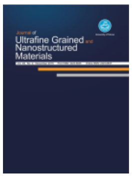

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Particle size and kind of mica in synthesis of nontoxic bronze and gold pearlescent pigments based on nanoencapsulated hematite

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Abstract

Nano-encapsulated iron oxide in Zirconium oxide-coated mica pigments are thermally stable, innocuous to human health, non-combustible, and they do not conduct electricity. They could be applied in several industries such as thermoplastics, cosmetics, food packaging, children toys, paints, automobiles coating, security purposes, and banknotes. Nowadays, they are highly desirable in ceramic decoration. In the present study, intensively dark gold to bronze colored mica clay pigments, which were based on mica flakes covered with a layer of nano-iron oxide-Zirconium oxide particles, were prepared by homogeneous precipitation of iron nitrate and Zirconium chloride ammonia in the presence of mica flakes in two kinds of ore clay-based phlogopite and muscovite minerals. The final color was obtained by thermal annealing of precipitates at a temperature of 800°C. The pigments were characterized by X-Ray Diffraction, Particle size analysis, Scanning electron microscopy, Transmission electron microscopy, X-Ray fluorescence, and Simultaneous thermal analysis. Results indicate that nano-encapsulated iron oxide in zirconia particles have been formed on mica flakes and kinds of clay-mica can be related to obtained shade from dark gold to bronze pearl. Higher particle size of mica flakes about phlogopite type of mica introduced pearl effects with higher L* changes in different angles. Muscovite performed higher hue and better pearl effect than phlogopite.

Keywords: *mica, muscovite, nano-encapsulation, pearl pigment, phlogopite, precipitation.*

1. Introduction

There are several kinds of mica; examples are biotite, lepidolite, muscovite, phlogopite, and vermiculite. All of them are based on complex hydrous potassium–aluminum silicate minerals that differ in chemical composition. Muscovite with $K\ Al_3\ Si_3\ O_{10}\ (OH)_2$ formula has more application than the other kinds of mica as pearlescent pigment [1-3].

Pearlescent pigments show optical effects due to angle-dependent deriving from alternating transparent layers with different refractive indices [4]. This luster effect is depended on the mica particle size. The stronger shine is related to coarser platelet (e.g., >50 mm) [4-6].

Iron oxide-coated mica pigments are thermally stable, innocuous to human health, environmental product, non-combustible, and they do not conduct electricity. Mica-based pearlescent pigments have been applied in several industries such as thermoplastics, cosmetics, food packaging, children toys, paints, automobiles coating, security purposes, and banknotes (since their angle-dependent optical effects) [4, 7]. Also, they are highly interesting in ceramic decoration because the possibility to get a luster effect, replacing precious metals, has been recently appraised in ceramic productions fired at low temperature. On the other hand, among synthetic ceramic pigments with luster effect, there is a restricted choice for colored shade; in fact, just gold and silver shades could be possible to apply current pearlescent pigments into glassy coatings preserving their optical appearance or third fire decoration and other low temperature ceramics [8].

Pearlescent pigments based on mica substrates coated with a metal oxide layer have been applied into predominantly lead and/or cadmium-containing glass frits and resulting colored pearl glaze could be fired within a limited temperature range of about 500˚C to 700˚C, while conventional glazes are fired at temperatures of up to 1000˚C or higher to obtain the desired appearance [9]. Therefore, synthesis of new colored pearl pigment with innovative aesthetic effects in decorated wares, especially wall and floor tiles or tableware is very important for the ceramic industry [4].

Hematite pigments have a long history as red/orange pigment and can be used for ceramic application by encapsulation. Hematite, as a natural and non-toxic red ceramic pigment has been known since prehistoric times. It is also plenty and cheap, therefore hematite is the best choice for coating mica in order to obtain bronze luster effect [10-15]. But no data are available in the literature and the previous studies only concern the utilization of mica [4]. Junru [16] synthesized cobalt blue mica coated titania pearlescent pigment from solution $Co(NO_3)_2.6H_2O$, $Al(NO_3)_3.9H_2O$, Na_2SO_4 and urea. Stengl et al prepared colored mica pigments based on muscovite flakes covered with surface oxide–hydroxide layer of different metals, such as Ti, Cr, Fe, Al, Co, Ni, Zn, and Cu by homogeneous precipitation of metal sulfates, but they did not describe details and did not study on the effect of mineral kind of mica, particle size of mica flakes, and layer morphology on the obtained pearlescent shade by the GonioSpectrophotometer and electron microscopy [17].

In this paper, preparation of intensively gold and bronze colored for two kinds of mica mineral particles was described based on iron oxide (hematite) and zirconium oxide (zirconia) in situ formed in aqueous media in the presence of mica particles, iron nitrate, zirconium chloride, and ammonia. Zirconia is a well-known material with high temperature stability that will cause possibility ceramic application of synthesized colored pearl pigments [Fetter, 2003]. Mica coated particles are possibly applied in the production of golden/bronze ceramic pigments. Golden ceramic pigments are normally obtained from gold, silver or copper metal particles. The use of mica coated particles was a cheaper alternative. This study was concerned with the synthesis and characterization of the pigments: composition, microstructure, and color. The technological behavior, microstructure, and thermal stability of pearlescent pigments have been assessed by simultaneous thermal analysis, evaluating colorimetric parameters, phase composition, particle size, and surface microstructure.

