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Synthesis and characterization of $Ca_2Sn_{1-x}Ce_xO_4$ with blue luminescence originating from Ce^{4+} charge transfer transition*

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Ce^{4+}-doped Ca_2SnO_4 with a one-dimensional structure, which emits bright blue light, is prepared by using a solid-state reaction method. The x-ray diffraction results show that the Ce^{4+} ions doped in Ca_2SnO_4 occupy the Sn^{4+} sites. The excitation and emission spectra of $Ca_2Sn_{1-x}Ce_xO_4$ appear to have broad bands with peaks at $\sim$268 nm and $\sim$442 nm, respectively. A long excited-state lifetime ($\sim 83\,\mu$s) for the emission from $Ca_2Sn_{1-x}Ce_xO_4$ suggests that the luminescence originates from a ligand-to-metal Ce^{4+} charge transfer (CT). The luminescent properties of $Ca_2Sn_{1-x}Ce_xO_4$ have been compared with those of Sr_2CeO_4, which is the only material reported so far to show Ce^{4+} CT luminescence. More interestingly, it is observed that the emission intensity of $Ca_2Sn_{1-x}Ce_xO_4$ with a small doping concentration (x $\sim$0.03) is comparable to that of Sr_2CeO_4 in which the concentration of active centre is 100%.

Keywords: $Ca_2Sn_{1-x}Ce_xO_4$, Ce^{4+}-O^{2-}, charge transfer, luminescent property
PACC: 7855

1. Introduction

The discovery and development of new compounds for ultraviolet-excited phosphor is of great importance for the advance of flat-panel display and illumination technology. Compared with organic materials and sulfide phosphors, oxide-based phosphors have the advantages: stable crystalline structure and high physical and chemical stability. Therefore, oxide-based phosphors, especially rare earth (RE)-based oxides, are attracting more and more attention.[1−5] For the full colour RE-based phosphors, the red and green emissions are generally generated by the f-f transitions of Eu^{3+} and Tb^{3+} while the blue one is caused by the d-f transitions of Eu^{2+} or Ce^{3+}. To date, satisfactory red and green phosphors have been commercially available. However, comparable materials for blue emission are still lacking, and they are the targets of many research work.[6,7]

It has been found that the luminescence materials with low-dimensional structures generally exhibit special luminescence properties.[8,9] Several years ago, a luminescence compound Sr_2CeO_4 was first discovered by Danielson *et al*[10] by using a combinatorial material synthesis technique. This phosphor exhibits efficient blue luminescence under the excitation of ultraviolet light, cathode rays or x-rays. It has been suggested that the luminescence of Sr_2CeO_4 originates from a ligand-to-metal Ce^{4+} charge transfer (CT) based on its long decay time (a few tenth μs). The Sr_2CeO_4, in structure, is comprised of one-dimensional chains of edge-sharing CeO_6 octahedra, in which the terminal Ce–O bonds are about 0.01 nm shorter than the equatorial Ce–O bonds.[11] To date, the Sr_2CeO_4 has been the only material in which the CT luminescence of Ce^{4+} is observed. The other known Ce^{4+}-based compounds such as $SrCeO_3$ and $BaCeO_3$, each with a three-dimensional CeO_6 framework structure, do not luminesce. Thus, the one-dimensional structure, with its Ce^{4+}–O^{2-} terminal bonds, is critical to the emission of Sr_2CeO_4. This implies that luminescence might also be observed for Ce^{4+}-doped materials with similar lattice structures. It has been known that Ca_2SnO_4 possesses the same crystal symmetry as Sr_2CeO_4.[11] Therefore, it is expected that the luminescence from Ce^{4+} ions doped in Ca_2SnO_4 may be observed if Ce^{4+} ions can substitute for the Sn^{4+} sites. Based on this idea, we have doped Ca_2SnO_4 with Ce^{4+} ions and found that Ce^{4+}-doped Ca_2SnO_4 exhibits strong blue luminescence. In

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this article, we report on the synthesis and characterization of Ce^{4+}-doped Ca_2SnO_4 powder phosphor and compare its luminescent properties with those of Sr_2CeO_4.

