The preparation of luminescent and reversible thermochromic Mn-doped Ca-Zn-Al-O inorganic materials

Vorrada Loryuenyong, Pitsinee Juikatu, Pichanut Sirisukha, Ukrit Kumleing and Achanai Buasri

Department of Materials Science and Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom, Thailand

ABSTRACT
In this research, we reported the thermochromic and luminescent behaviors of \( \text{Ca}_{1-x}\text{Zn}_x\text{Al}_{10-x}\text{Mn}_x\text{O}_{35} \) \((x = 0.05, 1.0, 1.5, 2)\) garnet materials prepared by a high-temperature solid-state reaction method. Thermochromism of all samples showed gradual tunability of color with a change in temperature. However, the optimal thermochromic performance was observed for \( \text{Ca}_{1-x}\text{Zn}_x\text{Al}_{10-x}\text{Mn}_x\text{O}_{35} \) samples with \( x = 1 \) and the sintering temperature of 1200°C. The resultant samples showed a reversible change in color from yellow to reddish yellow when heated to around 500°C. This was due to the changes in absorption bands of \( \text{Mn}^{4+} \) and \( \text{Mn}^{5+} \) in octahedral and tetrahedral sites, respectively. The materials also exhibited a deep red emission at around 710 nm. The existence of impurity phases was found to degrade the optical properties of the samples.

1. Introduction
Reversible thermochromic materials have recently attracted tremendous attention due to their durable, reversible, and controllable temperature-responsive color-change behaviors. These materials are normally used in temperature-indicating applications that require a reversible sharp visual color change. Most thermochromic materials are generally organic compounds, ionic liquids, inorganic-organic hybrid molecules, and composites. The thermochromism of these materials normally shows a reversible color change below 200°C. However, they typically suffer high-temperature thermal degradation, short storage life, and poor durability, which limit their applications to a large extent. Therefore, inorganic thermochromic materials are preferable.

Garnet has recently been reported as a new host for reversible intermediate-to-high temperature thermochromic materials [1,2]. The color transition is usually ascribed to the changes in absorption band induced by either reversible phase transition, the thermal expansion and contraction of crystal lattice, or electron transition. However, most of the thermochromic garnet materials are based on rare-earth garnets or an expensive gallium (Ga)-based garnets such as \( \text{Y}_2\text{Fe}_2\text{O}_{12}, \text{Ca}_3\text{Zn}_2\text{Ga}_{10}\text{O}_{35}, \) and \( \text{Sm}_3\text{Fe}_5\text{O}_{12}. \) Huanhuan et al. [1] reported that the thermochromic properties of \( \text{Ca}_3\text{Zn}_2\text{Ga}_{10}\text{O}_{35} \) were induced by the introduction of dopants such as chromium (Cr), manganese (Mn), iron (Fe), and cobalt (Co). The Mn-doped samples, however, showed the best thermochromic performance due to the contribution of \( \text{Mn}^{4+} \) and \( \text{Mn}^{5+} \). When heated to 460°C, these thermochromic materials change color from greenish to yellow.

Although \( \text{Ca}_3\text{Zn}_2\text{Ga}_{10}\text{O}_{35} \) has many interesting optical properties, it is very expensive because of the cost of the gallium metal. By replacing Ga with Al, the similar building units of garnets or \( \text{Ca}_3\text{Zn}_2\text{Al}_{10}\text{O}_{35} \) could be obtained. In the \( \text{Ca}_3\text{Zn}_2\text{Al}_{10}\text{O}_{35} \) structure [3], \( \text{Zn}^{2+} \) ions occupy tetrahedral sites, and \( \text{Al}^{3+} \) ions occupy both the tetrahedral and octahedral \( \text{AlO}_6 \) sites. There are, additionally, three independent \( \text{Ca}^{2+} \) ions. Two of them are in octahedral sites, and the third independent \( \text{Ca}^{2+} \) is seven-coordinated. With divalent ions such as \( \text{Ca}^{2+}, \) \( \text{Mn}^{4+} \) could be obtained due to the charge compensation [4]. The \( \text{Mn}^{4+} \) ions are preferentially accommodated at the \( \text{Al}^{3+} \) ion sites with an octahedral coordination due to their similar ionic radius [5,6]. The doping atoms with +2 and +3 valences normally occupy the tetrahedral and octahedral sites, respectively. Previous researches have been reported that \( \text{Mn}^{2+} \) ions tend to occupy \( \text{Zn}^{2+} \) sites, while \( \text{Mn}^{3+} \) ions tend to occupy \( \text{Al}^{3+} \) sites [7–9].

