



Color-tunable self-activated oxyfluoride phosphors induced by anion-defect with cation-disorder



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ABSTRACT

Cation-disordered oxyfluoride materials, $\text{Sr}_{3-p-q}\text{Ba}_p\text{Na}_q\text{Al}_{1-z}\text{Sn}_z\text{O}_4\text{F}$ ($p = 0-0.7$ and $q, z = 0, 0.05$) and $\text{Sr}_{2.975-p}\text{Ba}_p\text{Na}_{0.05}\text{AlO}_4\text{F}$ ($p = 0-0.7$), were prepared via solid-state reactions and subsequently induced with defects under appropriate reduction conditions. The anion-deficient self-activating phosphors can be identified using broadband-shaped emissions ranging from 300 to 700 nm when excited with ultraviolet (UV) light. The luminescence properties of the defect-induced self-activating phosphors were examined using cation-disordered $[(\text{Sr},\text{Ba})(\text{Al},\text{Sn})\text{O}_4]^{3-}$ and $[(\text{Sr},\text{Na})_2\text{F}]^{3+}$ clusters in the oxyfluoride lattice. The luminescent emissions of $\text{Sr}_{2.45}\text{Ba}_{0.5}\text{Na}_{0.05}\text{Al}_{0.95}\text{Sn}_{0.05}\text{O}_{4-z}\text{F}_{1-\delta}$ phosphors were significantly enhanced by the combination of the cation disorder with anion defect. Color-tunable emissions in the defect-induced self-activating $\text{Sr}_{2.45}\text{Ba}_{0.5}\text{Na}_{0.05}\text{Al}_{0.95}\text{Sn}_{0.05}\text{O}_{4-z}\text{F}_{1-\delta}$ phosphor were obtained. The desired Commission Internationale de l'Éclairage (CIE) values corresponding to the spectral emission from blue to white and yellow regions of the spectra were attained by exciting the defect-induced self-activating $\text{Sr}_{2.45}\text{Ba}_{0.5}\text{Na}_{0.05}\text{Al}_{0.95}\text{Sn}_{0.05}\text{O}_{4-z}\text{F}_{1-\delta}$ phosphors with UV light.

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1. Introduction

Rare-earth and transition ions - Ce^{3+} , Eu^{2+} , Eu^{3+} , Tb^{3+} , or Mn^{2+} ions - in various host lattices can be generally used as activators for an appropriate luminescence process, which is defined as the excitation and emission progression through the electronic transitions of the activators [1,2]. Line-shaped or broadband-shaped emission could arise from an activator, and is assigned to f-f, f-d, or d-d electronic transitions; especially, the activators showing broadband-shaped transitions can be affected by their coordinated environments in host lattices [1–5]. Notably, unusual emission without using the activators can be observed via an electronic transition between an anion electron and empty cation orbital; for example, an electron transfer from the 2p orbital of O^{2-} to the vacant 3d orbital of V^{5+} in the $(\text{VO}_4)^{3-}$ complex results in broadband-shaped emission [1,6]. Such phosphors are called self-activated phosphors because the activators of rare-earth or transition ions are not involved in the process. Similar luminescence phenomena were widely observed in $(\text{WO}_4)^{2-}$, $(\text{MoO}_4)^{2-}$, and $(\text{MnO}_4)^-$ complexes during the investigation of self-activated

CaWO_4 phosphors, which were used as a scintillator for the detection of X-rays in 1896 [7–10]. Furthermore, the defect-induced self-activating phosphors obtained owing to cation or anion vacancies in host lattices, which generate self-trapped electron or hole states, emit broadband-shaped luminescence lights without the activators [11–13]. These defects can be produced with cation-disordered substitutions in the host lattice or by altering material preparation conditions using X-ray irradiation, Ar^+ irradiation, or appropriate reduction environments [13–17]. In a previous study, defect-induced self-activating $(\text{Sr},\text{Ca},\text{Ba})_3\text{AlO}_{4-z}\text{F}_{1-\delta}$ phosphors controlled by anion defects were investigated [16]. In this study, cation-disordered $\text{Sr}_{2.5-q}\text{Ba}_{0.5}\text{Na}_q\text{Al}_{1-z}\text{Sn}_z\text{O}_4\text{F}$ ($p = 0-0.7$ and $q, z = 0, 0.05$) and $\text{Sr}_{2.975-p}\text{Ba}_p\text{Na}_{0.05}\text{AlO}_4\text{F}$ ($p = 0-0.7$) oxyfluorides are prepared. The luminescence properties of defect-induced self-activating oxyfluoride phosphors are examined by controlling the anion defect structure generated under post-synthesis reduction conditions when excited with ultraviolet (UV) light. A significant emission enhancement is expected to arise from a combination of the cation disorder with anionic defects. Color-tunable emissions of defect-induced self-activating $\text{Sr}_{2.45}\text{Ba}_{0.5}\text{Na}_{0.05}\text{Al}_{0.95}\text{Sn}_{0.05}\text{O}_{4-z}\text{F}_{1-\delta}$ phosphors are observed. The desired CIE values corresponding to the spectral emission regions from blue to white and yellow are attained using the defect-induced, self-activating oxyfluoride phosphors.

