Luminescence of delafossite-type CuAlO$_2$ fibers with Eu substitution for Al cations

Yin Liu$^a$, Yuxuan Gong$^a$, Nathan P. Mellott$^a$, Bu Wang$^a$, Haitao Ye$^b$ and Yiquan Wu$^a$

$^a$New York State College of Ceramics, Alfred University, Alfred, NY, USA
$^b$School of Engineering and Applied Science, Aston University, Birmingham, UK

1. Introduction

Delafossite-type CMO$_2$ ternary oxides (C represents monovalent ion and M represents the trivalent ion) have been widely studied as p-type transparent conducting oxides and exhibit promise for various optoelectronics applications.[1–5] This class of materials has a rhombohedral space group of R$\bar{3}$m. The c-direction of the layered delafossite is occupied by a linearly coordinated O-Cu-O dumbbell. The edge-sharing MO$_6$ octahedra constitute the MO$_2$ layer along the $ab$ plane, which is connected by the Cu$^+$ ions. CuAlO$_2$ is a typical p-type transparent oxide with a wide band-gap (>3 eV) and room temperature photoluminescence through its UV near-band-edge emission due to the recombination of free excitons.[1,6,7] The delafossite structure allows for chemical bond stretching from either the Cu-O bonds (xy-plane) or the Al-O bonds (z-direction) and the local lattice relaxations are crucial to electrical properties. By substituting the Al cation site with other trivalent ions, the conductivity could be enhanced due to the change of the electronic density via ligand field modification.[8,9]

While most researchers focus on the electrical properties of CuAlO$_2$ as a p-type transparent conducting oxide, there are few reports of CuAlO$_2$ as a potential phosphor material. In addition, with the development of field emission display and other flat display technologies,
new generation of phosphors with good luminescence, conductivity and stability are required. CuAlO$_2$ could be a promising host material in which the Al site could be substituted with various trivalent rare earth dopants, without changing the hole transport within the Cu$^+$ plane.\[9\] Since the main conduction path in delafossite crystals is close-packed Cu$^+$ layers,\[10\] the electrical properties could be sustained in addition to photoluminescence properties. Conventional solid-state synthesis of CuAlO$_2$ powders or thin films requires high temperature sintering and repeated thermal treatments. In this study, we prepared CuAlO$_2$ fibers via a cost-effective electrospinning method. The wire-like CuAlO$_2$ nanostructures possess higher surface area and sintering activity, which could lower the annealing temperature. Additionally, the one-dimensional material may also present extraordinary effectiveness in light emitting and transparent conducting.\[11–13\] The dopant cation, Eu$^{3+}$, was chosen as the emission activator and intense red emission from f-f transition of Eu$^{3+}$ was identified. The Eu$^{3+}$ activator center was successfully doped into the Al$^{3+}$ site and this delafossite-type material could be used as potential host for luminescence application.

2. Experimental details

The 0.01 mol CuAl$_{1-x}$Eu$_x$O$_2$ ($x = 0.001, 0.003, 0.01, 0.03, 0.05 and 0.1$) was prepared through stoichiometric mixing of copper nitrate, aluminum nitrate and europium nitrate in deionized water. Poly(vinylpyrrolidone) (PVP, molar weight ~140,000 g mol$^{-1}$) was then added into the aqueous solution to obtain desirable viscosity for electrospinning. The viscous solution was then electrospun onto aluminum foil via a self-made electrospinning device. The as-spun polymer fibers were collected and annealed in air at 1100 °C for 3 h.