The substitution of \( \text{Mn}^{4+} \) ions into the octahedral sites \( \text{AlO}_6 \) of \( \text{Ca}_3\text{Zn}_2\text{Al}_{10}\text{O}_{35} \) would induce the deep red luminescence [10–13]. This material has recently been attracted a great attention because of highly efficient emission in the spectral region of 650–700 nm, high thermal stability, and ease of preparation. Its efficient red emission is beneficial for uses in applications that require red spectral lighting such as indoor
plant cultivation [1,10–13]. Several methods have been reported to improve the luminescence of this material, including the determination of the optimal Mn⁴⁺ doping content [10], the use of oxygen-pressure method [12], and the co-doping with other ions to obtain a broadband near-infrared (NIR) emission [13,14]. Other improvements for the luminescence efficiency of light-emitting materials are the controls of defects and impurity phases [15] and the modification of the crystallinity [16,17].

To date, Ca₉Zn₆Al₁₀O₃₅ has been widely investigated as a deep red emitting phosphor. However, to our knowledge, the studies on the thermochromism of this material are rare. In this paper, we have, therefore, prepared Mn⁴⁺-doped Ca₁₄Zn₆Al₁₀O₃₅ materials by conventional solid-state reaction method. The effects of crystalline phases and valence states of manganese on the luminescence and thermochromic properties were discussed.

2. Experimental procedures

2.1. Chemicals and materials

The constituent oxides CaCO₃, Al₂O₃, ZnO, and MnCO₃ were used as raw materials. Calcium carbonate (CaCO₃, NPCC101, average particle size ~ 40 nm) was purchased from Nanomaterials Technology. Zinc oxide (ZnO ≥99%), manganese (II) carbonate (MnCO₃ ≥99.9%), and aluminum oxide (Al₂O₃, standard grade) were purchased from Sigma-Aldrich.

2.2. Synthesis of thermochromic materials

Mn-doped Ca-Zn-Al-O materials were synthesized by solid-state reaction. The composition of samples with different manganese doping levels is shown in Table 1. The starting materials were first mixed and ground in mortar and pestle for 30 min. The homogeneous mixture was then calcined in air at 800°C for 6 h at the heating rate of 5°C/min. After calcination, the mixture was ground in mortar and uniaxially pressed into 20-mm-diameter pellets under a pressure of 95 MPa. The pellets were then sintered at 1200°C in air for 5 h at a heating rate of 5°C/min.

### Table 1. Chemical compositions, preparations, and CIE values of samples.

| Samples    | Composition (wt.%) | CIE values | Color |
|------------|-------------------|------------|-------|
|            | CaCO₃ ZnO Al₂O₃ MnCO₃ |            |       |
| CZA00.0    | 58.40 20.35 21.25 0 | 97.1       | 3.4   | 14.3  |
| CZA00.5    | 57.63 20.09 19.92 2.36 | 75.2       | 5.5   | 32.0  |
| CZA01.0    | 56.88 19.82 18.63 4.67 | 72.5       | 8.6   | 47.9  |
| CZA02.0    | 56.16 19.57 17.37 6.91 | 55.0       | 3.4   | 18.1  |
| CZA02.0    | 55.44 19.32 16.14 9.10 | 48.2       | 3.2   | 19.7  |

2.3. Characterizations

X-ray diffraction patterns (XRD) were identified by a Shimadzu LabX XRD-6100. Scanning-electron-microscope (SEM) images and energy-dispersive-spectroscopy (EDS) spectra were detected by Tescan MIRA3. Photoluminescence (PL) spectra were recorded using a photoluminescence spectroscopy (Avantes Avaspec-2048TEC). Absorption spectra were determined using a UV-Vis-NIR spectrophotometer (Shimadzu 3600i plus). X-ray photoelectron spectroscopy (XPS) spectra are characterized using Kratos Axis Ultra DLD. FTIR spectra were obtained using a Bruker Vertex 70 spectrometer.