2. Experiments

Powder samples of $Ca_2Sn_{1-x}Ce_xO_4$ ($x = 0.01$–0.05) and Sr_2CeO_4 were prepared with a conventional solid-state reaction method using $CaCO_3$ (analytical grade), $SrCO_3$ (analytical grade), SnO_2 (analytical grade), and CeO_2 (99.99%) as the starting materials. The mixtures with stoichiometric ratios of the needed starting materials were calcined in air at 1250°C for 20 h with two intermediate regrindings. The final products were identified by x-ray diffraction (XRD) using a SHIMADZU XD-610 Powder Diffractometer with Cu Kα ($\lambda = 0.15405$ nm). The photoluminescence excitation and emission spectra were recorded at room temperature with a spectrofluorometer (Perkin Elmer LS55) using a Xe lamp as a light source. Fluorescence lifetimes were measured using a monochromator and a photomultiplier connected to a 500 M digital oscilloscope. A Nd-YAG laser was used as a pulsed excitation source.

3. Results and discussion

Figures 1(a) and (b) show the XRD patterns of the powder with a 2 : 1 ratio of Ca : Sn calcined in air at 1250°C for two different heating times. The XRD pattern in Fig.1(a) suggests the existence of the impurity phase of $CaSnO_3$ (Joint Committee on Powder Diffraction Standards (JCPDS) card No.77-1797) in the initial stage of the reaction. However, it was then converted to the more stable Ca_2SnO_4 upon further heating. As shown in Fig.1(b), the Ca_2SnO_4 sample (JCPDS card No.46-0112) with a single phase was obtained after heating for about 20 h. The formation process of Ca_2SnO_4 is quite similar to that of its isostructural compound Sr_2CeO_4.[11] When Ce ions are doped in Ca_2SnO_4, they can occupy either the Sn^{4+} sites or the Ca^{2+} sites. Figures 1(c) and (d) show the XRD patterns of Ca_2SnO_4 doped with Ce ions on the Sn^{4+} sites ($Ca_2Sn_{0.97}Ce_{0.03}O_4$) and the Ca^{2+} sites ($Ca_{1.97}Ce_{0.03}SnO_4$), respectively. Both of them indicate the formation of Ca_2SnO_4. However, the $Ca_2Sn_{0.97}Ce_{0.03}O_4$ sample has a single phase of the Ca_2SnO_4 material, while the $Ca_{1.97}Ce_{0.03}SnO_4$ sample has the impurities of $CaSnO_3$ and CeO_2 (JCPDS card No.34-0394). Thus, it is suggested that the Ce ions tend to occupy the Sn^{4+} sites in the Ca_2SnO_4 lattice.

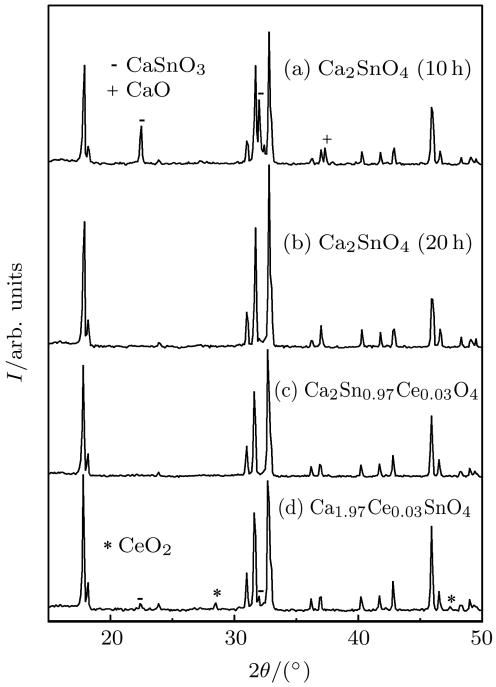


Fig.1. X-ray diffraction patterns of undoped and Ce^{4+}-doped Ca_2SnO_4.

