Journal of Luminescence 157 (2015) 69–73

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Mn^{4+} emission in pyrochlore oxides

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A R T I C L E I N F O

Article history:
Received 10 May 2014
Received in revised form
27 June 2014
Accepted 18 August 2014
Available online 27 August 2014

Keywords:
Red phosphor
Mn^{4+}
Pyrochlore
Fluorescent lighting

A B S T R A C T

Existing Mn^{4+} activated red phosphors have relatively low emission energies (or long emission wavelengths) and are therefore inefficient for general lighting. Density functional calculations are performed to study Mn^{4+} emission in rare-earth hafnate, zirconate, and stannate pyrochlore oxides ($RE_2Hf_2O_7$, $RE_2Zr_2O_7$, and $RE_2Sn_2O_7$). The results show how the different sizes of the RE^{3+} cation in these pyrochlores affect the local structure of the distorted MnO_6 octahedron, the Mn–O hybridization, and the Mn^{4+} emission energy. The Mn^{4+} emission energies of many pyrochlores are found to be higher than those currently known for Mn^{4+} doped oxides and should be closer to that of Y_2O_3:Eu^{3+} (the current commercial red phosphor for fluorescent lighting). The O–Mn–O bond angle distortion in a MnO_6 octahedron is shown to play an important role in weakening Mn–O hybridization and consequently increasing the Mn^{4+} emission energy. This result shows that searching for materials that allow significant O–Mn–O bond angle distortion in a MnO_6 octahedron is an effective approach to find new Mn^{4+} activated red phosphors with potential to replace the relatively expensive Y_2O_3:Eu^{3+} phosphor.

1. Introduction

Mn^{4+} can activate red emission in many materials [1,2]. The Mn^{4+} emission wavelengths in some fluorides [3–6] are close to that of Y_2O_3:Eu^{3+}, which is the current commercial red phosphor used in fluorescent lighting. (The Mn^{4+} emission wavelength in Na_2SiF_6 is 617 nm [5], compared with 611 nm for Y_2O_3:Eu^{3+}.) Therefore, Mn^{4+} has the potential to replace the more expensive Eu-activated red phosphors. However, the fluorides are not stable in the mercury vapor environment, which is present in fluorescent lamps. Many Mn^{4+} activated oxides are stable in mercury environment but their emission wavelengths are relatively too long compared to that of Y_2O_3:Eu^{3+}. The shortest reported Mn^{4+} emission wavelength in oxides is 648 nm for $Y_2Sn_2O_7$ [7]. It is important to note that human eye sensitivity to red light decreases rapidly when the emission wavelength goes above 611 nm (by more than 60% from 611 to 648 nm). Hence, the currently known Mn^{4+} activated oxide phosphors are inefficient for general lighting.

Mn can assume many oxidation states, such as 2+, 3+, 4+, and 5+, depending on the chemical environment of the Mn ion. An Mn ion usually assumes the 4+ oxidation state when it is located on an octahedral site in solids because the octahedral crystal field creates a large energy gap between the occupied t_{2g} and the empty e_g orbitals in Mn^{4+} [2]. The emission spectrum of Mn^{4+} typically shows a sharp line corresponding to the $^2E_g \rightarrow {}^4A_{2g}$ transition. The variation in the Mn^{4+} emission energies in different materials is attributed to different hybridization strength between Mn^{4+} and its ligands [1,2,8]. Weaker Mn^{4+}-ligand hybridization usually lead to higher emission energy (or shorter emission wavelength). Substitutional Mn^{4+} on large cation sites usually forms long Mn^{4+}-ligand bond, resulting in relatively weak hybridization and high emission energy. A recent study further shows that bond angle distortion around the Mn octahetral site significantly decreases the Mn^{4+}-ligand hybridization, thereby increasing the emission energy [2]. This explains, for instance, why the Mn^{4+} emission energies in pyrochlore oxides (with significant bond angle distortion in MnO_6 octahedra) are generally higher than those in perovskite oxides (with no or small bond angle distortion in MnO_6 octahedra). $Y_2Sn_2O_7$, which is the oxide with shortest reported Mn^{4+} emission wavelength [7], is a pyrochlore oxide.

