Near-Infrared Luminescence Investigation of Cr⁴⁺ ions Doped Germanate

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Abstract

In this paper, the preparation of a series of $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ phosphors by high-temperature solid-state reaction is reported. The results of X-ray diffraction show that the doping of Cr^{4+} ions makes the lattice expand to a larger size. X-ray photoelectron spectroscopy (XPS) analysis shows that the chromium ions in the sample are tetravalent, confirmed further by fluorescence spectroscopy. Under the excitation of 980nm laser, the Cr^{4+} ions $^3\text{T}_2$ doped $^3\text{A}_2$ radiates transition and emits light at 1300nm. At the same time, the luminescence lifetime decreases with the increase in Cr^{4+} ions doping concentration. $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ phosphors have a broad application prospect in near-infrared LEDs.

Highlights

1. The $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ phosphor was prepared by the high-temperature solid-phase reaction method.
2. The luminescence lifetime decreases with the increase in Cr^{4+} ions doping concentration..
3. $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ phosphors have a broad application prospect in near-infrared LEDs..

1. Introduction

Near infrared (NIR) light is the electromagnetic wave between visible (VIS) and mid-infrared (MIR) light. The near-infrared region is divided into near-infrared short-wave NIR I (780-1100nm) and near-red long-wave NIR II (1100-2526nm). Near infrared light has a potential application prospect in food quality detection, biological detection, biological imaging, and so on [1-8]. In recent years, the application of near infrared light in NIR phosphorescence conversion light-emitting diodes (pc-LED) has developed rapidly. At present, the common infrared LEDs in the market are primarily made of semiconductor chips, which have the disadvantages of generating low power, poor thermal stability, narrow emission spectrum, and high cost. The light source based on near-infrared pc-LED provides some notable advantages like low cost, ease of use, and long service life. Therefore, it is a promising way to replace the existing micro-commercial LEDs [9]. However, the emission band of near-infrared LED is very narrow ($< 50\text{nm}$) [10], which is not adequate for most spectral applications. To obtain a high-performance NIR pc-LED, we need a highly efficient broadband NIR phosphor that matches well with the blue LED chip [11-12]. To this end, a lot of research has been carried out. At present, there are two main types of NIR broadband emitting materials available for blue LED chips: rare-earth ions and transition metal ions doped phosphors. It is a well-known fact that the luminescence centers of these phosphors are trivalent rare-earth ions and the electronic transitions in the f-f electronic structure are odd and even, leading to a very weak absorption capacity. Therefore, the FWHM of rare-earth-doped broadband near-infrared phosphors is narrow. However, since the d-shell electrons of transition metal ions are easily affected by the crystal field, and their luminescence properties are easy to be controlled, these have attracted more and more attention. To expand the luminous region of LED-based light sources, our focus is on 3d transition metal ions. The optical transitions in 3d transition metals are affected by the symmetry and strength of the ligand field

since these are firmly bonded with the ligands in the host materials. Therefore, 3d transition metals typically show broadband emission and excitation spectra with adjustable wavelengths [13].

Among the 3d metals, chromium ions display near-infrared luminescence when stimulated by germanate. At room temperature, $\text{Li}_2\text{TiGeO}_5$ crystal has a tetragonal structure and its space group is $P4/nmm$ [14]. The germanium ions occupy a quadrilateral position and the titanium site is surrounded by five oxygen ions. The crystal structure is composed of the infinite angle shared GeO_4 units separated by the alkali metal ions (Li^+) and the $[\text{TiOGeO}_4]$ of the TiO_5 square pyramid. One interesting aspect of the chromium ions is that Cr^{4+} -doped materials have many advantages, including simple energy level structures, allowing continuous wave and pulse operation at low threshold pump power, and wide absorption bands overlapping with the working wavelengths of several commercial pump lasers. One disadvantage is that Cr^{3+} ions are often found to be accompanying Cr^{4+} ions. Finding a suitable medium for Cr^{4+} ions doping is still an active research field. At present, because a tetrahedral environment is the first choice for Cr^{4+} , germanate material is a promising candidate material [15].

Therefore, in this work, we studied the synthesis and structure of $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ phosphors. All the experimental samples were prepared by the high-temperature solid-state method and the emission characteristics of $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ was explored. The introduction of Cr^{4+} ions as dopant led to the emergence of a wide fluorescent band at 1100-1700nm.

