New Scheelite-based Environmentally Friendly Yellow Pigments: $(BiV)_x(CaW)_{1-x}O_4$

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New scheelite-based environmentally friendly yellow pigments with the general formula, $(BiV)_x(CaW)_{1-x}O_4$ ($x = 0.2$, 0.4, 0.6, and 0.8) have been synthesized by a solid-state route. The resulting colorants were characterized for their structural as well as optical properties. The color parameters, L^*, a^*, and b^* values have been significantly improved in the solid solutions of $(BiV)_x(CaW)_{1-x}O_4$ over those of $BiVO_4$. Further, the solid solutions allow fine tuning of the optical band gap resulting in various shades of yellow. The synthesized pigments were found to be interesting alternatives to existing toxic yellow pigments.

There is a strong incentive to design new colorants based on inorganic materials to substitute for industrial pigments that are based on heavy elements hazardous to health and the environment.[1] For decades $PbCrO_4$ was one of the most widely used yellow pigments, but concerns about the toxicity of both lead and chromate have significantly reduced its use.[2,3] Chrome yellows, oranges, and molybdate oranges are used in a large number of different paint systems, which are restricted mostly to maintenance and industrial finishes, because of their toxicity and potential carcinogenic nature. Traditional use of these pigments has been decreasing as a result of environmental regulations. Thus, serious need arises to search for environmentally friendly and economically viable materials for the replacement of toxic inorganic yellow pigments. Less toxic, inorganic metal–oxide yellow pigments, such as titanium–nickel yellow, bismuth vanadate, and their combinations with organic pigments, are being used increasingly as a replacement for lead chromate pigments.[4] Recent investigations reveal that the toxic yellow pigments can be replaced by solid solutions of CeO_2–SiO_2–Bi_2O_3[5] and CeO_2–ZrO_2–Bi_2O_3.[6]

Among transition metals, vanadium, and more particularly in the pentavalent state, is well known for its coloring properties. For example, vanadium pentaoxide V_2O_5, whose color is due to the charge-transfer band from $O_{2p}{}^{2-}$ to $V_{3d}{}^{5+}$, is commonly used as a classic yellow pigment in glazes.[7] The charge-transfer energy of the colorless $VO_4{}^{3-}$ ion is larger than that of the yellow $CrO_4{}^{2-}$ ion. Consequently, many vanadate salts are white. Numerous colored ternary oxides $A_xV_yO_z$ are described in the literature.[1] Among the compounds, $BiVO_4$ is particularly notable. $BiVO_4$ with scheelite structure, especially a tetragonal system at high temperature is found to exhibit murky yellow in contrast to monoclinic scheelite $BiVO_4$ which shows vivid yellow.[8] Bismuth vanadate ($BiVO_4$) is a yellow pigment widely used in ceramics and polymeric systems. However, it has been proven difficult to control the pigmentary colors of $BiVO_4$.[9] The extension of the color pallet of $BiVO_4$ is a factor that will increase the commercial competitiveness of this pigment. $CaWO_4$ is a white powder which absorbs below 400 nm with a wide band gap. Band structure engineering by making solid solutions between two compounds with different band gap can be regarded as an efficient method for producing various shades of colorants. In the present study, new yellow pigments having the formula $(BiV)_x(CaW)_{1-x}O_4$ ($x = 0.2$, 0.4, 0.6, and 0.8) have been synthesized by a solid-state method and characterized for their structural and optical properties.

Compositions based on $(BiV)_x(CaW)_{1-x}O_4$ ($x = 0.2$, 0.4, 0.6, and 0.8) were prepared from the corresponding oxides: $CaCO_3$, Bi_2O_3, V_2O_5, and WO_3 (99.9% purity Acros Organics). Stoichiometric proportions of the chemicals were weighed, were thoroughly wet mixed in an agate mortar with acetone as the wetting medium for 1 h, and dried in an air oven. This process of mixing and drying was repeated thrice to obtain a homogeneous mixture. The dried powders were then calcined at 900 °C in air for 6 h in a platinum crucible. The phase purity of the samples was investigated by powder X-ray diffraction analysis (XRD) with Ni-filtered Cu Kα radiation using a PANalytical X'pert Pro diffractometer. Optical reflectance of the powders was measured with UV–vis spectrophotometry (Shimadzu, UV-2401) using barium sulphate as a reference. Color coordinates were determined using CIE-LAB 1976 color scales.