Pyrochlore oxides are a large family of oxides with general formula of $A_2B_2O_7$ (space group Fd-3m) [9]. Fig. 1 shows the structure of rare-earth pyrochlore oxides ($A_2^{3+}B_2^{4+}O_7^{2-}$), where the A-site contains the large rare-earth cations (*RE*$^{3+}$) and the B-site consists of smaller (e.g., Sn^{4+}, Zr^{4+}, Hf^{4+}), higher-valence cations. The larger *RE*$^{3+}$ cations are eight-fold coordinated with oxygen and located within a distorted cubic polyhedron. The smaller B^{4+} cation is six-fold-coordinated with oxygen and located in a distorted octahedron, which is illustrated in Fig. 1.

This work employs density functional calculations [10] to show how the different sizes of the *RE*$^{3+}$ cation in rare-earth hafnate, zirconate, and stannate pyrochlore oxides ($RE_2Hf_2O_7$, $RE_2Zr_2O_7$, and $RE_2Sn_2O_7$) affect the local structure of the distorted MnO_6 octahedron, the Mn–O hybridization, and the Mn^{4+} emission

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http://dx.doi.org/10.1016/j.jlumin.2014.08.038
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energy. There are many rare-earth pyrochlores. Here, only those with large-sized tetravalent ions (i.e., Hf^{4+}, Zr^{4+}, and Sn^{4+}) are chosen since these ions, when substituted by Mn^{4+}, allow relatively long Mn–O bond length, which results in weak Mn–O hybridization and high Mn^{4+} emission energy. (The ionic radii of Hf^{4+}, Zr^{4+}, and Sn^{4+} are 0.85 Å, 0.86 Å, and 0.83 Å, respectively, much larger than that of Mn^{4+}, which is 0.67 Å [11].) The emission energies of a large number of Mn^{4+} doped rare-earth pyrochlores are found to be higher than those currently known for Mn^{4+} doped oxides and should be closer to that of Y_2O_3:Eu^{3+}.

2. Computational details

In this work, density functional theory (DFT) with standard Perdew–Burke–Ernzerhof (PBE) [12] is used to study the Mn^{4+} emission in rare-earth pyrochlore oxides. Since the $^2E_g \rightarrow {}^4A_{2g}$ emission at Mn^{4+} involves only a spin flip, the Mn^{4+} emission energy is calculated by taking the energy difference between the low- and the high-spin states of Mn^{4+}:

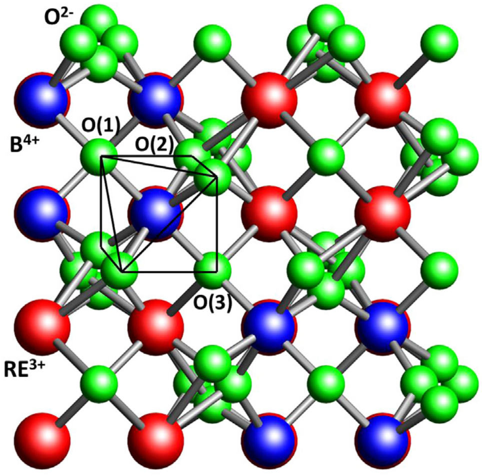

Fig. 1. Structure of rare-earth pyrochlore oxides ($RE_2B_2O_7$).

$$\Delta E_{em} = E(1\mu_B) - E(3\mu_B), \qquad (1)$$

where $E(1\mu_B)$ and $E(3\mu_B)$ are the total energies of structurally relaxed low-spin ($1\mu_B$) and high-spin ($3\mu_B$) states of Mn^{4+} [2].

