SYNTHESIS OF ENVIRONMENT-FRIENDLY (Bi, Ca, Zn)VO$_4$ INORGANIC YELLOW PIGMENTS

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ABSTRACT

In this paper, the synthesis of scheelite based environment-friendly inorganic yellow pigments was presented. The pigments of Bi$_{1-x-y}$Ca$_x$Zn$_y$VO$_{4-(x+y)/2}$ (x = 0.1 ÷ 0.9, y = 0.1 ÷ 0.9) have been prepared by the evaporation to dryness from BiONO$_3$, Ca(NO$_3$)$_2$.4H$_2$O, Zn(NO$_3$)$_2$.6H$_2$O and NH$_4$VO$_3$. The obtained powders were characterized by Thermal Analysis (TG-DSC), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and CIE L*a*b* colour measurement. The results showed that the pigments calcinated at 650 ^{o}C for 6 hours with the heating rate of 5 ^{o}C.min^{-1} possessed single phase of scheelite with good crystallinity. The yellow colour intensity was a function of the amount of calcium (II) and zinc (II) ions. The colour of Bi$_{0.70}$Zn$_{0.30}$VO$_{3.85}$ sample was similar to the lemon yellow PbCrO$_4$ (BASF1522) pigment made by Hangzhou Emperor Pigment Company (China).

Keywords: yellow pigments, scheelite, environment-friendly inorganic pigments.

1. INTRODUCTION

Inorganic pigments have been used extensively in many fields of porcelains, ceramic tiles, paints, inks, rubbers, plastics… due to their high thermal stability, weather resistance and high hiding power.

The factor creating the colour of pigments is the appearance of oxide, sulfide, phosphate of transition metals [1]. Among them, the yellow colour is usually prepared based on the appearance of compounds containing Pb, Cr, Cd, Se. For example, CdS is the main component of yellow powder or lemon yellow one widely-used is produced from PbCrO$_4$. However, the toxicity of these metals could cause a high contamination for soil and water, and affect to human and animal health, certainly. Therefore, the synthesis and using of environment-friendly pigments without toxic metals such as Pb, Cr, Cd, Se have interested many scientists and even normal people [2, 3, 4, 5, 6].

Dark yellow scheelite BiVO$_4$ mineral containing harmless metals (Bi and V) is well-known as an environmentally friendly pigment. The appearance of yellow colour from BiVO$_4$ monoclinic crystal lattice is based on the moving of electron from sp^3 hybridized orbital, created

from 6s orbital of Bi and 2p orbital of O to 3d orbital of V [3]. The isomorphous replacement of Bi^{3+} (r = 0.117 nm) by smaller diameter ions such as Ca^{2+} (r = 0.112 nm) and Zn^{2+} (r = 0.090 nm) would increase defects in BiVO$_4$ crystal lattice, change the valence band of 2p orbital of O and also decrease the energy of 6s orbital of Bi or 2p orbital of O on hybridized orbital [3]. In addition, both Ca^{2+} and Zn^{2+} ions are non-toxic and cheaper than Bi^{3+}.

In the present work, the study on the formation of light yellow pigment from substitutional solid solution of Bi$_{1-x-y}$Ca$_x$Zn$_y$VO$_{4-(x+y)/2}$ by isomorphous replacing of Bi^{3+} ~~ions~~ by Zn^{2+} and Ca^{2+} in BiVO$_4$ crystal lattice is shown.

2. EXPERIMENTS

BiONO$_3$, Ca(NO$_3$)$_2$.4H$_2$O, Zn(NO$_3$)$_2$.6H$_2$O và NH$_4$VO$_3$ (PA, China) were used as initial chemicals. Twenty-four samples of Bi$_{1-x-y}$Ca$_x$Zn$_y$VO$_{4-(x+y)/2}$, notated from M0 to M24, were prepared with different compositions (x = 0 ÷ 0.9, y = 0 ÷ 0.9) shown in Table 1.