The XRD patterns of the pigments are given in Figure 1. The intense and sharp peaks found in the diffraction patterns reveal the crystalline nature of the powders. All compounds crystallize with the tetragonal scheelite structure (space group $I4_1/a$), and the XRD patterns are in good agreement with the powder X-ray diffraction file: JCPDS card No. 77-2233. The formation of tetragonal scheelite type structure is confirmed by the absence of a characteristic scheelite monoclinic peak at 15°.[8] The crystallite size was calculated from the Debye–Scherrer formula $D = 0.9\lambda/\beta\cos\theta$, where D is the crystallite size, λ is the wavelength

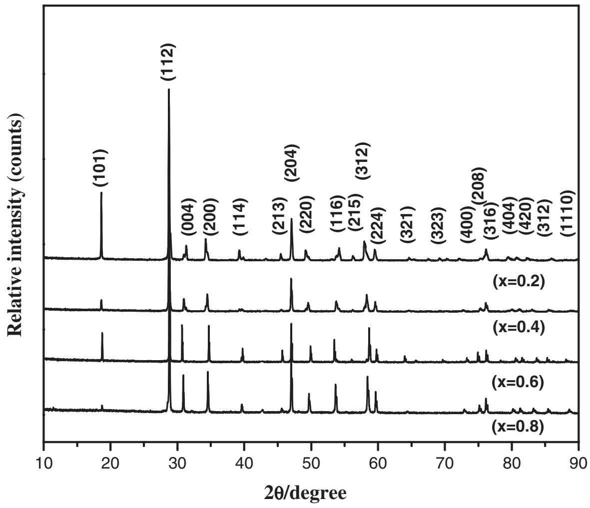

Figure 1. Powder XRD patterns of the pigments.

Table 1. Color coordinates of $(BiV)_x(CaW)_{1-x}O_4$ ($x = 0.2$–0.8)

x	L^*	a^*	b^*	C_{ab}	h_{ab}	E_g/eV
$x = 0.2$	90.6	−13.6	59.9	61.4	77.2	2.79
$x = 0.4$	89.4	−10.5	65.0	65.8	80.8	2.76
$x = 0.6$	79.3	−1.2	61.7	61.8	88.8	2.74
$x = 0.8$	76.7	13.2	68.9	70.1	79.1	2.51
$BiVO_4$[10]	68.0	16.5	42.3			2.34
Praseodymium yellow[5]	83.5	−3.28	70.3			2.43

[a]Purity of hue (0–100): $C_{ab} = (a^{*2} + b^{*2})^{1/2}$. [b]hue angle (yellow, 90°): $h_{ab} = \arctan(b^*/a^*)$.

of X-ray used, and β and θ are the half width of X-ray diffraction lines and half diffraction angle of 2θ, respectively. The crystal size is found to decrease with decrease in concentration of bismuth and vanadium in the range from 140–153 nm.

Color coordinates of the synthesized pigments are listed in Table 1. The pigments show lightness value L^* ranging from 76–90, color coordinates with low a^* and high b^* (+ve) values. Compared to $BiVO_4$, the L^*, a^*, and b^* values of the synthesized pigments were improved significantly in the solid solutions of $(BiV)_x(CaW)_{1-x}O_4$ and are also comparable to praseodymium yellow (Table 1). This may be due to the high refractive index (1.97) and opacity of $CaWO_4$.[11] An ideal yellow color is characterized by high lightness $L^* > 60$, yellowness $b^* > 50$, high purity C_{ab} (0–100), and hue angle ca. 90°. The pigment composition with $x = 0.6$, exhibits high lighteness, purity (C_{ab}), and hue angle, h_{ab}, close to 90°. By introducing bismuth and vanadium into $CaWO_4$, various shades of bright yellow pigments with greenness ($-a^*$) and redness ($+a^*$) can be produced along with high purity yellow pigment ($x = 0.6$).

