Sohail Ahmed,a Muhammad Adil Mansoor,a Muhammad Mazhar,*a Tilo Söhnel,b,c Hamid Khaledi,a Wan Jeffrey Basirun,d Zainudin Arifin,a Shahzad Abubakar,e and Bakhtiar Muhammadf

An octa-nuclear heterobimetallic complex \[ [Y_2Cu_6Cl_0.7(dmae)_6(OAc)_7.3(OH)_4(H_2O)_2] \cdot 3H_2O \cdot 0.3CH_3C_6H_5 \] (dmae = dimethylaminoethanoate; OAc = acetato) was synthesized, characterized by melting point analysis, elemental analysis, FT-IR, and single crystal X-ray diffraction analysis and implemented at 600 °C under an oxygen atmosphere for the deposition of \( Y_2CuO_4-5CuO \) composite thin films by aerosol assisted chemical vapor deposition (AACVD). The chemical composition and surface morphology of the deposited thin film have been determined by X-ray diffraction, scanning electron microscopy and energy dispersive X-ray analysis that suggest the formation of impurity-free crystallite mixtures of the \( Y_2CuO_4-5CuO \) composite, with well-defined evenly distributed particles in the size range of 19–24 nm. An optical band gap energy of 1.82 eV was estimated by UV-visible spectrophotometry. PEC studies show that under illumination with a 150 W halogen lamp and at a potential of 0.8 V, a photocurrent density of 9.85 µA cm\(^{-2}\) was obtained.

1. Introduction

Highly crystalline bi- and tri-metallic ceramic oxides constitute an important class of materials that have found a wide range of applications such as superconductors, structural ceramics, sensors, catalysts and actuators in addition to their use as ferroelectric and dielectric materials for microelectronic data processing devices.\(^1\)\(^,\)\(^2\) Several methods\(^3\)\(^–\)\(^8\) with their own merits and demerits are available for thin film fabrication, but the use of a single source precursor in chemical vapour deposition (CVD) is gaining more attention because it provides advantages of excellent film uniformity, high deposition rates, control over the material composition and phase, conformal coverage on complex geometries, controllability of film microstructures, low cost and scalability. An easily adaptable sub-branch of CVD known as aerosol assisted chemical vapour deposition (AACVD) provides an attractive method to deposit metal oxide thin films.\(^9\)\(^–\)\(^14\) The keen interest towards the synthesis of mixed yttrium, barium and copper heterotrimetallic complexes is to really fabricate the high temperature 1–2–3 superconductor \( YBa_2CuO_{7-x} \) from a single source and to further transform it into useful forms such as films, wires and fibers.\(^15\) These hetero-bimetallic complexes may not only model as intermediate species, but may also find direct application as precursors for the synthesis of high \( T_c \) superconductors. Although extensive work has been carried out on the development of heterometallic complexes of copper with yttrium and barium such as \( [Y_2Cu_8(\mu-PyO)_{12}(\mu-Cl)_2(\mu-Cl)(\mu-Cl)(\mu-Cl)(\mu-Cl)(\mu-Cl)(\mu-Cl)(\mu-Cl)] \( [BaCu[OCMe(CF_3)_{1/2}]_2] \), \( [CuCu[OCMe(CF_3)_{1/2}]_2] \), \( [BaCu_2(CF_3)O_2] \), \( [Me_3NC_2H_4O]_3(MeOH)]_3MeOH \), \( [BaCu(PyO)]_6(bdamap) \), \( [O_2CCF]_3) \), \( [BaCu(PyO)]_6(deac) \), \( [O_2CCF]_3) \), \( [BaCu(C_3H_8O)]_6(C_2H_4O)]_3 \), \( [BaCu(C_3H_8O)]_6(C_2H_4O)]_3 \), \( [BaCu(C_3H_8O)]_6(C_2H_4O)]_3 \), none of these compounds have been investigated for their implementation as precursors for chemical vapour deposition of \( Y-Cu \) ceramic oxides. In continuation of our efforts directed towards the development of bi- and trimetalloclic complexes,\(^11\)\(^,\)\(^12\)\(^,\)\(^13\) we focussed our attention on the use of multifunctional ligands, such as aminoalkoxides and acetate, as a tool to strengthen the interaction between the components of heterobimetallic species.
We utilized the tetrameric \([\text{Cu(dmae)Cl}]_4\) complex, for the preparation of a heterobimetallic complex in which 2-dimethylaminoethanol (dmae) serves as a bridging ligand to coordinate copper and yttrium and also imparts coordinative saturation and enhances the volatility and solubility of the complex, which is of utmost importance for AACVD. Hence, we synthesized the heterobimetallic complex \([\text{Y}_2\text{Cu}_6\text{Cl}_{0.7}(\text{dmae})_6(\text{OAc})_7.3(\text{OH})_4(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O} \cdot 0.3\text{CH}_3\text{C}_6\text{H}_5\) and used it as a precursor for the growth of impurity-free \(\text{Y}_2\text{CuO}_3\) composite thin films using the AACVD technique at 600 °C. The deposited films were characterized by XRPD, SEM, EDX and UV-visible spectrophotometry for their stoichiometry, morphology, thickness and optical band gap. Further scope of these thin films for application in harvesting sunlight for photoelectrochemical water splitting into hydrogen and oxygen is also investigated.