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2. Experimental details

Samples of $\text{Sr}_{3-p-q}\text{Ba}_p\text{Na}_q\text{Al}_{1-z}\text{Sn}_z\text{O}_4\text{F}$ ($p = 0-0.7$ and $q, z = 0, 0.05$) and $\text{Sr}_{2.975-p}\text{Ba}_p\text{Na}_{0.05}\text{AlO}_4\text{F}$ ($p = 0-0.7$) were prepared by heating the appropriate stoichiometric amounts of SrCO_3 (Alfa 99%), BaCO_3 (Alfa 99.8%), SrF_2 (Alfa 99%), Na_2CO_3 (Alfa 99.5%), Al_2O_3 (Alfa 99.95%), and SnO_2 (Alfa 99.9%) at temperature up to 1200°C for 3 h in air. The as-made samples were subsequently annealed at 800°C in reducing atmosphere (8% $\text{H}_2/92\%$ Ar) for 1 h to compose self-activating luminescent materials [15–18]. Phase identification of the phosphors was done using a Shimadzu XRD-6000 powder diffractometer using $\text{CoK}\alpha$ radiation and the unit cell parameters were determined by using the least squares refinement program Rietica. Ultraviolet–visible spectroscopy to measure the excitation and emission spectra of the fluoride phosphors was done with a spectrofluorometer (Sinco Fluoromate FS-2).

3. Results and discussion

The phase identification of $\text{Sr}_{2.5-p-q}\text{Ba}_p\text{Na}_q\text{Al}_{1-z}\text{Sn}_z\text{O}_4\text{F}$ ($p = 0-0.7$ and $q, z = 0, 0.05$) and $\text{Sr}_{2.975-p}\text{Ba}_p\text{Na}_{0.05}\text{AlO}_4\text{F}$ ($p = 0-0.7$) samples was performed by studying the powder X-ray diffraction (XRD) patterns after the Ba^{2+} , Na^+ , and/or Sn^{4+} ions were replaced with Sr^{2+} or/and Al^{3+} ions in the $\text{Sr}_3\text{AlO}_4\text{F}$ host lattice. The XRD patterns of the single-phase host lattice features without any evident impurities were observed. Fig. 1 (a)–(e) indicate the calculated $\text{Sr}_3\text{AlO}_4\text{F}$ (ICSD 50736, $a = 6.7822(1)$ and $c = 11.1437(2)$ Å) and the obtained $\text{Sr}_{3-p}\text{Ba}_p\text{AlO}_4\text{F}$ ($p = 0, 0.5$), $\text{Sr}_{2.475-q}\text{Ba}_{0.5}\text{Na}_q\text{AlO}_4\text{F}$ ($q = 0.05$), and $\text{Sr}_{2.5-q}\text{Ba}_{0.5}\text{Na}_q\text{Al}_{1-z}\text{Sn}_z\text{O}_4\text{F}$ ($q, z = 0.05$) XRD patterns. The larger Ba^{2+} ($r = 1.52$ Å, CN = 10) and smaller Na^+ ($r = 1.18$ Å, CN = 8) ions can be accommodated in the 10-coordinated Sr(1) ($r = 1.36$ Å, CN = 10) and 8-coordinated Sr(2) ($r = 1.26$ Å, CN = 8) sites in the structure, respectively. Sr^{2+} in the obtained $\text{Sr}_3\text{AlO}_4\text{F}$ lattice ($a = 6.7735(2)$ and $c = 11.12840(5)$ Å) was partially substituted by Ba^{2+} ($p = 0.5$) in $\text{Sr}_{3-p}\text{Ba}_p\text{AlO}_4\text{F}$ ($a = 6.8378(2)$ and $c = 11.1615(6)$ Å) and this resulted in a slight shift in the positions of the Bragg reflections between $2\theta = 35^\circ$ and 37° to lower angles as the cell size increased as shown in Fig. 1 (c). Furthermore, when Sr^{2+} ions were replaced by smaller Na^+ ions in $\text{Sr}_{2.475}\text{Ba}_{0.5}\text{Na}_{0.05}\text{AlO}_4\text{F}$ ($a = 6.8373(3)$ and $c = 11.1563(8)$ Å), a slight peak shift from the XRD pattern of the $\text{Sr}_{2.5}\text{Ba}_{0.5}\text{AlO}_4\text{F}$ lattice was observed in Fig. 1 (d). It is conceivable that an Sr^{2+} ion was replaced by two Na^+ ions in the host lattice. The substitution of Al^{3+} ($r = 0.395$ Å, CN = 4) ions by Sn^{4+} ($r = 0.55$ Å, CN = 4) ions in the $\text{Sr}_{2.45}\text{Ba}_{0.5}\text{Na}_{0.05}\text{AlO}_4\text{F}$ structure resulted in a clear shift to lower angles as the cell size increased to $a = 6.8484(3)$ and $c = 11.1765(5)$ Å for the