It is well known that Ca_2SnO_4 does not luminesce. When doped with Ce ions, however, it exhibits strong blue luminescence to the naked eye at room temperature under the excitation of ultraviolet light. The emission of $Ca_2Sn_{1-x}Ce_xO_4$ ($x = 0.01$–0.05) increases with the Ce concentration increasing up to $x = 0.03$. After that, it decreases gradually. The excitation and emission spectra of the $Ca_2Sn_{0.97}Ce_{0.03}O_4$ sample are shown in Figs.2 and 3, respectively. The excitation spectrum appears to have a broad band with a peak at $\sim$268 nm and a shoulder at $\sim$325 nm. The emission spectrum recorded for the excitation at 268 nm shows a broad band with a peak at $\sim$442 nm and a full width at half maximum (FWHM) of $\sim$68 nm. The spectral features remain almost unchanged when the sample is excited at 325 nm except for the difference in intensity. The Stokes shift determined by the difference between the first excitation peak (325 nm) and the emission maximum (442 nm) is calculated to be 8100 cm^{-1}. In addition, no obvious changes are found in the excitation and emission spectra when the samples are annealed at 1250°C in air or at 1000°C in a reducing atmosphere (N_2).

Moreover, blue luminescence is also observed when this phosphor is excited by x-rays.

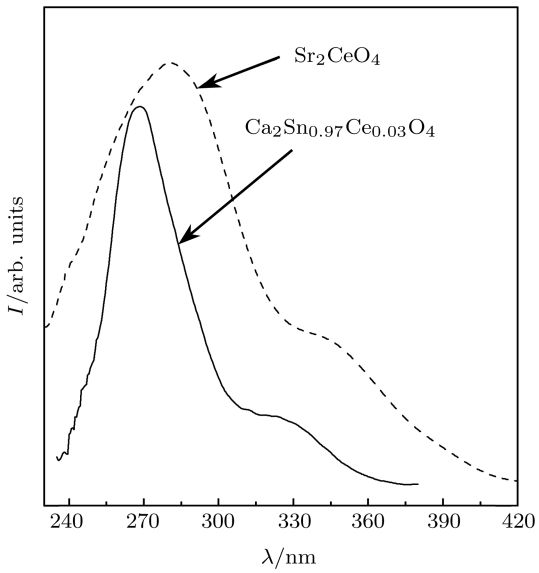


Fig.2. Excitation spectrum of $Ca_2Sn_{0.97}Ce_{0.03}O_4$ (solid curve) monitored at $\lambda_{em} = 442$ nm and the excitation spectrum of Sr_2CeO_4 recorded at $\lambda_{em} = 465$ nm (dashed curve) that is shown for comparison.

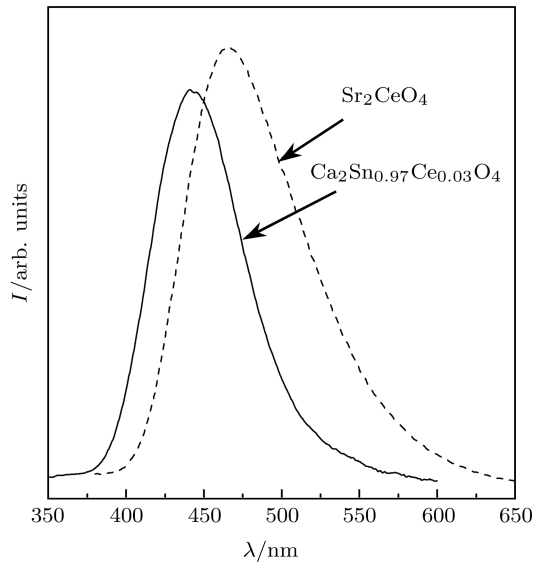


Fig.3. Emission spectrum of $Ca_2Sn_{0.97}Ce_{0.03}O_4$ (solid curve) recorded at $\lambda_{ex} = 268$ nm and the emission spectrum of Sr_2CeO_4 recorded at $\lambda_{ex} = 280$ nm (dashed curve) that is provided for comparison.