2. Experimental

2.1. Materials and methods

All experiments were carried out under an inert atmosphere of dry argon gas using Schlenk tube and glove box techniques. All solvents were purchased from Fluka Chemical Company. Toluene was rigorously dried over sodium benzoenate and methanol was purified by distilling over reagent grade magnesium powder. \(\text{N}_2\text{N}\text{-Dimethylaminoethanol (dmaeH)}\) was purchased from Aldrich, purified by refluxing over \(\text{K}_2\text{CO}_3\) for 10 h and distilled immediately before use. The melting point was determined in a capillary tube using electrothermal melting device and is uncorrected. The microanalyses were performed using a Leco CHNS 932. FT-IR spectra were recorded on a single reflection ATR instrument (4000 – 8529 cm\(^{-1}\)) with a heating rate of 5 °C min\(^{-1}\). Data reduction was carried out using the SAINT\(^{23}\) program. Semi-empirical absorption corrections were applied based on equivalent reflections using SADABS.\(^{24}\) The structure solution and refinements were performed with the SHELXL-2013 program package.\(^{25}\) All the non-hydrogen atoms were refined anisotropically and all the C-bound hydrogen atoms were placed at calculated positions and refined isotropically. O-bound hydrogen atoms were located in difference Fourier maps and refined with a distance restraint of O–H 0.84(2) Å. The Cl atom has substitutional disorder with acetate with an occupancy ratio of 0.7 : 0.3. Crystal data: \(\text{C}_{40.70}\text{H}_{98.30}\text{Cl}_{0.7}\text{Cu}_6\text{N}_6\text{O}_{29.60}\text{Y}_2\), blue prism, 0.14 × 0.12 × 0.08 mm\(^3\), \(\alpha = 25.110(17)\) Å, \(\beta = 15.773(10)\) Å, \(\gamma = 105.863(3)\) °, \(V = 4382.8(3)\) Å\(^3\), \(Z = 4\); \(50\) reflections observed \([I > 2\sigma(I)]\), final \(R\) indices \([I > 2\sigma(I)]\) \(R_1 = 0.0393, wR_2 = 0.0787\).