Figure 2 shows the diffuse reflectance spectra of the pigment samples. The diffuse reflectance spectra of both $BiVO_4$ and $CaWO_4$ show a shape of two overlapping absorption bands (Figure 2 inset).[12] This feature is weakened in the quarternary solid solutions, and a steep absorption can be observed. In the diffuse reflectance spectra it is seen that with increase in concentration of bismuth and vanadium a red shift is observed, and consequently the band gap is also seen to be decreasing. The apparent band gap energies are also listed in Table 1. The steep absorption at higher energies is attributable to the fine tuning of the band gap. The band gap energy strongly depends on the composition and varies with x from 2.79–2.50 eV. The band gaps of $BiVO_4$ and $CaWO_4$ were detected as 2.34 and 3.8 eV, respectively.[12] The band gap of $Ca_{1-x}Bi_xV_xW_{1-x}O_4$ compounds which is intermediate between either end member clearly indicates the possibility of tuning the band gap by mixing two solid solutions with different band gaps to produce pigments with different shades.

$CaWO_4$ has large, nearly identical band gap that falls in the UV region. Walsh et al.[13] reports that $BiVO_4$ is found to be a direct band gap semiconductor and that direct gap is maintained via coupling among V 3d, O 2p, and Bi 6p, which lowers the conduction band minimum. $Ca_{1-x}Bi_xV_xW_{1-x}O_4$ pigments absorb in the visible blue region which arises due to three main charge-transfer transitions, O_{2p}–V_{3d}, O_{2p}–W_{5d}, and O_{2p}–Bi_{6p}. Doping of Bi^{3+} and V^{5+} into $CaWO_4$ lattice results in enhancement of visible blue light absorption due to the transition from a new hybrid band made up of hybrid orbitals of Bi 6s, V 3d, and O 2p into the W 5d conduction band. When Ca^{2+} is replaced by Bi^{3+}, the filled Bi 6s orbitals raise the top of the valence band while the Bi 6p orbitals lower the bottom of the conduction band, resulting in a reduction in the band gap with $\Delta E = 1.01$ and 1.30 for the typical compositions with $x = 0.2$ and 0.8, respectively. Thus, these solid solutions allow fine band gap tuning resulting in various shades of yellow.

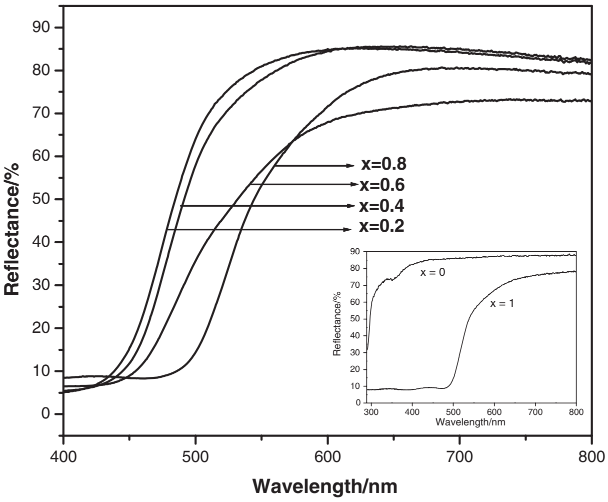

Figure 2. Reflectance spectra of the pigments.

In summary, new inorganic yellow pigments, $(BiV)_x(CaW)_{1-x}O_4$ ($x = 0.2$, 0.4, 0.6, and 0.8), have been synthesized, and the characteristics of the pigments suggest that these products have potential to be used as environmentally benign yellow pigments as interesting alternatives to existing toxic yellow pigments.

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