In general, oxide compounds such as CaO and silica exhibit a strong, broad, and efficient emission from oxygen defects.[12,13] In our experiments, it is observed however that the annealing in air or in a reducing atmosphere has no large influence on the luminescence of $Ca_2Sn_{1-x}Ce_xO_4$. This indicates that oxygen vacancies are not the luminescent centres responsible for the efficient luminescence because the emission based on oxygen defects is not stable and its brightness is strongly dependent on the synthesis conditions. Therefore, the luminescence of $Ca_2Sn_{1-x}Ce_xO_4$ should be related to the doped Ce ions. Two possible origins are the Ce^{3+} d–f transition and Ce^{4+} CT transition. So far, Sr_2CeO_4 has been the only material in which the CT luminescence of Ce^{4+} is observed. For other Ce-based phosphors, their luminescence arises from the d-f transitions of Ce^{3+}. The emission from Sr_2CeO_4 has a relatively long excited-state lifetime (a few tenth μs) compared with that from d-f transitions in the Ce^{3+} excited states (a few tenth ns). Thus, an analysis of the fluorescence decays will provide the information on the origin of $Ca_2Sn_{1-x}Ce_xO_4$ luminescence. Figure 4 shows the measured fluorescence decay curve for the $Ca_2Sn_{0.97}Ce_{0.03}O_4$ sample.

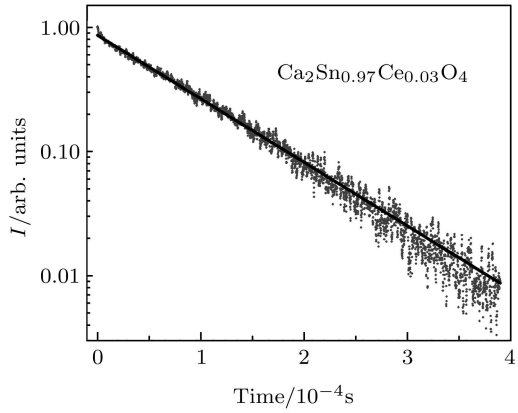


Fig.4. Fluorescence decay curve for $Ca_2Sn_{0.97}Ce_{0.03}O_4$, where the solid line represents the one-exponential fit to the decay curve.

The lifetime can be extracted by the exponential fitting of the decay curve. The lifetime for $Ca_2Sn_{0.97}Ce_{0.03}O_4$ is estimated to be 83 μs. This value is quite similar to that reported for Sr_2CeO_4 ($\sim 51\,\mu$s).[10] In general, the phosphor materials containing Ce^{3+} ions are fabricated by calcinating the reaction mixtures at high temperatures in a reducing atmosphere (N_2+H_2). In our case, the Ce atoms in the $Ca_2Sn_{1-x}Ce_xO_4$ samples prepared by a solid-state reaction method in air are expected to be present in the form of Ce^{4+}. Therefore, the long fluorescence lifetime, combined with the synthesis conditions of the sample, strongly suggests that the emission from $Ca_2Sn_{1-x}Ce_xO_4$ originates from the Ce^{4+}-O^{2-} CT transition. The unique one-dimensional structure of

the Ca_2SnO_4 host lattice is critical to the Ce^{4+} CT luminescence. Since the Ce^{4+} ions have no 4f electrons, an electron can be transferred from an oxygen ligand to the shell of Ce^{4+} under the ultraviolet excitation. Subsequently, the electron relaxes nonradiatively to the lowest energy excited state where the Ce^{4+}–O^{2-} CT luminescence occurs. The long lifetime can be explained by the spin-forbidden transition of the luminescence proposed by Pieterson *et al.*[14]