The thermo-gravimetric (TG) and differential thermal analyses (DTA) were carried out on Q600 TG/DTA (TA Instruments, New Castle, DE) in flowing air. The powder X-ray diffraction measurement was performed on Bruker D2 Phaser (Bruker-AXS, Madison, WI) using Cu Kα radiation line. The Rietveld refinement was carried out by TOPAS software kits (Bruker-AXS, Madison, WI). The microstructure of the electrospun fibers was observed through an FEI Quanta 200F environmental scanning electron microscope (ESEM) (Fei, Hillsboro, OR) combined with energy dispersive spectroscopy (EDS). Steady state photoluminescence (PL) spectrum measurements were performed on a Spex FluoroLog Tau-3 (HORIBA John Yvon, Edison, NJ) at 300 K. A Fourier-transform Raman spectrometer (Thermo Nicolet 6700, Thermo Nicolet Corp., Madison, WI) was used to record room-temperature Raman spectra of the delafossite samples. X-ray photoelectron spectroscopy (XPS) (PHI Quantera, ULVAC-PHI, Chanhassen, MN) was used to examine the local chemical environment in the doped samples ($x = 0.001, 0.003, 0.01$). The X-ray source was a monochromated Al Ka line at 1486.6 eV. The beam sweeps for each high resolution scan were adjusted (three sweeps: Al$_{2p}$/Cu$_{2p}$; one sweep: O$_{1s}$ and C$_{1s}$) to yield a signal-to-noise ratio of >100:1 with exception of doping agents Eu$_{3d}$ (three sweeps), which were adjusted to yield a signal-to-noise ratio of >50:1. The Hall measurement (MMR Technologies, San Jose, CA) was conducted at room temperature to determine the carrier type and density. The fibrous mat was cold pressed onto a square glass substrate and coated with silver electrodes on the four corners.

3. Results and discussion

Thermal treatment of electrospin fibers involves the burnout of organics and simultaneous crystallization. The thermo-gravimetric and differential thermal analyses are shown in Figure 1. The TG curve consists of three stages of weight loss. The first weight loss event occurred at ~100 °C, which could be attributed to the volatilization of adsorbed water and surface organics. The second event, at ~225 °C, is accompanied by a strong thermopositive peak in the DTA signal. This is due to the decomposition of PVP lateral chains and the nitrate salts. The third stage of weight loss begins at 400 °C, with a small thermal positive peak, which could correspond to the further burnout of PVP fundamental chains.\[14,15\] At above 800 °C, the TG curve exhibits a broad endothermic peak in the DTA curve. The TG plateau indicates that the thermal decomposition process was complete and the decomposed copper and aluminum nitrate undertook a combination reaction to finally form CuAlO$_2$. The overall weight loss is nearly 80%, given the large amount of PVP addition into the precursors required to yield ideal elasticity for electrospinning.

The X-ray diffraction (XRD) patterns together with the RWP (residual weight pattern) values from the refinement are shown in Figure 2 along with the standard CuAlO$_2$ (R3m) phase for comparison. All samples show a single CuAlO$_2$ phase with no other crystal structure identified. This shows that the post annealing condition is sufficient to transform the polymeric as-spun fibers into a single, crystalline delafossite structure. In addition, samples (not shown in Figure 2) with a higher annealing temperature of 1200 °C show undesired CuAl$_2$O$_4$ phase due to the oxidation of cuprous ions. Annealing at lower temperatures than 1040 °C, both CuAlO$_2$ and CuO phases result, due to the insufficient reaction between CuO and CuAl$_2$O$_4$.\[16,17\] It is noteworthy that crystallinity differs among samples with different Eu doping. Samples with the 0.001 and 0.003 Eu doping show lower degree of crystallinity corresponding to broader diffraction peaks. However, when the doping concentration exceeds 0.01, well-defined CuAlO$_2$, delafossite peaks are exhibited. According to the bonding environment shown later, the substituted Eu and resultant Eu-O bond may alter the bonding environment, allowing for higher mass...
The lattice parameters extracted from the Rietveld refinement of the delafossite phase CuAl$_{1-x}$Eu$_x$O$_2$ are shown in Figure 3. The lattice parameter $a$ increases with increasing Eu concentration while $c$ remains nearly constant. This behavior could be explained by a pseudo-linear relationship between lattice constant and trivalent ion radius $r_R$ in a delafossite structure.[19] According to our host material, CuAlO$_2$, the lattice constant could be estimated by