The synthetic proceduce of Bi$_{1-x-y}$Ca$_x$Zn$_y$VO$_{4-(x+y)/2}$ pigments is shown in Figure 1. Briefly, the initial mixture was dissolved in 3M HNO$_3$ solution and diluted by an appropriate volume of distilled water. Then, the pH of solution was adjusted to 6.5 by 5 % NH$_3$ solution and was stirred for 1 hour. The solution was heated at 180 ^{o}C for many hours to evaporate water and obtain powder mixture dried at 105 ^{o}C and grinded. Finally, the obtained powder was calcinated in furnace (Lennton, England), grinded and sieved through the mesh with the diameter of 4900 hole.cm^{-1}.

The obtained precursor of the M0 sample was characterized by Thermogravimetry - Differential Scanning Calorimetry (TG-DSC) using Labsys TG/DSC Setaram (France) in ambient atmosphere with the maximum temperature of 800°C, heating rate of 5°C.min^{-1}.

The crystalline phase of the pigments was determined by X-ray diffraction (XRD) using Brucker D8 Advance (Germany) with Cu anode X-ray source ($\lambda_{CuK\alpha}$ = 1.5406 Å). The crystalization of monoclinic scheelite phase of the pigments was assessed by full width at half maximum (FWHM) of diffraction peak, diffraction intensity (I) and crystal size (D). The more completely the crystal grows, the smaller FWHM and the bigger D and I value are. In order to determine FWHM, D and I values, the diffraction peak of BiVO$_4$ with highest intensity at 2θ = 28,90^o (013) was selected. The FWHM value was calculated from data of XRD diagram of samples by Origin 6.0 software. The D value of scheelite was calculated by P. Scherrer equation [7]:

$$D = \frac{0,9\lambda}{FWHM \times \cos\theta}$$

where λ is the X-ray wavelength (Å), θ is the diffraction angle (rad) of the (013) peak with highest intensity.

The morphology and the particle size of obtained pigments were observed by scanning electron microscope (SEM) using Hitachi S4800 (Japan).

The lemon-yellow pigment PbCrO$_4$ (BASF1522) made by Hangzhou Emperor Pigment Company (China) was used as comparative sample (MSS). The colour intensity of samples was measured by colour coordinate of CIEL*a*b* using Micromath Plus device (Instrument, England) at Hue Frite Joint-stock company. The difference between two samples was

Table 1. Initial composition of $Bi_{1-x-y}Ca_xZn_yVO_{4-(x+y)/2}$ samples.

Notation	X	y	Percentage composition (w/w)			
			$BiONO_3$	$Ca(NO_3)_2.4H_2O$	$Zn(NO_3)_2.6H_2O$	NH_4VO_3
M0	0.00	0.00	71.0	0.00	0	29.0
M1	0.10	0.00	64.8	5.90	0	29.3
M2	0.20	0.00	58.3	12.0	0	29.7
M3	0.30	0.00	51.7	18.2	0	30.1
M4	0.40	0.00	44.9	24.6	0	30.5
M5	0.50	0.00	37.9	31.2	0	30.9
M6	0.60	0.00	30.7	37.9	0	31.3
M7	0.70	0.00	23.4	44.9	0	31.8
M8	0.80	0.00	15.8	52.0	0	32.2
M9	0.90	0.00	8.0	59.3	0	32.7
M10	0.00	0.10	63.8	0	7.3	28.9
M11	0.00	0.20	56.6	0	14.6	28.8
M12	0.00	0.30	49.4	0	21.9	28.7
M13	0.00	0.40	42.2	0	29.1	28.7
M14	0.00	0.50	35.1	0	36.3	28.6
M15	0.00	0.60	28.0	0	43.5	28.5
M16	0.00	0.70	20.9	0	50.6	28.5
M17	0.00	0.80	13.9	0	57.7	28.4
M18	0.00	0.90	6.9	0	64.7	28.3
M19	0.40	0.10	37.3	24.5	7.7	30.4
M20	0.40	0.20	29.8	24.5	15.4	30.3
M21	0.40	0.30	22.3	24.4	23.0	30.3
M22	0.40	0.40	14.8	24.4	30.7	30.2
M23	0.40	0.50	7.4	24.3	38.2	30.1
M24	0.40	0.60	0.0	24.2	45.7	30.0

determined by the equation $\Delta E = \sqrt{(L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2}$, the smaller ΔE was, the more similar colour was and reverse. The synthesis root of $Bi_{1-x-y}Ca_xZn_yVO_{4-(x+y)/2}$ is shown in Figure 1.