2. Experiments

2.1. Synthesis of gold and bronze colored mica pigments

The preparation of surface-treated muscovite and phlogopite was performed using controlled homogeneous hydrolysis, in which a mixture of iron and zirconium oxides-hydroxides was co-precipitated onto the lamellar particle surface. Mica was obtained from high quality ores located in north (phlogopite) and northwest (muscovite) of Iran. Table 1 shows their chemical composition.

At first, in order to study on particle size as an effective factor on pearl shade in a comparable condition, phlogopite type of mica was milled and screened to 4 groups with different particle sizes. Particle size analyses of phlogopite used in this study are presented in Table 1 and Figure 1.

Table 1. Chemical analysis of the muscovite and phlogopite by X-ray fluorescence

Chemical analysis	(%) in phlogopite	(%) in muscovite
SiO_2	10.783	18.835
Al_2O_3	11.136	46.496
TiO_2	33.428	6.271
MgO	26.844	0.698
K_2O	9.439	19.36
Na_2O	-	0.664
Fe_2O_3	4.855	2.917
P_2O_5	-	0.03
CaO	-	0.237
Rb	0.019	0.043
Sr	0.015	-
LOI	3.48	4.45

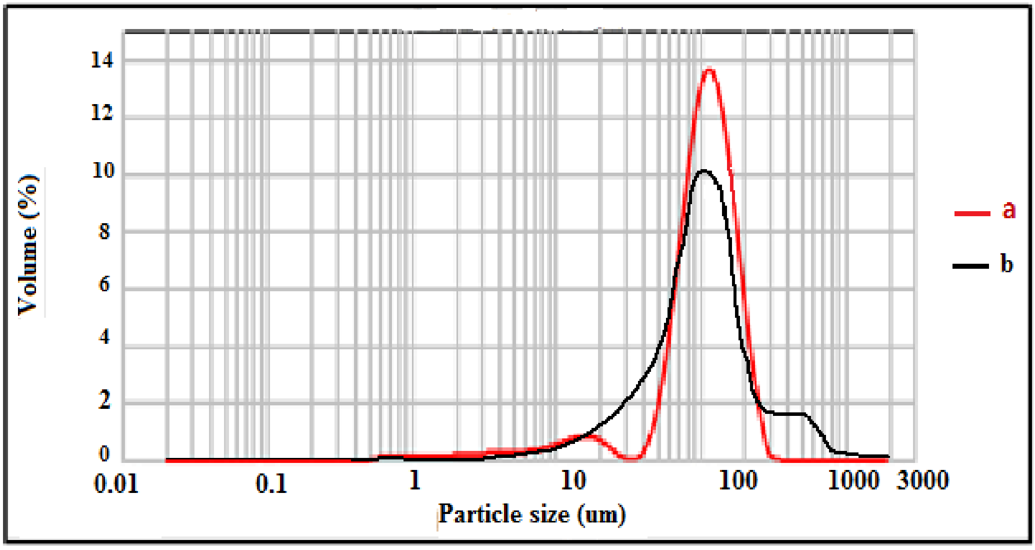


Fig. 1. Particle size analyses of phlogopite which were used in preparation of samples with codes of a) 1 and b) 2.

25 g of mica was suspended in 1litre of distilled water, iron nitrate (Merck). Zirconium chloride (Merck) and a necessary amount of ammonia solution (Merck) droplet was added to the mixture. The synthesis was complete after reaching a pH of about 7. The particles of the hydrolysis products can better develop a crystal structure. The gradual rise in pH results in the nucleation and growth of nano-size particles of the solid hydrolysis products. These particles are precursor of hematite and zirconium oxide. Depending on the reaction conditions, these nanoparticles either agglomerate into spherical clusters or can be deposited onto the surface of a suitable substrate present in the reaction mixture [17]. The final composition of coated particles was 1Mole ZrO_2-0.5Mole Fe_2O_3, in which raw materials were calculated based on weight percent of X against 100 gram mica. The effect of X changes (weight percent of coated particles), particle sizes, and kind of mica were also studied. The condition and code of synthesized samples are shown in Table 2. The product was obtained by filtration and drying at 110°C. The dry pigment was annealed at a temperature of 800°C for 2 hours.

