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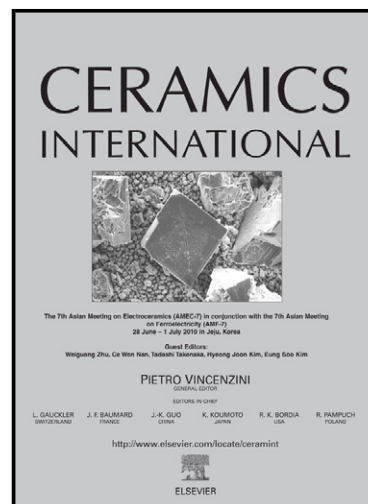
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# Author's Accepted Manuscript

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# Optical properties and thermal durability of copper cobalt oxide thin film coatings with integrated silica antireflection layer

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## Abstract

Copper cobalt oxide ( $\text{Cu}_2\text{CoO}_3$ ) thin film coatings integrated with silica ( $\text{SiO}_2$ ) antireflection (AR) layer have been deposited on the top of aluminum substrates using a simple sol-gel dip-coating method. Reflectance spectra of the coatings were generated using spectroscopic methods while the coatings were subjected to an accelerated thermal durability test. The addition of silica changed the reflectance spectra of coatings within the wavelength range of 0.3-15.4  $\mu\text{m}$ . The absorptance decreased with the increase of the withdrawal rate in range of 10-40 mm/min, while the emittance increased with the increase of the withdrawal rate. The optimum optical parameters for this study were absorptance,  $\alpha_S = 84.96\%$ ; emittance,  $\varepsilon_T = 5.63\%$  corresponding to the coating with a silica AR layer at withdrawal rate of 10 mm/min. The coatings with the silica AR layer were shown to be thermally durable in which no discernible ‘cracking’ phenomenon was observed. The degradation of the coatings with the silica AR layer was predominantly governed by temperature changes rather than exposure time.

**Keywords:** Copper-cobalt oxide; Silica antireflection layer; Sol-gel dip-coating, Accelerated thermal durability test.

## 1. Introduction

Solar thermal collectors such as the ubiquitous solar hot water panels are designed to collect solar radiation and convert it into useful heat energy for various industrial and domestic applications. A significant component that affects the efficiency of a solar thermal collector system is the solar selective absorber (SSA) coating [1] which, ideally, should

absorb the incoming solar radiation (high solar absorptance) as much as possible with concurrent low thermal emittance. The most frequently used industrial SSAs in recent years are the metal particles in ceramic (cermet) structures which can be synthesized *via* electroplating/electrochemical or sputtering/vacuum deposition techniques [2, 3]. Though these techniques are effective, they are, nonetheless, not environmentally-friendly [4-6] and sputtering/vacuum deposition processes are technically complicated and not cost-effective [3, 7-11]. Concerted efforts by materials scientists are currently underway in seeking alternative SSA materials synthesis processes which exhibit benefits such as simplicity, cost-effectiveness and environmentally-friendly aspect.

Cobalt copper oxides ( $\text{Cu}_x\text{Co}_y\text{O}_z$ ) are versatile metal oxides which have applications in a variety of important catalytic reactions such as conversion of syngas to higher alcohols, oxidation of carbon monoxide (CO) by  $\text{O}_2$ , oxygen evolutions reaction (EOR), Fischer-Tropsch synthesis and for thermoelectric power generation material [12-17]. Numerous studies have been conducted to establish the physicochemical, magnetic, conductivity, electrochemical and thermal properties of copper-cobalt oxides [14, 15, 18-20]. On the other hand, solar-based optical properties of the copper-cobalt oxides thin film coating are comparatively less well-studied [14].

In our previous studies, we prepared copper cobalt oxide ( $\text{Cu}_2\text{CoO}_3$ ) thin film coatings deposited on highly reflecting aluminum substrate *via* a simple, cost-effective and environmentally-friendly sol-gel dip-coating route [21-24]. Our coatings (before the addition of antireflection layer) exhibited promising absorptance properties as compared to other selective absorber materials synthesized from more complicated sol-gel process routes [25, 26]. The light absorption selectivity behavior is due to the combination of

factors of the intrinsic properties of coating, the film thickness and reflectivity properties of substrate [24]. However, to maximize the absorptance in UV-Vis range and to protect the coatings from any degradation due to external factors, an antireflection (AR) layer on the top of the absorber layer is, therefore, needed [27, 28]. The aim of the present work is to investigate the optical properties and the thermal durability of copper cobalt oxide thin film coatings with a silica anti reflection layer ( $\text{Cu}_2\text{CoO}_3 - \text{SiO}_2$ ). A material which will be used as antireflective layer should have a refractive index value between the value of the material underneath and the value of air ( $n=1$ ) [2]. For the case of  $\text{Cu}_2\text{CoO}_3$ , to the best of our knowledge, no previous data on refractive index has been published. Since most copper cobalt oxide family and spinel minerals have refractive indices of around 1.75 [2], we utilized such value for our compound. Therefore, as  $\text{SiO}_2$  refractive index is widely known to be about 1.5 [2, 29], we surmise that  $\text{SiO}_2$  should be a good choice as antireflective material for our absorber layer. Besides that  $\text{SiO}_2$  is well-known to be a very resilient with favorable mechanical characteristics. The durability data obtained from this study are also useful in establishing the physical (wear and thermal) resistance of the coatings against extreme weather and external conditions.