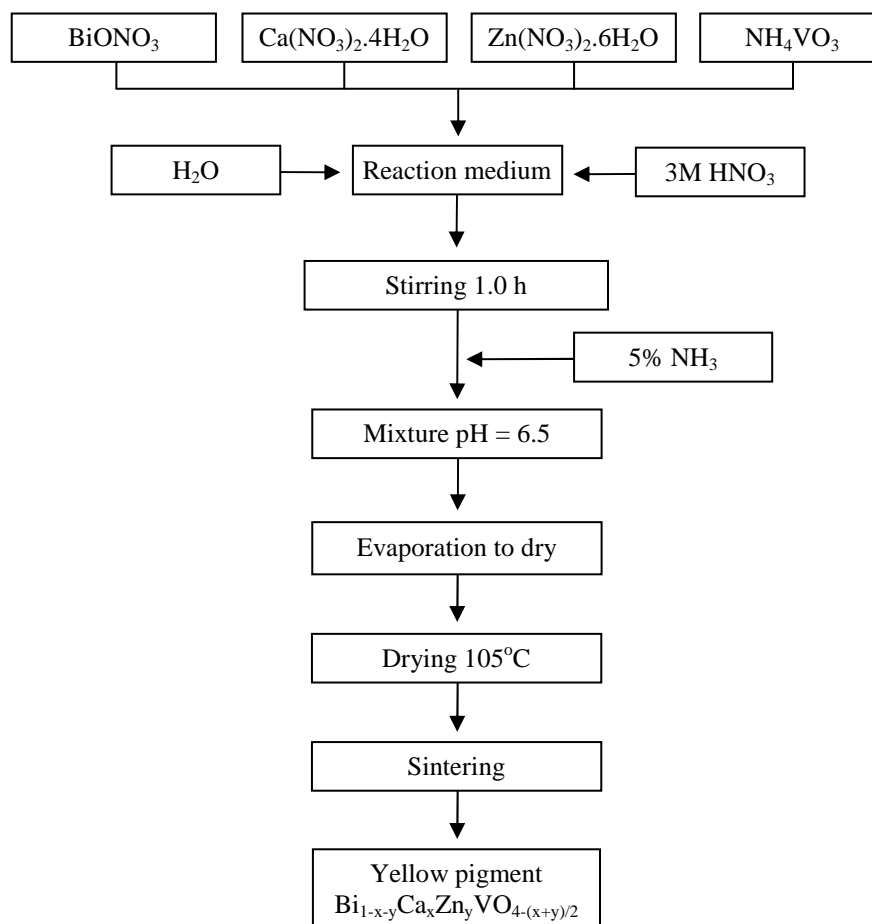*Figure 1.* The diagram of the synthetic procedure of yellow pigment Bi$_{1-x-y}$Ca$_x$Zn$_y$VO$_{4-(x+y)/2}$.

3. RESULTS AND DISCUSSION

In Figure 2, the DSC-TG plot of M0 sample was analyzed to detemine the physical and chemical process during the calcination of pigment samples. As can be seen, there was endothermic peak when the temperature rose from room temperature to 131 ^{o}C in the TG curve, the weight loss of 0.5 %, was observed which caused by the evaporation of adsorptive water in the sample. Continuously, a weight loss of 3 % at 150 ^{o}C – 450 ^{o}C appeared when increasing the temperature to 243 ^{o}C, that was referred to decomposition of nitrate salts, corresponded with the only exdothermic peak on the plot. There was no thermal effect in the TG curve during the calcination of sample to 800 ^{o}C, weight loss of 0.6 % was observed at 550 ^{o}C. Hence, the suitable calcinated temperature of pigments should be from 550 ^{o}C.
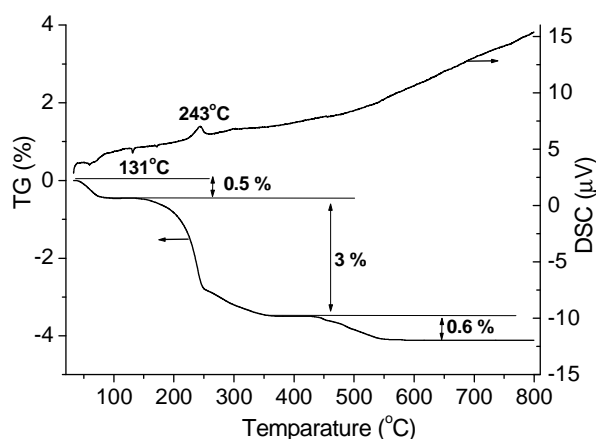
Figure 2. TG-DSC diagram of M0 sample.

