Blue and red up-conversion light emission in Tm-doped A₂B₂O₇ oxides

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Abstract

The crystal structure and light emission property of Yb/Tm doped gadolinium titanate and gadolinium zirconate with chemical composition of A₂B₂O₇ were studied by x-ray diffraction (XRD) and optical spectroscopy measurements, respectively. XRD results suggest that the rare earth titanates have an ordered pyrochlore structure and a defect-fluorite structure for the zirconates. Photoluminescence activated with 1064 nm infrared laser light shows different light emission behaviors for the titanate and zirconate samples, which is related to the different site occupancy of Tm³⁺ in the lattice of the samples. Only a weak near-infrared (NIR) (~800 nm) light emission was observed in the titanate samples while a strong blue and red up-conversion emission was detected in the Tm³⁺-doped zirconate samples. The strong blue and red emission is due to the 7-fold coordinated Tm³⁺ in the structure.

KEY WORDS: light emission, pyrochlore, defects

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Introduction

The outside shell electrons of rare earth elements have very rich energy levels because of their unfilled 4f orbits. By absorbing external energy, the electrons can be easily activated to higher level orbits and jump back to ground state or lower energy levels via emission of light. Rare earth elements play a key role in various fluorescent materials. Upon the activation source, they can be divided as photon-activated, electron-activated, x-ray activated and electron field activated [1-3] **phosphors**. The photon-activated fluorescence has been widely investigated before [1-2, 4-8] and both down-conversion and up-conversion processes have been observed. Up-conversion is a multi-photon process, which the host material absorbs low energy photons (usually IR) and emits light in the visible frequency range [9-13]. It is expected that up-conversion has great application in solar cell and other photo-electron conversion devices. It was reported that the quantum efficiency can be enhanced by ~2.5% for a Si-solar cell when NaYF₄:Er³⁺ up-conversion layer was coated [14].

Up-conversion light emission is a multiple photon process, and the effect of different **dopants** and **the** size of crystallites in various insulators have been broadly reported before [15-18]. However, there are seldom reports on the effect of **atomic-level defects (point defects)** and occupancy **of rare earth elements** in host materials on the light emission behaviors. In this letter, doping **of** rare earth elements in materials with similar **crystal** structures and the effect of defects on the light emission in atomic scale were investigated.

Rare earth titanates and zirconates with chemical composition of A₂B₂O₇ have two **closely** relevant structures—pyrochlore and defect-fluorite [19, 20]. Most rare earth titanates RE₂Ti₂O₇ have the pyrochlore structure. The ideal pyrochlore **structure** is an ordered state with space group

of Fd-3m, and cations RE^{3+} and Ti^{4+} reside on the A- and B-site (*16d* and *16c*), respectively, and the two anion sites (*8b* and *48f*) are also fully occupied (Fig.1a). The A-site cations are 8-fold coordinated with oxygen and usually occupied by larger cations, like rare earth elements. The B-site is 6-fold coordinated with oxygen and usually occupied by cations with smaller size, like transition metals. When the size difference of cations between the A- and B-site is not so distinct, the two cations have chance to swap their sites in the lattice, which yields cation anti-site defects. If the size of cations on A- and B-sites is comparable ($r_A/r_B < 1.46$), the pyrochlore structure is not stable and a defect-fluorite structure becomes favorable [21]. The defect-fluorite structure has a space group of Fm-3m and the lattice parameter is half of that of pyrochlore. In the fluorite structure, there is only one cation and one anion site (*4a* and *8c*) in the unit cell, and both cations are randomly distributed on the *4a* site. Since there is one-eighth oxygen missing from the standard fluorite AX_2 , oxygen vacancies in the fluorite are also randomly distributed on the anion site (Fig. 1b). The structural transformation from pyrochlore to defect-fluorite is an order-disorder transition process, which accompanies distinct changes in physical properties, such as the compressibility and ionic conductivity [22-24]. The order-disorder transition in $\text{A}_2\text{B}_2\text{O}_7$ oxides can be realized by various factors, such as chemical doping [25], treatment by high temperature [26], high pressure [29-30] and high energy ion irradiation [31-33]. Phase stability of $\text{A}_2\text{B}_2\text{O}_7$ compounds at extreme conditions and the associated property changes have been intensively reported before [34-36], however, the associated light emission behavior has not been studied. The cations on the A- and B-site in the structure have different bonding environments (8- and 6-fold coordination) and the corresponding crystal field is thus different. It is expected that the doped rare earth elements will show different light emission behaviors when they occupy the A- or B-sites in these compounds. In this paper, the light emission from Tm^{3+}

