHI-FENG, *et al.* Enhanced broadband near-infrared luminescence in Bi-doped glasses by co-doping with Ag. *J. Appl. Phys.*, 2013, **113**(18): 183506.
- [2] PENG MINGYING, LOTHAR W. Bi^{2+} -doped strontium borates for white-light-emitting diodes. *Opt. Lett.*, 2009, **34**(19): 2885–2887.
- [3] FRANK K, DIRK R, AND ALAN F. Mid-Infrared Laser Applica-

- tions in Spectroscopy. Springer Berlin Heidelberg, 2003: 458–529.
- [4] FUJIMOTO Y, NAKATSUKA M. Optical amplification in bismuth-doped silica glass. *Appl. Phys. Lett.*, 2003, **82**(19): 3325–3326.
- [5] LI CHEN, LI YONG-JIN, SONG ZHI-GUO, *et al.* Study on the effect of apatite structure on spectroscopic properties of bismuth activated alkaline earth metal chlorophosphate $[M_5(PO_4)_3Cl]$; $M = Ca, Sr$ and Ba . *Mater. Chem. Phys.*, 2013, **139**(1): 220–224.
- [6] WAN RONG-HUA, SONG ZHI-GUO, LI YONG-JIN, *et al.* Investigation on the near-infrared-emitting thermal stability of Bi activated alkaline earth aluminoborosilicate glasses. *J. Appl. Phys.*, 2015, **117**(5): 053107.
- [7] LI CHEN, SONG ZHI-GUO, QIU JIAN-BEI, *et al.* Broadband yellow–white and near infrared luminescence from Bi-doped $Ba_{10}(PO_4)_6Cl_2$ prepared in reductive atmosphere. *J. Lumin.*, 2012, **132**(7): 1807–1811.
- [8] SUN HONG-TAO, AKINOBU H, FUMIAKI S, *et al.* Strong ultra-broadband near-infrared photoluminescence from bismuth-embedded zeolites and their derivatives. *Adv. Mater.*, 2009, **21**(36): 3694–3698.
- [9] SUN HONG-TAO, ZHOU JIA-JIA, QIU JIAN-RONG. Recent advances in bismuth activated photonic materials. *Prog. Mater. Sci.*, 2014, **64**: 1–72.
- [10] PENG MING-YING, DONG GUOPING, WONDRAKZEK L, *et al.* Discussion on the origin of NIR emission from Bi-doped materials. *J. Non-Cryst. Solids.*, 2011, **357**(11): 2241–2245.
- [11] WAN RONG-HUA, SONG ZHI-GUO, LI YONG-JIN, *et al.* Influence of alkali metal ions on thermal stability of Bi-activated NIR-emitting alkali-aluminoborosilicate glasses. *Chinese Optics Letters*, 2014, **12**(11): 111601.
- [12] PENG MING-YING, ZOLLFRANK C, WONDRAKZEK L. Origin of broad NIR photoluminescence in bismuthate glass and Bi-doped glasses at room temperature. *J. Phys.: Condens. Matter*, 2009, **21**(28): 285106.
- [13] NIKL M, NOVOSELOV A, MIHOKOVA E, *et al.* Photoluminescence of Bi^{3+} in $Y_3Ga_5O_{12}$ single-crystal host. *J. Phys.: Condens. Matter*, 2005, **17**(21): 3367.
- [14] SUN HONG-TAO, SHIMAOKA F, QIU JIANRONG, *et al.* Sensitized superbroadband near-IR emission in bismuth glass/Si nanocrystal superlattices. *Opt. Lett.*, 2010, **35**(13): 2215–2227.
- [15] PENG MING-YING, DA NING, KROLIKOWSKI S, *et al.* Luminescence from Bi^{2+} -activated alkali earth borophosphates for white LEDs. *Opt. Express*, 2009, **17**(23): 21169–21178.
- [16] PENG MING-YING, QIU JIAN-RONG, CHEN DAN-PING, *et al.* Superbroadband 1310 nm emission from bismuth and tantalum codoped germanium oxide glasses. *Opt. Lett.*, 2005, **30**(18): 2433–2435.
- [17] SUN HONG-TAO, MATSUSHITA Y, SAKKA Y, *et al.* Synchrotron X-ray, photoluminescence, and quantum chemistry studies of bismuth-embedded dehydrated zeolite Y. *J. Am. Chem. Soc.*, 2012, **134**(6): 2918–2921.
- [18] LIU BO-MEI, ZHANG ZHI-GANG, SUN HONG-TAO, *et al.* Unconventional luminescent centers in metastable phases created by topochemical reduction reactions. *Angew. Chem. Int. Ed.*, 2016, **55**(16): 4967–4971.
- [19] SUN HONG-TAO, SAKKA Y, GAO HONG, *et al.* Ultrabroad near-infrared photoluminescence from $Bi_5(AlCl_4)_3$ crystal. *J. Mater. Chem.*, 2011, **21**(12): 4060–4063.
- [20] SUN HONG-TAO, SAKKA Y, SHIRAHATA N, *et al.* Experimental and theoretical studies of photoluminescence from Bi_8^{2+} and Bi_5^{3+} stabilized by $[AlCl_4]^-$ in molecular crystals. *J. Mater. Chem.*, 2012, **22**(25): 12837–12841.
- [21] PENG MING-YING, WONDRAKZEK L. Orange-to-red emission from Bi^{2+} and alkaline earth codoped strontium borate phosphors for white light emitting diodes. *J. Am. Ceram. Soc.*, 2010, **93**(5): 1437–1442.
- [22] HAMSTRA M A, FOLKERTS H F, BLASSE G. Red bismuth emission in alkaline-earth-metal sulfates. *J. Mater. Chem.*, 1994, **4**(8): 1349–1350.
- [23] ZHOU YANG, YONG ZI-JUN, SUN HONG-TAO, *et al.* Ultrabroad photoluminescence and electroluminescence at new wavelengths from doped organometal halide perovskites. *J. Phys. Chem. Lett.*, 2016, **7**(14): 2735–2741.
- [24] BLASSE G. Classical phosphors: a Pandora's box. *J. Lumin.*, 1997, **72**: 129–134.
- [25] ARIMILLI S, NAG B, SRIVASTAVA A M. Luminescence of divalent bismuth in $M^{2+}BPO_5$ ($M^{2+} = Ba^{2+}, Sr^{2+}$ and Ca^{2+})-Condens. Matter. *J. Lumin.*, 1998, **78**(4): 239–243.
- [26] SCHETTLER G, GOTTSCHALK M, HARLOV D E. A new semi-micro wet chemical method for apatite analysis and its application to the crystal chemistry of fluorapatite-chlorapatite solid solutions. *Am. Mineral.*, 2011, **96**(1): 138–152.
- [27] LI CHEN, SONG ZHI-GUO, QIU JIAN-BEI, *et al.* Broadband orange emission from Bi activated calcium fluorophosphate. *Mater. Res. Bull.*, 2014, **50**: 490–493.
- [28] HONG B C, KAWANO K. Syntheses of CaF_2 : Eu nanoparticles and the modified reducing TCRA treatment to divalent Eu ion. *Opt. Mater.*, 2008, **30**(6): 952–956.
- [29] PENG MING-YING, PEI ZHI-WU, HONG GUANG-YAN, *et al.* Study on the reduction of $Eu^{3+} \rightarrow Eu^{2+}$ in $Sr_4Al_{14}O_{25}$: Eu prepared in air atmosphere. *Chem. Phys. Lett.*, 2003, **371**(1): 1–6.