On the purpose of determination of suitable sintering temperature for producing $BiVO_4$ cheelite phase, M0 sample was calcinated at the different temperatures of 550, 650 and 750 °C, corresponding to the notations of N550, N650 and N750, respectively. XRD patterns of samples were showed in Figure 3. The highest peak of each sample was chosen to calculate FWHM value, diffraction intensity (I) and crystallite size (D), shown in Table 2. Figure 3 presented that at all of above sintering temperatures, the characteristic peaks of monoclinic scheelite $BiVO_4$ at the diffraction angles 18.70° (d_{011}), 28.9° (d_{013}), 30.58° (d_{004}) with high intensity appeared. These peaks were also observed in the study of Sivakumar et. al. [8]. Combining with the results in Table 2, at temperature of 650 °C, the diffraction peak intensity was higher than and the value of FWHM was smaller in comparison with two others. This indicates crystallite of scheelite $BiVO_4$ was formed almost completely at 650 °C. For this reason, the sintering temperature of 650 °C was fixed for later experiments. This sintering temperature was much lower than the one of the synthesis of $YTbO_3$ based yellow pigments (1300 °C) [2].
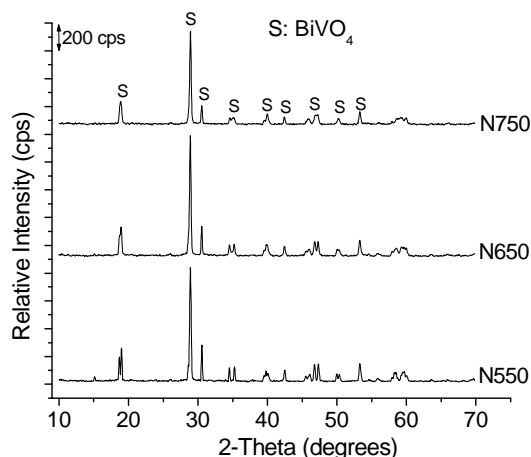

Table 2. FWHM value, diffraction intensity (I) and crystal size (D) of N550, N650 and N750.

Notion	FWHM (°)	I (cps)	D (nm)
N550	0.280	841	29
N650	0.262	890	31
N750	0.269	690	30

Figure 3. XRD diagram of M0 sample at diferent temparatures.

The samples from M1 to M24 were sintered at temperature 650 °C for 6 hours with the heating rate of 5 °C.min^{-1}. The images of pigment samples shown in Figure 4 indicated the difference of colour between the substrated sample (M0) and others. As can seen, the yellow

