Deep-red emission of Mn^{4+} and Cr^{3+} in $(\text{Li}_{1-x}\text{A}_x)_2\text{MgTiO}_4$ (A = Na and K) phosphor: Potential application as W-LED and compact spectrometer

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Abstract

Mn^{4+} doped and $\text{Mn}^{4+}/\text{Cr}^{3+}$ co-doped alkali metal titanate phosphors have been prepared by solid state reaction method. A part of Li^+ ions in the $\text{Li}_2\text{MgTiO}_4$: Mn^{4+} are substituted with Na^+ and K^+ ions and consequently the intensity of Mn^{4+} emission at 678 nm is enhanced by 1.7 and 2.5 times, respectively. In the $\text{Mn}^{4+}/\text{Cr}^{3+}$ co-doped $(\text{Li}_{0.95}\text{K}_{0.05})_2\text{MgTi}_{0.999}\text{O}_4$, both emission of Cr^{3+} at 726 nm and emission of Mn^{4+} at 678 nm of Mn^{4+} are observed. It is interesting to find that the intensity ratio of 726 nm to 678 nm emissions in the $\text{Mn}^{4+}/\text{Cr}^{3+}$ phosphor continually increases with excitation wavelength increasing from 290 nm to 455 nm, which means that the intensity ratio in turn can be used to identify the excitation light wavelength. This refers a possible approach to design novel compact light-wavelength detector or spectrometer based on the phosphor. The mechanism of Na^+ or K^+ substitution induced luminescence enhancement in the Mn^{4+} phosphor and the competition between the Cr^{3+} and Mn^{4+} emissions in the $\text{Mn}^{4+}/\text{Cr}^{3+}$ co-doped has been discussed.

Keywords

Deep-red phosphors; Light-wavelength detector;
Spectrometer; W-LED; $\text{Li}_2\text{MgTiO}_4$

1. Introduction

White light-emitting diodes (W-LED) have been extensively regarded as the new generation of solid-state lightings, attracted substantial attentions due to their many advantages such as high efficiency, life-durable, compactness, low energy consumption, high reliability, good stability and environmental friendliness properties [1-7]. Currently, the leading commercial W-LEDs are achieved by combination of InGaN blue-emitting LED chip with a yellow phosphor (YAG: Ce^{3+}) packed on the chip surface using epoxy resin or silicone [8-10]. However, in practical applications, w-LEDs fabricated by this method do not reach the optimal requirements for white light due to some deadly weaknesses, such as low color rendering index and high color correlated temperature caused by the innate deficiency in the red spectral region [7, 11]. Thus, it is quite important to find a suitable red phosphor which can convert blue light into long wavelength region with high efficiency in order to improve the aforementioned weaknesses and attain the

optimal quality requirements for W-LEDs.

Recently, rare-earth (RE) elements, in particular Eu^{2+} or Ce^{3+} , are widely used in the outstanding red emitting phosphors and meet the actual requirement of practical application, such as $\text{Sr}_2\text{Si}_5\text{N}_8: \text{Eu}^{2+}$ [12], $\text{M}[\text{Mg}_3\text{SiN}_4]: \text{Eu}^{2+}/\text{Ce}^{3+}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Eu}$) [13], $\text{CaAlSiN}_3: \text{Eu}^{2+}$ [14], $\text{BaCa}_2\text{Y}_6\text{O}_{12}: \text{Eu}^{3+}, \text{Dy}^{3+}$ [15] and $(\text{SrCa})\text{AlSiN}_3: \text{Eu}^{2+}$ [16]. However, besides the high-cost, rare-earth (RE) elements, especially europium, usually have strong photon re-absorption in green or yellow spectral region due to the 4f-5d transitions and synthesis of most nitride phosphors requires extremely high temperature, high pressure reaction condition and harsh synthesis procedures [17]. Therefore, it is necessary to develop new red phosphors without RE elements that can be produced by simple synthesis process for the future W-LED market.

