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Electronic structure and photoluminescence properties of a novel single-phased color tunable phosphor $KAlGeO_4:Bi^{3+},Eu^{3+}$ for WLEDs

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A series of novel single-component color tunable phosphors $KAlGeO_4:Bi^{3+},Eu^{3+}$ were synthesized by high-temperature solid state reaction. The crystal structure and electronic structure were analyzed by Rietveld refinement method and density functional theory (DFT) calculations, from which the lattice parameters and bandgap energy were determined. Photoluminescence properties, fluorescence decay and the energy transfer process have been investigated systematically. Under 320 nm excitation, $KAlGeO_4:Bi^{3+},Eu^{3+}$ shows both blue emission of Bi^{3+} and red emission of Eu^{3+}, originating from the allowed $^3P_1–^1S_0$ transition of Bi^{3+} and the $^5D_0–^7F_J$ transitions of Eu^{3+}, respectively. By adjusting the mole ratio of Bi^{3+} to Eu^{3+}, the color of $KAGO:Bi^{3+},Eu^{3+}$ can be tuned from blue to orange-red. The energy transfer mechanism was determined, and the energy transfer efficiency from Bi^{3+} to Eu^{3+} increased linearly with the increasing of Eu^{3+} concentration. Moreover, $KAGO:Bi^{3+},Eu^{3+}$ has good thermal quenching properties.

1. Introduction

Recently, as an energy-saving and environmentally friendly candidate for general lighting, white light-emitting diodes (WLEDs) have attracted intense attention due to their prominent advantages, such as high luminous efficiency, high brightness, low power consumption, long operation time and great stability [1–3]. They are considered to be the next generation lighting sources, which are replacing the traditional incandescent and fluorescent lamps [4] The main strategy to generate white light is by the combination of a LED chip with an appropriate phosphor, i.e. phosphor-converted white LEDs (pc-LEDs) [5]. Therefore, phosphors play a vital part in WLEDs and numerous investigations have been devoted to the development of new phosphors. Commonly, the commercial WLEDs are obtained by coupling blue InGaN LED chips with yellow-emitting phosphor $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce^{3+}). However, the lack of red component leads to cool white light with poor color rendering index (CRI) and relatively high correlated color temperature (CCT), which restricts their application in more vivid practical fields [6,7]. To overcome these drawbacks, considerable investigations have been directed to combine UV LED chips with tricolor (blue, green and red) phosphors. WLEDs obtained by this method can exhibit better color stability as well as outstanding CRI, because white light is absolutely generated by phosphors [8]. Hence, novel phosphors with different emission colors are a hotspot for research, of which red-emitting phosphors are highly desired.

It is well-known that Eu^{3+} is regarded as typical red-emitting activators due to its $^5D_0–^7F_J$ ($J = 0$, 1, 2, 3, 4) transitions, and numerous Eu^{3+}-doped phosphors with red emission have been investigated, such as, $Sr_{1.7}Zn_{0.3}CeO_4:Eu^{3+}$ [9], $Ca_{19}Mg_2(PO_4)_{14}:Eu^{3+}$ [10], $KGdTiO_4:Eu^{3+}$ [11], and $Na_3Sc_2(PO_4)_3:Eu^{3+}$ [12]. The excitation spectra of Eu^{3+} are usually composed of charge transfer bands in the short-wavelength UV region and direct excitation peaks in n-UV to blue region. The direct excitation peaks of Eu^{3+} ions are sharp lines and ascribed to intra-configurational 4f–4f forbidden

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transitions, which leads to poor emission intensity from Eu^{3+}-singly doped phosphors. Thus, sensitizers usually need to be introduced into the system to improve the emission intensity of Eu^{3+}. As is well known, Bi^{3+} ions can serve as activators, exhibiting blue to green emission with the wavelength ranging from 400 to 550 nm, deriving from its 6s6p–$6s^2$ transition upon UV excitation [13]. Generally, the absorption bands of Bi^{3+} originate from the allowed $^1S_0$–$^3P_1$ and $^1S_0$–$^1P_1$ transitions [14]. The photoluminescence properties of Bi^{3+} depend on the coordination environment [15]. In addition, Bi^{3+} ions can act as sensitizers to enhance the emission of Eu^{3+} based on the energy transfer process, as reported in many phosphors, such as, $MgY_2Si_3O_{10}:Eu^{3+},Bi^{3+}$ [15], $Sr_3YAl_2O_{7.5}:Bi^{3+},Eu^{3+}$ [16], and $Ba_3Y_4O_9:Bi^{3+},Eu^{3+}$ [13]. With the mixture of blue-green emission from Bi^{3+} and red emission from Eu^{3+}, color tunable emission can be achieved by regulating the mole ratio of Bi^{3+} to Eu^{3+} in Bi^{3+}/Eu^{3+} co-doped phosphors. In addition, blue emission (400–500 nm) and red emission (600–720 nm) are indispensable for plant growth because they match well with the absorption wavelengths of carotenoids and chlorophyll. They can improve the photosynthesis of plants, and thus increase the crop yield and tune the plant growth process [17,18].