2. Experimental

2.1 Raw materials and Synthesis

$\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ phosphors were prepared by high-temperature solid-state synthesis. Using TiO_2 , Li_2CO_3 , GeO_2 and Cr_2O_3 as starting materials, a series of $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ ($x = 0.002, 0.004, 0.006$ and 0.008) samples were prepared and sintered at 900°C for 5h in stoichiometric air. After the samples were taken out, these was put into an agate mortar for fine grinding and subsequently characterized.

2.2 Characterization Method

The crystal structures of all the samples were examined by X-ray powder diffractometer (XRD) (Ultima IV-X) at room temperature with $\text{CuK}\alpha$ radiation of 40kV and 20mA, and the data were collected in the range of 10 - 80° . (XPS) analysis of, C (1s) signal (284.6eV) using an equipped EP13-002 electronic analyzer was used as a reference for calibrating the binding energy of different elements to correct the charge effect. The infrared absorption spectra of the samples were recorded by a PerkinElmer Frontier infrared spectrometer. The sample surfaces were analyzed by an FE-SEMSU6600 scanning electron microscope ((SEM)). The luminescence properties of the samples were studied by using a steady-state Fluorolog- π spectrofluorometer with a high spectral resolution at room temperature. The fluorescence lifetimes of the samples with varying doping concentrations were recorded on a Fluorolog- π fluorescence spectrofluorometer. All measurements were carried out at room temperature.

3. Results And Discussion

3.1 Structure Analysis of $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$

As shown in the figure above, the phase structure of the sample $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ is analyzed by XRD. The XRD spectra of 0.2%, 0.4%, 0.6% and 0.8% doped Cr^{4+} ions are shown in Fig. 1(a). From the illustration, it is obvious that all of the four samples with different doping concentrations in the scanning range of 10° - 80° show the characteristic peaks of pure $\text{Li}_2\text{TiGeO}_5$, and the diffraction peak has no special deviation. This shows that no other phases or impurities have been detected, which is completely in line with the basic parameters of $\text{Li}_2\text{TiGeO}_5$. This observation also indicates that the $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ phosphor has been successfully prepared and that the $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ sample prepared by the solid-state method has good crystallization. From Fig. 1(b), it is obvious that the diffraction peak shifted slightly to a small angle because the radius of the doped Cr^{4+} ions is larger than the radius of the Ge^{4+} ions, resulting in the crystal volume expansion. At the same time, it also shows that Cr^{4+} ions successfully bind to the $\text{Li}_2\text{TiGeO}_5$ matrix lattice by replacing some of the Ge^{4+} ions.

Fig. 2 shows the X-ray photoelectron spectroscopy (XPS) image of $\text{Li}_2\text{TiGe}_{0.994}\text{Cr}_{0.006}\text{O}_5$. The signals of lithium (Li), titanium (Ti), germanium (Ge), oxygen (O), and carbon (C) can be clearly observed. At the same time, a relatively weak chromium (Cr) signal is also observed. When carbon (C) is not an inherent component in the sample, the function of carbon is to calibrate the binding energy. Li^+ , Ti^{4+} and Cr^{4+} ions show peak positions at (55.6eV) and (458.3eV) and (578.6eV), respectively. The peak position at 578.6eV corresponds to Cr^{4+} ions, while no peak position corresponding to Cr^{3+} ions is found. Therefore, it can be concluded that Cr^{4+} ions were successfully introduced into the $\text{Li}_2\text{TiGeO}_5$ sample [16-18].