As a non-rare-earth activator, Mn^{4+} or Cr^{3+} doped phosphors with broad band excitation and deep-red narrow band emission may be an alternative choice. $^4\text{A}_2 - ^4\text{T}_1$ and $^4\text{A}_2 - ^4\text{T}_2$ transitions in Cr^{3+} or Mn^{4+} in octahedral coordination environment exhibit respective near UV and visible light absorption, so that the luminescence of Cr^{3+}

or Mn^{4+} doped phosphors is always dominated by the spin-forbidden transition (${}^2\text{E}_g - {}^4\text{A}_{2g}$) under near UV or blue light excitation. Recently Cr^{3+} or Mn^{4+} -doped crystals have been drawing attention as candidate materials for the red phosphor used in W-LEDs.

According to Tanabe–Sugano diagram, the Cr^{3+} and Mn^{4+} emission is almost independent on the crystal field splitting but is significantly influenced by different host lattice ^[7]. For Cr^{3+} or Mn^{4+} activated oxide phosphors, aluminates are investigated as major hosts such as $\text{MgAl}_2\text{O}_4\text{:Cr}^{3+}$ ^[18], $\text{SrMgAl}_{10}\text{O}_{17}\text{:Mn}^{4+}$, M ($\text{M} = \text{Li}^+$, Na^+ , K^+ , Cl^-) ^[19], $\text{Sr}_4\text{Al}_{14}\text{O}_{25}\text{:Mn}^{4+}$ ^[20], $\text{CaAl}_4\text{O}_7\text{:Mn}^{4+}$ ^[21] and $\text{Y}_3\text{Al}_{5-x}\text{Ga}_x\text{O}_{12}\text{:Cr}^{3+}$ ^[22] so far. Whereas titanates can be treated as a potential host group for Mn^{4+} substitution because of suitable characteristics, that is, the similarity of ionic radius between Ti^{4+} (60.5 pm) and Mn^{4+} (53 pm) and non-necessity of substitution for charge compensation owing to the same oxidation number. Recently, some Mn^{4+} -activated titanates are reported as phosphors, for example, $\text{Mg}_2\text{TiO}_4\text{:Mn}^{4+}$ ^[23], $\text{La}_2\text{MTiO}_6\text{:Mn}^{4+}$ ($\text{M} = \text{Mg}$ and Zn) ^[24], $\text{Li}_2\text{TiO}_3\text{:Mn}^{4+}$ ^[25] and $\text{Gd}_2\text{ZnTiO}_6\text{:Mn}^{4+}$ ^[26]. Thus, it is of great significance to incorporate Mn^{4+} ions

into titanate hosts with abundant octahedral sites and to gain insight into what influences and determines the emission of Mn^{4+} [7].

Considering that $\text{Li}_2\text{MgTiO}_4$ with rock salt structure type contains three types of octahedral sites ($[\text{TiO}_6]$, $[\text{MgO}_6]$ and $[\text{LiO}_6]$) and can be synthesized easily with cheap raw materials. In this work, Mn^{4+} doped and $\text{Mn}^{4+}/\text{Cr}^{3+}$ co-doped $\text{Li}_2\text{MgTiO}_4$ was prepared by a conventional solid-state reaction method in air atmosphere. A part of the Li^+ ions were tried to be substituted with other alkaline metal ions (Na^+ or K^+), in order to enhance the luminescence efficiency and improve the excitation properties. Meanwhile, the luminescence properties the $\text{Mn}^{4+}/\text{Cr}^{3+}$ co-doped phosphor have also been investigated.