2.2. Deposition of thin films by AACVD

The thin films were deposited on commercially available FTO-coated glass substrates using self-designed AACVD assembly as described elsewhere.\(^{26}\) FTO-coated glass substrates of size \(2 \times 1\) cm \((L \times W)\) purchased from Sigma Aldrich were cleaned by ultrasonic washing with distilled water, acetone, and ethyl alcohol prior to their use. Finally, they were washed with distilled water, stored in ethanol and dried in air. Substrate slides were placed inside the reactor tube and then heated up to the deposition temperature for 10 min before carrying out the deposition. The aerosol of the precursor solution was formed by keeping the round bottom flask in a water bath above the piezoelectric modulator of an ultrasonic humidifier. The generated aerosol droplets of the precursor were transferred into the hot wall zone of the reactor by compressed air. At the end of the deposition, the aerosol line was closed and only carrier gas was passed over the substrate to cool to room temperature before it was taken out from the reactor. In a typical experiment, 50 mg of the precursor 1 was dissolved in 30 mL of toluene to deposit thin films of the composite \(\text{Y}_2\text{CuO}_3\) composite.
on FTO-conducting glass under compressed air with a flow rate of 150 cm$^3$ min$^{-1}$ at 600 °C. The deposited thin films are light yellow in colour, transparent, uniform, robust, and stable towards atmospheric conditions and adhere strongly on the FTO substrate as verified by the “scotch tape test”.27

2.4.1. Characterisation of thin films. The surface morphology of thin films was studied using a field-emission gun scanning electron microscope (FESEM, FEI Quanta 400) coupled with an Energy Dispersive X-ray spectrometer EDX (INCA Energy 200 (Oxford Inst.)), at an accelerating voltage of 10 kV, and a working distance of 6 mm. The final products were characterised by X-ray powder diffraction (XRD) on a D8 Advance X-ray Diffractometer (Bruker AXS) using CuKα radiation ($\lambda = 1.540\AA$), at a voltage of 40 kV and a current of 40 mA at ambient temperature. The optical absorption spectrum of the thin films having a thickness of 310 nm as measured using a profilometer KLA Tencore P-6 surface profiler was recorded on a Lambda 35 Perkin-Elmer UV-visible spectrophotometer in the wavelength range of 350–850 nm.

The photo-electrochemical response of fabricated Y$_2$CuO$_5$–5CuO layers was studied by electrochemical techniques such as linear scanning voltammetry (LSV) in the absence and presence of light (150 W halogen lamp). A three-compartment cell consisting of discrete heterometallic complexes cocrystallized with a partially occupying toluene and three water molecules.

3. Results and discussion

3.1. Synthesis and characterization

The tetrameric complex [Cu(dmae)Cl]$_4$ reacts quantitatively with Y(acetate)$\cdot$3H$_2$O in toluene solution to yield complex 1 (m.p. = 137 °C) as shown in chemical eqn (1).

$$\frac{3/2[Cu(\text{CH}_3)_2NCH_2CH_2O)]Cl_4 + 3Y(\text{CH}_3COO)_3 \cdot xH_2O}{\text{Toluene}} \rightarrow [Y_2Cu_6Cl_{0.7}(\text{dmae})_6(OAc)_{7.3}(OH)_{4}\cdot(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O} \cdot 0.3\text{CH}_3\text{C}_6\text{H}_5 \cdot 1$$

Complex 1 is soluble in common organic solvents such as dichloromethane, chloroform and tetrahydrofuran, and is stable in air under normal conditions. The structure and stoichiometry of the complex was ascertained by single crystal analysis, micro-analysis and FT-IR that revealed formation of the Y–Cu bimetallic complex in which two Y and six Cu atoms are bridged through oxygen atoms of acetato and dimethylamino-ethanolato ligands in addition to four hydroxo groups. The use of multifunctional ligands coordinatively saturates each metal atom and restricts its ability to oligomerize at the same time enhancing its solubility in organic solvents and making it useful as a precursor to fabricate bimetallic composite oxide thin films. In the FT-IR spectrum, an absorption band at 3295 cm$^{-1}$ is due to water molecules; the presence of both carboxy whole and aminoalcoholate ligands in the complex was also identified by their vibration signals. The two strong absorption bands between 1400 and 1700 cm$^{-1}$ for the carboxylate group suggest a dominant chelating or bridging–chelating behaviour for the acetate ligands. The anti-symmetric and symmetric stretching vibrations for CO$_2$ were assigned at 1571 cm$^{-1}$ and 1415 cm$^{-1}$, respectively.29 The difference of 156 cm$^{-1}$ between the anti-symmetric and symmetric stretching vibrations suggests a chelating or bridging–chelating behaviour for carboxylate ligands.30,31 The presence of three strong absorption bands in the range of 1120–1270 cm$^{-1}$ for ν(C–O) stretching corresponds to carboxylate ligands.29 The absorptions at the low frequencies of 512 and 464 cm$^{-1}$ are probably due to M–O and M–N stretching vibrations, respectively (Fig. S1†).

