Extending the Luminescence Properties of Zinc Gallogermanate via Co-doping with Cost Effective Metals Ions ($\text{Cr}^{3+}/\text{Mg}^{2+}$, $\text{Cr}^{3+}/\text{Ca}^{2+}$ and $\text{Cr}^{3+}/\text{Sr}^{2+}$)

Moustafa M.S. Sanad (✉ mustafa_sanad2002@yahoo.com)

Central Metallurgical R & D Institute <https://orcid.org/0000-0002-4312-7234>

Research Article

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Abstract

The huge applications of red-light emitting materials paying the research attention to reduce the cost of production and raw materials. Therefore, abundant cations of alkaline earth metals e.g. Mg^{2+} , Ca^{2+} and Sr^{2+} were successfully incorporated with Cr^{3+} : $\text{Zn}_3\text{Ga}_2\text{Ge}_2\text{O}_{10}$ (Cr-ZGGO) as co-activators via simple solid-state method. The X-ray diffraction (XRD) results of all samples confirmed the formation of zinc gallogermanate superstructure with two cubic phases ZnGa_2O_4 and Zn_2GeO_4 . The particle imaging of Cr-ZGGO and Ca@Cr-ZGGO via field emission scanning electron microscopy (FE-SEM) reveals a significant change in morphology and particle size by Ca^{2+} co-doping. Meanwhile, the energy dispersive X-ray spectroscopic analysis (EDS) and mapping techniques elucidate the exact chemical composition of the calculated stoichiometric substitution and illustrate the equal distribution of all elements over the whole sample. Optical band gap energy of Mg^{2+} , Ca^{2+} and Sr^{2+} co-doped phosphors are lower than Cr-ZGGO. The Sr@Cr-ZGGO displays the most intense photoluminescence (PL) peak and the broadest emission in the near infra-red region (NIR) as a result of increasing light traps and generation of new paths between the energy levels of trapping centers.

1. Introduction

The need for low cost, highly stable and eco-friendly luminescent materials enforced the scientists to focus their research on metal oxide phosphors rather than metal sulphides [1]. Certain types of luminescent materials with long lasting phosphorescence are widely used in various applications such as optical imaging, light emitting diodes and spectral converters [2–4]. It has been reported that Cr^{3+} doped metal based gallogermanate such as $\text{La}_3\text{Ga}_5\text{GeO}_{14}$, $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ and $\text{Sr}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ displayed unique capabilities for near-infra red (NIR) emissions upon excitation with ultraviolet and visible light irradiation [5–7]. In recent years, zinc gallogermanate compounds have emerged as one of the most popular hosting materials to be applied for long persistent phosphors [8–10]. The reason for long red persistent luminescence in $\text{Zn}_3\text{Ga}_2\text{Ge}_2\text{O}_{10}$ (ZGGO) as hosting material could be attributed to the presence of tetrahedral and octahedral sites available from the formed solid solution of two crystal structures, spinel ZnGa_2O_4 and willemite Zn_2GeO_4 [9, 11]. Therefore, single doping of ZGGO with Cr^{3+} or Mn^{2+} ions possessed red and green emissions as a result of ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transitions caused by the lattice distortion in the octahedral positions [12–14]. Actually, the co-doping of Cr-ZGGO with Pr^{3+} was found to be an effective way to improve emissions performance up to 695 nm and prolong the afterglow properties especially at near infra-red region [15]. Similarly, the incorporation of Eu^{3+} in spinel Cr-ZGGO yielded a persistent NIR emission at 697 nm for in vitro bio-imaging applications [16]. In addition, Lin et al discovered that the co-doping of $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ with Nd^{3+} and Cr^{3+} would lower the energy transitions paths as a result of deeper traps generation between these energy levels achieving better and broader photoluminescence features [17]. Moreover, the photo-stimulation of spinel phosphors $\text{Cr}^{3+}:\text{ZnGa}_2\text{O}_4$ was clearly confirmed to achieve long persistent red emissions via complete or partial substitution of Zn^{2+} with Mg^{2+} [18, 19] and Ga^{3+} substitution with Sn^{4+} or Al^{3+} [20, 21]. This significant enhancement in these