## 2. Experimental

### 2.1. Preparation of thin film coatings with silica antireflection layer

The cobalt copper oxides thin film coatings were prepared from their respective chemical precursors (0.25 M copper acetate and 0.25 M cobalt chloride) using a sol-gel dip-coating method as specified in our previous studies [21, 22]. The dip-coating withdrawal rate was fixed at 120 mm/min. Final annealing was conducted at 500°C for 1

hour. The heating rate of the annealing process was 50°C/min, while cooling was performed inside the furnace for 10 minutes before allowed to cool to room temperature. The copper-cobalt oxides (Cu<sub>2</sub>CoO<sub>3</sub>) thin film coatings were obtained using this route.

To prepare the silica antireflection layer, tetraethyl orthosilicate/TEOS (C<sub>8</sub>H<sub>20</sub>O<sub>4</sub>Si, Alfa Aesar, >99%), absolute ethanol (Merck), Milli-Q water, hydrochloric acid (32% w/w) were used as received. Commercial aluminum (2 × 4 cm<sup>2</sup>) was used as substrate. This AR layer was synthesized using a sol-gel method customized from Bostrom et al. [28]. Firstly, TEOS was mixed with ethanol while 0.06 wt% HCl solution was gradually added to the TEOS-ethanol solution. The molar ratios of ethanol and water to the TEOS were 5 and 4, respectively. To ensure complete hydrolysis process, the resulting mixture was stirred for 24 hours in a closed container. The obtained solution with pH of 2.1 was used for the AR layer deposition by dip-coater with withdrawal rates ranging from 10 to 40 mm/min. The wet AR layer was subsequently stored in a desiccator before final annealing to 400°C for 30 minutes in an oven furnace and finally allowed to cool to room temperature overnight inside the furnace. All samples were kept in vacuum desiccator with silica gel and the samples were further dried in laboratory vacuum drying oven at 60 °C overnight prior to any characterisation analysis.

## 2.2. Characterizations

The optical performance of the coatings with silica the AR layer on reflective aluminum substrates (opaque surfaces) was calculated based on the absorptance ( $\alpha_S$ ) and emittance ( $\epsilon_T$ ) values. These values were obtained from the measurements of monochromatic reflectance in the wavelength area from 0.3 to 2.7  $\mu\text{m}$  by using an Ultra

violet– visible-near infrared (UV-Vis-NIR) spectrometer and wavelength area more than 2.7  $\mu\text{m}$  by using a FTIR spectrometer.

The solar absorptance and emittance values of the samples were calculated based on the reflectance data as elucidated by Duffie and Beckman [29]. A template of reflectance data against spectral distribution (using Air Mass standard of AM1.5 for absorptance and blackbody radiation standard of 100°C for emittance) in equal energy increment was created using an *Excel* worksheet. The near-normal hemispherical solar reflectance spectrum was recorded from 0.3 to 2.7  $\mu\text{m}$  using a UV–Vis-NIR Jasco V-670 double beam spectrophotometer with 60 mm integrating sphere. Deuterium and halogen lamp were used as the light source. Infrared reflectance spectra in the wavelength area from 2.7 to 15.4  $\mu\text{m}$  were obtained using a reflected-off type of Perkin Elmer Spectrum 100 FTIR spectrometer with integrating sphere within the range from 500 to 4000  $\text{cm}^{-1}$ . The coating surface was contacted on the diamond surface area and a pressure arm was positioned and locked at force of 80 N to maintain homogenous attachment onto the surface. The reflectance spectrum was obtained after four scans with resolution of 2  $\text{cm}^{-1}$ . Background correction was performed before the collection of each spectrum.

The accelerated thermal durability test was conducted using an oven furnace based on the PC (performance criterion) value of IEA SHC Task 27 [30] while the adhesion effectiveness between the film absorber and substrate was evaluated by the physical/cracking inspection before and after thermal test. The PC value is defined as the following equation:

$$PC = -\Delta\alpha_s + 0.5\Delta\varepsilon_{100} \quad (1)$$



where  $\Delta\alpha_S$  is the difference of absorptance values before and after the thermal test while  $\Delta\varepsilon_{100}$  is the difference of emittance values (where the emittance values were measured at the blackbody radiation standard of 100°C) before and after the thermal test [30]. In this test, the initial  $\alpha_S$  and  $\varepsilon_T$  values of the coatings were determined before the thermal test, and they became the basis to establish the temperature ( $T_1$ ) applied in the thermal test. The PC values were evaluated after  $t = 18, 36, 75, 150, 300$  and 600 hours of thermal testing. The time  $t_1$  was defined as the last testing time where the PC value was still less than 0.05. If the PC value was similar to or less than 0.01 after  $t_1 = 600$  hour and there was no cracking, then the absorber coating was deemed to have passed the accelerated thermal test. If PC value was more than 0.05 at  $t_1 = 300$  hour or the PC value was higher than 0.01 after  $t_1 = 600$  hour, then an additional thermal test at a higher temperature ( $T_3$ ) for  $t_3$  hours would be required ( $t_3$  corresponded to the previously determined  $t_1$ ). After this additional test, if  $PC(T_3, t_3) \geq PC(T_1, t_1)$  and the coatings did not crack, the coating had passed the accelerated thermal test. Lastly, if the PC value was greater 0.05 at  $t_1 \leq 150$  hours, an additional test using a lower temperature ( $T_2$ ) for  $t_2$  hours would be required (where  $t_2$  corresponded to the previously determined  $t_1$ ). If  $PC(T_2, t_2) \leq PC(T_1, t_1)$  and there was no cracking, the absorber had passed the accelerated thermal test.

