Preparation and spectroscopic properties of Ca$_2$MgTeO$_6$:Tm$^{3+}$ blue-emitting tellurate phosphors

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Abstract. Various novel Ca$_2$MgTeO$_6$:Tm$^{3+}$ blue-emitting tellurate materials were synthesized via solid-state reaction. The structure and phase purity of prepared Ca$_2$MgTeO$_6$:xTm$^{3+}$ ($x = 0.0025-0.10$) were examined by X-ray powder diffraction. The Ca$_2$MgTeO$_6$:Tm$^{3+}$ phosphors emit blue emission at 359 nm excitation. The optimum doping concentration was 0.02 mol. The concentration quenching mechanism in the Ca$_2$MgTeO$_6$:host was due to the electric dipole-dipole interaction. The CIE chromaticity coordinates of Ca$_2$MgTeO$_6$:Tm$^{3+}$ phosphors located in the blue region. These results validated the Ca$_2$MgTeO$_6$:Tm$^{3+}$ tellurate phosphor can be used as good blue-emitting candidate for W-LEDs.

1 Introduction

White light-emitting diodes (W-LEDs), particularly phosphors-covered LEDs, have replaced traditional lighting sources (e.g., incandescent light, halogen tungsten lamp, and fluorescent lamp) owing to their energy conservation, long lifetime, high efficiency, and environment-friendly properties [1-5]. The common combination of commercial W-LEDs is that of blue InGaN chips and Y$_2$Al$_2$O$_3$:Ce$^{3+}$ yellow phosphors. Given the lack of a red component, this combination has a low rendering index and correlated color temperature (CCT). The other common method combines near-ultraviolet (n-UV) LED chips with trichromatic phosphors (yellow-, blue-, and red-emitting phosphors) [6-9]. It is imperative to fabricate a novel blue-emitting phosphor with effective absorption in the near-UV region.

There are many kinds of phosphors those have been reported. Rare-earth ions doped tellurates have arisen extensive interest due to excellent chemical and physical stability, such as Li$_2$Gd$_2$Te$_5$O$_{12}$:Dy$^{3+}$, Ca$_2$TeO$_5$:Eu$^{3+}$, and NaLaCaTeO$_5$:Mn$^{4+}$ [10-13]. Tm$^{3+}$ is widely used as an efficient blue light emitting center, such as CaHfO$_4$:Tm$^{3+}$, Li$_3$Gd$_2$Te$_5$O$_{12}$:Tm$^{3+}$, Ca$_2$NaGd$_{2/3}$(PO$_4$)$_2$:Tm$^{3+}$, and CaBi$_2$Ti$_5$O$_{15}$:Tm$^{3+}$, Yb$^{3+}$ many alternative Tm$^{3+}$-doped phosphors have been reported [14-17]. Ca$_2$MgTeO$_6$ ceramics were reported to a double porosokite family member and exhibited a monoclinic $P2_1/n$ structure [18]. Recently, Ca$_2$MgTeO$_6$:Eu$^{3+}$, Ca$_2$MgTeO$_6$:Sm$^{3+}$ phosphors emitted bright red/orange-emitting light under UV excitation [19, 20]. However, the Tm$^{3+}$-doped Ca$_2$MgTeO$_6$ phosphors had not been reported. In this work, Tm$^{3+}$-doped Ca$_2$MgTeO$_6$ blue-emitting phosphor has been synthesized by solid-state reaction. The powder X-ray diffraction (XRD), the photoluminescence excitation (PLE) properties, the photoluminescence emission (PL) spectra, and concentration quenching mechanism were investigated in depth.

2 Experimental section

The Ca$_2$MgTeO$_6$:xTm$^{3+}$ powders were achieved through the solid-phase synthesis method. CaCO$_3$ (analytical reagent), TeO$_2$ (99.99%), MgCO$_3$-4Mg(OH)2·5H2O (analytical reagent), Tm$_2$O$_3$ (99.99%), and Na$_2$CO$_3$ (analytical reagent). Na$_2$CO$_3$ was taken as charge compensation. They were mixed in a muffle furnace cooled down to near room temperature, after the muffle furnace cooled down to near room temperature, the products were ground for luminescence characterization. The structural properties of phosphor were measured by XRD through a Bruker D2 PHASER X-ray diffractometer with Cu Kα radiation source (λ = 0.15405 nm) operated at 40 kV with results between the range of 20 = 15°-70°. The morphology was tested through scanning electron microscopy (JEOL, JSM-6490). The photoluminescence spectra and decay curves of the samples were characterized by the Edinburgh spectrometer (FLS 980).

3 Results and discussion

Fig. 1 presents the XRD patterns of Ca$_2$(1-x)Tm$_{x}$Na$_{2}$MgTeO$_6$ ($x = 0.0025, 0.005, 0.01, 0.02, 0.03, 0.05, and 0.10$) phosphors. Obviously, with the increase
of Tm3+ dopant concentration, all the diffraction peaks were in accordance with the standard card (ICPDS no. 48-0108) of Ca2MgWO6 [21, 22]. It indicated that the small amount of Tm3+ ions does not evidently influence the crystal structure of Ca2MgTeO6. The ionic radii of the Ca2+ and Tm3+ ions are approximate corresponding to 1.12 Å and 0.994 Å (coordination number, CN = 8), respectively [23]. Apparently, a small amount of Ca2+ ions can be readily replaced by Tm3+ ions in the Ca2MgTeO6 host lattice. The as-prepared samples were with high phase purity.