$$a = 2.784 \times r_R + 1.437,$$

in which the constant 2.784 was calculated from the $a$ value at zero doping level from the standard powder diffraction file (PDF#35-1401). The trivalent ion radius $r_R$ follows a weighted sum of both Al$^{3+}$ radius and Eu$^{3+}$ radius ($r_R = (1 - x)r_{Al} + xr_{Eu}$).[20] By employing the Vegard’s law, the Eu$^{3+}$ ions are assumed to exclusively occupy the Al$^{3+}$ sites, due to their equivalent charge and more difficulties in impurity doping of Cu-O dumbbells with strong covalency between Cu$^+$ d$^{10}$ levels and O-2p orbitals. Based on the two equations above, the calculated value is shown as a dashed line in Figure 3. It can be seen that both experimental and calculated parameters follow a similar trend as a function of Eu concentration. The deviation could be attributed to the stoichiometric variation in starting precursors and the difference between nominal and doped Eu ion concentrations. The $c$ value diffusivity and more sufficient crystallization, which might explain the promotional effect of Eu on CuAlO$_2$ crystallization. In summary, the nanofiber-derived single-phase CuAlO$_2$ via single step annealing and relatively short dwelling time implies that one-dimensional ceramic fibers have higher sintering activity than powders or thin films.[18]
is independent of $r_R$ and at various doping levels, the lattice parameter $c$ remains almost constant. The trends in both $a$ and $c$ in terms of dopant concentration imply that Eu$^{3+}$ substitutes Al$^{3+}$ site in this delafossite structure. The SEM micrographs are shown in Figure 4. After thermal annealing, the smooth polymeric as-spun fibers become coarse and rough, with nano-sized polygonal grains observed on the fibers. The microstructure evolution with the increasing doping concentration is also prominent, from well-sustained non-woven fibers to a disconnected porous structure. According to the significant radius difference between Eu$^{3+}$ and Al$^{3+}$ ions, the introduction of Eu$^{3+}$ in the Al$^{3+}$ site may cause lattice distortions and unrelaxed strains. Additionally, the radial crystallization on self-supported fibers imposes excess surface strain on the crystallites. As a result, excess enthalpy was produced for crystallization and a higher crystallinity is expected with a further increasing in Eu level, in a similar manner revealed from XRD patterns. When the Eu concentration increased with further increase in crystallinity to a degree that the bonding to crystallites cannot hold the accumulated stress in the cylindrical fibrous structure, the non-woven fibers break up and the crystallites start growing as isolated particles.

During the annealing process of the electrospun fibers, the organics derived from the PVP addition must be eliminated in order to achieve well-crystallized ceramic fibers suitable for luminescence application. EDS was employed to confirm the burn-out of the polymers shown in Figure 5. Before thermal annealing, the energy peaks associated with C and N were prominent because of the existence of PVP (${(\text{C}, \text{H}, \text{N})_n}$). After 1100 °C annealing, there were no C or N peaks identified; only Cu, Al, O, and Eu (enlarged inset in Figure 5) peaks were observed. The polymer burn-out, thermal decomposition and crystallization proceeded simultaneously during the annealing, which shows that

![Figure 4](image_url) **Figure 4.** SEM microstructure of CuAl$_{1-x}$Eu$_x$O$_2$ ($x=0.001, 0.003, 0.01, 0.03, 0.05$ and $0.1$) electrospun fibers annealed at 1100 °C for 3 h.
this delafossite-type phosphor could be synthesized as one-dimensional fibers.