The surface morphologies of the thin film samples were analyzed using FESEM (Zeiss Neon 40EsB). Prior to the analysis, the sample was mounted on the substrate holder using carbon tape and sputter-coated with platinum to reduce any charging effects. InLens detectors were used at magnifications of 1  $\mu\text{m}$  with an aperture size of 30  $\mu\text{m}$  while the extra high tension voltage field emission gun was set at 5 kV.

### 3. Results and Discussion

#### 3.1. Reflectance spectra and solar absorptance

Figure 1 shows the reflectance spectra (wavelength range of 0.3-2.7 $\mu$ m) of the copper cobalt oxide thin film coatings with the silica AR layer synthesized at different withdrawal rates. The spectrum of copper cobalt oxide coating without a silica AR layer which has the thickness of around 320 nm is also presented for comparison purposes. Interestingly, it can be clearly seen that the addition of a silica AR layer at increasing dip-coating speeds has a substantial effect on the reflectance curves profile. The relatively significant changes occur when the AR layer was deposited at withdrawal rates of 20 and 40 mm/min where their interference peaks (labeled “\*”) and the absorption edges (labeled “#”) positions shift to the lower wavelengths area compared to the coating with silica synthesized using withdrawal rate 10 mm/min or coating without silica (see the lines labeled “2” and “3” versus lines labeled “0” and “1” in Fig. 1). Likewise, the distance between the interference peak and absorption edge (amplitude) of these two former silica coatings decreases ~60% compared to the amplitude of coating with silica synthesized using the withdrawal rate of 10 mm/min or the coating without silica. Theoretically, the increase of the withdrawal rate would increase the thickness of the silica AR layer [31]. However, even though the thicknesses of silica layer were not measured directly and the thickness of copper cobalt oxide layer was kept similar, from the reflection curve of the silica coated samples, it may be expected that the physical thickness for the withdrawal speed of 20 mm/min is equivalent to that for the speed of 40 mm/min. These observations evidently imply that the reflectance spectra profile relatively alters with the increase in the thickness of the silica AR layer.

Low spectral reflectance in the solar wavelength area indicates high absorptance and *vice versa*. The increases of absorptance values for the three coatings with silica AR layers are *ca* 1.0-1.5% while the AR layer synthesized with dip-speed of 10 mm/min exhibits the highest absorptance among all the samples. The increase of absorptance after the addition of silica is attributed to the enhanced solar absorption by the silica network which reduces the reflective properties of copper cobalt oxide coating surface where the variation of reflective properties here are related to interference phenomena governed by film thickness and refractive index ratios. Further increases of withdrawal rates, however, seem to have marginal effect on the absorptance values which suggests that the AR layer thickness does not significantly influence absorptance (as opposed to reflectance spectra profile, especially in the NIR area ( $>0.8 \mu\text{m}$ )). This may be elucidated based on the characteristic of the Duffie and Beckman method [29] in counting the absorptance value where the denser count occurred in the UV-Vis wavelengths area compared to the NIR area due to the denser spectral distribution of solar irradiance in the UV-Vis area [32, 33], therefore the reflectance spectra curve profile below  $0.8 \mu\text{m}$  becomes crucial to note.

### 3.2. Emittance and selectivity

The reflectance spectra of copper cobalt oxide thin film coatings with and without a silica AR layer within the mid-far infrared wavelength range are presented in Figure 2. Similarly, the addition of silica AR layer at increasing dip-coating speeds has a substantial effect on the reflectance curves profile. Within the wavelength range of around  $3 - 8 \mu\text{m}$ , the addition of an AR layer increases the reflectance. However, within the wavelength range of around  $8-10 \mu\text{m}$ , the AR layer absorbs too much infrared light, thus increasing the

thermal emittance ( $\epsilon_T$ ). Within this range, the thicker the AR layer, the higher the infrared absorption. This phenomenon is due to the strong phonon absorption of the Si-O stretching modes as also reported by other researchers [26, 34]. The relatively weaker phonon absorption in the wavelength range of around 15  $\mu\text{m}$  is also observed and can be attributed to the phonon absorption typically exhibited by the copper cobalt oxide family [26].