As is well-known, the photoluminescence properties of phosphors are closely related to the chemical composition, crystal structure and electronic structure. $KAlGeO_4$ was reported firstly by Lampert et al. in 1986 [19]. In this work, we applied Rietveld refinement method and density functional theory (DFT) calculation to analyze the crystal structure and the electronic structure of KAGO. KAGO is a stuffed derivative of tridymite. It crystallizes in a hexagonal unit cell with the space group $P6_3$. There are six kinds of K^+ sites in the structure: the ones on the 6_3 and triad axes are coordinated by nine oxygen atoms, and the others on general positions are surrounded by four oxygen atoms. KAGO is a kind of direct bandgap materials with appropriate bandgap energy. All these enable KAGO to be an appropriate host for luminescent materials. In addition, as far as we know, the photoluminescence properties of $KAlGeO_4$ based phosphors have not been investigated yet. Therefore, in this work, we synthesized a novel single-component color tunable phosphor $KAlGeO_4:Bi^{3+},Eu^{3+}$ with efficient energy transfer from Bi^{3+} to Eu^{3+} for white LEDs. The crystal structure, electronic structure, photoluminescence properties, thermal stability and the energy transfer process were investigated in detail.

2. Experimental section

2.1. Materials and synthesis

$KAlGeO_4:xBi^{3+},yEu^{3+}$ ($KAGO:xBi^{3+},yEu^{3+}$) ($x = 0$–0.07, $y = 0$–0.10) phosphors were synthesized by high-temperature solid state method. The raw materials K_2CO_3 (A.R.), Al_2O_3 (A.R.), GeO_2 (A.R.), Bi_2O_3 (A.R.) and Eu_2O_3 (99.99%) were weighted in the stoichiometric ratio, ground thoroughly and then sintered at 1323 K for 10 h in air. After calcination, the samples were ground into powder for further characterization.

2.2. Materials characterization

The powder X-ray diffraction (XRD) patterns were collected by a Bruker D8 focus diffractometer at the scanning rate of $8^\circ\ min^{-1}$ in the 2θ range from 10 to 80° with graphite-monochromatized Cu Kα radiation ($\lambda = 0.15405$ nm) operating at 40 kV and 40 mA. GSAS software was utilized to perform the Rietveld refinements. The photoluminescence excitation (PLE) and photoluminescence (PL) spectra were obtained with a Hitachi F-7000 spectrophotometer with a 150 W xenon lamp as the excitation source. The diffuse reflectance spectra were detected by a 3600 UV-VIS-NIR spectrophotometer with the reference of barium sulphate. The fluorescence decay curves were detected on a Lecroy Wave Runner 6100 Digital Oscilloscope (1 GHz) with a tunable laser (pulse width = 4 ns, gate = 50 ns) as the excitation source. The temperature-dependent PL spectra were measured by an FLS-920-Combined Fluorescence Lifetime and steady state spectrometer (Edinburgh Instruments) with the excitation source of a 450 W xenon lamp. All the characterizations were completed at room temperature except those for the TL spectra.

2.3. Details of the calculation

DFT calculations on KAGO matrix were performed with the CASTEP code [20]. Geometry optimization and the calculation of properties were conducted to identify crystal structure, electronic structure and the orbital population. The Vanderbilt ultrasoft pseudopotential with a cutoff energy of 340.0 eV was adopted, and *k*-points of $1 \times 1 \times 2$ were generated with the Monkhorst–Pack scheme [21]. The exchange and correlation functionals were handled by the generalized gradient approximation (GGA) in the formulation of PBE, and the local density approximation (LDA) in the formulation of CA-PZ [22]. Atomic positions and lattice parameters were optimized simultaneously in the geometry optimization. For self-consistent field iterations, the convergence tolerance of geometry optimization was selected with the differences in total energy, the stress tensor, the maximal ionic Hellmann–Feynman force and the maximal displacement being within 1.0×10^{-5} eV/atom, 5.0×10^{-2} GPa, 3.0×10^{-2} eV/Å and 1.0×10^{-3} Å, respectively.

3. Results and discussion

3.1. Phase identification and crystal structure

Powder X-ray diffraction was applied to attest the phase purity. XRD profiles of $KAGO:xBi^{3+},yEu^{3+}$ and the standard pattern of $KAlGeO_4$ (JCPDS 78-1173) were shown in Fig. 1(a). It is obvious that all the diffraction peaks of $KAGO:xBi^{3+},yEu^{3+}$ can be well indexed to the standard profiles of KAGO, which indicates that Bi^{3+} and Eu^{3+} ions have been incorporated into KAGO host successfully without generating any notable impurities. With respect to the site occupancy, we suppose that Bi^{3+} and Eu^{3+} ions tend to occupy the sites of K^+ ions, because the ionic radii of Bi^{3+} (1.03 Å) and Eu^{3+} (0.947 Å) are similar to that of K^+ (1.38 Å) with the same coordination number, while much larger than those of Al^{3+} (0.535 Å) and Ge^{4+} (0.53 Å) [23].

The Rietveld refinement was conducted to obtain the detailed crystal structure information. The single crystallographic data of KAGO was used as the initial model. Fig. 1(b) depicts the observed and calculated XRD patterns, as well as their difference for the refinement of KAGO matrix. The lattice parameters are listed in Table 1^a. The refinement finally converged to $\chi^2 = 9.327$, $R_p = 3.59\%$, $R_{wp} = 5.30\%$, which indicates that the fraction factor, atom position, and temperature factor of the sample coincide well with the reflection conditions. In addition, the structure optimization of KAGO was carried out by using DFT calculations with the generalized gradient approximation (GGA) and the local density approximation (LDA). The obtained lattice parameters are also summarized in Table 1^{bc}. Atom positions of KAGO obtained from Rietveld refinement, GGA and LDA are listed in Table A1–A3 for comparison. The refinement and DFT calculation results all reveal that KAGO has the hexagonal structure with the space group $P6_3$. The cell volumes of KAGO were determined to be 2661.238 $Å^3$ (GGA) and