host luminescent materials could be attributed to the enlarged numbers of energy levels (i.e. crystal field splitting) which extend the trapping/de-trapping kinetics as a result of crystal structure distortion and the created vacancies in both octahedral and tetrahedral sites [22, 23]. Inspired by the previous concepts, this work suggests the substitution of Zn^{2+} in the ZGGO with different codopant ions $\text{Cr}^{3+}/\text{Mg}^{2+}$, $\text{Cr}^{3+}/\text{Ca}^{2+}$ and $\text{Cr}^{3+}/\text{Sr}^{2+}$ to induce synergistic activation effects owing to the produced distorted spinel structure, cation vacancies and localized traps causing a strong red emission performance and significant delay for relaxation processes through a resonant energy transfer steps. Moreover, avoiding the utilization of rare earth activators such as (Eu^{3+} , Pr^{3+} , Nd^{3+} , ... etc.) and only use small portions of alkaline metals as co-activators will reduce the cost of these red phosphors. Hence, the present study aims at investigating the physicochemical, morphology, optical and photoluminescence properties of Cr^{3+} -doped ZGGO and their activated compounds with three types of earth abundant alkaline metals (Mg^{2+} , Ca^{2+} and Sr^{2+}) in order to achieve high persistent red emission characteristics.

2. Experimental

2.1. Sample preparation

Pink powder samples of $\text{Cr}_{0.015}\text{Zn}_{2.985}\text{Ga}_2\text{Ge}_2\text{O}_{10}$ (Cr-ZGGO) and $\text{M}^{2+}_{0.015}\text{Cr}_{0.015}\text{Zn}_{2.97}\text{Ga}_2\text{Ge}_2\text{O}_{10}$ ($\text{M}^{2+} = \text{Mg}^{2+}$, Ca^{2+} or Sr^{2+}) were prepared via high temperature solid state route. The starting materials for chemical synthesis are $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (Fischer, 99%), Ga_2O_3 (Sigma-Aldrich, 99, 99%), GeO_2 (MSE Supplies, 99, 99%), Cr_2O_3 (Alfa Aesar, 99%), $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich, 99, 5%), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich, 99, 99%), $\text{Sr}(\text{NO}_3)_2$ (Sigma-Aldrich, 99, 99%). The stoichiometric mass of all components was placed together in a planetary ball mill to perform grinding at 400 rpm for 6 hours. The ground powder then pre-calcined in muffle furnace at 800°C for 2 hours in air. The pre-calcined powders were subsequently calcined at 1200°C for 6 hours in air with heating rate 5°min^{-1} . The obtained four samples are ground again in an agate mortar for further physical and optical characterization.

2.2. Powder characterization

The crystal structure of the prepared samples was investigated using powder X-ray diffraction (XRD) of model Bruker AXS diffractometer (D8-ADVANCE Germany) with $\text{Cu K}\alpha$ ($\lambda = 1.54056 \text{ \AA}$) radiation, operating at 40 kV and 40 mA in the 2θ range 20° and 60° and the scanning rate about $0.02^\circ / 0.4 \text{ sec}$. The microstructure of the powder samples was disclosed by field emission scanning electron microscopy FE-SEM (JEOL-JSM-5410 Japan). The chemical analysis and elemental mapping were carried out by the energy dispersive X-ray spectrometer (EDS) Model: Apollo x attached with SEM with resolution 133 eV. Fourier transform infrared (FTIR) was employed for investigation using Jasco-6300 spectrometer (Japan) in the range $400\text{--}4000 \text{ cm}^{-1}$. The optical properties were tested using UV/VIS/NIR spectrophotometer (Model: Jasco-V-570, Japan) based on an integrating sphere reflectance unit in the wavelength range $250\text{--}1000 \text{ nm}$ at room temperature. The fluorescence spectrophotometer (SHIMADZU RF-5301PC

Japan) was utilized to measure the photoluminescence emission peaks at room temperature after excitation of samples at $\lambda = 515$ nm with xenon discharge lamp of power ~ 150 W.