The photoluminescence of CuAl$_{1-x}$Eu$_x$O$_2$ ($x = 0.001, 0.003, 0.01, 0.03, 0.05$ and $0.1$) electrospun fibers has been studied at two excitation wavelengths (365 and 420 nm). Delafossite-type CuMO$_2$ has room temperature luminescence due to its UV near-band-edge emissions [21–24]. The Cu-O bonds in the O-Cu-O dumbbell layers determine the electronic structure near the band-gap and lead to strong localization of excitons in the $x$–$y$ plane as well as larger binding energy. This causes hybridization between the $3d^2$ and $4s$ orbitals in the CuMO$_2$ delafossite. Since the binding energy exceeded the room temperature thermal energy ($kT = 0.025$ eV), room temperature PL emissions were presented.[6,7] We herein reported the room temperature near-band-edge emissions from the Eu-doped CuAlO$_2$ fibers with slightly different peak energies compared to other studies.[7,25] The peak positions in terms of relative intensity shown in Figure 6 mainly centered at ~407 nm, indicating a 0.3 eV decrease in the direct band-gap compared to a normal 370 nm emission in thin films or bulks. Since the reported direct band-gap values of CuAlO$_2$ vary from 3.0 to 3.8 eV and highly depend on fabrication method, the near-band-edge emission is supposed to shift accordingly. The oxygen vacancies, surface defects and crystallinity associated with fabrication methods in low dimensional CuAlO$_2$ thin films or nanoparticles often yield dispersed band-gap values. In this particular study, the energy peak shift is also attributed to a fiber-derived band-gap energy change. A similar phenomenon has been observed in TiO$_2$ ceramic fibers,[26] i.e. that band-gap increases with the excess pressure on the fiber circular cross section. The inset in Figure 6 shows the measured optical band gap in our study, the absorption edge (3.084 eV corresponds to ~402 nm) of which is similar to the PL peak energy, which leads to the conjecture that the emission with the excitation wavelength of 365 nm results from the CuAlO2 near-band-edge transition. We also need to consider other factors regarding to the violet emission. The defect origin from VCu in the delafossite material is assumed to form an acceptor level above the zero vibrational level,[27,28] leading to a Stokes shift in the spectrum. Since our experiments were performed at room temperature and no other peaks associated with Eu$^{3+}$ activators were observed from the emission spectra, the broad violet emission is unlikely from transition to defect levels. Byrne et al. [25] recently observed a coexistence of both a near-band-edge UV emission and a blue emission at ~430 nm at 14.5 K, with almost 100 nm Stokes shift. Revisiting the study by Jacob et al. [29] on CuYO$_2$ and CuLaO$_2$, the prolific hybridization from Cu 4p/3d orbitals and the resultant $3d^2$ and $4s$ split only give rise to an asymmetric and overlapped peak feature rather than large Stokes shift. In addition, the effect of defect states on room temperature excitation still remains unclear, which definitely requires further investigation. The one-dimensional fibrous microstructure with major surface defects may also cause a band-gap narrowing in some oxide materials.[30] However, since there have been no reports on the photoluminescence of CuAlO$_2$, in the form of fibers to the best of our knowledge, at the current stage we may conjecture that the decrease in the band-gap associated with low excitation energy (365 nm in our case) leads to the red shift in the PL emission spectra. At different dopant levels, the band-gap extracted from the PL peak energies in Figure 6 decreases with the increase of Eu level, indicating the further band modifications as a result of trivalent ion substitution and change of degree in Cu 4p/3d hybridization.

We also compared the peak energies in terms of doping levels. Regardless of the variation in relative PL emission

Figure 5. EDS spectra of as-spun polymeric fibers and annealed CuAl$_{0.97}$Eu$_{0.03}$O$_2$ ceramic fibers. The enlarged inset shows the presence of Eu.

Figure 6. Near-band-edge photoluminescence of CuAl$_{1-x}$Eu$_x$O$_2$ excited at 365 nm. Inset shows the Tauc plot used for evaluating the optical band gap of CuAl$_{0.999}$Eu$_{0.001}$O$_2$. 
indicating the environment around the activator centers. The increasing $5D_0 \rightarrow 7F_2$ emission intensity from samples with $x = 0.001–0.01$ indicates a higher symmetry local site. Upon the occupancy of Eu$^{3+}$ ions in the octahedral center, the lattice was distorted and the local symmetry of Eu$^{3+}$ continued to change with increasing Eu$^{3+}$ doping level. As a consequence, the probability of each $5D_0 \rightarrow 7F_J$ transition channels may change, which leads to the variation of intensity of the six $5D_0 \rightarrow 7F_2$ emissions shown in Figure 8(b). The overall red emission intensity increases with the increase of doping concentration up to 0.01Eu. Above this doping level, the intensity significantly drops due to the concentration quench effect [33,34] shown in Figure 8(c). With the increase of Eu$^{3+}$ concentration, the cross-relaxation becomes dominant due to the reduced distance between two Eu$^{3+}$ ions. Therefore, the luminescence emission intensity almost vanishes at higher Eu$^{3+}$ concentration. Since the activator is introduced solely on the Al$^{3+}$ site, the critical transfer distance ($R_c$) could be estimated by the following equation:

$$R_c \approx 2 \left( \frac{3V}{4\pi\chi N} \right)^{1/3}$$

where $V$ is the unit cell volume, $\chi$ is the critical concentration and $N$ is the number of Al$^{3+}$ ions per unit cell. For CuAlO$_2$, host ($N = 3$), $\chi$ is roughly equal to 0.01 at which concentration the maximum luminescent intensity was observed. The cell volume from XRD refinement is 120.75 Å$^3$ and the $R_c$ was calculated to be approximately 20 Å. For a Eu$^{3+}$–Cu$^{2+}$ distance larger than 5 Å, the multipolar interaction is dominant and the exchange interaction is negligible. Therefore, the main mechanism for concentration quenching in the CuAlO$_2$:Eu$^{3+}$ phosphor is the multipolar interaction.

Room temperature Raman spectra are shown in Figure 9. It has been widely acknowledged that in delafossite structure with $\Gamma = A_1 g + E_g + 3A_2u + 3E_u$, only the first

![Figure 7. Photoluminescence excitation spectrum (a) showing the direct band-gap transition in CuAlO$_2$ host, and the emission spectrum (b) of CuAl$_{0.99}$Eu$_{0.01}$O$_2$.](image-url)
of Cu-O bonds and the E modes represent the vibrations in the perpendicular direction. A previous report on particulate CuAlO$_2$ [25] shows two sharp peaks at 418 and 767 cm$^{-1}$, respectively. However, the Raman scattering peaks could shift to a large extent depending on the trivalent ion species. CuLaO$_2$ with the same crystal geometry has two peaks centered at 318 and 652 cm$^{-1}$. [38] The lowered frequencies could be due to a higher M atom mass and weaker M-O bond. The room temperature Raman spectrum that we obtained here shows a similar Eg position but a slight lower frequency of A$_{1g}$ mode, which might provide supplementary information on trivalent substitution. Upon the introduction of larger Eu$^{3+}$ ions, the MO$_6$ along the ab-plane would go through a decrease in bonding energy, which is also confirmed by XPS in later discussion. Therefore the Eg characterized by the vibration along the ab-plane mode should shift to lower frequency. However from the experimental data, the Eg shows a typical CuAlO$_2$ peak position whereas the A$_{1g}$ peak shifts to lower frequency for both undoped and doped samples, which might lead to the conjecture that the decrease of the A$_{1g}$ frequency might due to the electrospinning synthesis during which the MO$_6$ octahedral two modes are Raman active. [36,37] The A modes correspond to the vibrational movements in the direction

Figure 8. Schematic diagram of photoluminescence emission channels in the rare-earth doped delafossite CuAlO$_2$ (a), $^5$D$_{0} \rightarrow ^7$F$_{j}$ and $^7$F$_{j}$ transitions with respect to doping concentration (b) and integrated PL intensity of 610 nm emission as a function of doping concentration (c).