colours of all the samples (M1 ÷ M24) were much lighter than substrate one (M0) due to the partly replacement of Bi^{3+} by Ca^{2+} (M1 ÷ M9) or Zn^{2+} (M10 ÷ M18) or both (M19 ÷ M23) and totally replacement of Bi^{3+} by Ca^{2+} and Zn^{2+} (M24). This was demonstrated by the higher values of L* and b* of all the samples, comparing to the substrated one shown in Table 3. The images of samples from M1 to M9 expressed that the higher content of Ca^{2+} in crystalized lattice was, the lighter colour intensity was.
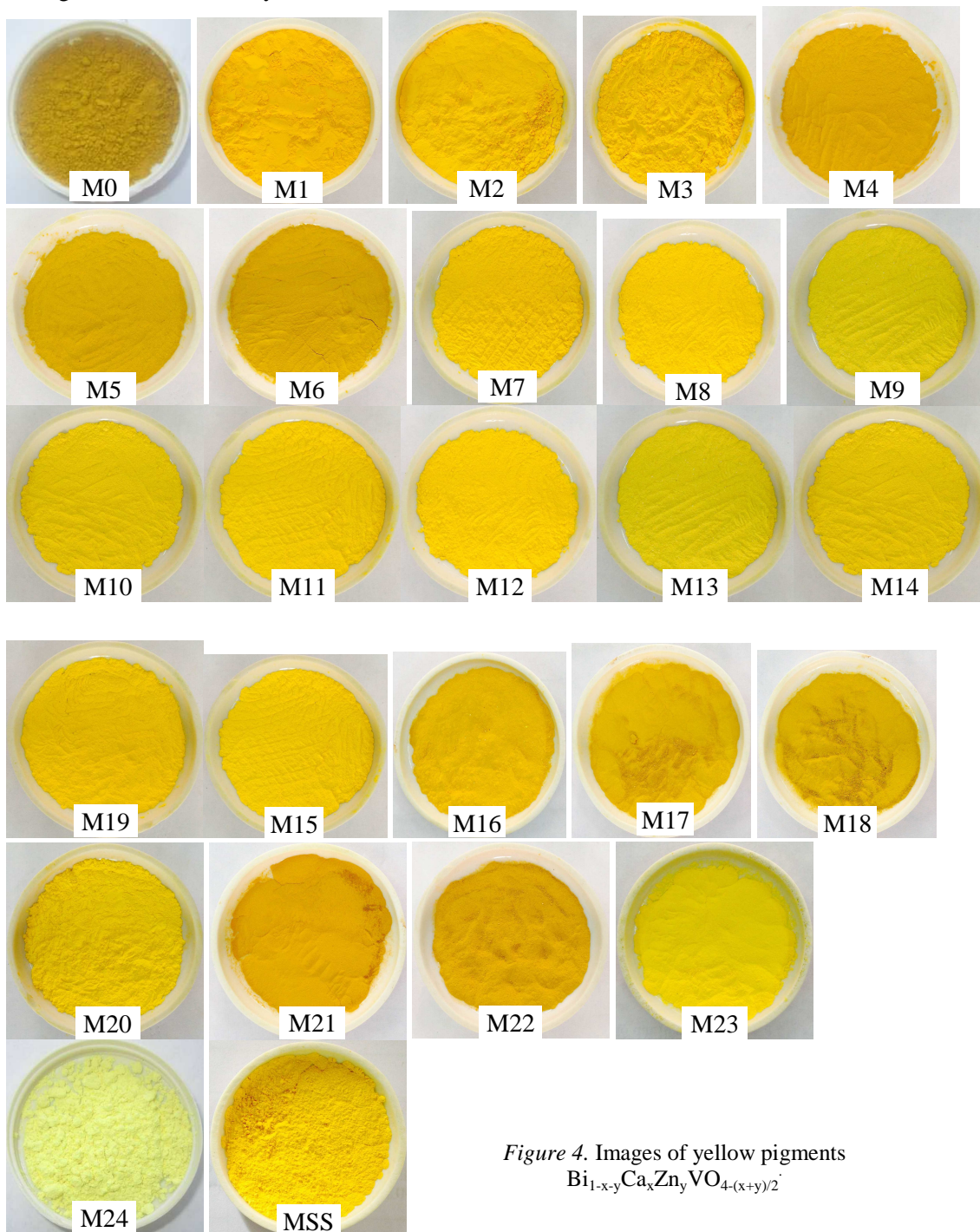

Figure 4. Images of yellow pigments
Bi$_{1-x-y}$Ca$_x$Zn$_y$VO$_{4-(x+y)/2}$.

In contrast, the appearance of Zn^{2+} with higher content could formed pigments with darker colour intensity. By the partly doping of Bi^{3+} ions by both Ca^{2+} and Zn^{2+} ions (M19 ÷ M23), the yellow colour of pigments could be darker than samples containing Bi^{3+} and Ca^{2+} or Zn^{2+} (M1 ÷ M18). The values of ΔE of all samples were rather small explaining the yellow colours of all samples, except M24 one, were similar to the compared sample (MSS). M24 sample without Bi^{3+} ions in crystal lattice was white representing the role of Bi^{3+} ions in producing yellow pigment. L*, a* and b* values of M1, M2, M3, M7, M8, M11, M12, M15 samples were similar to the results of Masui et al. [3].