ions doped in pyrochlore $(\text{GdYb})_2\text{Ti}_2\text{O}_7$ and defect-fluorite $(\text{GdYb})_2\text{Zr}_2\text{O}_7$ was studied with a 1064 nm infrared (IR) laser as the activation source, and the corresponding light emission mechanisms were also discussed.

Experimental Details

All the doped samples were prepared by conventional high-temperature solid-state reaction method. The starting powders of Ti_2O_3 , Yb_2O_3 , TiO_2 and ZrO_2 are from Alfa Aesar with purity of more than 99.5%. The Gd_2O_3 powder is from MTI with purity of 99.9%. Weighted powders in the desired chemical composition of $(\text{Gd}_{0.98-x}\text{Yb}_x\text{Ti}_{0.2})_2\text{Ti}_2\text{O}_7$, and $(\text{Gd}_{0.98-x}\text{Yb}_x\text{Ti}_{0.2})_2\text{Ti}_2\text{O}_7$ ($x=0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5$) were well mixed in a mortar with acetone as the medium. The mixed powder was pressed into half inch diameter pellets by using a hydraulic press and then heat treated at 1300 °C for 15 hours in air. In order to enhance the homogeneity, the pellets were ground into powder and reshaped, and finally heated at 1500 °C for another 15 hours. The structure of the synthetic samples was checked with a lab x-ray diffraction machine (Rigaku MiniFlex). The crystal structure and lattice parameters of the synthetic samples were analyzed through full pattern fitting with Rietveld refinement method by using program Fullprof [37]. The light emission was measured with a Raman facility SPEX-1250M, which is modified by changing the visible light beam splitter with a 1064 nm dichroic beam splitter in the system. An IR laser (YAG: 1064 nm) was used as the activation light source. The power of the IR laser shooting on the sample is less than 200 mW. The emission light was collected with a liquid nitrogen cooled CCD detector. The CCD detector (Symphony, Horiba Jobin Yvon) has good quantum yield efficiency to collect light from near UV to near infrared region (400-1100 nm).

Results and Discussion

Pyrochlore and defect-fluorite have very similar structural characters. Both are in cubic symmetry. Fig. 1 illustrates the local bonding environments of the two structure types. Generally, pyrochlore can be regarded as a 2×2 superstructure of the defect-fluorite if the cation antisite defects in the latter are not considered. In pyrochlore structure, the larger rare earth cations and smaller transitional cations occupy the A- and B-sites respectively, which has different coordination numbers (8 and 6) with oxygen. In the defect-fluorite structure, all the cations share to occupy the same cationic site. Since the chemical composition of $(A/B)_4O_7$ has 1/8 less anion from the ideal fluorite, the anion vacancy is randomly distributed in the lattice and all the cations have 7-fold coordination with oxygen. Previous experiments suggested that all rare earth titanates have the ordered pyrochlore structure and rare earth zirconates can crystallize in either pyrochlore or fully disordered defect-fluorite structure depending on the size ratio of cations A and B and their thermal histories. Fig. 2 shows the XRD patterns of the prepared samples. All the titanates have the pyrochlore structure and the defect-fluorite structure for the zirconates. Comparing the XRD patterns of the two different compounds, all the main diffraction peaks are the same, but titanates have more weak diffraction peaks than those of the zirconates, which suggest that pyrochlore is a superstructure of the fluorite. The cations in titanates with pyrochlore structure are ordered and all rare earth ions occupy the A-site only, including the doped Tm^{3+} . There is one sole cation site in the fluorite structure, so all the cations in zirconates are disordered. Tm^{3+} cations are randomly distributed on the cationic site and share with Gd^{3+} , Yb^{3+} and Zr^{4+} . To anion sublattice in zirconates, the anion vacancy is also evenly distributed in the structure. The diffraction maxima of both titanates and zirconates shift to larger 2θ angles with the increase of doped Yb^{3+} because of the smaller size of Yb^{3+} compared with Gd^{3+} . Rietveld

analysis indicated that the lattice parameter decreased by 2.1% and 2.2%, respectively, when 50% Yb^{3+} cation doped in Gd-Ti-O and Gd-Zr-O systems.