3. Results and discussion

Figure 1 shows XRD patterns of the samples prepared by a solid state reaction method. All the samples have the diffraction peaks corresponding to a cubic structure of Ca₁₄Zn₆Al₁₀O₃₅ (JCPDS card no. 50-0426). However, there is also the existence of secondary phases, including CaO (JCPDS card no. 37-1497), ZnO (JCPDS card no. 01-79-0206), and Ca₉Zn₆Al₁₀O₃₅ (JCPDS card no. 49–0280). According to a typical phase diagram of 14CaO-6ZnO-5Al₂O₃ system [18], there are generally 3 equilibrium phases, i.e., ZnO, Ca₉Zn₆Al₁₀O₃₅, and Ca₉Zn₆Al₁₀O₃₅ in the current composition. The substitution of manganese ions into the crystalline sites of zinc and calcium ions could also result in the remaining ZnO and CaO oxide precursors as secondary phases.

At the optimal manganese content (CZA01.0), most of the precursors participate in a complete reaction for the formation of Ca₁₄Zn₆Al₁₀O₃₅. The samples, therefore, exhibit the smallest amount of impurity phases. An increase in manganese content, however, could induce the formation of MnO₃ (peaks at 2-Theta = 33.0° and 34.6°) [1]. In addition, it could be observed that the manganese doping results in the shifts of XRD peaks of Ca₁₄Zn₆Al₁₀O₃₅ to higher angles. These shifts are attributed to the difference in ionic radius between Mn⁴⁺ and Al³⁺ ions, leading to the shrinkage of the lattice. It could also be observed that the intensity of the peak decreases with the doping level. This is likely due to the existence of structural defects associated with the incorporation of a large amount of manganese ions into Ca₁₄Zn₆Al₁₀O₃₅ lattice.

The morphology and compositional analysis of the samples were obtained from SEM and EDS analysis as shown in Figure 2. The appearance of impurity phases could be observed. For undoped sample (CZA00.0), the image shows particles with polygonal shape of Ca₁₄Zn₆Al₁₀O₃₅. The SEM images of Mn-doped samples, however, show rod-shaped crystals with the sizes in the range of sub-micrometers to a few micrometers. The EDS spectrum clearly shows that these crystals contain the peaks
of zinc (Zn), aluminum (Al), calcium (Ca), manganese (Mn), and oxygen (O). The decrease in Al ratio, compared to that of CZAO0.0, suggests that manganese ions have been substituted into Al sites in $\text{Ca}_{14}\text{Zn}_6\text{Al}_{10}\text{O}_{35}$ structure.

The absorption spectra of $\text{Ca}_{14}\text{Zn}_6\text{Al}_{10}\text{O}_{35}$ host and Mn-doped $\text{Ca}_{14}\text{Zn}_6\text{Al}_{10}\text{O}_{35}$ are shown in Figure 3. With no manganese doping, there is a rapid increase in the absorption below 400 nm with a shoulder in the vicinity of 400–600 nm. The absorption band in the UV region below 400 nm is due to the charge transfer transition of metallic ions such as Al$^{3+}$, Ca$^{2+}$, and Zn$^{2+}$ and O$^{2-}$ ions. Mn-doped samples, however, show two absorption bands, which are originated from the absorption by Mn$^{4+}$ ion. The absorption band centered at 461 nm is due to the $^4\text{A}_2 \rightarrow ^4\text{T}_2$ transitions of Mn$^{4+}$ ion and attributes the yellowish color to the sample. Samples with no manganese doping (CZAO0.0) do not show any sharp absorption bands in this region and appear yellowish-white in color. An additional strong absorption band in the UV region of the doped samples is caused by the characteristic absorption of manganese ions, which is overlapped with that of the charge transfer between the metallic ions and O$^{2-}$ ion. A further increase in manganese doping results in the existence of a broad absorption band toward long-wavelength region, making the sample appear more greenish (Table 1). With increasing amount of manganese content, the band becomes wider, and the absorption intensity is increased. This band is attributed to the absorption of Mn$^{4+}$, whose band gap is approximately 1.29 eV [19], and any possible Mn$^{5+}$ in the tetrahedral site [1]. The latter is attributed to the transition from the ground state ($^4\text{A}_2$) to $^3\text{T}_1$, $^3\text{T}_2$, and $^1\text{A}_1$ of Mn$^{5+}$ ion [20].