The FT-IR spectrum of $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ in the range of 4000 - 400cm^{-1} , is shown in Fig. 3(a). The vibrational peaks of all samples are the same, which proves that the main lattice structure does not change after doping, which corroborates well with the XRD analysis of $\text{Li}_2\text{TiGeO}_5$. The main vibrational peak of the sample is concentrated in the range of 4000 - 1000cm^{-1} where two peaks are at 3445 and 1443cm^{-1} . The peak at 3445cm^{-1} is a result of the tensile vibration of OH in water, and the peak at 1443cm^{-1} owes its origin to the bending vibration of OH. Fig. 3(b) shows the peaks in the FT-IR spectrum between 1000 and 400cm^{-1} . In this range, $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ shows three main vibration peaks, at 746cm^{-1} , 512cm^{-1} and 425cm^{-1} . Among these, the peak at 746cm^{-1} is attributed to the asymmetric tensile vibration of the Ge-O-Ge bond, the peak at 512cm^{-1} is attributed to the symmetrical tensile vibration of the Ge-O-Ge bond, and the peak at 425cm^{-1} can be attributed to the deformation vibration of O-Cr-O bond. This observation also confirms that Cr^{4+} ions are indeed doped into $\text{Li}_2\text{TiGeO}_5$ [19-21]. At the same time, with the increase in the Cr^{4+} ions doping concentration, the vibration of the Ge-O bond increases, and the peak at 878cm^{-1} increases. This is because when the Cr^{4+} ions occupy the quadrilateral position of the Ge^{4+} ions in the $\text{Li}_2\text{TiGeO}_5$, the Cr^{4+} ions combine with the O^{2-} ions to form an O-Cr-O bond to break the Ge-O-Ge bond, and thus some of the Ge-O-Ge bonds become Ge-O bonds.

3.2 Morphology Analysis of $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$

Fig. 4 shows the scanning electron microscope image of $\text{Li}_2\text{TiGe}_{0.994}\text{Cr}_{0.006}\text{O}_5$, from which it can be concluded that the average particle size of the sample is about 900 nm. The sample shows particles with good shape, most of which are spherical or ellipsoidal. The micron structure is stable, and the content of impurities is less. It confirms that the calcination temperature and doping concentration of the samples are suitable for doping, which is consistent with the results of XRD. According to the Wulff rule, the morphology of the equilibrium grains follows the principle of minimum surface free energy [22].

3.3 Luminescence Characteristics of $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$

As shown in Fig. 5(a), the relationship between the emission spectrum of $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ excited by 980 nm laser and the doping concentration of Cr^{4+} ions has been studied. A broadband emission peak near 1100-1700 nm ($\lambda_{\text{ex}}=980\text{nm}$) is obtained. The single band at 1300 nm ($\lambda_{\text{ex}} = 980\text{nm}$) is attributed to the Cr^{4+} ions. The luminescence here is produced by the transition from the $^3\text{T}_2$ excited state of Cr^{4+} to its $^3\text{A}_2$ ground state [23]. When the doping concentration of Cr^{4+} ions increases from 0.2 mol% to 0.8 mol%, the emission intensity increases initially and then decreases, reaching the maximum when the concentration of Cr^{4+} ions is 0.6 mol%. The main reason for this phenomenon is the concentration quenching of Cr^{4+} ions. With the increase in Cr^{4+} ions doping concentration, the average distance between Cr^{4+} ions decreases, increasing the interaction between Cr^{4+} ions, which leads to energy transfer and concentration quenching. Fig. 5(b) shows the Cr^{4+} ions energy level diagrams of the two lowest high spin terms $^3\text{T}_1$ and $^3\text{T}_2$. Consistent with the Tanabe-Sugano diagram of Cr^{4+} ions, the lowest free ion level of $d^2\text{-Cr}^{4+}$ ions is ^3F at the ideal tetrahedral position of T_d -symmetry. Owing to the splitting of the crystal field, the free ions energy levels split in the following way: $^3\text{F} \rightarrow ^3\text{A}_2 + ^3\text{T}_2 + ^3\text{T}_1$. The energy levels of these levels are as follows: $^3\text{T}_1 > ^3\text{T}_2 > ^3\text{A}_2$. In general, the $^3\text{A}_2$ level can be thought of as the ground state. The $^3\text{A}_2 \rightarrow ^3\text{T}_1$ transition is the permissible electric dipole (spin permissible), and the $^3\text{A}_2 \rightarrow ^3\text{T}_1$ is the permissible magnetic dipole. According to the structure of $\text{Li}_2\text{TiGeO}_5$, the local environmental symmetry is less than T_d -symmetry, and the tetrahedron is deformed along two axes. The $^3\text{T}_1$ and $^3\text{T}_2$ bands are divided into three parts. The most likely sequence of symmetry decline is $\text{T}_d \rightarrow \text{C}_{3v} \rightarrow \text{C}_s$.