2. Experimental

A series of $(\text{Li}_{1-x}\text{A}_x)_2\text{MgTi}_{0.999-y}\text{O}_4:0.001\text{Mn}^{4+}, y\text{Cr}^{3+}$ ($\text{A} = \text{Na}, \text{K}$ and $x = 0 - 0.1$, $y = 0 - 0.012$) phosphors samples were synthesized by a traditional high temperature solid-state reaction method with Li_2CO_3 , K_2CO_3 , Na_2CO_3 , MgO , TiO_2 , Cr_2O_3 and MnCO_3 as starting materials. All the chemicals used in the experiments were of analytical reagent (AR) grade. Stoichiometric

amounts of raw materials were weighed according to the chemical proportion of $(\text{Li}_{1-x}\text{A}_x)_2\text{MgTi}_{0.999-y}\text{O}_4: 0.001\text{Mn}^{4+}, y\text{Cr}^{3+}$ ($\text{A} = \text{Na}, \text{K}$ and $x = 0 - 0.1$, $y = 0 - 0.012$) with thoroughly mixed and ground to fine particle in an agate mortar. Subsequently, the mixtures were filled in corundum crucibles and preheated at 1000 °C for 4 h under air atmosphere, and then cooled down naturally to room temperature. After the reactants were milled again to improve the homogeneity, they were heated up to 1300 °C and held for 2 h in air atmosphere. Finally, the samples were cooled down to room temperature naturally for further characterization.

The crystalline phases of the phosphors were identified by a D/MAX 2500 X-ray diffract (XRD) meter using Cu tube with $\text{K}\alpha$ radiation in the 2θ range of $20^\circ \sim 90^\circ$. The excitation and emission spectra were obtained by a monochromator (Zolix Instrument, Omni- λ 320i) coupled with photomultiplier (PMTH-S1-CR131), which is equipped with a 150 W xenon lamp as the excitation source. The luminescence decay curves were measured by PTI QM 40 spectrofluorometer using a pulse xenon lamp as the excitation source. The temperature dependent

photoluminescence spectra of the phosphors under 470 nm excitation were measured with an FLS920 (Edinburgh) spectrometer.

3. Results and discussion

Fig. 1(a) shows the representative XRD patterns of $(\text{Li}_{0.95}\text{A}_{0.05})_2\text{MgTi}_{0.999-y}\text{O}_4: 0.001\text{Mn}^{4+}, y\text{Cr}^{3+}$ (A= Na and K, $y = 0, 0.003$ and 0.008). Pure phase $\text{Li}_2\text{MgTiO}_4$ (JCPDS#89-7118) ^[27] has a cubic rock salt structure belonging to Fm-3m (225) space group. All the diffraction peaks of as-prepared samples can be matched well with the data of pure $\text{Li}_2\text{MgTiO}_4$ and no obvious peaks of impurity phase have been observed, indicating that the doping of Mn^{4+} , Cr^{3+} and alkaline metal ions (Na^+ or K^+) into the host lattice does not cause significant influence on the host crystal structure. **Fig. 1(b)** further shows the enlarged XRD patterns of $(\text{Li}_{0.95}\text{A}_{0.05})_2\text{MgTi}_{0.999-y}\text{O}_4: 0.001\text{Mn}^{4+}, y\text{Cr}^{3+}$ (A= Na and K, $y = 0, 0.003$ and 0.008) at $2\theta = 43^\circ - 44^\circ$. The peaks at 43.46° and 43.58° correspond to the Cu-Ka1 and Cu-Ka2 ray diffractions from the (200) plane of the $\text{Li}_2\text{MgTiO}_4$, respectively. Although 5 mol% of Li^+ sites are substituted with other alkaline metal ions (Na^+ or K^+) or 0.8 mol% of Cr^{3+} ions

are incorporated in the $\text{Li}_2\text{MgTiO}_4$ powder, no shift of the diffraction peak is observed.

