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SYNTHESIS AND CHARACTERIZATION OF A NEW SERIES OF $BiOI_{1-x-y}Br_xCl_y$ PIGMENTS

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Abstract—New bismuth oxyhalides of the type $BiOI_{1-x}Br_x$ form a complete solid solution series and crystallize in a layered tetragonal matlockite structure. Color varies from yellow to red as x decreases from 0.75 to 0 and layer separation, c, increases from 8.45 to 9.16 Å. The compounds have large intrinsic optical absorption coefficients ($\alpha > 10^5$ cm^{-1}). Used as pigments, they are light-fast but show less color saturation than $PbCrO_4$ of the same hue.

INTRODUCTION

Concern over the toxicity of the traditional yellow, orange, and red pigments lead chromate, lead chromate-molybdate, cadmium sulfide and cadmium sulfoselenide, has led to increased efforts in the search for pigments containing elements of lower toxicity [1-3]. Several new yellow and orange pigments containing the elements Bi and Zn have recently been discovered [4-8]. In this paper we describe the synthesis and characterization of $BiOI_{1-x-y}Br_xCl_y$, a series of Bi-containing pigments with colors that may be continuously varied from yellow to red-orange [9].

The compound BiOCl is colorless and is used as a nacreous or pearlescent pigment in cosmetics [10]. The end member of the new series, BiOI, is a coral red material proposed as a nacreous pigment but not generally used as such [10, 11]. Both materials crystallize in the tetragonal matlockite structure, a layer structure characterized by Bi_2O_2 layers interleaved by double layers of halogen atoms [12, 13]. Each Bi atom is surrounded by 4 (O) in one layer and five halogen atoms, four from the immediately adjacent layer and one from the other halogen layer. Typical distances are d(Bi-O) = 2.33 Å, d(Bi-Br) = 3.2 Å and d(Bi-I) = 3.4 Å [12].

EXPERIMENTAL

The new $BiOI_{1-x-y}Br_xCl_y$ solid solutions were prepared by combining an aqueous solution containing Bi nitrate and acetic acid with a solution containing KI, KBr, KCl and Na acetate. In a typical experiment to prepare $BiOI_{0.5}Br_{0.5}$, 60-g $Bi(NO_3)_3 \cdot 5H_2O$ dissolved in 90-cc glacial acetic acid was added rapidly to a solution of 10.371-g KI, 7.435-g KBr and 20.5-g Na acetate in 1500-cc H_2O at 65°C. After the yellow-orange precipitate formed, the solution was stirred for 24 h and decanted four to five times. The precipitate was filtered and dried at 120°C. The procedure was used to prepare solid solutions with x = 0 to 1. Two Cl-containing compositions with x = 0.20, y = 0.25 and x = 0.35, y = 0.40 were also prepared. Table 1 gives constituent quantities for several of the preparations.

The products typically consisted of micalike platelets 0.1-3.0-μ wide and 100-700 Å thick. Larger crystallites (1-3 μ by 700 Å) were achieved by stirring for 24 h at 95°C, whereas the smaller crystallites (0.1-0.3 μ by 200 Å) were prepared at 25°C. The platelike morphology with the c-axis perpendicular to the plate was also noted for BiOCl by Patel *et al* [14]. Photographs of $BiOI_{0.6}Br_{0.4}$ are shown in Fig. 1.

In the final products, Bi was analyzed gravimetrically. Oxygen analyses were obtained by a catalytic fusion method using a LECO nitrox 2400 c unit. To obtain the I and Br contents, the samples were decomposed by NaO_2 fusion in a Parr bomb acidified with conc. HNO_3 and titrated potentiometrically with $AgNO_3$. The Bi analyses in $BiOI_{1-x}Br_x$ appear to be somewhat low whereas the Br analyses in $BiOI_{1-x-y}Br_xCl_y$ were 2-3% low, presumably because all the Br was not reduced to Br^0. In the latter two samples Br was determined by difference. As shown in Table 2, the compositions of the products correspond approximately to the composition of the starting solutions.

X-Ray diffraction patterns were obtained with a Guinier-Hägg focusing camera (r = 40 mm). The radiation was monochromatic CuKα_1 (λ = 1.54051 Å). KCl (a = 6.2931 Å) was used as an internal standard. Line positions on the film were determined to ±5 μ with a David Mann film reader. Cell dimensions, given in Table 3, were obtained by least-squares refinement.

The X-ray diffraction patterns of samples prepared at 25°C showed broadening of the h0l and 0kl lines. Only the hk0 lines (110, 200, 220 and 310) were sharp. This is consistent with platelets having dimensions of 100-500 Å along c.

To evaluate the potential intensity (also called saturation or color purity) and lightfastness of the

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Table 1 Preparation of $BiOI_{1-x-y}Br_xCl_y$

x	y	$Bi(NO_3)_3 \cdot 5H_2O$	Acetic Acid	KI	KBr	KCl	Na Acetate
0.75		20 g	30 cc	1.711	3.680		10 000
0.60		20	30	2.766	2 974		10 000
0.50		60	90	10.371	7.435		20 500
0.40		20	30	3.720	2.480		6.833
0.25		20	30	4 875	1 625		6.764
0.20	0 25	20	30	3.800	0.991	0 776	6 830
0.35	0.40	20	30	1.728	1.735	1.240	6 830

bismuth oxyhalide pigments, a paint was made by dispersing pigment into a binder in a 2:1 weight ratio of pigment to binder using a Hoover muller. The binder was composed of 98.9 parts by weight of a transparent varnish,† 1 part by weight as lead of lead Nuodex® drier (contains 24% lead), and 0.1 part by weight of manganese Nuodex® drier (contains 6% manganese). The paint was spread onto Crane 100% rag paper using a 0.1-mm knife. These "drawdowns" were dried for about 72–120 h in a well-ventilated room at 25°C and less than about 50% relative humidity. Such drawdowns, in which only colored pigment with no diluent pigment is used, are commonly referred to as "mass-tones".