Table 3. Colour intensity of samples $Bi_{1-x-y}Ca_xZn_yVO_{4-(x+y)/2}$ on colour coordinate of CIE L*a*b*.

Notion	Formula	L*	a*	b*	ΔE
M0	$BiVO_4$	64.32	10.25	44.21	25.31
M1	$Bi_{0.90}Ca_{0.10}VO_{3.95}$	83.45	6.24	62.33	2.14
M2	$Bi_{0.80}Ca_{0.20}VO_{3.90}$	81.77	6.55	63.88	4.04
M3	$Bi_{0.70}Ca_{0.30}VO_{3.85}$	84.56	6.68	64.15	4.19
M4	$Bi_{0.60}Ca_{0.40}VO_{3.80}$	69.25	7.38	69.68	17.03
M5	$Bi_{0.50}Ca_{0.50}VO_{3.75}$	70.46	6.90	58.21	13.10
M6	$Bi_{0.40}Ca_{0.60}VO_{3.70}$	68.24	6.30	54.48	16.18
M7	$Bi_{0.30}Ca_{0.70}VO_{3.65}$	86.01	5.47	60.38	2.68
M8	$Bi_{0.20}Ca_{0.80}VO_{3.60}$	84.27	6.25	60.38	1.11
M9	$Bi_{0.10}Ca_{0.90}VO_{3.55}$	85.09	5.62	42.13	18.22
M10	$Bi_{0.90}Zn_{0.10}VO_{3.95}$	84.56	5.14	67.56	7.41
M11	$Bi_{0.80}Zn_{0.20}VO_{3.90}$	85.33	5.91	65.34	5.45
M12	$Bi_{0.70}Zn_{0.30}VO_{3.85}$	83.46	6.12	60.17	0.49
M13	$Bi_{0.60}Zn_{0.40}VO_{3.80}$	84.26	6.34	43.57	16.74
M14	$Bi_{0.50}Zn_{0.50}VO_{3.75}$	83.16	5.84	66.32	6.06
M15	$Bi_{0.40}Zn_{0.60}VO_{3.70}$	84.37	5.67	64.12	3.99
M16	$Bi_{0.30}Zn_{0.70}VO_{3.65}$	71.53	6.58	57.84	12.09
M17	$Bi_{0.20}Zn_{0.80}VO_{3.60}$	66.72	7.15	54.69	17.59
M18	$Bi_{0.10}Zn_{0.90}VO_{3.55}$	66.73	7.68	57.53	16.96
M19	$Bi_{0.50}Ca_{0.40}Zn_{0.10}VO_{3.75}$	81.24	6.86	66.41	6.60
M20	$Bi_{0.40}Ca_{0.40}Zn_{0.20}VO_{3.70}$	84.90	7.24	65.31	5.51
M21	$Bi_{0.30}Ca_{0.40}Zn_{0.30}VO_{3.65}$	69.44	7.44	59.27	14.05
M22	$Bi_{0.20}Ca_{0.40}Zn_{0.40}VO_{3.60}$	67.12	6.48	54.48	17.24
M23	$Bi_{0.10}Ca_{0.40}Zn_{0.50}VO_{3.55}$	85.21	3.41	56.98	4.40
M24	$Ca_{0.40}Zn_{0.6}VO_{3.50}$	91.24	1.13	55.27	10.39
MSS		83.34	5.66	60.27	