$Ca_2Sn_{1-x}Ce_xO_4$ is found to have the same mechanism of luminescence as Sr_2CeO_4. For the purpose of comparison, we have presented their excitation and emission spectra in Figs.2 and 3, respectively. In Fig.2, it is observed that each excitation spectrum appears to have a broad band with a peak and a shoulder. They are located at $\sim$280 nm and $\sim$340 nm for Sr_2CeO_4 and $\sim$268 nm and $\sim$325 nm for $Ca_2Sn_{0.97}Ce_{0.03}O_4$, respectively. Apparently, the CT excitation of $Ca_2Sn_{1-x}Ce_xO_4$ exhibits a blue shift as compared with that of Sr_2CeO_4. However, the energy separation between the peak and the shoulder for $Ca_2Sn_{1-x}Ce_xO_4$ ($\sim 6500\,cm^{-1}$) is almost the same as that for Sr_2CeO_4 ($\sim 6300\,cm^{-1}$). In addition, the FWHM of excitation spectrum for Sr_2CeO_4 is much broader than that for $Ca_2Sn_{1-x}Ce_xO_4$. The FWHM of the strong excitation band is $\sim$58 nm for Sr_2CeO_4 which is obtained by Gaussian fitting,[15] while that for $Ca_2Sn_{0.97}Ce_{0.03}O_4$ is estimated to be $\sim$35 nm. In Fig.3, it is found that the emission from $Ca_2Sn_{1-x}Ce_xO_4$ shows a blue shift with respect to that from Sr_2CeO_4. For Sr_2CeO_4, a broad emission band is observed with a peak at $\sim$465 nm. The FWHM and the Stokes shift are extracted to be $\sim$88 nm and $\sim 7900\,cm^{-1}$. In the case of $Ca_2Sn_{0.97}Ce_{0.03}O_4$, the broad emission band is centred at $\sim$442 nm with a FWHM of $\sim$68 nm and a Stokes shift of $\sim 8100\,cm^{-1}$. More interestingly, it is noticed that the emission intensity of Ca_2SnO_4 doped with a small number of Ce^{4+} ions (x $\sim$ 0.03) is comparable to that of Sr_2CeO_4 in which the concentration of active centre is 100%.

It has been recognized that the CT transition is sensitive to the ligand environment. The compound Sr_2CeO_4 belongs to the orthorhombic crystal system in a space group *Pbam* with cell parameters $a = 0.6119$ nm, $b = 1.0350$ nm, and $c = 0.3597$ nm.[11] The Sr_2CeO_4, in structure, is comprised of linear chains of edge-sharing CeO_6 octahedra running parallel to the [001] crystallographic direction. These chains are separated from and charge-balanced by seven-coordinated Sr^{2+} chains surrounding the octahedra chains. In CeO_6 octahedra there exist two trans-terminal Ce^{4+}-O^{2-} bonds and four equatorial Ce^{4+}-O^{2-} bonds. The former are about 0.01 nm shorter than the latter. Ca_2SnO_4 possesses the same crystal symmetry as Sr_2CeO_4. However, the parameters of the unit cell decrease to $a = 0.5753$ nm, $b = 0.9701$ nm, and $c = 0.3266$ nm because the six-coordinated radius of Sn^{4+} (0.071 nm) is smaller than that of Ce^{4+} (0.087 nm) while the seven-coordinated radius of Ca^{2+} (0.099 nm) is also smaller than that of Sr^{2+} (0.121 nm). The CT energy levels are related to the Ce^{4+}-O^{2-} distances and the nearest-neighbouring environment of Ce^{4+} ion. There exists a tendency to find the CT band at higher energies for shorter metal-to-ligand distances.[16] Hence, the CT band of Ce^{4+}–O^{2-} in $Ca_2Sn_{1-x}Ce_xO_4$ appears at a higher energy than that in Sr_2CeO_4. On the other hand, compared with the bond structure of Ce^{4+}–O^{2-}–Ca^{2+} in $Ca_2Sn_{1-x}Ce_xO_4$, Ce^{4+}–O^{2-}–Sr^{2+} in Sr_2CeO_4, Ca^{2+} can attract the electrons of O^{2-} more strongly than Sr^{2+} because of the larger electronegativity and smaller radius. Thus, the energy of the electronic transition from O^{2-} to Ce^{4+} is expected to be higher in $Ca_2Sn_{1-x}Ce_xO_4$ than in Sr_2CeO_4. The two reasons mentioned above explain why the Ce^{4+}-O^{2-} CT band of $Ca_2Sn_{1-x}Ce_xO_4$ is observed at a higher energy than that of Sr_2CeO_4.