Fig. 2(a) shows the excitation spectra of $(\text{Li}_{0.95}\text{A}_{0.05})_2\text{MgTi}_{0.999}\text{O}_4: 0.001\text{Mn}^{4+}$ ($\text{A} = \text{Na}$ and K). When monitored at 678 nm, the excitation spectra between 250 nm and 600 nm present two peaks at about 352 nm and 470 nm assigned to the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ and ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ transitions of Mn^{4+} ions, respectively. The emission spectra exhibit a broad emission band covering from 600 to 800 nm with a maximum at 678 nm, as show in **Fig. 2(b)**. This emission is ascribed to transitions ${}^2\text{E} \rightarrow {}^4\text{A}_2$ of Mn^{4+} suited in an octahedral site. Usually the Mn^{4+} emission is composed of some distinguishable sharp R lines and Stokes/anti-Stokes side-peaks due to different vibration modes for the 3d^3 electrons when Mn^{4+} is of octahedral structure^[28-30]. However, the abnormal red emission in Mn^{4+} -doped $\text{Li}_2\text{MgTiO}_4$ phosphor shows an undistinguishable broad asymmetric band, which is rarely observed in Mn^{4+} -doped oxides. Though the Ti, Mg and Li occupy the octahedral sites in $\text{Li}_2\text{MgTiO}_4$ structure randomly, the occupancy probability of corners of a given octahedron is affected by the nearest neighbor sites. In the

$\text{Li}_2\text{MgTiO}_4$ structure, the relaxation of one set of Ti-O (Mg-O or Li-O) tends to interfere with the relaxation of the other set of Ti-O (Mg-O or Li-O). The overlap of the corresponding ions is increased, leading to the enhancement of chemical bond strength and nephelauxetic effect, which may cause the seemingly broadened emission of Mn^{4+} [7]. Although there was no peak shift in the excitation spectra for these alkaline metal-doped samples, the excitation intensity is effectively enhanced at both 352 nm and 470 nm when part of Li^+ is substituted by other alkaline metal (Na^+ or K^+). The substitution of Li^+ by other alkaline metal (Na^+ or K^+) also increases the luminescence intensity. **Fig. 2(c)** further shows the dependence of luminescence intensity on the concentration of substituted alkaline metal ions. The luminescence intensities of $(\text{Li}_{0.97}\text{A}_{0.05})_2\text{MgTi}_{0.999}\text{O}_4: 0.001\text{Mn}^{4+}$ (A = Na and K) were 1.7(Na) and 2.5(K) times higher than that of $\text{Li}_2\text{MgTi}_{0.999}\text{O}_4: 0.001\text{Mn}^{4+}$, respectively. This result suggests that the substituted Na^+ or K^+ ions might slightly change the local crystal field around Mn^{4+} ions [25], improving the luminescence properties.

The room temperature fluorescence decay curves of $(\text{Li}_{0.95}\text{A}_{0.05})_2\text{MgTi}_{0.999}\text{O}_4: 0.001\text{Mn}^{4+}$ ($\text{A} = \text{Na}$ and K) phosphors monitored at 678 nm with excitation of 470 nm are shown in **Fig. 3**. The long decay time for all the phosphors suggests that the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transition of Mn^{4+} is a spin-forbidden transition of the intra-d-shell electrons. However, it is also seen that the substitution of Li^+ sites by Na^+ or K^+ can prolong the luminescence decay time of 678 nm emissions. The average lifetime (τ_{avg}) of the Mn^{4+} emission of at 678 nm is expressed as ^[31]

$$\tau_{\text{avg}} = \frac{\int_0^\infty tI(t)dt}{\int_0^\infty I(t)dt}. \quad (1)$$

Where $I(t)$ is the time dependent luminescence intensity of $(\text{Li}_{0.95}\text{A}_{0.05})_2\text{MgTi}_{0.999}\text{O}_4: 0.001\text{Mn}^{4+}$ ($\text{A} = \text{Na}$ and K) phosphors at 678 nm. The calculated mean decay lifetimes (τ_{avg}) are also given in **Fig. 3**. Considering that the emission and excitation spectral shapes have not changed, the slightly increased τ_{avg} when a small amount of Li^+ is replaced by Na^+ or K^+ might be ascribed to the reduced non-radiative transition of Mn^{4+} . Presumably, the substituted Na^+ or K^+ ions might weaken the electron-phonon coupling strength of Mn^{4+} in the host. Thus the probability of non-radiative transition of Mn^{4+} is

reduced. Correspondingly the luminescence lifetime is prolonged and the emission at 678 nm is intensified.