The  $\epsilon$  value is defined as a weighted fraction between emitted radiation and the Planck black body distribution. It may be determined based on the reflectance spectrum data [29]. This parameter is generally used to explain the performance of a solar selective absorber in the mid-far infrared wavelength range. High spectral reflectance within this range indicates low thermal emittance and vice versa. From Figure 2, the overall thermal emittance of copper cobalt oxide thin film coatings with a silica AR layer increases with the increase of dip-speed. The significant increase of emittance at ca 50% occurs when the dip-speed is increased from 20 to 40 mm/min which implies increased heat loss from the coating surface and decreased efficiency. The marginal increase of emittance value is shown by the coating with the AR layer synthesized using dip-speed 10 mm/min.

Figure 3 shows the optimal reflectance curve of copper cobalt oxide thin film coating with silica AR layer (dip-speed of 10 mm/min) within the wavelength range of 0.3-15.4  $\mu\text{m}$  corresponding to the optimum absorptance value of  $\alpha_S = 84.96\%$  and emittance value of  $\epsilon_T = 5.63\%$  (selectivity,  $s = 15.1$ ). An emittance value below 10% can be categorized as a good emittance performance for a selective absorber material [3, 4, 35]. The dashed line in Figure 3 is the extrapolation line created in place of ‘noisy’ spectrum at the end of the spectrum measurement range generated by the equipments used (UV-Vis-NIR and FTIR).

### 3.3. Accelerated thermal durability test

The accelerated thermal durability test was conducted to determine the estimated service lifetime of a selective absorber surface based on its thermal behavior at a high temperature range. This is because the real application of a selective absorber is strictly insulated under a transparent glass cover; therefore the thermal behavior became the essential factor determining the quality of the absorber film. The International Energy Agency (IEA) developed an accelerated thermal durability test to assess the thermal collector performance called performance criterion (PC) through the IEA SHC Task 27 [30]. This test procedure assumes that the activation energy of a certain degradation process is sufficient to ensure absorber durability under natural working conditions of a flat thermal collector [36].

Table 1 shows the PC values of the coatings with a silica AR layer based on the thermal test of the IAEA SHC Task 27. Based on this procedure, it was selected the temperature of 265°C as applied in the thermal test ( $T_1$ ) for several testing times ( $t_1$ ) as our coating showed the optimum absorptance value of around 84-85% and emittance value of around 5-6%. From Table 1, it can be seen that the variations of emittance before and after the thermal test ( $\Delta\epsilon_T$ ) are much higher than the variations of absorptance ( $\Delta\alpha_S$ ). The change of emittance ( $\Delta\epsilon_T$ ) values increases with the increase of testing time, while the change of absorptance ( $\Delta\alpha_S$ ) values is relatively small and negligible. As such, the PC values absorber coatings are more influenced by the changes in emittance. The significant change of spectral reflectance in the mid-IR area ( $\geq 2.5\mu\text{m}$ ) after the thermal test is due to the thermal load that causes the thermo-chemical redox reactions experienced by absorber coating materials which increase the IR absorption [30, 37, 38]. The PC values increase with the

increase in the testing times while for the testing times of 75 and 150 hours, the recommended PC value ( $PC = 0.05$ ) for a qualified absorber was exceeded. As such, longer testing times were not required. Instead, an additional test was carried out using a lower temperature ( $T_2 = 235^\circ\text{C}$ ) for  $t_2=179$  hours. It is observed that the PC ( $235^\circ\text{C}; 179\text{h}$ ) is less than PC ( $265^\circ\text{C}; 36\text{h}$ ). Based on the PC value criteria, the coatings with the silica AR layer pass the accelerated thermal durability test. Figure 4 shows the reflectance spectra of copper cobalt oxide thin film coatings with an AR layer within the wavelength range of 0.3-15.4  $\mu\text{m}$  before and after the thermal test at  $265^\circ\text{C}$  for 36 h and  $235^\circ\text{C}$  for 179 h.

The possibility of residual water content that may influence the optical performance of coatings can be dismissed since all coatings were synthesized at temperatures above  $400^\circ\text{C}$  and the samples were treated as described in Section 2.1. None of the samples showed observable visual changes and cracks before or after the thermal test, see Figure 5. The thermal tests even improve the appearance of film coating (i.e. smoother) with integrated silica antireflection layer (Figure 5b). This indicates the high thermal endurance of coatings and the good adhesion between the coating and the substrate. Based on the physical and cracking inspections, the coatings with AR layers fulfill the performance criteria as good material for solar selective absorber. Nonetheless, the results in Table 1 reveal that the degradation of the coatings with the silica AR layer is more governed by the temperature regime than the exposure time. This may be detected by comparing the PC values between temperatures  $235^\circ\text{C}$  and  $265^\circ\text{C}$  where the PC value can be retained remain low ( $<0.05$ ) by decreasing the temperature test even though the test was carried out at a longer of exposure time. As such, the coatings are qualified for uses within an extended timeframe but in low

temperature range applications ( $\leq 150^{\circ}\text{C}$ ) [39] such as for domestic solar water heating systems or for façade coating applications.

#### **4. Conclusions**

The copper cobalt oxide thin film coatings with the silica antireflection (AR) layer have been successfully deposited on reflective aluminum substrates using the sol-gel dip-coating method. The addition of silica changed the reflectance spectra of coatings within the wavelength range of 0.3-15.4  $\mu\text{m}$ . The PC values results and physical inspections showed that the coatings with silica AR layer passed the accelerated thermal durability test without any cracking detected. The degradations of the copper cobalt oxide thin film coating with silica AR layer is governed more by the temperature changes regime than the exposure time indicating that the coating is qualified for long periods of uses in low temperature applications such as for domestic solar water heater systems or for façade coating applications.