Table 2. The condition of the synthesized samples with codes

Sample code	Mica type	PSA_d(0.1) µm	PSA_d(0.5) µm	PSA_d(0.9) µm	%X
1	phlogopite	51.494	107.621	182.084	3
2	phlogopite	32.313	86.84	190.554	3
3	phlogopite	17.559	51.172	115.455	3
4	phlogopite	13.048	30.86	58.872	3
5M	Muscovite				9
6	phlogopite	17.559	51.172	115.455	9

2.2. Characterization methods

The spectral reflectance of the colored mica powders was measured using a GretagMacbeth GonioSpectrophotometer Color-Eye741GL with a special silica glass cup.

The microstructure studies were performed using a transmission electron microscopy (Jeol JEM 2010 equipped with a GIF Multiscan Camera 794) and scanning electron microscopy SEM Leo 1455 VP microscope equipped with SE (secondary electron) detector and backscattered (BS) Robinson and solid state BSE detectors (to display the chemical contrast in the observed objects). Simultaneous thermal analysis was carried out using a Pyris Diamond TG/DTA (SII) model of PerkinElmer Company. To identify the crystalline phases present in the raw and annealed samples, X-ray diffraction patterns were collected using a conventional powder technique in a Siemens Diffractometer Siemens (D500 mod) employing Cu Ka Ni-filtered radiation.

3. Results and Discussion

3.1. Thermal behavior by simultaneous thermal analysis

The analysis was carried out in air atmosphere in a temperature up to 1200 °C with a heating rate of 10 °C/min. Figure 2 shows the typical STA thermos-diagrams for the unwashed (unwashed condition is due to the detection of evaporate temperature, i.e. evaporation can help to control nano-size particles) raw sample 5M.

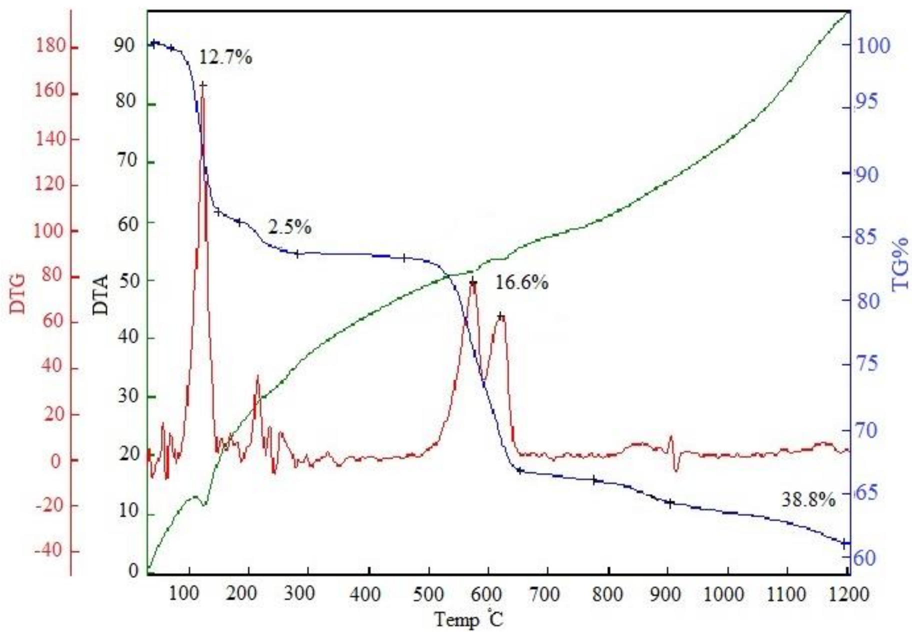


Fig. 2. STA of unwashed raw sample 5M

This analysis shows several weight losses even up to 38.8% in higher temperatures as a result of evaporated gas and moisture, such as HCl, SOx, and H2O. It can be concluded that weight losses have been taken place in 3 steps. It is assumed that the endothermic below 250°C is due to the removal of structural water and dehydroxylation [6], regardless of the amount of water. Moreover, the 2.5 weight percent endothermic weight losses at peaks about 220°C-240°C is due to the decomposition of the condensation of no bonded oxygen, residual –OH groups and chloride ions [18] and perhaps ammonium sulfate decomposes at about 240°C.

In addition, the peak at 122°C is related to 12.7 weight percent endothermic weight losses because of humidity. The peaks at 574°C and 620°C correspond to the elimination of sulfate ions and crystallization of the amorphous phase into hematite and zirconium oxide phase with 16.6 weight percent endothermic weight losses [11].

There is a peak about 900°C with high weight loss equal to 1.7% which can be as a result of muscovite to feldspar transformations. Pearlescent mica based pigments are stable in glassy coatings up to 1000°C, any deterioration of their optical properties being due to muscovite-to-feldspar transformations occur at higher temperatures or after long firing times [4]. Therefore, annealing at 800°C is suitable and this pigment type with a bronze shine is particularly suitable for third fire decoration of ceramic tiles, involving low temperatures and fast firing schedules, where it can replace expensive precious metals lustrous. No destruction or sintering of the mica particles was observed after the annealing process, but only changes of color, which resulted from the crystallization of the nano-hematite. Due to its chemical and thermal stability, this pearl pigment type may be considered to be used in various applications such as organic coatings, plastics, glass, ceramics, and paper; particularly suitable for third fire decoration of ceramic applications, involving low temperatures and fast firing schedules.