In an attempt to further improve the emission intensity, Cr^{3+} ions of different concentration have also been introduced in to the newly optimized host. **Fig. 4** shows the emission and excitation spectra of the $(\text{Li}_{0.95}\text{K}_{0.05})_2\text{MgTi}_{0.999-y}\text{O}_4: 0.001\text{Mn}^{4+}, y\text{Cr}^{3+}$ ($y= 0 - 1.2\%$) phosphors. The excitation spectra of $\text{Mn}^{4+} - \text{Cr}^{3+}$ co-doped samples with various Cr^{3+} concentration monitored at 726 nm emission of Cr^{3+} are shown in **Fig. 4(a)**. All the excitation spectra by monitoring at 726 nm emission of Cr^{3+} contains three broad band with peaks located at 348 nm, 470 nm and 617 nm, which correspond to spin-allowed transitions of $^4\text{A}_{2g}(\text{F}) - ^4\text{T}_{1g}(\text{F})$, $^4\text{A}_{2g}(\text{F}) - ^2\text{T}_{2g}(\text{F})$ and $^4\text{A}_{2g}(\text{F}) - ^4\text{T}_{2g}(\text{F})$ of Cr^{3+} ions ^[32], respectively. It is found that the excitation intensity of Cr^{3+} increases with the increase of Cr^{3+} concentration. The excitation spectra of $\text{Mn}^{4+}/\text{Cr}^{3+}$ co-doped $(\text{Li}_{0.95}\text{K}_{0.05})_2\text{MgTiO}_4$ with various concentration of Cr^{3+} monitored at 678 nm emission of Mn^{4+} are also measured and shown in **Fig. 4(b)**. The excitation bands located at 352 nm and 470 nm are ascribed to $^4\text{A}_{2g} - ^4\text{T}_{1g}$ and $^4\text{A}_{2g} - ^4\text{T}_{2g}$ spin-allowed

transitions ^[33] of Mn⁴⁺ ions, respectively. The excitation intensity of Mn⁴⁺ decreases with the increasing concentration of Cr³⁺.

All the emission spectra of the Mn⁴⁺/Cr³⁺ co-doped phosphors under 470 nm excitation share the similar spectral profile with two conjoint emission bands centered located at 678 nm (Mn⁴⁺: ²E_g – ⁴A_{2g}) and 726 nm (Cr³⁺: ²E_g(G) – ⁴A_{2g}(F)), respectively, as shown in **Fig. 4(c)**. The integrated intensity of the 678 nm emission slightly decreases while the integrated intensity of the 726 nm emission continues to increase with the increasing concentration of Cr³⁺. It is found that the Cr³⁺ and Mn⁴⁺ luminescence centers give almost the same intensity at Cr³⁺ concentration of 0.8%.

The increase of excitation and emission intensity of Cr³⁺ with its concentration increasing is easy to understand, since the enhanced Cr³⁺ concentration increases the number of luminescence center of Cr³⁺. On the other hand, the decreased Mn⁴⁺ excitation and emission at higher Cr³⁺ concentration suggests that the co-doped Cr³⁺ leads to the luminescence quenching of Mn⁴⁺. However, the total integrated intensity in the region of 600 - 750 nm slightly

increases with the increasing concentration of Cr^{3+} , as shown in the insert of **Fig. 4(c)**. Unfortunately, the increased total emission intensity appears to be no advantage in W-LED application because the wavelength of the enhanced Cr^{3+} emission is too long and thus the luminous flux constantly decreases with Cr^{3+} concentration increasing. Nevertheless the enhanced total luminescence intensity of the phosphor is still of great significance because it may meet other applications such as solar cells.