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**Table 1.** Accelerated thermal durability parameter values obtained in the thermal test.

Parameters	Testing times ( $t_1$ ) at 265°C			
	18 h	36 h	75 h	150 h
$\Delta\alpha_S$	-0.005	0.002519	0.000628	0.001132
$\Delta\varepsilon_T$	0.0283	0.08412	0.10895	0.14197
PC	0.01915	0.039541	0.053847	0.069853
<b>Thermal test at 235°C for 179 h</b>				
$\Delta\alpha_S$	-0.0019			
$\Delta\varepsilon_T$	0.060247			
PC	0.032024			

**Figure captions**

**Fig. 1.** Reflectance spectra of copper cobalt oxide thin film coatings with and without the silica AR layer within a wavelength range of 0.3-2.7 $\mu\text{m}$  with corresponding solar absorptance ( $\alpha_s$ ) values.

**Fig. 2.** Reflectance spectra of copper cobalt oxide thin film coatings with and without silica AR layer within wavelength range of 3.0-15.4  $\mu\text{m}$  with corresponding solar emittance ( $\epsilon_T$ ) values.

**Fig. 3.** Reflectance spectrum of copper cobalt oxide thin film coatings with AR layer (dip-speed of 10 mm/min) within wavelength range of 3.0-15.4  $\mu\text{m}$ .

**Fig. 4.** Reflectance spectra of copper cobalt oxide thin film coatings with AR layer before and after accelerated thermal durability test at: a) 265 $^{\circ}\text{C}$  for 36 h and, b) 235 $^{\circ}\text{C}$  for 179 h