DFT is a ground-state single-particle theory, which in principle is incapable of calculating the transition energy between multi-electronic states. The calculated Mn^{4+} emission energies based on DFT–PBE method have been found to be significantly lower than those measured experimentally, as expected [2]. However, PBE calculations can efficiently screen a large number of materials. More importantly, PBE calculations of a large number of oxide and fluoride hosts have been shown to produce a trend of Mn^{4+} emission energies consistent with the experimental results (see Ref. [2] for details). The reason is that the variation of the Mn^{4+} emission energy in different hosts is caused by the different Mn-ligand hybridization strengths [1,2,8], which can be distinguished by DFT–PBE calculations. Therefore, although calculating Eq. (1) using the DFT–PBE method cannot give the correct Mn^{4+} emission energy, it produces a correct trend, which can be used for predicting Mn^{4+} emission energies in new oxide materials. For example, one can identify new Mn^{4+} doped oxides with emission energies that are higher than those currently known and closer to that of Y_2O_3:Eu^{3+}, as has been done in Ref. [2].

All the calculations were performed using the VASP codes [13,14]. The electron–ion interactions were described using projector augmented wave potentials [15,13]. The 4f electrons of the rare-earth cations are frozen in the core because the 4f states are highly localized and have little interaction with valence states. The valence wavefunctions were expanded in a plane-wave basis with cut-off energy of 400 eV. All the atoms were relaxed to minimize the Feynman–Hellmann forces to below 0.02 eV/Å. The previously calculated structures of rare-earth titanate pyrochlores, which

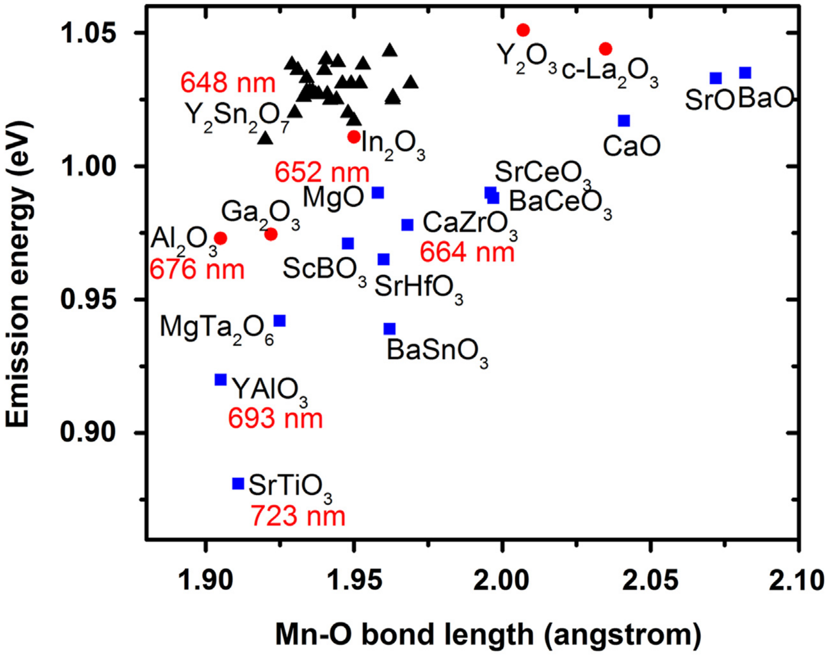

Fig. 2. PBE-calculated Mn^{4+} emission energies as functions of Mn–O bond length for oxides. The Mn–O bond length is the average over the six Mn–O bond lengths in the MnO_6 octahedron. The experimental values are shown (in red) wherever available (i.e., for $SrTiO_3$, $YAlO_3$, Al_2O_3, $CaZrO_3$, MgO, and $Y_2Sn_2O_7$). Some of the materials shown in the figure have no or small ($< 2°$) O–Mn–O bond angle distortion (blue squares) while some other have relatively large ($> 4°$) O–Mn–O bond angle distortion (red circles and black triangles). Black triangles represent pyrochlore oxides, which are shown in more details in Fig. 3. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)