- [30] PENG MING-YING, PEI ZHI-WU, HONG GUANG-YAN, *et al.* The reduction of Eu^{3+} to Eu^{2+} in $\text{BaMgSiO}_4 : \text{Eu}$ prepared in air and the luminescence of $\text{BaMgSiO}_4 : \text{Eu}^{2+}$ phosphor. *J. Mater. Chem.*, 2003, **13**(5): 1202–1205.
- [31] ZENG Q, PEI Z, WANG S, *et al.* The reduction of RE^{3+} in $\text{SrB}_6\text{O}_{10}$ prepared in air and the luminescence of $\text{SrB}_6\text{O}_{10} : \text{RE}^{2+}$ (RE= Eu, Sm, Tm). *Spectroscopy Letters*, 1999, **32**(6): 895–912.
- [32] SALEM L. The sudden polarization effect and its possible role in vision. *Acc. Chem. Res.*, 1979, **12**(3): 87–92.
- [33] PRITCHARD H, SKINNER H. The concept of electronegativity. *Chem. Rev.*, 1955, **55**(4): 745–786.
- [34] CZAJA M, BODYL S, GLUCHOWSKI P, *et al.* Luminescence properties of rare earth ions in fluorite, apatite and scheelite minerals. *J. Alloy Compd.*, 2008, **451**(1): 290–292.
- [35] SABINA B. Luminescence properties of Ce^{3+} and Eu^{2+} in fluorites and apatites. *Mineralogia*, 2009, **40**(1–4): 85–94.
- [36] LI LI-YI, VIANA B, PAUPORTÉ T, *et al.* Deep Red Radioluminescence from a Divalent Bismuth Doped Strontium Pyrophosphate $\text{Sr}_2\text{P}_2\text{O}_7 : \text{Bi}^{2+}$. SPIE OPTO. International Society for Optics and Photonics, 2015: 936423.
- [37] BLASSE G, MEIJERINK A, NOMES M, *et al.* Unusual bismuth luminescence in strontium tetraborate ($\text{SrB}_4\text{O}_7 : \text{Bi}$). *J. Phys. Chem. Solids*, 1994, **55**(2): 171–174.
- [38] LI LI-YI, PENG MING-YING, VIANA B, *et al.* Unusual concentration induced antithermal quenching of the Bi^{2+} emission from $\text{Sr}_2\text{P}_2\text{O}_7 : \text{Bi}^{2+}$. *Inorg. Chem.*, 2015, **54**(12): 6028–6034.
- [39] GAFT M, REISFELD R, PANCZER G. Luminescence Spectroscopy of Minerals and Materials. Berlin Springer, 2005, 356.

F/Cl 比对卤磷酸钙固溶体 Bi 离子掺杂位点及价态的调控

张庆福¹, 李 臣², 宋志国¹, 李永进², 邱建备¹, 杨正文¹

(1. 昆明理工大学 材料科学与工程学院, 昆明 650093; 2. 云南工商学院, 昆明 651700)

摘 要: 本工作研究了卤素离子含量对卤磷酸钙固溶体中 Bi 离子的价态和发光性能的影响。荧光分析表明, 卤素磷酸钙中的 $\text{Bi}^{2+}/\text{Bi}^{3+}$ 可以通过其 F/Cl 组分变化实现有效调控; 当卤素离子全部为 Cl 离子时, 晶体中 Bi^{2+} 全部消失。上述现象的主要原因在于, 当卤素离子为 F 或者 Cl 时, 晶体中与其邻近的 Ca(2) 位点可以被分裂为 Ca(2)a 或 Ca(2)b 两种不同的格位, 而 Ca(2)a 位点则有利于实现 Bi^{3+} 的自还原。上述研究结果可以为 Bi 离子在晶体中的价态调控提供指导。

关 键 词: 卤磷酸钙; Bi; 发光性能; 调控

中图分类号: O482

文献标识码: A