(L: 0 ÷ 100: black ÷ white, a*: + ÷ - : red ÷ green, b*: + ÷ -: yellow ÷ dark blue)*
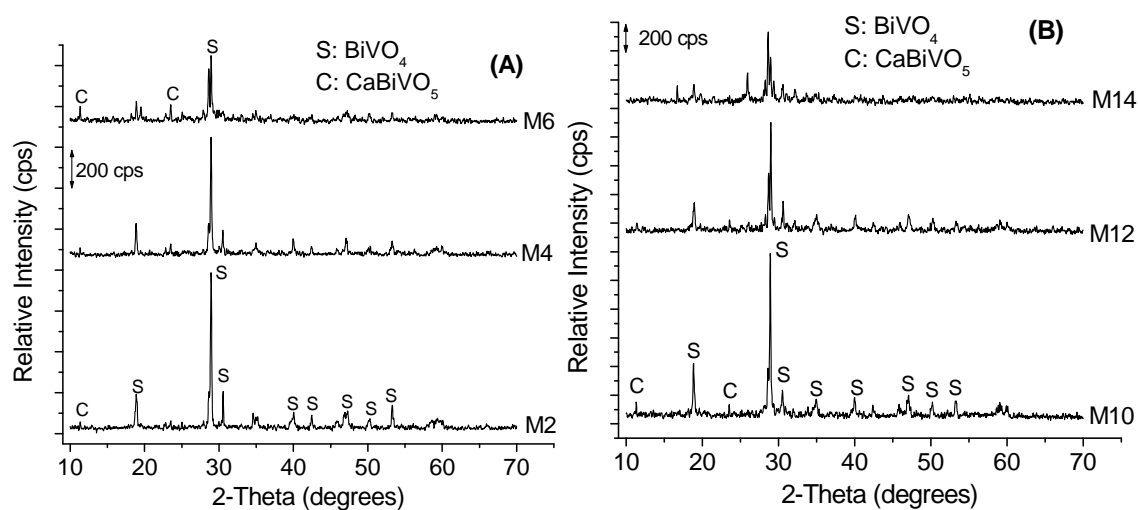
Figure 5. XRD diagram of M2, M4, M6 (A) and M10, M12, M14 samples.

XRD patterns of M2, M4, M6, M10, M12 and M14 pigments were displayed in Figure 5. The results showed that some low intensity peaks of CaBiVO$_5$ appeared beside main crystalized phase of BiVO$_4$ scheelite. CaO and ZnO peaks were not observed because Ca^{2+} and Zn^{2+} were doped into Bi^{3+} sites. As can be seen, the higher x, y values were, the lower peaks' intensity of BiVO$_4$ pigment was. This proved that it was difficult to carry out the solid reaction between Bi$_2$O$_3$, V$_2$O$_5$, CaO, ZnO oxides and resulted in the multi-phase of obtained pigment. These results were similar to T. Masui et al. report [3], in case of isomorph replacement of Bi^{3+} by Ca^{2+} (Bi$_{1-x}$Ca$_x$VO$_{4-x/2}$) or Zn^{2+} (Bi$_{1-y}$Zn$_y$VO$_{4-y/2}$), the single phase of BiVO$_4$ pigment was obtained only when x, y $\leq$ 0.1.

The values of the distances between d$_{013}$, d$_{004}$, d$_{011}$ planes of BiVO$_4$ pigments, expressed in Table 4, proved the partly replacement of Bi^{3+} ions by Ca^{2+} and Zn^{2+} resulting a slight decrease of lattice parameter. This can be explained by smaller ionic radius of Ca^{2+} (0.106 nm) and Zn^{2+} (0.083 nm) in comparison with Bi^{3+} (0.117 nm) [9].

Table 4. The distance between characterization lattice planes (d$_{hkl}$) of BiVO$_4$ pigments.

Notion	M0	M2	M4	M6	M10	M12	M14
d$_{013}$ (Å)	3.087	3.085	3.085	3.083	3.085	3.078	3.075
d$_{004}$ (Å)	2.929	2.925	2.920	2.919	2.927	2.920	2.918
d$_{011}$ (Å)	4.693	4.689	4.688	4.682	4.692	4.690	4.690
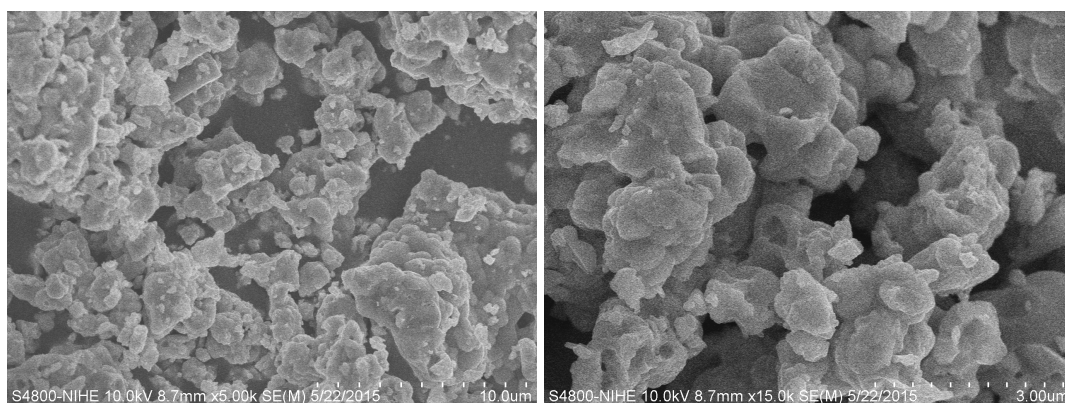
Figure 6. SEM images of $Bi_{0.70}Zn_{0.30}VO_{3.85}$ sintering at 650 ^{o}C.