3.2. Thermal evolution of crystalline phases by XRD analysis

The XRD patterns of samples with 3 percent nanoparticles coated phlogopite (codes: 1-4) show that raw and annealed samples are approximately similar. Figure 3, for example, presents XRD pattern of annealed sample 1, only indicating the phlogopite phase. It can be related to low percent of colored phases that is lower than XRD detection power. Moreover, raw samples can have amorphous phases.

Figure 4 shows XRD pattern of a) raw sample 5M and b) annealed sample 5M. In case of 9% nanoparticles coated muscovite, the annealed sample 5M at a temperature of 800°C contains crystalline phases (hematite, baddeleyite, and tetragonal zirconium oxide) whereas raw samples were amorphous. Baddeleyite is the low temperature monoclinic form of zirconium oxide.

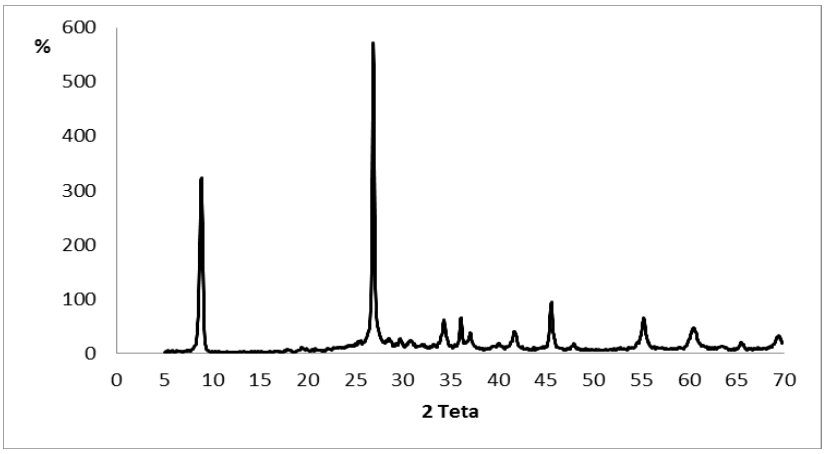
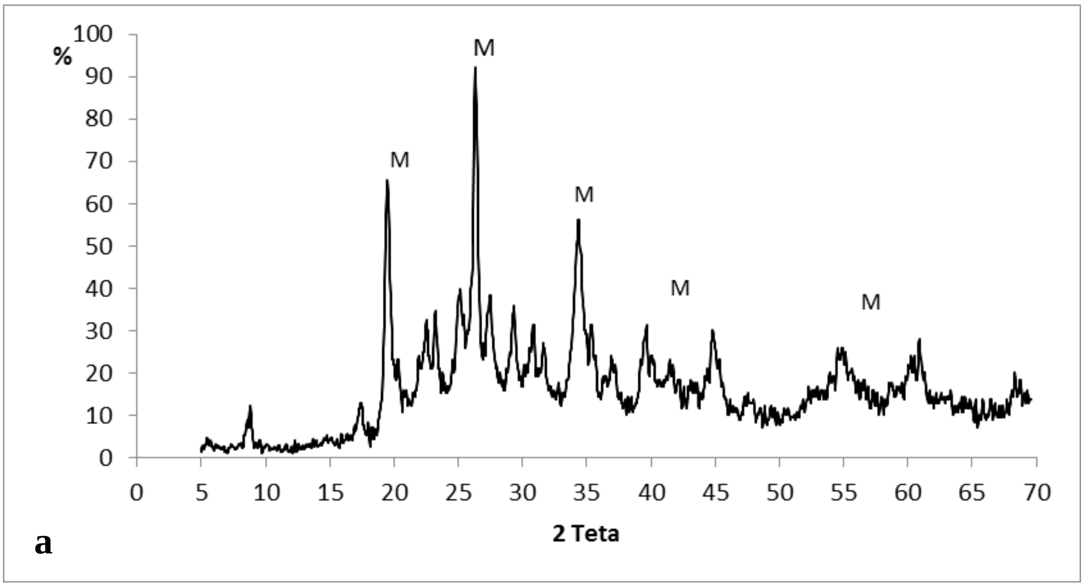