It is noted that there is overlap between the excitation bands of Mn^{4+} and Cr^{3+} ions. Especially, both Cr^{3+} and Mn^{4+} have a strong excitation peak at about 470 nm, as shown in **Fig. 5**. Obviously there exists a competition between the increased Cr^{3+} emission and the quenched Mn^{4+} emission in the $\text{Mn}^{4+}/\text{Cr}^{3+}$ co-doped phosphors when excited at 470 nm. Although the Mn^{4+} emission intensity tends to decrease with Cr^{3+} concentration increasing, the emission intensity of Cr^{3+} increases and this increase exceeds the reduction of the Mn^{4+} emission. Resultantly the total emission intensity is still enhanced with Cr^{3+} concentration increasing.

To understand the interaction between the Mn^{4+} and Cr^{3+} ions, the decay curves monitoring at 678 nm emission of Mn^{4+} for the $(\text{Li}_{0.95}\text{K}_{0.05})_2\text{MgTi}_{0.999-y}\text{O}_4: 0.001\text{Mn}^{4+}, y\text{Cr}^{3+}$ ($y = 0.0\%, 0.1\%, 0.3\%, 0.5\%, 0.8\%$ and 1.0%) phosphors excited at 470 nm are also measured, as show in **Fig. 6**. It is seen that the luminescence lifetime of 678 nm emission decreases with the Cr^{3+} concentration increasing. The average lifetimes have been calculated according to Eq. (1) and given in **Fig. 6**. The average lifetime decreases monotonously from 420us to 309us with the increase of the doping concentration of Cr^{3+} , which manifests that the introduced Cr^{3+} ions accelerate non-radiative energy migration among the doped ions and thus cause the non-radiative quenching of Mn^{4+} luminescence, shortening the average lifetime and reducing the intensity of Mn^{4+} emission.

To further explore the luminescence properties of the phosphors of double luminescence centers, the emission spectra for the $(\text{Li}_{0.95}\text{K}_{0.05})_2\text{MgTi}_{0.991}\text{O}_4: 0.001\text{Mn}^{4+}, 0.008\text{Cr}^{3+}$ are measured excited with different wavelength. **Fig. 7** gives the emission spectra of $(\text{Li}_{0.95}\text{K}_{0.05})_2\text{MgTi}_{0.991}\text{O}_4: 0.001\text{Mn}^{4+}, 0.008\text{Cr}^{3+}$ excited at

several typical wavelengths. It is found that with the change of excitation wavelength, the relative integrated intensity of the Cr^{3+} emission (726 nm) and Mn^{4+} emission (678 nm) is also changed. The reason lie in that the difference of the excitation spectra of Cr^{3+} and Mn^{4+} , just as shown in **Fig. 5**. The integrated intensity ratio(R) of the Cr^{3+} emission peaking at 726 nm to Mn^{4+} emission peaking at 678 nm for different excitation wavelength is carefully calculated. **Fig. 8** shows the dependence of the integrated intensity ratio R on the excitation wavelength (290 nm – 455 nm). It is interesting to find that with excitation wavelength increasing from 290 nm to 455 nm, the integrated intensity ratio R monotonically increases. This means that by measuring the emission intensity at 726 nm and 678 nm and calculating their integrated intensity ratio, in turn the excitation wavelength can be conveniently identified. The result indicates that the luminescence properties of the $\text{Mn}^{4+}/\text{Cr}^{3+}$ co-doped phosphor permit it to act as a light wavelength detector, which refers a possible and interesting approach to design novel compact light detector or spectrometer based on this phosphor in the future.