Fig. 1. XRD patterns of the Ca2(1-x)Tm xNa xMgTeO6 phosphors (x = 0.0025, 0.005, 0.01, 0.02, 0.03, 0.05, and 0.10).

The morphology of the Ca2MgTeO6:0.02Tm3+ phosphor was characterized through scanning electron microscopy (SEM) and is shown in Fig. 2. The shapes of the particles are irregular and non-uniform, and some clusters are present. The existence of agglomerates is ascribed to high-temperature sintering. Particle size has a range of 1-2 μm.

The excitation spectrum of representative sample Ca2MgTeO6:0.02Tm3+ is monitored at 457 nm and shown in Fig. 3 curve (a). A broadband in the range of 200-250 nm related to O2−→Tm3+ charge transfer band [10]. Another peak in the excitation spectrum at 359 nm is assigned to the typical 4f−4f transition of 3H6→1D2 of Tm3+. Fig. 3 curve (b) displays the emission spectrum of Ca2MgTeO6:0.02Tm3+ at near-UV light λex = 359 nm. The main emission band at 457 nm due to the electronic dipole transition of 1D2 →3F4 of Tm3+. Importantly, the blue region's emission peaks suggested that Ca2MgTeO6:Tm3+ can be promising blue-emitting phosphors.

The PL spectra of Ca2(1-x)Tm xNa xMgTeO6 (x = 0.0025, 0.005, 0.01, 0.02, 0.03, 0.05, and 0.10) phosphors as with different Tm3+ ions content are presented in Fig. 4. It is obvious that all the emission spectra have similar shape profiles with the increasing concentration. When the doping Tm3+ concentration in Ca2(1-x)Tm xNa xMgTeO6 was x = 0.02 mol, the emission intensity of sample reached the most intense. Subsequently, exceeding 0.02 mol, the emission intensities of Tm3+ began to decrease gradually due to concentration quenching phenomena induced through the resonant energy transfer.

Blasse proposed the critical transfer distance (Rc) for analyzing the energy transfer mechanism, and the value can be estimated by this equation (1) [24, 25]:

$$R_c \approx \frac{2}{3\pi N X_c V}$$

where V (238.31 Å3) referred to the cell volume, Xc (0.02) represented the best doping concentration, and N (2) was the number of substitutable cations in a unit cell, the critical transfer distance Rc was estimated to be 22 Å,
much higher than that of exchange interaction distance (5.0 Å). Therefore, the electric multipole interactions between Tm3+ ions will be responsible for the concentration quenching phenomenon.

Furthermore, the following equation was used to evaluate the specific type of interaction mechanism in the energy transfer process of Tm3+ ions [26]:

\[
\frac{I}{x} = K \left[ 1 + \beta(x)^{Q/3} \right]^{-1}
\]  

(2)

Here, Q is constant at 6, 8, and 10. They represent different energy transfer interactions, such as electric dipole-dipole (Q=6), dipole-quadrupole (Q=8), or quadrupole-quadrupole (Q=10) interactions, respectively. x stood for the activator concentration, K and β were constants at the same excitation condition [27]. Fig. 5 illustrates the linear plot. The slope parameter of the line was found to be −1.6. The Q value was fitted to 4.8, which approaches 6, indicating that the electric dipole-dipole interaction was the primary reason for the concentration quenching of Ca2MgTeO6:Tm3+ phosphors [28].

![Fig. 5. Dependence of lgi on lgi(x) of CaMgTeO6:Tm3+ phosphors.](image)

Conclusions

The Ca2MgTeO6:Tm3+ phosphors with different concentrations were successfully synthesized by the solid-state reaction method at 1100 °C for 24 h. Their phase purity was checked by XRD measurement. Particle size has a range of 1-2 μm. When excited at 359 nm, the Ca2MgTeO6:Tm3+ phosphors presented prominent emission peaks at 457 nm. The highest relative intensity was at 0.02 mol doping level. The concentration quenching was due to the electric dipole-dipole interaction. The critical distance related to concentration quenching to be 22 Å. The decay lifetimes were calculated to be 1.007, 0.566, and 0.267 ms when the concentrations were 0.005, 0.02, and 0.05 mol, respectively. The decay time decreased with the enhancement of Tm3+ concentration. When the doping concentration of Tm3+ increases, the interaction between Tm3+-Tm3+ gradually strengthens, resulting in an increase in non-radiative transition possibility.