3.2. Structural analysis of [Y$_2$Cu$_6$Cl$_{0.7}$(dmae)$_6$(OAc)$_{7.3}$(OH)$_4$(H$_2$O)$_2$]$\cdot$3H$_2$O$\cdot$0.3CH$_3$C$_6$H$_5$ 1

A schematic drawing of the Y–Cu complex is shown in Fig. 1 and the crystal structure is depicted in Fig. 2–4. The structure consists of discrete heterometallic complexes cocrysalized with a partially occupying toluene and three water molecules.

![Fig. 1 Schematic diagram of Y$_2$Cu$_6$Cl$_{0.7}$(dmae)$_6$(OAc)$_{7.3}$(OH)$_4$(H$_2$O)$_2$]$\cdot$3H$_2$O$\cdot$0.3CH$_3$C$_6$H$_5$ 1.](image)

![Fig. 2 The molecular structure of 1. C-bound hydrogen atoms and the solvent molecules are omitted for clarity.](image)
The metal complex molecule contains two Y³⁺ and six Cu²⁺ metal centres. Each Y³⁺ atom is eight-fold coordinated in a dodecahedral geometry by three \( \mu_3\text{-OH}^- \), three \( \mu_2\text{-ODMAE} \) and one bidentate acetate group with Y–O distances ranging between 2.250(3) and 2.503(3) Å. Each Cu²⁺ center is five-fold coordinated in a square-pyramidal geometry by an N, O-bidentate chelate of dmae, one \( \mu_3\text{-OH}^- \) and one bridging acetate O atom. The fifth ligand in three of the copper centers (Cu₂, Cu₃ and Cu₅) is an equatorially placed monodentate acetate group and in two centers (Cu₁ and Cu₄) it is an apically bound water molecule. In the case of Cu₆, the fifth ligand is a Cl ligand in the equatorial plane, which is partially replaced by a monodentate acetate group.