$\text{Sr}_{2.45}\text{Ba}_{0.5}\text{Na}_{0.05}\text{Al}_{0.95}\text{Sn}_{0.05}\text{O}_4\text{F}$ lattice as shown in Fig. 1 (e).

In Fig. 2 (a), the broadband emission spectra and photos in the blue, green, white, yellow, and orange regions of the visible light with UV excitation light ranging from 254 to 313 nm are shown when $\text{Sr}_{3-p}\text{Ba}_p\text{AlO}_{4-x}\text{F}_{1-\delta}$ ($p = 0-0.7$) powder was exposed to a reducing atmosphere (8% $\text{H}_2/92\%$ Ar) at 800°C . The structure of $\text{Sr}_3\text{AlO}_4\text{F}$ lattice contains two types of 10-fold and 8-fold coordinated Sr^{2+} ions, Sr(1) O_8F_2 and Sr(2) O_6F_2 , with 4-fold coordinated Al^{3+} cation (AlO_4) in the stacking Sr(1) AlO_4^{3-} and Sr(2) F_3^{3+} layers [16,19]. As reported before, the anion-deficient self-activating photoluminescence of $\text{Sr}_3\text{AlO}_{4-x}\text{F}_{1-\delta}$ was suggested to be induced by two defect clusters— $[\text{SrAlO}_4]^{3-}$ and $[\text{Sr}_2\text{F}]^{3+}$ blocks along the c -axis [16]. When the content of Ba^{2+} ions was increased, the emission spectra exhibited a red shift from 467 to 582 nm. The energy gap steadily increased with the substitution with larger Ba^{2+} ions, which occupy the 10-fold Sr(1) site in the $\text{Sr}_3\text{AlO}_4\text{F}$ host lattice with the local electronic structure of $[(\text{Sr},\text{Ba})\text{AlO}_4]^{3-}$ clusters. The maximum intensity of the photoluminescence emission under UV excitation light was observed for the solid-state series $\text{Sr}_{3-p}\text{Ba}_p\text{AlO}_{4-x}\text{F}_{1-\delta}$ with $p = 0.5$. When the defect-induced $\text{Sr}_{3-p}\text{Ba}_p\text{AlO}_{4-x}\text{F}_{1-\delta}$ ($p = 0-0.7$) phosphors were doped with Na^+ ions, the emission bands showed a clear shift to the yellow region. The blue emission of the $\text{Sr}_{3-p}\text{Ba}_p\text{AlO}_{4-x}\text{F}_{1-\delta}$ ($p = 0$) phosphor evidently shifted to the green region when substituted by Na^+ ions; furthermore, the green emission was observed in $\text{Sr}_{2.975-p}\text{Ba}_p\text{Na}_{0.05}\text{AlO}_{4-x}\text{F}_{1-\delta}$ ($p = 0.3$) phosphors under the excitation of 254 and 312 nm with a hand lamp as shown in Fig. 2 (b). The maximum intensity of the yellow photoluminescence emission of $\text{Sr}_{2.5}\text{Ba}_{0.5}\text{AlO}_{4-x}\text{F}_{1-\delta}$ with $p = 0.5$ under UV excitation light was enhanced by Na^+ substitution in the structure; in addition, reddish emission was observed in $\text{Sr}_{2.975-p}\text{Ba}_p\text{Na}_{0.05}\text{AlO}_{4-x}\text{F}_{1-\delta}$ ($p = 0.5, 0.7$) under 365 nm excitation with a hand lamp. The Sr^{2+} ion was replaced by two Na^+ ions in the $\text{Sr}_{2.975-p}\text{Ba}_p\text{Na}_{0.05}\text{AlO}_{4-x}\text{F}_{1-\delta}$ lattice. The Na^+ ions can play the role of a charge compensator; moreover, the over-doped Na^+ ions will possibly occupy the interstitial positions in the defect-induced oxyfluoride lattice. Na^+ ions promote the emission of the self-activating phosphors, when the anion defect process occurs, thereby reducing the number of cation vacancies. The defect-induced $\text{Sr}_{2.95-p}\text{Ba}_p\text{Na}_{0.05}\text{Al}_{0.95}\text{Sn}_{0.05}\text{O}_{4-x}\text{F}_{1-\delta}$ ($p = 0-0.7$) phosphors show two excitation and emission centers as shown in Fig. 2 (c). In the $\text{Sr}_{2.95-p}\text{Ba}_p\text{Na}_{0.05}\text{Al}_{0.95}\text{Sn}_{0.05}\text{O}_4\text{F}$ host lattices, Na^+ and Sn^{4+} ions occupy Sr^{2+} and Al^{3+} sites, respectively. The cation disorders in the host structures exhibited defect-trap centers and unusual emission spectra according to the previous reports [11,13]. When the $\text{Sr}_{2.95-p}\text{Ba}_p\text{Na}_{0.05}\text{Al}_{0.95}\text{Sn}_{0.05}\text{O}_4\text{F}$ lattice was induced with defects by substituting Sr^{2+} and Al^{3+} with Na^+ and Sn^{4+} ,