Fig. 3. XRD pattern of annealed sample 1 indicates phlogopite peaks



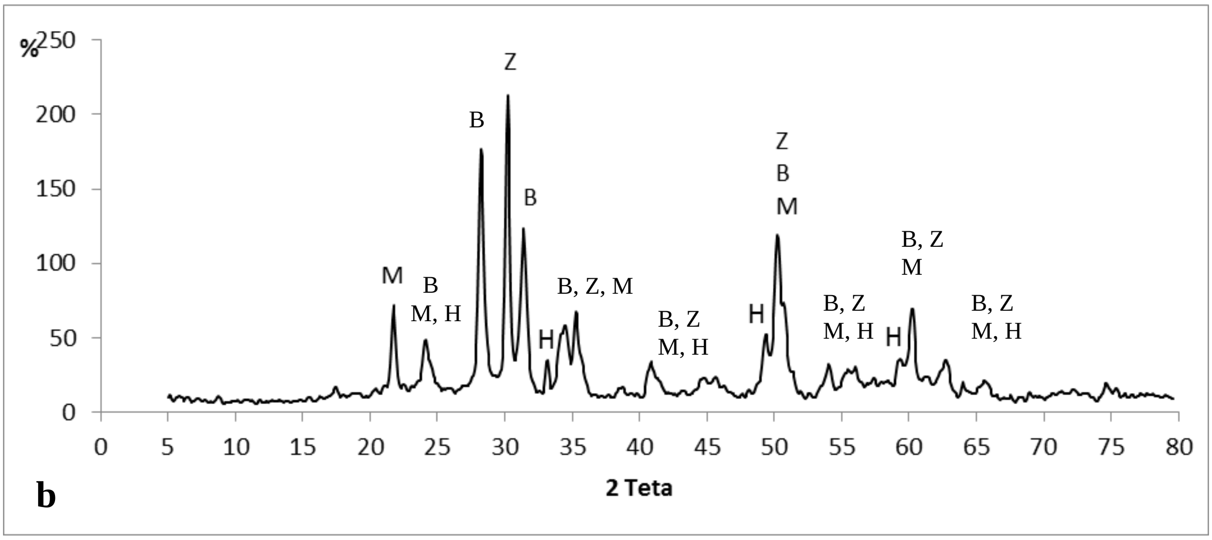


Fig. 4. XRD pattern of sample a) raw sample 5M and b) annealed sample 5M. M: muscovite H: hematite (PDF 33-0664), B: baddeleyite (PDF 72-1669) and Z: zirconium oxide (PDF 79-1771)

In order to evaluate crystalline size of hematite, the Scherrer equation has been calculated and the conclusion is compared with TEM findings, based on X-ray diffraction pattern:

$$D = \frac{K\lambda}{\beta \operatorname{Cos}\theta_{\beta}} \qquad (1)$$

where D is the mean crystallite size λ is the radiation wavelength (0.15406 nm for copper lamp), K= 0.89. β is the most intense line, for the hematite phase and θ the Bragg angle [2]. The crystalline size of hematite was evaluated about 28 nm.

3.3. Colorimetric analysis of samples by CIElab values

The layer of nanoparticles of encapsulated hematite on the mica surface results in colored mica in various shades. The color shade of the final pigment depends on the granularity, mica particle sizes, and the amount of hematite deposit [17]. The prepared pearl pigments with 3 percent nanoparticles coated phlogopite present dark gold shade. The color changes of pigments which are based on different particle sizes of mica (in system CIE L*a*b) are shown in Table 3. Magnitude of error of their irreproducibility was about $\Delta E_{ab}^{*} \leq 0.4$.

Table 3. Color scheme for prepared dark gold pearl pigments (in system CIE L*a*b) based on different particle sizes by Illum D65

Sample Name	Angle	L*	a*	b*	C*	h°
1	20°	81.449	10.437	31.354	33.045	71.588
1	45°	44.045	9.32	23.882	25.636	68.682
1	75°	29.236	8.711	18.704	20.633	65.027
1	110°	25.007	8.866	19.136	21.09	65.141
2	20°	72.563	9.053	26.442	27.949	71.101
2	45°	39.82	9.049	21.86	23.659	67.513
2	75°	29.586	9.464	19.795	21.941	64.448
2	110°	25.688	10.183	20.987	23.327	64.117
3	20°	67.053	6.568	21.407	22.392	72.942
3	45°	37.948	7.45	19.713	21.074	69.297
3	75°	30.474	7.572	17.863	19.401	67.029
3	110°	25.988	8.314	19.19	20.913	66.575
4	20°	71.71	7.844	24.078	25.324	71.956
4	45°	44.994	9.268	23.937	25.669	68.834
4	75°	36.092	10.349	23.714	25.874	66.423
4	110°	32.679	10.91	24.131	26.483	65.672

Compared to codes 1-4, sample 3 has a higher and best hue than the others. Higher changes in red factor (a*) with changes of observer angle is related to sample 4 but color concentrating factor (c*) is more important. Data of L* and c*at different observer angle indicate that higher particle size has a higher pearl effect. In sample 1, c* is from 20.633 to 33.045 while it is about 25 in sample 4.

Table 4 shows the Color scheme for prepared bronze pearl pigments (in system CIE L*a*b) based on mica type and particle sizes of samples which are approximately constant around 40µm. Mica types in stable X value (mole ratio of nano-hematite) a little effect on shade of bronze pearl pigment. Muscovite performs higher hue and better pearl effect than phlogopite because c* has changed 15 steps, 16.43_31.42.