It is interesting that the samples show different light emission behavior with IR laser light irradiation. Upon 1064 nm IR laser excitation, titanate samples show only weak NIR emission at around 800 nm (Fig. 3). In addition, IR emission with wavelength above 900 nm was also detected. The light emission behavior of zirconate samples irradiated with 1064 nm IR light is different, and a red and blue light emission is detected in the visible light range, which is even observable with naked eyes in dark. Fig. 4 shows the measured emission spectrum from zirconates. Besides the similar NIR emission with titanates at ~ 800 nm, a strong blue emission with wavelength of 460-490 nm and a red emission centered at 655 nm were detected. The red emission peak is sharp and the blue emission band contains several peaks with slightly different wavelength.

To most up-conversion light emission, combination of two different ions, such as $\text{Yb}^{3+}/\text{Tm}^{3+}$, or $\text{Yb}^{3+}/\text{Er}^{3+}$ is usually required. The active light has a photon energy (usually with wavelength 980 nm) slightly higher than the energy gaps of Yb^{3+} , and Yb^{3+} ions absorb laser energy through a multi-photon process, and a final up-conversion light emission occurs through energy transfer from Yb^{3+} ions to Tm^{3+} or Er^{3+} . In our study, the laser light have a wavelength of 1064 nm, and the photon energy is less than the energy gaps of Yb^{3+} , and Yb^{3+} thus does not act as a laser absorber. However, doping of Yb^{3+} in the zirconate samples can change the crystal structure from the ordered pyrochlore to a disordered defect-fluorite structure. A pyrochlore structure was formed in the titanate samples because the size of Ti^{4+} cation is much smaller than that of rare earth elements, and all Tm^{3+} occupy the A-site (16d) only. Our previous experiments [22, 29] have revealed that undoped $\text{Gd}_2\text{Zr}_2\text{O}_7$ sample crystallized in a pyrochlore structure and

the degree of structural disordering depends on the sampling history. Since Yb^{3+} has smaller size than Gd^{3+} , the doping of Yb^{3+} in $\text{Gd}_2\text{Zr}_2\text{O}_7$ can further decrease the size difference (r_A/r_B) between cations. In this study, the zirconates all have a defect fluorite-type structure when Yb^{3+} cations are doped. In the fluorite-type structure, Tm^{3+} cations randomly occupy both cationic sites and are 7-fold coordinated with oxygen. That is why we observe a similar blue and red emission in Yb^{3+} -free zirconate sample. Compared with the Yb^{3+} -doped zirconates, there are some small differences in the Yb^{3+} -free sample, such as no weak shoulder at 495 nm (blue region), the red emission has lower intensity and the NIR region has no double bands. These may be related to Yb^{3+} ions in the samples which need to be further identified.

Fig. 5 shows the schematic energy levels of Tm^{3+} and possible energy transfer mechanisms for both titanates and zirconates are illustrated. Since all the observed emission light has energy higher than that of the IR laser we used, the Tm^{3+} ions must be activated to high energy levels through self-multi-photon processes. The energy transfer process in titanates is shown in Fig 5a. In titanate samples, Tm^{3+} ions first absorb laser energy to level of $^3\text{H}_5$, then absorb another laser photon to levels of $^3\text{F}_2/^3\text{F}_3$. Since no red emission ($^3\text{F}_2/^3\text{F}_3 \rightarrow ^3\text{H}_6$) was observed in titanates, the $^3\text{F}_2/^3\text{F}_3$ electrons must release the energy through intermediate levels. The ~800 nm emission is from the relaxation of $^3\text{H}_4 \rightarrow ^3\text{H}_6$. The energy transfer of $^3\text{F}_2/^3\text{F}_3 \rightarrow ^3\text{F}_4$ may occur, which emits light with wavelength more than 900 nm and is not our interest. In zirconates, since blue light emission is observed, the electrons must be further activated to higher energy levels, such as $^1\text{G}_4$ and $^1\text{D}_2$ through multi-photon processes (Fig. 5b). The blue light emission (460 nm – 490 nm) comes from the energy transfer of $^1\text{D}_2 \rightarrow ^3\text{F}_4$ and $^1\text{G}_4 \rightarrow ^3\text{H}_6$. Different from titanates, the electrons can release energy from $^3\text{F}_2/^3\text{F}_3$ orbits and transform directly to the ground level of $^3\text{H}_6$ and emit red light (655 nm). The ~ 800 nm NIR light emission in both titanate and zirconate