**Fig. 5.** Surface morphology of coatings for a) before and b) after thermal durability test

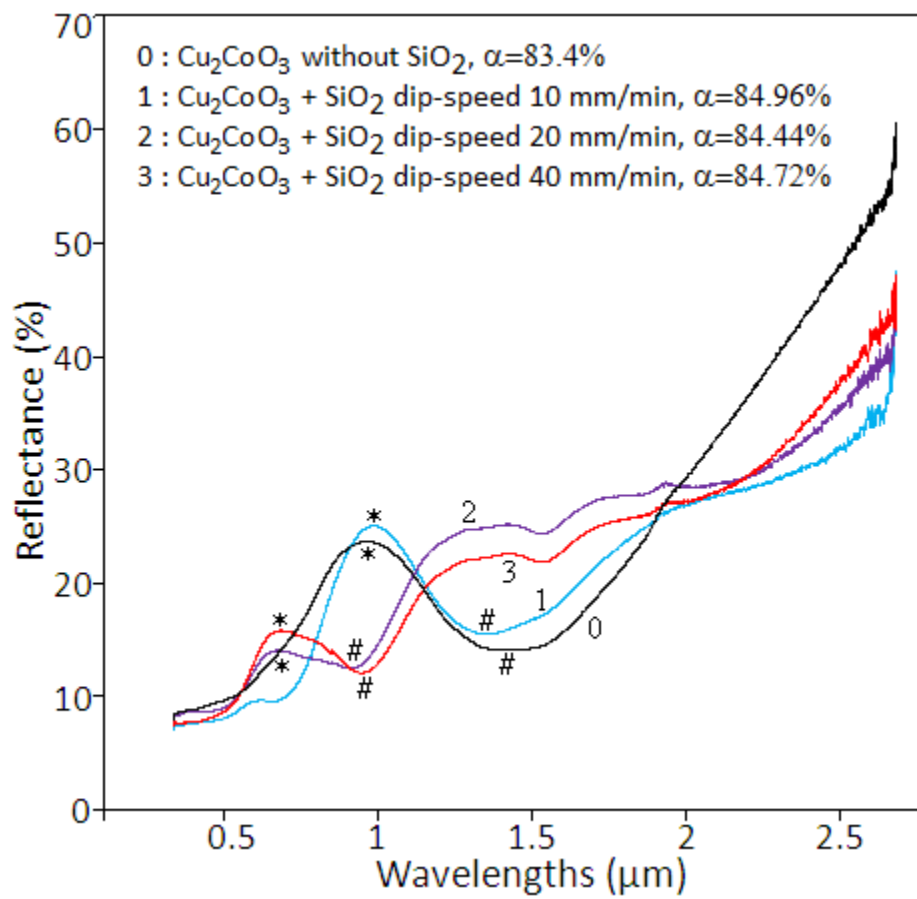
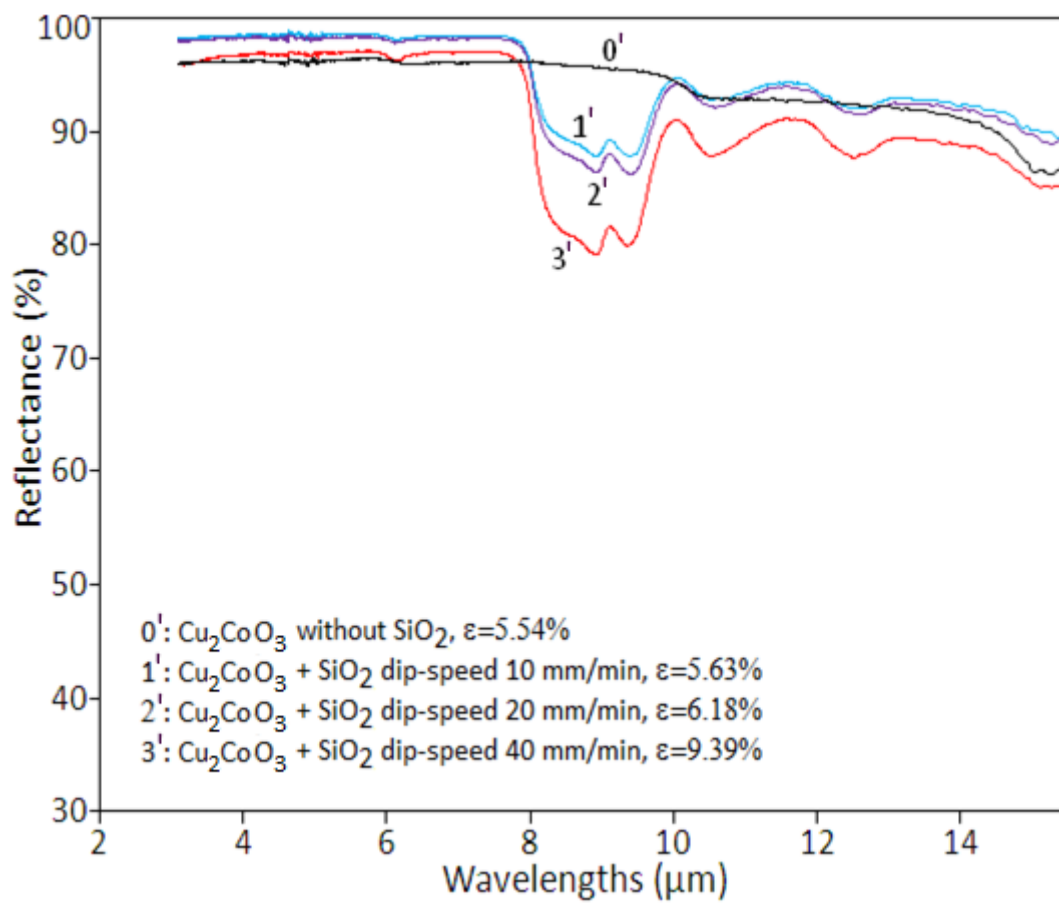
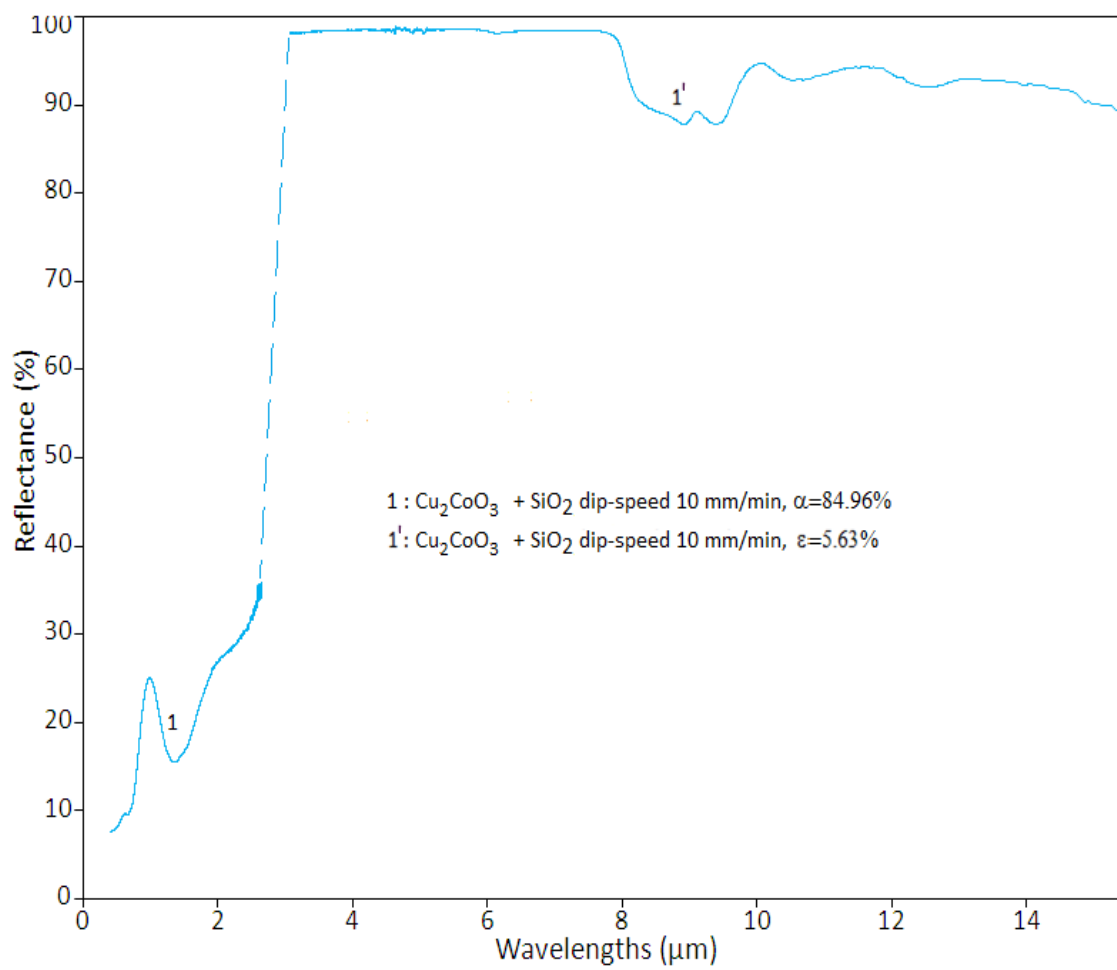