Samples 3 and 6 are comparable regarding X value changes in Tables 3 and 4. Therefore various shades from gold to bronze can be performed depending on the mole ratio or weight percent of the nano hematite.

3.4. Microstructure analysis of samples by SEM and TEM techniques

Figures 5 and 6 show SEM Micrographs of annealed samples 3 and 6 with different magnification by secondary and backscattered detectors respectively.

Table 4. Color scheme for prepared bronze pearl pigments (in system CIE L*a*b) based on mica type by Illum D65

Sample Name	Angle	L*	a*	b*	C*	h°
5M	20°	48.38	11.95	11.28	16.43	43.37
5M	45°	38.50	16.69	15.40	22.71	42.69
5M	75°	38.92	20.69	19.27	28.27	42.97
5M	110°	40.18	22.97	21.43	31.42	43.01
6	20°	59.80	19.53	14.94	24.59	37.41
6	45°	51.37	23.54	18.43	29.89	38.05
6	75°	50.44	25.44	20.18	32.47	38.43
6	110°	51.71	25.98	20.97	33.38	38.91

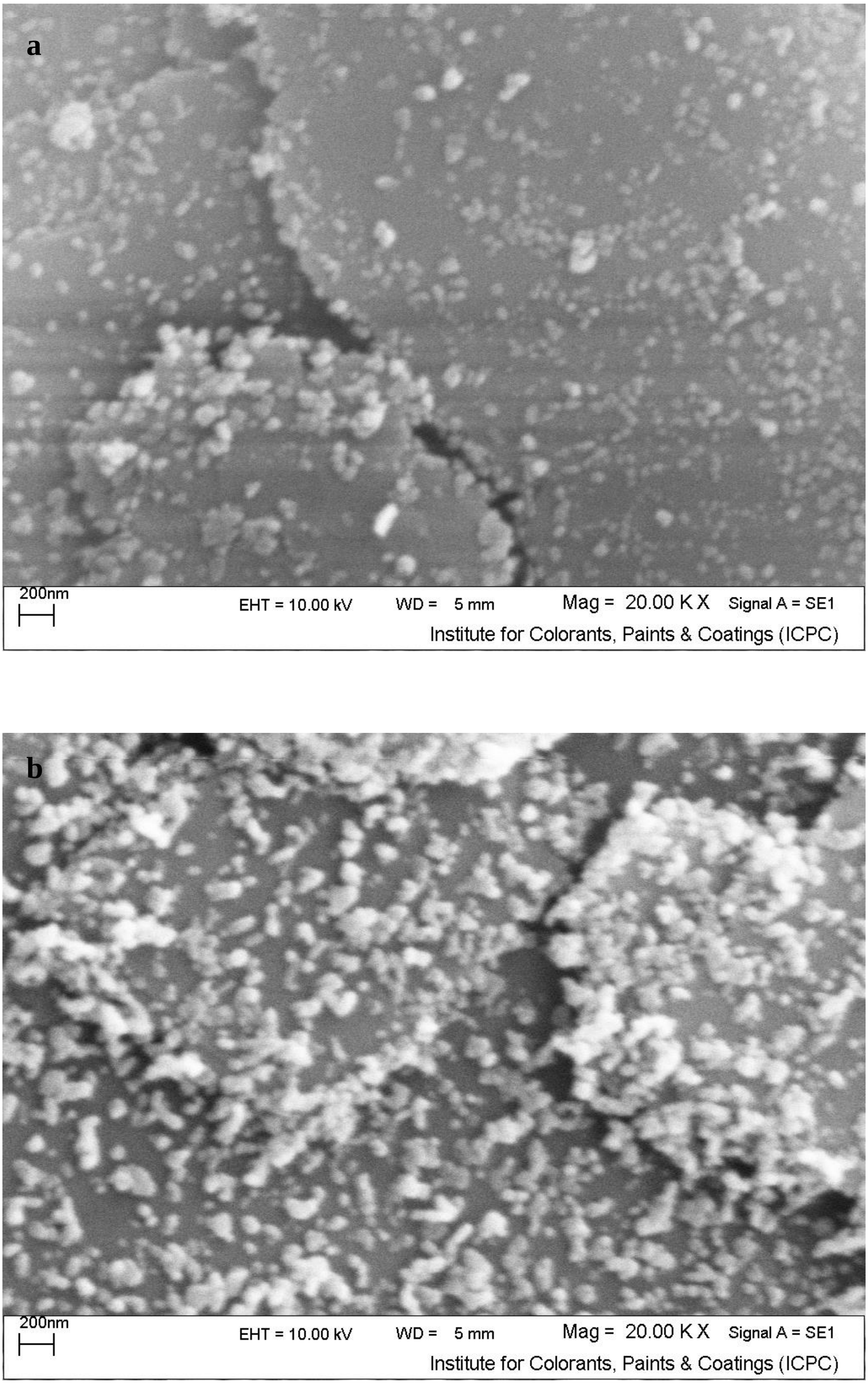


Fig. 5. SEM micrographs of annealed sample number a) 3 and b) 6 with magnification of 20.00K by secondary detector