4. Conclusions

A new Ce^{4+}-doped Ca_2SnO_4 phosphor with a one-dimensional structure has been prepared by using a solid-state reaction method. It exhibits bright blue luminescence under the excitation of ultraviolet light or x-rays. The excitation and emission spectra appear to have broad bands with peaks at $\sim$268 and $\sim$442 nm, respectively. A long excited-state lifetime ($\sim 83\,\mu$s) for the emission from $Ca_2Sn_{1-x}Ce_xO_4$ suggests that the luminescence originates from a ligand-to-metal Ce^{4+} charge transfer. The CT bands of $Ca_2Sn_{1-x}Ce_xO_4$ have a blue shift with respect to those of Sr_2CeO_4.More interestingly, it is noticed that the emission intensity of $Ca_2Sn_{1-x}Ce_xO_4$ with a small doping concentration (x $\sim$ 0.03) is comparable to that of Sr_2CeO_4. The excellent luminescence properties make it a promising candidate for display and illumination in the blue region.

References

[1] Danielson E, Golden J H, McFarland E W, Reaves C M, Weinberg W H and Wu X D 1997 *Nature* **389** 944

[2] Wang J, Yoo Y, Gao C, Takeuchi I, Sun X, Chang H, Xiang X D and Schultz P G 1998 *Science* **279** 1712

[3] Fu S L, Yin T, Qing Q K and Zhao W R 2006 *Acta Phys. Sin.* **55** 4940 (in Chinese)

[4] Yang Z P and Liu Y F 2006 *Acta Phys. Sin.* **55** 4946 (in Chinese)

[5] Peng Z W, Wang L L, Liu H Q, Huang W Q and Zou B S 2007 *Acta Phys. Sin.* **56** 1162 (in Chinese)

[6] Jiang Y D, Zhang F, Summers C J and Wang Z L 1999 *Appl. Phys. Lett.* **74** 1677

[7] Lee Y E, Norton D P, Budai J D, Rack P D and Potter M D 2000 *Appl. Phys. Lett.* **77** 678

[8] Blasse G and Van Tol F 1995 *Solid State Commun.* **95** 465

[9] Van Schaik W and Blasse G 1994 *J. Lumin.* **62** 203

[10] Danielson E, Devenney M, Giaquinta D M, Golden J H, Haushalter R C, McFarland E W, Poojary D M, Reaves C M, Weinberg W H and Wu X D 1998 *Science* **279** 837

[11] Danielson E, Devenney M, Giaquinta D M, Golden J H, Haushalter R C, McFarland E W, Poojary D M, Reaves C M, Weinberg W H and Wu X D 1998 *J. Mol. Struct.* **470** 229

[12] Green W H, Le K P, Gray J, Au T T and Sailor M J 1997 *Science* **276** 1826

[13] Chen Y, Orera V M, Gonzalez R, Williams R T, Williams G P, Rosenblatt G H and Pogatshnik G J 1990 *Phys. Rev.* B **42** 1410

[14] Van Pieterson L, Soverna S and Meijerink A 2000 *J. Electrochem. Soc.* **147** 4688

[15] Fu S L, Dai J, Qing Q K and Zhao W R 2005 *Acta Phys. Sin.* **54** 2369 (in Chinese)

[16] Xu X R and Su M Z 2004 *Luminescence Theory and Material* (Beijing: Chemical Industry Press) p567 (in Chinese)