SEM image of $Bi_{0.70}Zn_{0.30}VO_{3.85}$ pigment sintering at 650 ^{o}C is showed in Figure 6. The colour of materials were equitable, that demonstrated the composition of samples were identical. The pigment particles were uniform and agglomerated together into large particles with the size in the range of $1 \div 2$ µm. In comparison with gel method carried out by dispersing ammonium metavanadate and bismuth nitrate into 1-dodecanol solvent [8], the evaporation to dryness method could form $BiVO_4$ pigment with much higher particle size.

4. CONCLUSION

Environment-friendly inorganic yellow pigments of $Bi_{1-x-y}Ca_xZn_yVO_{4-(x+y)/2}$ (x = 0.1 ÷ 0.9, y = 0.1 ÷ 0.9) were synthesized by the evaporation to dryness. Molar proportion of sample is $(Ca^{2+} + Zn^{2+} + Bi^{3+})/V^{5+} = 1/1$. The precursor was dried at 105 ^{o}C and sintered at 650 ^{o}C for 6 hour with heating rate of 5 ^{o}C.min^{-1}. The pigments with main crystalized phase of $BiVO_4$ scheelite were yellow, in which, the colour intensity depends on the calcium (II) and zinc (II) ions content. The $Bi_{0.70}Zn_{0.30}VO_{3.85}$ sample was bright lemon-yellow, which was similar to lemon-yellow pigment commercial pigment made by Hangzhou Company (China).

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TÓM TẮT

TỔNG HỢP BỘT MÀU VÀNG (Bi, Ca, Zn)VO₄ THÂN THIỆN VỚI MÔI TRƯỜNG

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Bài báo này trình bày kết quả tổng hợp bột màu vàng vô cơ thân thiện với môi trường trên nền khoáng scheelite BiVO₄. Các mẫu chất màu có thành phần ứng với công thức $Bi_{1-x-y}Ca_xZn_yVO_{4-(x+y)/2}$ (x = 0,1 ÷ 0,9, y = 0,1 ÷ 0,9) được tổng hợp từ BiONO₃, Ca(NO₃)₂.4H₂O, Zn(NO₃)₂.6H₂O và NH₄VO₃ theo phương pháp cô bay hơi đến khô. Các mẫu bột màu được nung thiêu kết ở 650 °C, thời gian lưu nhiệt 6 giờ, tốc độ nâng nhiệt 5 °C/phút. Các đặc trưng của sản phẩm được xác định bằng các phương pháp XRD, TG-DSC, SEM, CIE L*a*b*. Bột màu thu được có thành phần pha tinh thể chủ yếu là khoáng scheelite BiVO₄ với mức độ tinh thể hóa cao. Cường độ màu vàng của sản phẩm phụ thuộc vào hàm lượng ion canxi và kẽm thay thế. Mẫu bột màu ứng với công thức $Bi_{0.70}Zn_{0.30}VO_{3.85}$ có màu vàng tươi sáng, tương đương với mẫu bột màu vàng chanh PbCrO₄ (BASF1522) của hãng chất màu Hangzhou (Trung Quốc).

Từ khóa: bột màu vàng, khoáng scheelite, bột màu vô cơ thân thiện môi trường.