Fig. 6 shows the luminous decay curve of $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ at 1300 nm excited by 980 nm laser. A single exponential decay formula can be used for all luminous decay curves, as follows:

$$I(t) = I_0 + Ae(-t/\tau) \quad (1)$$

I is the photoluminescence intensity of $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$; $I(t)$ and I_0 represent the photoluminescence intensity at times t and 0 respectively. For the single exponential lifetime formula, the fluorescence intensity is proportional to the number of molecules in the excited state, where A is the fitting parameter

and τ is the component of the luminescence decay time. According to the above fitting equation, the attenuation time of $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ ($x = 0.002, 0.004, 0.006$ and 0.008) is calculated to be 13.552 ms, 13.181 ms, 12.914 ms and 12.224 ms, respectively. With the increase in Cr^{4+} ions doping concentration, the fluorescence lifetime of the sample decreases gradually. This may be due to the increase in the cross-relaxation between the two adjacent Cr^{4+} ions caused by the increase in Cr^{4+} doping concentration. Moreover, the molecules in the excited state not only return to the ground state through fluorescence but also through some other processes (such as quenching and energy transfer). As a result, the process of returning to the ground state from the excited state is accelerated and the fluorescence lifetime is reduced.

As shown in Fig. 7, the color coordinates of the $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ samples were drawn in the (CIE) chromaticity diagram of the International Lighting Commission in 1931. The concentration of Cr^{4+} ions change from 0.2mol% to 0.8mol%, while the chromaticity coordinate (x,y) changes from (0.3854-0.3616) to (0.3901-0.3641). The samples emit orange light, and the doped Cr^{4+} ions can improve the UC emission intensity and the green light emission intensity of the sample, which is a promising luminescence mechanism.

4. Conclusions

To sum up, a series of $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ phosphors have been synthesized by solid-state reaction, and the structures of the doped $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ have been characterized by XRD and FTIR. Because the ionic radius of Cr^{4+} is larger than that of Ge^{4+} , the lattice parameters increase after doping. The tetravalency of the doped chromium ions is proved by X-ray photoelectron spectroscopy (XPS). All the samples are excited under 980 nm LD and show an emission peak centered on 1300 nm, corresponding to the $^3\text{T}_2 \rightarrow ^3\text{A}_2$ energy transfer in Cr^{4+} ions. Due to the excellent luminous properties of $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ phosphors in the near-infrared wide band, it has the opportunity to become a new near-infrared LED application material in the future.

Declarations

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Tables

Table.1 Calculated values of CIE chromaticity coordinates (x, y) for $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_{5a}$

Point	Sample	CIE chromaticity coordinate	
		X	Y
a	$\text{Li}_2\text{TiGe}_{0.098}\text{Cr}_{0.002}\text{O}_5$	0.3854	0.3616
b	$\text{Li}_2\text{TiGe}_{0.096}\text{Cr}_{0.004}\text{O}_5$	0.3801	0.3590
c	$\text{Li}_2\text{TiGe}_{0.094}\text{Cr}_{0.006}\text{O}_5$	0.3945	0.3668
d	$\text{Li}_2\text{TiGe}_{0.092}\text{Cr}_{0.008}\text{O}_5$	0.3901	0.3641

Figures

Figure 1

(a) XRD of $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$; (b) $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ XRD main peak shift map (c) $\text{Li}_2\text{TiGeO}_5$ polyhedron crystal structure diagram.

Figure 2

XPS spectrum of (a) $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$, XPS spectrum of; (b) Cr-2p_{3/2}, XPS spectrum of; (c) Ti-2p, XPS spectrum of; (d) Ge-3d.

Figure 3

Infrared spectrum of (a) 4000 cm^{-1} -400 cm^{-1} (b) 1000 cm^{-1} -400 cm^{-1} $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ phosphor.

Figure 4

SEM photos of $\text{Li}_2\text{TiGe}_{0.994}\text{Cr}_{0.006}\text{O}_5$ phosphors.

Figure 5

The emission spectrum of (a) excited by 980 nm laser and the energy level of; (b) Cr⁴⁺ ion in Li₂TiGe_{1-x}Cr_xO₅.

Figure 6

Decay curve of luminescence lifetime of $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$ at 1300 nm excited by 980 nm laser.

Figure 7

CIE diagram of $\text{Li}_2\text{TiGe}_{1-x}\text{Cr}_x\text{O}_5$.