Fig. 1.

**Fig. 2.**



**Fig. 3.**

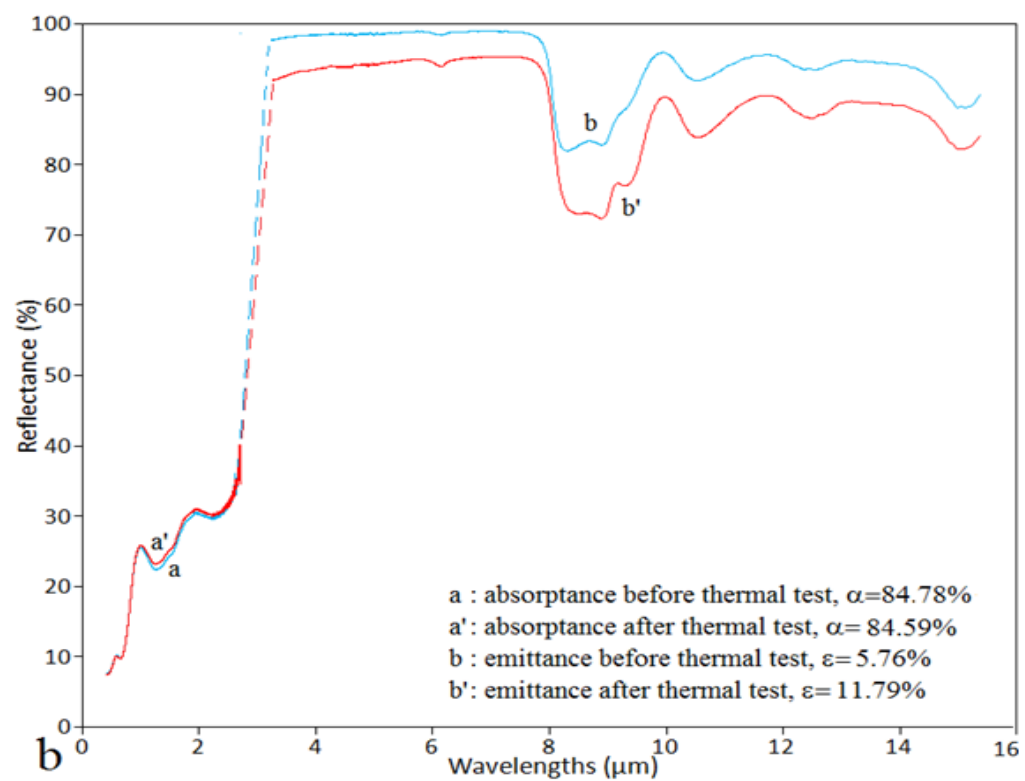
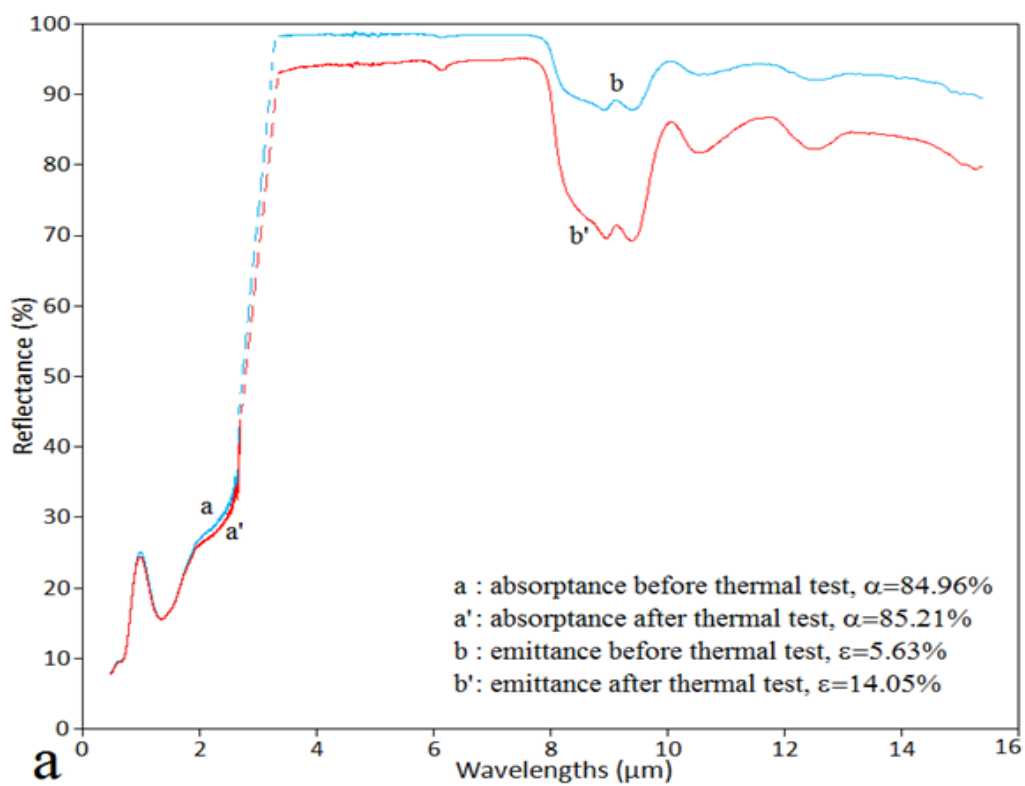
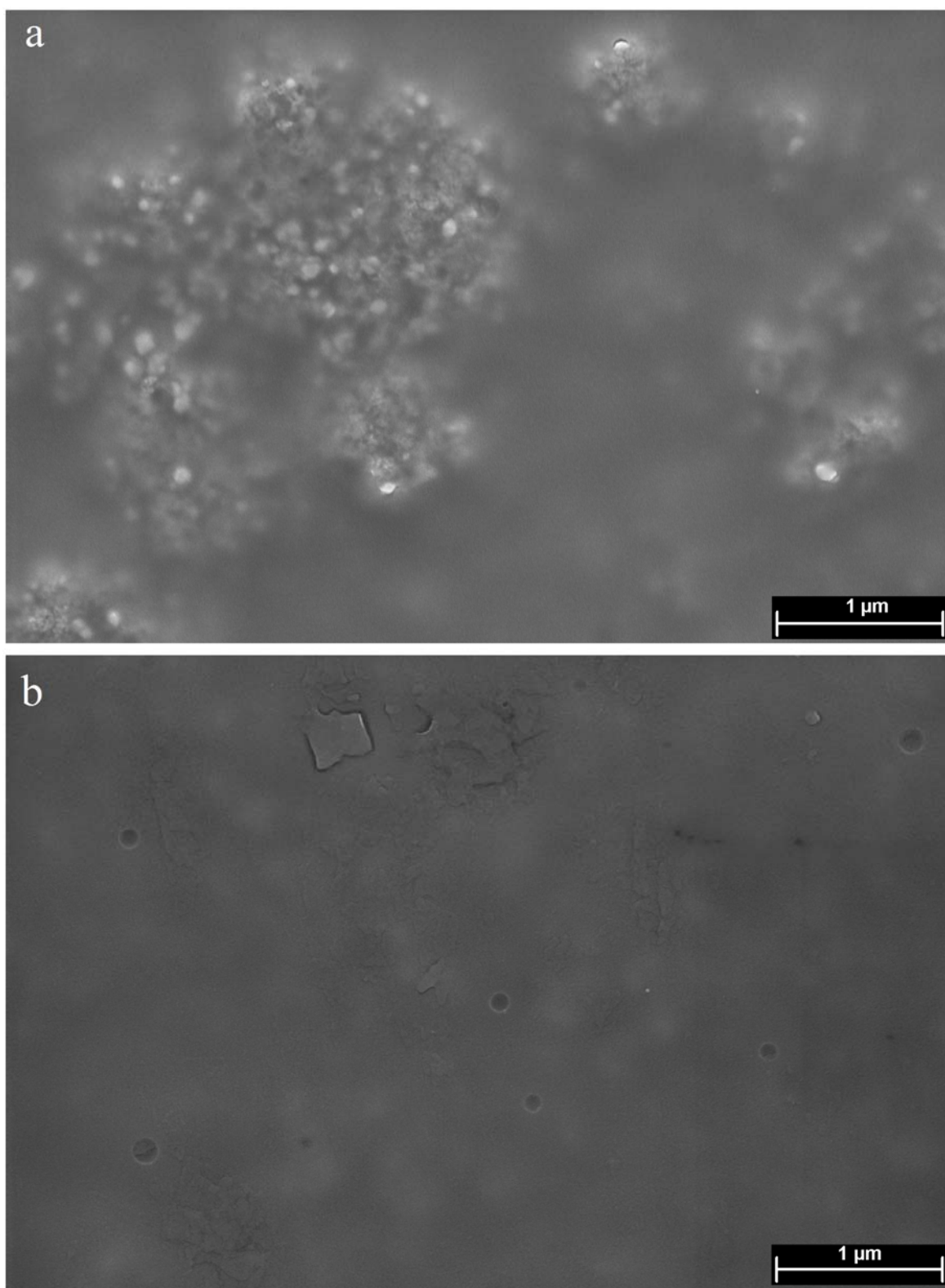


Fig. 4.



**Fig. 5.**