3. Results And Discussions

3.1. XRD analysis

Figure 1 shows the XRD patterns of Cr-ZGGO; Mg@Cr-ZGGO; Ca@Cr-ZGGO and Sr@Cr-ZGGO powders calcined at 1200°C for 6 hours. The crystal structure of all samples reveals the formation of cubic superstructure of mixed spinel phase of ZnGa_2O_4 with JCPDS card no. 38-1240 and Zn_2GeO_4 with JCPDS card no. 25-1018. The hexagonal GeO_2 phase with JCPDS card no. 34-1089 is also detected as minor phase in Cr-ZGGO and Sr@Cr-ZGGO samples. However, it is associated with larger percentage in Mg@Cr-ZGGO and Ca@ZGGO samples. The slight shift in the diffraction peaks of ZGGO crystal planes at 111, 220, 311, 222, 400, 422, 511, 440, 620, 533, 622 confirms the incorporation of Mg, Ca, and Sr in the ZGGO crystal structure. It is worth to note that the coincide of all patterns with both ZnGa_2O_4 and Zn_2GeO_4 phases indicates the formation of zinc gallogermanate solid solution. The envisaged results are comparable to the reported XRD data in the literature [24–26]

3.2. SEM, EDS and Elemental Mapping

Figure 2 (a, b) reveals the morphology of Cr-ZGGO particles which formed in large lumps with irregular shape and their main size was about $3\text{--}5\text{ }\mu\text{m}$. Meanwhile, Ca@Cr-ZGGO sample appears with sphere-like morphology and smaller particle size about $1\text{--}3\text{ }\mu\text{m}$ as shown in Fig. 2 (c). The EDS analysis in Fig. 2 (d) illustrates chemical composition of Ca@Cr-ZGGO sample confirms the actual weight percentage of each element which is very close to the calculated composition. Figure 3 (a-e) shows the elemental mapping for Cr-ZGGO sample which indicates the uniform distribution of each element resulting in homogeneous solid solution of zinc gallogermanate. Moreover, the EDS analysis in Fig. 3 (f) reveals the actual chemical composition of Cr-ZGGO is approximately similar to the calculated formula. The observed morphology and particle size are in a good agreement with previously reported studies [27, 28].

3.3. FTIR analysis

Figure 4 reveals the FTIR absorption spectra of Cr-ZGGO and alkaline metal co-doped Cr-ZGGO samples. The broad and shallow absorption band observed around $300\text{--}3600\text{ cm}^{-1}$ in Cr-ZGGO sample could be assigned to the stretching vibration of O-H bonds in the absorbed water molecules [29]. The incorporation of Mg^{2+} and Sr^{2+} ions shifts this band to lower wave numbers, while the Ca^{2+} addition diminishes this absorption peak. The two weak absorption peaks at 2850 and 2920 cm^{-1} can be attributed to the stretching vibrations of C-H bonds [30]. The two overlapped peaks detected at 1500 and 1650 cm^{-1} are usually attributed to the bending vibrations of O-C = O and H-O-H bonds, respectively [31]. Therefore, lower absorption and shift to higher wave numbers are noticeably occurred to these peaks by doping Cr-ZGGO with Mg^{2+} , Ca^{2+} or Sr^{2+} ions. This behavior could be explained by the enhanced crystallinity of the

primary superstructure phase. The absorption bands in the range $750\text{--}900\text{ cm}^{-1}$ correspond to the stretching vibration modes of asymmetric metal-oxygen bonds such as Zn-O-Ga, Zn-O-Ge and Ga-O-Ge bonds where Mg@Cr-ZGGO and Sr@Cr-ZGGO possessed higher intense peaks than Cr-ZGGO and Ca@ZGGO samples [32]. Meanwhile, the two weak absorption bands at 480 and 610 cm^{-1} are assigned to the symmetric stretching vibrations of O-Ga-O/O-Ge-O and O-Zn-O bonds, respectively.

3.4. Optical and luminescence properties

3.4.1. Band gap energy

The diffuse reflectance of the Cr-ZGGO and alkaline metal co-doped Cr-ZGGO samples were measured and converted to Kubelka-Munk function $F(R_\infty)$ for calculation of optical band gap according to the Tauc's law [33].

$$[\hbar\nu \times F(R_\infty)]^2 = A \times (\hbar\nu - E_g)$$

The band gap values can be obtained from the intercept of the extrapolated straight line of $(\alpha h\nu)^2$ - $h\nu$ plot as shown in Fig. 5 (a-d). It is noticed that the band gap energy (E_g) of Cr-ZGGO ~ 4.9 eV decreased by the additional doping with alkaline metals. The E_g values of about 4.2, 4.1 and 4.0 eV are found to be gradually decrease with increasing ionic radius of the alkaline metal according to the order $\text{Sr} < \text{Ca} < \text{Mg}$. The results are consistent with the reported approach about Cr^{3+} -doped gallogermanate materials [34–36].