Figure 4 shows the emission spectra of the samples excited at 345-nm UV light. It is noticeable that only samples with manganese doping exhibit the red luminescence under UV irradiation. The broad red emission centered at around 710 nm is originated from the $^2\text{E} \rightarrow ^4\text{A}_2$ transition of Mn$^{4+}$ ions. This corresponds well with the emission peak around 480 nm, which can be attributed to the $^4\text{A}_2 \rightarrow ^4\text{T}_2$ transitions of Mn$^{4+}$, and those reported in
with this, there are three superimposed emission peaks at around 410 nm (3.02 eV), 480 nm (2.58 eV), and 530 nm (2.34 eV) nm. This is due to the transition with shallow and deep defect levels as a result of possible Al or Mn doping in ZnO structure [22]. The UV-sided shoulder in the emission spectra at 364 nm (3.41 eV) could be attributed to the transitions from excitonic levels and/or zinc interstitials (Zn$_i$) to the conduction band (CB). As a result, for the lighting applications, controlling defects and impurity phases could play an important role to enhance the luminescence efficiency [16,17].

Figure 5 shows Mn 2p3/2 and Mn 2p1/2 XPS spectra of the samples. In general, manganese could be in the various oxidation states such as Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$ cations or a mixture of these [23,24]. When heated to high temperatures, these ions could occupy tetrahedral or octahedral sites of the garnet structure. Previous research [25] has demonstrated that Mn$^{2+}$ and Mn$^{3+}$ could also be incorporated in the Mn$^{4+}$-doped Ca$_{24}$Zn$_{6}$Al$_{10}$O$_{35}$ structure. The existence of these ions, especially Mn$^{2+}$, could cause the reduction of the red emission intensity of the samples. Considering the XPS peaks corresponding to Mn 2p3/2, compared with the literature data reported for Mn$^{2+}$, Mn$^{3+}$, Mn$^{4+}$, and Mn$^{6+}$ [26,27], it appears that the CZAO0.5 and CZAO1.0 have the binding energy of the Mn 2p3/2 close to that of Mn$^{4+}$ (641.9 eV) [27]. The results confirm that most of the valence states for manganese in the structure is +4. For higher manganese doping levels, the Mn 2p3/2 peaks consist of additional peak at larger binding energy between that of Mn$^{4+}$ and Mn$^{6+}$. This could be due to the existence of higher valence states of manganese such as Mn$^{5+}$, which is consistent with the light absorption behavior of the samples.

The intense broad emission band between 350 and 600 nm could be observed for the undoped samples, which gives consistent results with the absorption shoulder in Figure 3. The intensity of this band decreases with an increase in manganese doping level. This could be due to the transition in ZnO impurity phase. Previous research [21] has stated that undoped ZnO could emit intense visible light from its sub-band transition. Along
summary, although Mn$^{2+}$, Mn$^{3+}$, Mn$^{4+}$, and Mn$^{5+}$ were contained in all samples, the optimal red emission would be achieved in samples that predominantly contain Mn$^{4+}$ ions. The intensity of the red emission decreases as the manganese ions incorporated as other valence states. The same analysis occurs for the 2p1/2 peaks.