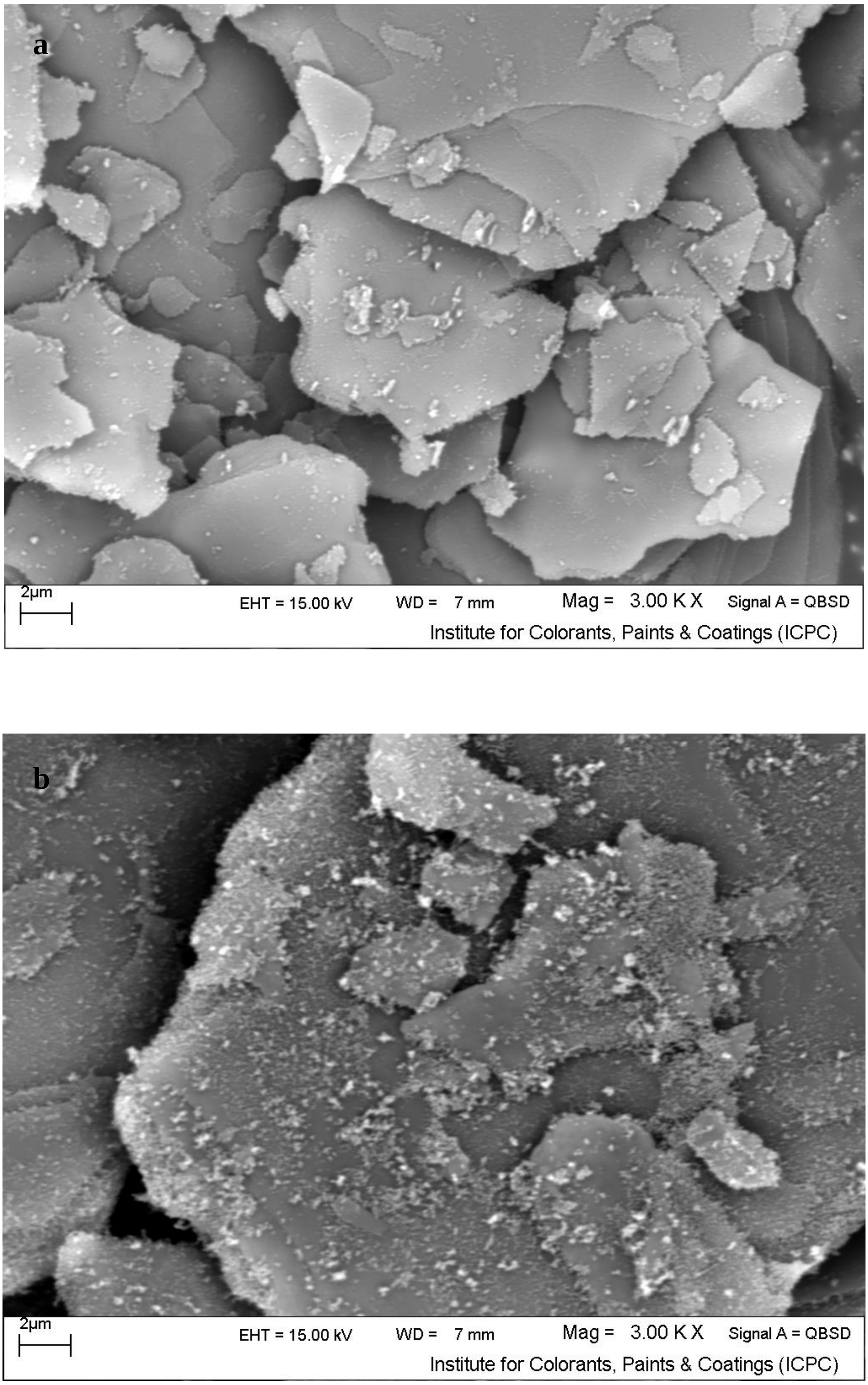


Fig. 6. SEM micrographs of annealed sample number a)3 and b)6 with magnification of 3.00K by backscattered detector

The pearl pigment consists of well distinguishable spherical nanoparticles, covering the surface of the phlogopite mica. The diameter of spherical nanoparticles is about 50 nanometer and it seems higher X value up to 1.5 did not size of nanoparticles but improve their distribution and result contact them to form a layer. No significant amounts of nanoparticles precipitated outside the mica surface were observed.

TEM micrographs of a hematite encapsulate crystal can be seen in Figure 7. It shows that the diameter of spherical nanoparticles is about 50 nanometer and contains nano encapsulated hematite. Probably nano hematite has formed single crystal because it seems parallel direction.