3.4.2. Photoluminescence properties

Figure 6 (a) represents the produced emission spectra of Cr-ZGGO; Mg@Cr-ZGGO; Ca@Cr-ZGGO and Sr@Cr-ZGGO samples upon excitation at $\lambda_{\text{Ex}} = 515\text{ nm}$. The produced PL spectra for all samples appeared as broad peak with wavelength range $600\text{--}850\text{ nm}$ and band maxima at 697 nm . The intensity and full width at half maximum (FWHM) of emission peaks are linearly increase with increasing ionic radius of the alkaline metal according to the order $\text{Sr} < \text{Ca} < \text{Mg}$ as revealed in Fig. 5 (b). It is known that the Cr^{3+} introduction to ZGGO host compound creates sub-levels of energy states below the conduction band which act as trapping centers for enhancing the photoluminescence properties [35, 37, 38]. Accordingly, the incorporation of Mg^{2+} , Ca^{2+} or Sr^{2+} is expected to increase the number of trapping levels which may enlarge the energy transfer from Cr^{3+} levels to Mg, Ca or Sr levels. These new energy transfer paths could clearly improve the photoluminescence response as previously discussed in the literature [17, 39]. It is worth to mention that the obtained PL results of Sr@Cr-ZGGO are better than previously reported results of $\text{Cr}^{3+}/\text{Pr}^{3+}$ co-doped ZGGO [15].

4. Conclusion

The present work practically compared the employing of three types of alkaline earth metals ($\text{M}^{2+} = \text{Mg}^{2+}$, Ca^{2+} or Sr^{2+}) as cheap co-activators in Cr-doped zinc gallogermanate red phosphors via simple solid-

state pathway. The XRD results revealed the formation of mixed solid solution of two spinel phases, ZnGa_2O_4 and Zn_2GeO_4 . The successful incorporation of $\text{Cr}^{3+}/\text{Mg}^{2+}$, $\text{Cr}^{3+}/\text{Ca}^{2+}$ and $\text{Cr}^{3+}/\text{Sr}^{2+}$ was clearly elucidated using XRD, FE-SEM, EDS and FTIR characterization tools. The Ca@Cr-ZGGO particles appeared with sphere-like morphology and particle size range about 1–3 μm while Cr-ZGGO particles have non-distinct shape and larger particle size range about 3–5 μm . Both Mg@Cr-ZGGO and Sr@Cr-ZGGO samples exhibited FTIR absorption bands for Zn-O-Ga, Zn-O-Ge and Ga-O-Ge bonds with higher intensity than Cr-ZGGO and Ca@ZGGO samples. Tauc's plot results indicated that the band gap energy of Cr-ZGGO decreased by co-doping with Mg^{2+} , Ca^{2+} and Sr^{2+} cations. All metal co-doped Cr-ZGGO samples showed improved photoluminescence characteristics due to generation of new energy transfer paths between the increased number of trapping levels resulting in persistent red-light emission.

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Figures

Figure 1

XRD diffraction patterns of Cr-ZGGO; Mg@Cr-ZGGO; Ca@Cr-ZGGO and Sr@Cr-ZGGO powders calcined at 1200°C, (*) Hexagonal GeO₂ phase

Figure 2

SEM images of Cr-ZGGO sample at two magnifications (a, b), SEM image of Ca-doped Cr-ZGGO sample (c), EDX analysis of Ca-doped Cr-ZGGO sample (d)

Figure 3

(a-e) Elemental mapping of Cr-ZGGO sample, (f) EDX analysis of Cr-ZGGO sample

Figure 4

FTIR absorption spectra of Cr-ZGGO and alkaline metal doped Cr-ZGGO samples

Figure 5

Band gap energy plots of Cr-ZGGO sample (a) Mg@Cr-ZGGO sample (b) Ca@Cr-ZGGO sample (c) Sr@Cr-ZGGO sample (d)

Figure 6

(a) Photoluminescence spectra, (b) emission intensity and FWHM of Cr-ZGGO; Mg@Cr-ZGGO; Ca@Cr-ZGGO and Sr@Cr-ZGGO samples at excitation wavelength = 515 nm