Figure 9. Room temperature Raman spectrum under 1064 nm excitation provided by a Nd:YVO$_4$ laser.
plots were used to identify the thermal-activation type of these wide band-gap materials. DC current was applied through a piece of fiber mat sandwiched by two rectangular graphite foils, which were used to minimize the contact resistance. The conductivity increases as the temperature increases, showing semiconduction. At ~300 K, the electrical conductivity for 0.1% Eu doped CuAlO₂ fibers is ~0.05 S cm⁻¹ with a thermal activation energy of ~0.09 eV. The room temperature conductivity increased with elevated Eu doping levels, from 0.05 to 0.17 S cm⁻¹. This could be attributed to the substitution of Eu cations which induced the lattice distortion and increased the hole concentrations. On the other hand, the substitution of Eu on the Al site may introduce a smaller band-gap associated with CuEuO₂ and this modification at the near-band-edge may also contribute to the hole conductivity enhancement. Based on the plot shown in Figure 11, when the doping level is as small as 0.1%, logσ decreases linearly with the reciprocal of temperature. However as the doping concentration increased, a variable-range hopping mechanism occurred,[41] which could be seen from the segmented slopes at different temperature ranges. The slope at higher temperature range...
between 570 and 800 K is lower than that at a lower temperature range between 300 and 400 K. A revisit to PL energy peaks shown Figure 6 could lead to the conjecture that the change in thermal activation may result from the various band-gaps induced by Eu partial substitution, since the band-gaps decrease with the increase of Eu concentration. In addition to the DC temperature-dependent conductivity measurement, the Hall coefficient ($R_{\text{H}}$) for the 0.1% Eu doped sample determined by Hall measurement is $+5.48 \text{ cm}^3/\text{C}$, corresponding to a carrier density of $1.14 \times 10^{18} \text{ cm}^{-3}$, while the heavily doped 1% sample has a $R_{\text{H}} = +6.94 \text{ cm}^3/\text{C}$ and a carrier density of $8.99 \times 10^{17} \text{ cm}^{-3}$, both showing a p-type semiconductor.

4. Conclusions

Cu$_{1-x}$Eu$_x$AlO$_2$ ($x = 0.001, 0.003, 0.01, 0.03, 0.05$ and $0.1$) fibers have been fabricated through a combination of a chemical solution method and electrospinning technique. This method could effectively synthesize single-phase CuAlO$_2$ via one-step annealing in air. The lattice parameter $a$ follows a pseudolinear relationship with Eu concentration while the lattice parameter $c$ remains almost constant with Eu concentrations. This implied that the delafossite-type CuAlO$_2$ could be used as a potential host material for the rare-earth Eu$^{3+}$ partial substitution on trivalent site. Further photoluminescence measurements indicated that upon two excitation wavelengths of 390 and 465 nm, the Cu$_{1-x}$Eu$_x$AlO$_2$ exhibits two emission behaviors from both intrinsic near-band-edges in the Eu doped delafossite structure. Different hopping mechanisms occur at inhomogeneous activation energy as a result of Eu substitution indicates an increase of Eu concentration. The variation in thermal conductivity increased monotonically with Eu concentration while the lattice parameter $c$ follows a pseudolinear relationship with Eu concentrations. This method could effectively synthesize single-phase CuAlO$_2$ via one-step annealing in air. The lattice parameter $a$ follows a pseudolinear relationship with Eu concentration while the lattice parameter $c$ remains almost constant with Eu concentrations. This implied that the delafossite-type CuAlO$_2$ could be used as a potential host material for the rare-earth Eu$^{3+}$ partial substitution on trivalent site. Further photoluminescence measurements indicated that upon two excitation wavelengths of 390 and 465 nm, the Cu$_{1-x}$Eu$_x$AlO$_2$ exhibits two emission behaviors from both intrinsic near-band-edges in the Eu doped delafossite structure. Different hopping mechanisms occur at inhomogeneous activation energy as a result of Eu substitution indicates an increase of Eu concentration. The variation in thermal conductivity increased monotonically with Eu concentration. This effect is +5.48 cm$^3$/C, corresponding to a carrier density of $1.14 \times 10^{18} \text{ cm}^{-3}$, while the heavily doped 1% sample has a $R_{\text{H}} = +6.94 \text{ cm}^3/\text{C}$ and a carrier density of $8.99 \times 10^{17} \text{ cm}^{-3}$, both showing a p-type semiconductor.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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