The FT-IR spectra and analysis of samples are shown in Figure 6 and Table 2. All the samples exhibit the absorption bands for Al-O, Zn-O, and Ca-O vibrations (Table 2). The bands at 935–950 cm$^{-1}$ and 1154 cm$^{-1}$ are attributed to the Al-O vibrations in AlO$_6$ tetrahedron, while the peak at 680 cm$^{-1}$ is ascribed to the AlO$_6$ octahedron band. The absorption bands at around 440 cm$^{-1}$ and 520 cm$^{-1}$ are attributed to Zn-O stretching vibration, and the band at around 850 cm$^{-1}$ is related to the Ca-O vibration. With Mn doping, there is the presence of a band around 560–570 cm$^{-1}$, which is a characteristic of Mn-O stretching vibrational mode [28]. At the optimal concentration of manganese (CZA01.0), there are two sharp and intense peaks centered at around 680 cm$^{-1}$ and 753 cm$^{-1}$. The former or the AlO$_6$ octahedron band slightly shifts toward lower frequency, indicating the substitution of Mn$^{4+}$ ions in the octahedral sites (AlO$_6$). This is due to the higher cation mass of Mn$^{4+}$. The sharp peaks with high intensity indicate the high crystallinity and small amount of structural defects of the Ca$_{5}$Zn$_{5}$Al$_{10}$O$_{35}$ host.

Figure 7 shows the images of the samples annealed at various temperatures from 30°C to 460°C. At 30°C, the color difference among the samples is due to the different absorption behavior. Without manganese doping, the color is originated from the charge transfer between oxygen ligand and metal. With an increase in manganese concentration, the color change is associated with the transition of Mn$^{4+}$ and Mn$^{5+}$ in the structure. The samples also show the thermochromic behavior due to the alteration of the absorption bands with increasing temperatures. Based on previous researches [1], the bands for $^{4}$A$_{2}$→$^{4}$T$_{2}$ transitions of Mn$^{4+}$ across 420–540 nm not only shift to a higher wavelength but also have a decreased intensity, indicating the transformation in oxidation states from Mn$^{4+}$ ions to other states. The absorption intensity of the bands between 540 and 850 nm also decreased dramatically with temperature. The strongest color change with the change

![Figure 6. FTIR spectra of Ca-Zn-Al-O samples with different manganese doping levels: (a) CZA00.0, (b) CZA06.5, (c) CZA01.0, (d) CZA01.5, and (e) CZA02.0.](image)

![Figure 7. Photographs of samples at different temperatures.](image)
of temperature occurs with CZAO1.0 sample. As the annealing temperature increases, CZAO1.0 sample exhibit colors ranging from yellow (30–189°C) to light reddish yellow (260–340°C) and dark reddish yellow (400–460°C). This confirms a redshift of the absorption band with increasing temperatures. When the annealing temperature was 460°C or above, i.e., 500°C, the samples are obtained with red shades. The color recovers when the temperature decreases to room temperature. Excessive amount of manganese doping, however, deteriorates thermochromic properties due to the wide light absorption in visible region from the presence of manganese oxide. The color change in response to a change in temperature could then mix with the dark color tone of manganese oxide, causing an unclear difference in color.

4. Conclusions

In summary, Mn-doped Ca$_{14}$Zn$_6$Al$_{10}$O$_{35}$ materials were successfully prepared by a conventional solid-state reaction method. The samples with optimal manganese doping level could behave both as thermochromatic and luminescent materials. The materials were yellow in daylight and had reddish glow under UV exposure. They also showed a color change from yellow to yellowish-red when heated from room temperature to around 500°C. Nevertheless, their thermochromism and luminescence properties were found to be related to the phase purity and crystallinity as well as the valence states of manganese. These findings could significantly contribute to further improvements and developments in inexpensive solid-state lighting as well as sensor applications.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

ORCID

Vorrada Loryuenyong http://orcid.org/0000-0002-9319-6211
Achanai Buasri http://orcid.org/0000-0002-1948-2518

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