To know the thermal quenching behavior, PL spectra for $(\text{Li}_{0.95}\text{K}_{0.05})_2\text{MgTi}_{0.991}\text{O}_4: 0.001\text{Mn}^{4+}, 0.008\text{Cr}^{3+}$ sample under 470 nm excitation in the different temperature (77K, 127K, 177K, 227K, 277K and 300K) have been measured, displayed in **Fig. 9(a)**. It is notable that the integral emission intensity of the PL spectrum increases continuously with temperature decreasing. The decrease in emission intensity with increasing temperature can be explained by thermal quenching at configurationally coordinate diagram ^[7, 34]. Upon 470 nm excitation, the Mn^{4+} and Cr^{3+} are excited from the ground state to their excited state $^4\text{T}_{2g}$, respectively. Luminescence can be observed after electrons non-radiative relaxation to their lowest excited state and radiative transition to the ground state. When the temperature is elevated, electrons in the lowest excited state have greater possibility to be thermally excited via the cross point between the lowest excited state and ground states with non-radiative decay to the ground state, resulting in the decrease of Mn^{4+} and Cr^{3+} emission. In order to further understand the thermal quenching characteristic, the activation energy (ΔE) can be evaluated by the equation ^[34]

$$I(T) = \frac{I(0)}{1 + A \exp(-\Delta E / k_B T)} \quad (2)$$

Where $I(0)$ and $I(T)$ is the initial intensity and the intensity at temperature T , ΔE is the activation energy, A is a constant and k_B is Boltzmann constant ($8.629 \times 10^{-5} \text{ eV K}^{-1}$). The experimental data are well-fitted by Eq. 2, as shown in **Fig. 9(b)**. The activation energy (ΔE) of Mn^{4+} in $(\text{Li}_{0.95}\text{K}_{0.05})_2\text{MgTi}_{0.999}\text{O}_4$ host is 0.40 eV. The value is slightly higher than that of Cr^{3+} ($\Delta E = 0.38 \text{ eV}$).

The temperature dependent luminescence behavior suggests that the color parameter of the $\text{Mn}^{4+}/\text{Cr}^{3+}$ co-doped phosphor can keep stable at relatively low temperature (<277 K). More importantly, the intensity ratio (R) of the Cr^{3+} emission (726 nm) to Mn^{4+} emission (678 nm) is not sensitive to the temperature variation below 227 K. The feature is very beneficial to its application as light wavelength detector.

Conclusion

In this work, Mn^{4+} doped and $\text{Mn}^{4+}/\text{Cr}^{3+}$ co-doped $\text{Li}_2\text{MgTi}_{0.999}\text{O}_4$ deep-red emitting phosphors have been synthesized via solid-state reaction method. When a small amount of Li^+ is replaced by Na^+ or K^+ in the host, the luminescence intensity is effectively enhanced. The Mn^{4+}

– Cr^{3+} co-doped $(\text{Li}_{0.95}\text{K}_{0.05})_2\text{MgTiO}_4$ has a broad luminescence band in range of 600 nm – 850 nm comprised by Mn^{4+} and Cr^{3+} emission. The total emission intensity of the co-doped phosphor can also be increased as compared with the Mn^{4+} single doped one. With excitation wavelength increasing from 290 nm to 455 nm, the integrated intensity ratio R of Cr^{3+} to Mn^{4+} emissions continues to increase, which provide a meaningful reference for designing compact wavelength detector with this phosphor.

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Figures and captions

Fig. 1

Fig. 1 (a) XRD patterns of $(\text{Li}_{0.95}\text{A}_{0.05})_2\text{MgTi}_{0.999-y}\text{O}_4: 0.001\text{Mn}^{4+}, y\text{Cr}^{3+}$ (A= Na and K, $y = 0, 0.003$ and 0.008) and the JCPDS card #89-7118 for $\text{Li}_2\text{MgTiO}_4$. (b) Enlarged XRD patterns of $(\text{Li}_{0.95}\text{A}_{0.05})_2\text{MgTi}_{0.999-y}\text{O}_4: 0.001\text{Mn}^{4+}, y\text{Cr}^{3+}$ (A= Na and K, $y = 0, 0.003$ and 0.008) at $2\theta = 43 - 44$.