3.3. Thermal studies of complex 1

The thermal behaviour of 1 has been examined by thermogravimetric and derivative thermogravimetric (TGA/DTG) analyses performed under an oxygen and inert nitrogen atmosphere with flowing gases at 25 cm³ min⁻¹ at a heating rate of 20 °C min⁻¹. The DTG (Fig. 5) curve indicates that the initial decomposition steps of complex 1 in both the oxygen and nitrogen atmosphere are very similar except that all the main heat intake steps appear late by about 10 °C in nitrogen as compared to the oxygen atmosphere. DTG curves indicate systematic five distinct stages of heat gain at 76, 120, 222, 336 and 505 °C giving weight losses of 2.4, 8.7, 36.8, 51.5 and 58.1% respectively in an oxygen atmosphere, whereas in a nitrogen atmosphere mass losses occur at 62, 105, 195, 232 and 348 °C yielding mass losses of 1.9, 9.9, 15.2, 38 and 57% respectively. In an oxygen atmosphere the final pyrolysis step occurs at 466 °C where a slight gain in weight along with a change in phase takes place to give a stable residual mass of 41.9% at 505 °C from complete decomposition of complex 1. Further heating of the residue to 600 °C did not bring any change in mass loss indicating formation of the stable Y₂CuO₄–5CuO composite. FT-IR of the residue obtained from decomposition of complex 1 under an oxygen atmosphere (Fig. S3a†) shows absorptions at 630 cm⁻¹ and 528 and 557 cm⁻¹ confirming the presence of Cu–O⁻⁵³ and Y₂O₃ respectively. The thermogram recorded under a nitrogen atmosphere shows a loss of 57% of the total mass of complex 1 at 348 °C. Further heating of the sample to 600 °C shows a gradual mass loss indicating incomplete decomposition of complex 1 at this temperature. This observation has also been affirmed by FT-IR of the residue, which showed strong absorption bands in the region 3300–3500 cm⁻¹ and at 1470 cm⁻¹ respectively (Fig. S3b†), indicating the presence of nitrogenous water solvent clusters \((\text{H}_2\text{O})_₃\) forming a two-dimensional network parallel to the \( (bc) \) plane (Fig. S2f). The toluene molecules are placed in the cavities between these layers. There is no significant intermolecular hydrogen bonding interactions between the metal complex molecules.
and carbonaceous impurities in the residue. The total mass loss of complex 1 in a nitrogen atmosphere is more than in an oxygen atmosphere. It is alleged that under a nitrogen atmosphere loss in weight is taking place through β-hydrogen abstraction followed by reductive elimination that reduces most of the Cu(II) to Cu(I) and Cu(0) triggering reduction in abstraction followed by reductive elimination that reduces the tetragonal phase of Y2CuO4 and the monoclinic phase of ICDD standard card no. [00-046-0622] and [00-002-1040] for composite thin films deposited on FTO matches very well with the monoclinic structure, space group

3.4. Powder X-ray diffraction studies of thin films

The powder diffraction pattern (Fig. 6) of Y2CuO4–5CuO composite thin films deposited on FTO matches very well with ICDD standard card no. [00-046-0622] and [00-002-1040] for the tetragonal phase of Y2CuO4 and the monoclinic phase of CuO respectively. The stick pattern matching is available in the ESI (Fig. S4†). The relative peak intensities and the position of the diffraction peaks of the Y2CuO4–5CuO composite thin films match with the tenorite phase of CuO that crystallizes in the monoclinic structure, space group C2/c with \( a = 4.6539 \) Å, \( b = 3.4100 \) Å, \( c = 5.1080 \) Å and \( \beta = 99.48^\circ \). The Y2CuO4 crystallizes in the tetragonal structure with the space group I4/mmm resulting in a larger unit cell with lattice parameters of \( a = 3.860 \) Å and \( c = 11.7000 \) Å. In the XRD, peaks at 2θ values of 26.41°, 33.70°, 37.70°, 51.59°, and 64.50° correspond respectively to (110), (101), (200), (211), and (310) lattice reflection planes of SnO2 (substrate), peaks at 2θ values of 35.46°, 38.70°, 48.81°, 54.74°, 58.22°, 61.72°, 65.74° and 66.54° correspond respectively to (002), (111), (−202), (020), (−113), (022), and (113) lattice reflection planes of the monoclinic CuO phase whereas peaks at 2θ values of 32.57°, 46.19°, 58.22° and 65.02° correspond respectively to (103), (200), (116) and (220) lattice reflection planes of the tetragonal Y2CuO4 phase. The XRD pattern of the thin film indicates dominant phases of FTO and monoclinic CuO whereas tetragonal Y2CuO4 gives weak signals possibly due to the low deposition temperature of 600 °C where most of this phase remains in the amorphous form. A particle size of 38.6 nm has been estimated as calculated from Scherrer’s equation.

The EDX spectrum (Fig. S5a and S5b†) confirmed the presence of Cu, Y and O elements in the deposited films. The silicon, tin and calcium signals appear from the FTO substrate. The Y:Cu in the films is 0.90 : 3, which is in agreement with the expected elemental ratio of 1 : 3 present in complex 1.