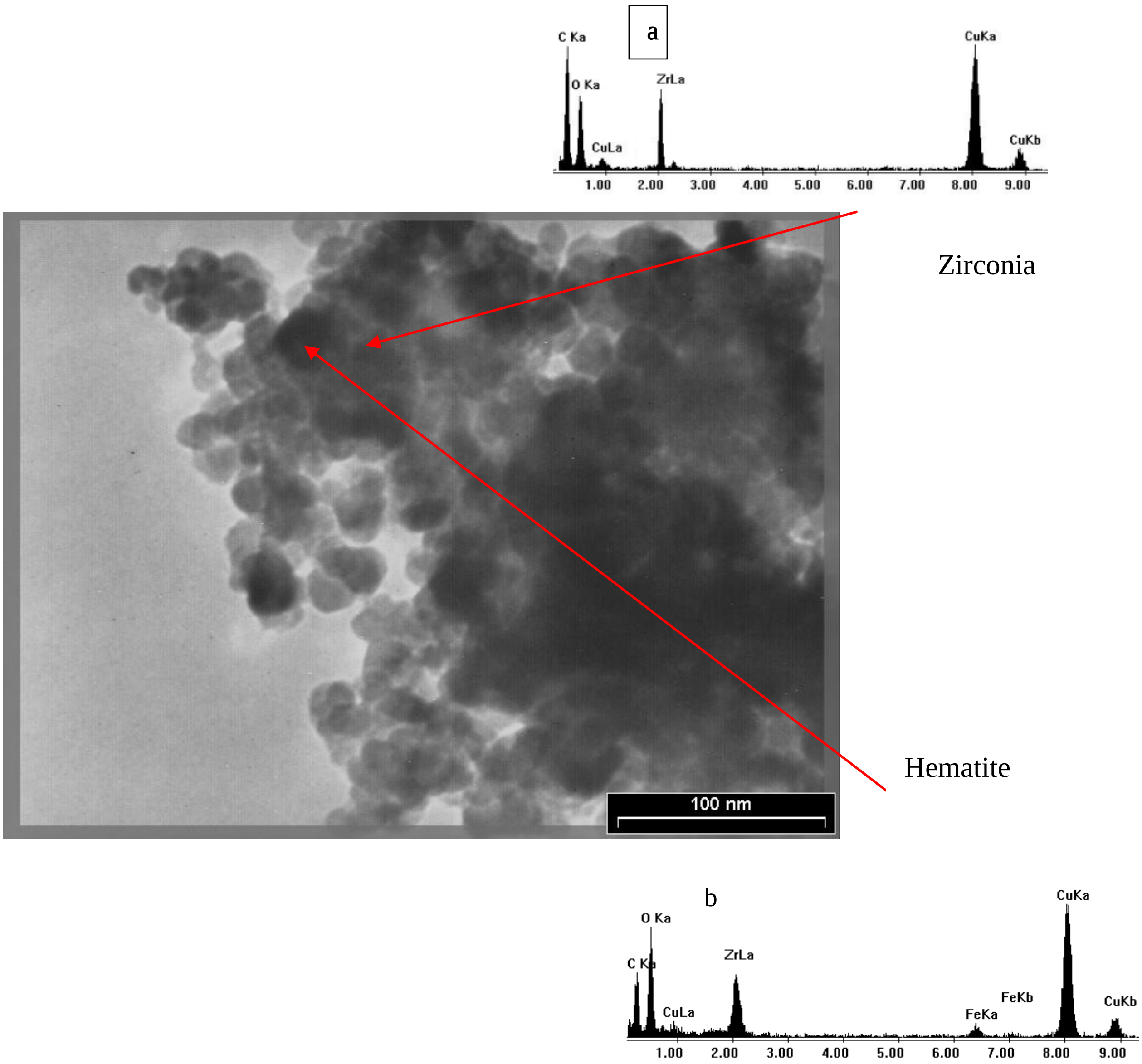


Fig. 7. TEM micrographs of the spherical nanoparticles a) gray matrix and b) black particle

4. Conclusion

In order to prepare bronze and gold pearl pigment ecologically friendly by a co-precipitation process, nano-hematite encapsulated particles in situ formed on phlogopite and muscovite flakes.

The method of synthesis is simple and the obtained pigments seem to have the needed thermal stability for the application to ceramics coloring.

Simultaneous thermal analysis, X-ray diffraction patterns, GonioSpectrophotometer and scanning electron microscopy results indicate that:

- Nano hematite particles covering on phlogopite and muscovite product gold and bronze pearl pigment.
- Synthesized pigment is thermally stable up to 1000°C.
- Data of c* at different observer angle indicate that higher particle size has higher pearl effect.
- Muscovite perform higher hue and better pearl effect (c* has been changed more) than phlogopite.
- Gold pearl pigment based on phlogopite type with d (0.5) particle size of 50 μm has higher and best hue.
- Various shades from gold to bronze can be performed depending on the weight percent of the nano particles of hematite and zirconia.
- The pearl pigment consists of well distinguishable spherical nanoparticles, covering the surface of the phlogopite mica.
- Diameter of spherical nanoparticles is approximately 50 nanometers.

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