Fig.2

Fig. 2 (a) Excitation spectra ($\lambda_{\text{em}} = 678$ nm) of $(\text{Li}_{0.95}\text{A}_{0.05})_2\text{MgTi}_{0.999}\text{O}_4:0.001\text{Mn}^{4+}$ (A = Na and K). (b) Emission spectra ($\lambda_{\text{ex}} = 470$ nm) of $(\text{Li}_{0.95}\text{A}_{0.05})_2\text{MgTi}_{0.999}\text{O}_4:0.001\text{Mn}^{4+}$ (A = Na and K). (c) Dependence of relative integrated intensity on substituted Na^+ or K^+ concentration.

Fig.3

Fig. 3 Decay curves of Mn^{4+} luminescence in $(\text{Li}_{0.95}\text{A}_{0.05})_2\text{MgTi}_{0.999}\text{O}_4$: 0.001Mn^{4+} (A = Na and K) phosphors monitored at 678 nm with excitation at 470 nm.

Fig.4:

Fig. 4 (a) Excitation spectra ($\lambda_{em} = 726$ nm) of $(Li_{0.95}K_{0.05})_2MgTi_{0.999-x}O_4$: $0.001Mn^{4+}$, xCr^{3+} ($x = 0\% - 1.2\%$), in which the insert gives the excitation spectra of Cr^{3+} single doped sample $(Li_{0.95}K_{0.05})_2MgTi_{0.992}O_4$: $0.008Cr^{3+}$. (b) Excitation spectra ($\lambda_{em} = 678$ nm) of $(Li_{0.95}K_{0.05})_2MgTi_{0.999-x}O_4$: $0.001Mn^{4+}$, xCr^{3+} ($x = 0\% - 1.2\%$). (c) Emission spectra ($\lambda_{ex} = 470$ nm) of $(Li_{0.95}K_{0.05})_2MgTi_{0.999-x}O_4$: $0.001Mn^{4+}$, xCr^{3+} ($x = 0\% - 1.2\%$). The inset shows the integrated intensity of 600 – 750 nm tendencies when changing the Cr^{3+} concentration.

Fig.5:

Fig. 5 Excitation spectra of $(\text{Li}_{0.95}\text{K}_{0.05})_2\text{MgTi}_{0.991}\text{O}_4: 0.001\text{Mn}^{4+}, 0.008\text{Cr}^{3+}$ monitored at 678 nm and 726 nm.

Fig. 6:

Fig. 6 Decay curves of Mn⁴⁺ luminescence in (Li_{0.95}K_{0.05})₂MgTi_{0.999-x}O₄:0.001Mn⁴⁺, xCr³⁺ (x = 0.0%, 0.1%, 0.3%, 0.5%, 0.8% and 1.0%) monitored at 678 nm excited at 470 nm light.

Fig. 7:

Fig. 7 Emission spectra (the different excitation wavelength) of $(\text{Li}_{0.95}\text{K}_{0.05})_2\text{MgTi}_{0.991}\text{O}_4: 0.001\text{Mn}^{4+}, 0.008\text{Cr}^{3+}$.

Fig. 8:

Fig. 8 Integrated intensity ratio of the Cr^{3+} emission (726 nm) to the Mn^{4+} emission (678 nm) of $(\text{Li}_{0.95}\text{K}_{0.05})_2\text{MgTi}_{0.991}\text{O}_4: 0.001\text{Mn}^{4+}, 0.008\text{Cr}^{3+}$ excited at the different excitation wavelength.

Fig. 9:

Fig. 9 (a) Emission spectra of $(\text{Li}_{0.95}\text{K}_{0.05})_2\text{MgTi}_{0.991}\text{O}_4: 0.001\text{Mn}^{4+}$,

0.008Cr³⁺ under 470 nm excitation at different temperatures.(b)
Temperature dependent relative emission intensity of
(Li_{0.95}K_{0.05})₂MgTi_{0.991}O₄: 0.001Mn⁴⁺, 0.008Cr³⁺ in Mn⁴⁺ (circle dotes)
and Cr³⁺ (square dotes) upon excitation of 470 nm.