3.5. Surface morphology and film thickness

The surface morphology of Y2CuO4–5CuO composite thin films grown on FTO glass substrates is presented in Fig. 7. The films deposited at 600 °C comprise spherical particles in the grain size range of 19 to 24 nm scattered evenly with small void spaces. A particle size of 38.6 nm calculated from the XRD peak at 2 theta of 32.57° is in good agreement with that determined from the SEM image.

3.6. Optical band gaps

The optical absorption spectrum of thin films was recorded in the wavelength range of 350–850 nm using a similar FTO coated glass substrate as a reference to exclude the substrate contribution in the spectrum. The UV-visible spectrum of the Y2CuO4–5CuO composite thin film shows wide range absorption which gradually increases towards lower wavelengths and shows the maximum absorption in the range of 540–375 nm. The film shows an direct optical band gap of a band energy of 1.82 eV as calculated from the Tauc plot\(^{40}\) of energy versus \((ah\nu)^2\) (Fig. 8). It is reported that the optical band gap of CuO falls in the range of 1.2–1.5 eV\(^{41,42}\), but we could not find any literature reference regarding the optical band gap of either Y2CuO4 or the composite of Y2CuO4–5CuO thin films. Our

Fig. 6 Powder X-ray diffraction (XRD) pattern of Y2CuO4–5CuO composite thin films deposited from precursor 1 at 600 °C in an atmosphere of oxygen for 45 minutes.

Fig. 7 SEM image of thin films of Y2CuO4–5CuO deposited from 1 at 600 °C in an atmosphere of oxygen for 45 minutes showing spherical granules.
The reported band gap value of 1.82 eV for the Y$_2$CuO$_4$–5CuO composite suggests a slight increase in the band gap of CuO by the addition of yttrium to it. This observation is in accordance with the known fact that the band gap is seriously affected by the addition of dopants and composite formation.\(^{23}\)

### 3.7. Photoelectrochemical studies

Fig. 9 shows current–voltage characteristics in the dark and under simulated sunlight in 0.01 M phosphate buffer (NaH$_2$PO$_4$ and Na$_2$HPO$_4$) for the Y$_2$CuO$_4$–5CuO electrode deposited using the optimum conditions of the deposition temperature of 600 °C, deposition time of 45 min, and 0.0026 M solution of yttrium to it. The photocurrent density at 0.8 V vs. SCE is about 9.85 which is higher than 7.5 µA cm$^{-2}$ in the dark. These observations indicate a 24% enhancement in the band gap of CuO by the addition of yttrium to it. This observation is in accordance with the known fact that the band gap is seriously affected by the addition of dopants and composite formation.\(^{23}\)

In summary the synthesised octa-nuclear Y–Cu complex provides an opportunity to fabricate Y$_2$CuO$_4$–5CuO composite thin films on the glass substrate by AACVD at a relatively low temperature of 600 °C. The characterisation of the thin film by XRPD, SEM, EDX, profilometry, and UV-visible spectrophotometry provides information about the crystallinity, surface morphology, particle shape and size, elemental composition, thickness of the film and direct energy band gap of the composite to determine their technological applications.

### 4. Conclusions

We have developed a synthetic route for the synthesis of an octanuclear heterobimetallic Y–Cu complex 1 that was implemented to develop Y$_2$CuO$_4$–5CuO composite thin films under an oxygen atmosphere from toluene solution by AACVD. The TG/DTG study of the decomposition of complex 1 in an oxygen and nitrogen atmosphere and FT-IR of the residues revealed the dependence of the decomposition mode of complex 1 on the environment. The Y$_2$CuO$_4$–5CuO composite thin film has well-defined, evenly distributed particles in the size range of 19–24 nm and offers an optical band gap energy of 1.82 eV and a photocurrent density of 9.85 µA cm$^{-2}$ at 0.80 V vs. SCE. All these observations indicate that the thin film is photoactive and generates holes and electrons that can be utilised for photoelectrochemical and solar energy applications.

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