samples have similar mechanism, but multi channels may exist in the latter, such as $^1D_2 \rightarrow ^3F_2$ and $^1G_4 \rightarrow ^3H_5$. The ~800 nm NIR emission in zirconate samples has much stronger intensity which also suggests the emission is from different high energy levels.

The different light emission behaviors from titanates and zirconates upon IR irradiation originate from the different bonding environment of Tm^{3+} in the samples which were determined by their crystal structures. In titanates with pyrochlore structure, all the rare earth cations Gd^{3+} , Yb^{3+} and Tm^{3+} occupy the A-site (*16d*) which is 8-fold coordinated with oxygen, while Ti^{4+} occupy the B-site. The outside electrons of Tm^{3+} can only absorb double photons and emit the ~800 nm NIR light with relatively weak intensities. In zirconates, the structure is defect-fluorite and all the cations share to occupy the same cationic site (*4a*) and are 7-fold coordinated with oxygen. Since there are more defects, especially cation sublattice, in the zirconate samples, the electrons can easily absorb photons and be activated to higher energy orbits through multi-photon processes, and emit also blue and red light during relaxation.

Summary

The light emission in Tm^{3+} -doped Gd/Yb-titanates and Gd/Yb-zirconates was studied by 1064 nm IR laser irradiation. Both samples have NIR emission with wavelength ~800 nm. Zirconates show strong blue and red light emission which comes from the relaxation of electrons from high energy levels. The different light emission behavior originates from the different bonding environments and crystal structures. In titanates with pyrochlore structure, Tm^{3+} can only occupy the A-site, which is 8-fold coordinated and there is less defects in the structure. In zirconates with defect-fluorite structure, however, Tm^{3+} ions occupy the unique cation site which is 7-fold coordinated with oxygen, and there are more defects for both the cation and anion sublattice. The

defect in the structure is favorable for the activation of electron to different higher energy levels through multi-photon absorption processes. The strong blue and red light emission from zirconate samples came from the relaxation of those high energy orbits to lower energy orbits.

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Figure Captions

Fig. 1 Schematic crystal structures (a) Ordered pyrochlore structure for titanates, all the larger cations $Gd^{3+}/Yb^{3+}/Tm^{3+}$ occupy the larger A-site (16d) with 8-fold coordination with oxygen. The smaller Ti^{4+} cation occupies the B-site (16c) and is 6-fold coordinated. The red and white spheres represent oxygen atoms on the 48f and 8b sites, respectively; (b) Defect fluorite structure for zirconate samples, all the cations of $Gd^{3+}/Yb^{3+}/Tm^{3+}$ occupy the unique cation site with 7-fold coordination

Fig. 2 XRD patterns for samples (a) $(Gd_{0.98-x}Yb_xTm_{0.02})_2Ti_2O_7$ and (b) $(Gd_{0.98-x}Yb_xTm_{0.02})_2Zr_2O_7$. All the Ti-based samples have a pyrochlore structure and Zr-based samples are in the fluorite-type structure.

Fig. 3 Light emission spectrum of $(Gd_{0.98-x}Yb_xTm_{0.02})_2Ti_2O_7$ activated by 1064 nm laser. The NIR light with multi-peaks has weak intensity compared to the corresponding zirconate samples

Fig. 4 Light emission spectrum of $(Gd_{0.98-x}Yb_xTm_{0.02})_2Zr_2O_7$ activated by 1064 nm IR laser. Three strong bands are observable (a) blue; (b) red and (c) NIR.

Fig. 5 Tm^{3+} energy levels and light emission mechanisms. (a) The case of Tm^{3+} in titanate samples and only ~800 nm light emission through double photon absorption can occur; (b) Light emission in zirconate samples. Electrons can be activated to higher energy levels through multi-photon processes, blue, red and NIR light emission can occur during the relaxation of electrons from those high energy levels.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5