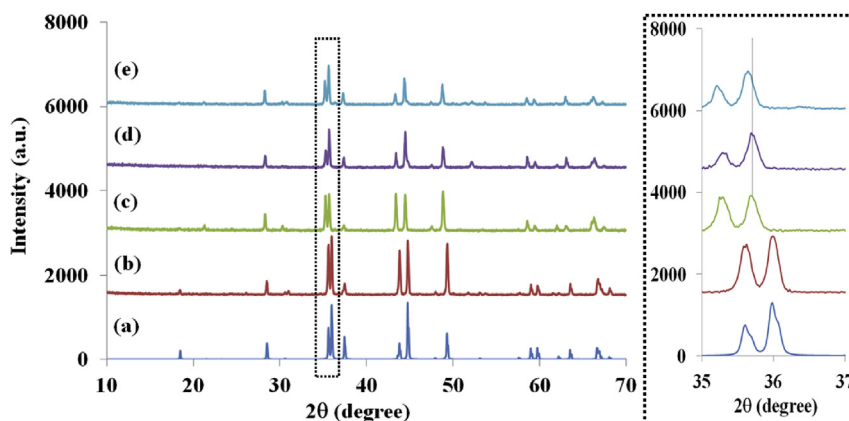


Fig. 1. XRD patterns of the calculated $\text{Sr}_3\text{AlO}_4\text{F}$ (ICSD 50736) and observed (b) $\text{Sr}_3\text{AlO}_4\text{F}$, (c) $\text{Sr}_{2.5}\text{Ba}_{0.5}\text{AlO}_4\text{F}$, (d) $\text{Sr}_{2.425}\text{Ba}_{0.5}\text{Na}_{0.05}\text{AlO}_4\text{F}$, and (e) $\text{Sr}_{2.45}\text{Ba}_{0.5}\text{Na}_{0.05}\text{Al}_{0.95}\text{Sn}_{0.05}\text{O}_4\text{F}$.

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