4 Conclusions

The Ca2MgTeO6:Tm3+ phosphors with different concentrations were successfully synthesized by the solid-state reaction method at 1100 °C for 24 h. Their phase purity was checked by XRD measurement. Particle size has a range of 1-2 μm. When excited at 359 nm, the Ca2MgTeO6:Tm3+ phosphors presented prominent emission peaks at 457 nm. The highest relative intensity was at 0.02 mol doping level. The concentration quenching was due to the electric dipole-dipole interaction. The critical distance related to concentration quenching to be 22 Å. The chromaticity coordinates of Ca2MgTeO6:0.02Tm3+ are (0.147, 0.029). The decay time of Ca2(1-x)Tm3+ in Na2MgTeO6 decreased with the increase of Tm3+ concentration. In conclusion, the Ca2MgTeO6:Tm3+ phosphor is a promising blue-emitting candidate for W-LEDs.

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References

1. L. Han, S. Xie, M. Wang, T. Sun, Q. Liu, G. Jiang, Y. Shi, Y. Tang, Mater. Lett. 234, 241 (2019)
2. Y. Chen, X. Li, N. Li, Y. Quan, Y. Cheng, Y. Tang, Mater. Chem. Front. 3, 867 (2019)
3. Q. Zhao, G.H. Tao, C.W. Ge, Y. Cai, Q.C. Qiao, X.P. Jia, Spectrosc. Lett. 51, 216 (2018)
4. X. Zhang, N. Bao, X. Luo, S.-N. Ding, Biosens. Bioelectron. 114, 44 (2018)
5. Y. Jin, C. Shi, X. Li, Y. Wang, F. Wang, M. Ge, Dyes Pigm. 139, 693 (2017)
6. R. Yu, C. Wang, J. Chen, Y. Wu, H. Li, H. Ma, ECS J. Solid State Sci. Technol. 3, R33 (2014)
7. G. Zhu, Y. Huang, C. Wang, L. Lu, T. Sun, M. Wang, Y. Tang, D. Shan, S. Wen, J. Zhu, Spectrochim. Acta, Part A 210, 105 (2019)
8. D. Wang, X. Fan, S. Sun, S. Du, H. Li, J. Zhu, Y. Tang, M. Chang, Y. Xu, Sens. Actuators, B 264, 304 (2018)
9. J. Shen, S. Shang, X. Chen, D. Wang, Y. Cai, Sens. Actuators, B 248, 92 (2017)
10. S. Liu, J. He, Z. Wu, J.H. Jeong, B. Deng, R. Yu, J. Lumin. 200, 164 (2018)
11. F. Fan, L. Zhao, Y. Shang, J. Liu, W. Chen, Y. Li, J. Lumin. 211, 14 (2019)
12. K. Li, R. Van Deun, Chem. Commun. 55, 10697 (2019)
13. H. Deng, Z. Gao, N. Xue, J.H. Jeong, R. Yu, J. Lumin. 192, 684 (2017)
14. H. Fukushima, D. Nakauchi, T. Kato, N. Kawaguchi, T. Yanagida, Radiat. Meas. 133, 106280 (2020)
15. B. Deng, C.S. Zhou, H. Liu, J. Chen, Mater. Sci. Forum 921, 111 (2018)
16. B. Deng, J. Chen, C.-s. Zhou, H. Liu, Optik 202, 163658 (2020)
17. T. Fu, X. Wang, H. Ye, Y. Li, X. Yao, J. Electron. Mater. 49, 5047 (2020)
18. A. Dias, G. Subodh, M.T. Sebastian, M.M. Lage, R.L. Moreira, Chem. Mater. 20, 4347 (2008)
19. L. Zhang, J. Che, Y. Ma, J. Wang, R. Kang, B. Deng, R. Yu, H. Geng, J. Lumin. 225, 117374 (2020)
20. L. Zhang, Y. Xie, X. Geng, B. Deng, H. Geng, R. Yu, J. Lumin. 225, 117365 (2020)
21. A. S.Y., F. N.F., A. I.F., Inorg. Mater. 921 (1975)
22. www.springermaterials.com/docs/VSP/summary/lpf-sd/00022668.html, E3S Web of Conferences 213, 01034 (2020)
23. R.D. Shannon, Acta Crystallogr., Sect. A: Found. Crystallogr. 32, 751 (1976)
24. G. Blasse, B.C. Grabmaier, Springer-Verlag, Berlin, Heidelberg (1994)
25. W. Yang, C. Liu, S. Lu, J. Du, Q. Gao, R. Zhang, Y. Liu, C. Yang, J. Mater. Chem. C 6, 290 (2018)
26. L.G. Van Uitert, J. Electrochem. Soc. 114, 1048 (1967)
27. L. Tang, L. Zhou, X. Yan, K. Zhong, X. Gao, X. Liu, J. Li, Dyes Pigm. 182, 108644 (2020)
28. L. Tang, L. Zhou, X. Yan, K. Zhong, X. Gao, J. Li, J. Photochem. Photobiol., A 387, 112160 (2020)
29. L. Tang, J. Xia, K. Zhong, Y. Tang, X. Gao, J. Li, Dyes Pigm. 178, 108379 (2020)
30. G. Zhang, L. Zhao, F. Fan, Y. Bai, B. Ouyang, W. Chen, Y. Li, L. Huang, Spectrochim. Acta, Part A 223, 117343 (2019)