Dried drawdowns were continuously exposed for 200 h in an Atlas Color Fade-Ometer® Type FDA-P. The color change was visually estimated after exposure.

To quantify the color properties of the pigment, diffuse reflectance spectra of drawdowns were measured relative to that of pure $BaSO_4$ powder on a Cary 14 double beam spectrophotometer fitted with an integrating sphere. The procedure is standard and is discussed by Kortum [15]. To obtain absolute reflectance, the observed relative reflectance was multiplied by the absolute reflectance of pure $BaSO_4$‡ as published by Grum and Wightman [16]. Since the drawdowns transmit some light in the spectral region of nominal transparency (long wavelengths), they were backed with a thick $BaSO_4$ pellet.

A critical property of a pigment is its strength as a colorant. The strength is related to the intrinsic absorption coefficient, α, in the strongly absorbed part of the spectrum. Pigments with $\alpha < 10^4$ cm^{-1} are not generally useful. The spectrum of intrinsic-absorption coefficients was determined by application of the Kubelka–Munk theory to the diffuse reflectance spectrum of dilute (approximately 1%) mixtures of bismuth oxyhalide pigment in $BaSO_4$ standard. This dilution method and the Kubelka–Munk theory are discussed by G. Kortum [17].

For accurate measurements, the individual colored pigment particles must not be thick compared with the optical absorption depth of light in the solid. For strong pigments, the optical absorption depth in the

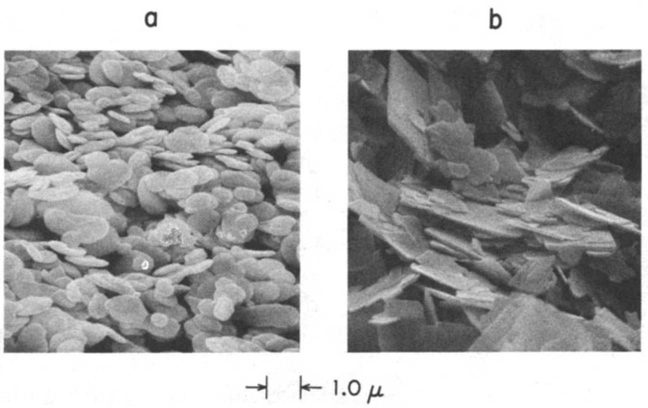

Fig 1 The crystallite habit of $BiOI_{0.6}Br_{0.4}$. The tetragonal c axis is perpendicular to the tabular surface (a) Reaction mixture stirred for 24 h at 25°C; (b) reaction mixture stirred for 4 h at 95°C

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† Number 2 varnish, Superior Varnish and Drier Company, Merchantville, New Jersey

‡ Eastman No 6091 White Reflectance Standard

Table 2. Chemical analyses of $BiOI_{1-x-y}Br_xCl_y$

Nominal Composition	$BiOI_{.25}Br_{.75}$	$BiOI_{.5}Br_{.5}$	$BiOI_{.55}Br_{.20}Cl_{.25}$	$BiOI_{.25}Br_{.35}Cl_{.40}$
%I	10.3	19.8	23.00	9.41
%Br	16.0	13.8	3.77[a]	9.26[a]
%Cl			2.67	4.83
%Bi	60.5	60.6	65.46	71.17
%O	5.0	4.9	4.92	5.33
Analyzed Composition	$Bi_{.92}OI_{.26}Br_{.69}$	$Bi_{.95}OI_{.51}Br_{.56}$	$BiOI_{.98}Br_{.18}Cl_{.24}$	$BiOI_{.22}Br_{.38}Cl_{.40}$

[a] By difference.

visible part of the spectrum can be 10^{-5} cm (0.1 μ) or less. Furthermore, the particles must not be agglomerated into lumps larger than the absorption depth. For the measurements described here, pigment particles were suspended in water with an anionic surfactant, which gives them a negative surface charge. The suspension was then centrifuged to remove large particles and agglomerates. Next the remaining suspension of fines was heteroagglomerated onto the $BaSO_4$ diluent particles, which adopt a positive surface charge at pH 7. These conditions discourage self-agglomeration of colored pigment particles with each other.

It was necessary to limit the concentration of surfactant to a level just sufficient to suspend the colored pigment. Otherwise the anionic surfactant was adsorbed on the $BaSO_4$ diluent particles, thus changing their surface charge and preventing heteroagglomeration. Alternatively, the suspension of fines was washed to remove unadsorbed surfactant.

The dried mixture was pressed into flat disc pellets at 2.4 × 10^6 Pascals (350 pounds/in.^{2}).

The intrinsic absorption coefficient, α, was calculated with eqn (1)

$$\alpha = \frac{S}{2v_p}\left[F_m - \frac{(P - v_p)}{p} F_d\right], \tag{1}$$

where F is the Kubelka–Munk function

$$F = \frac{(1 - R_\infty)^2}{2R_\infty} \tag{2}$$

R_∞ is the absolute diffuse reflectance of a thick sample. Subscript m indicates R_∞ for the pigment

Table 3. Cell dimensions of $BiOI_{1-x-y}Br_xCl_y$

x	y	a, Å	c, Å
0.0	0.0	3.9956(3)	9.155(1)
0.1	0.0	3.9849(5)	9.1354(6)
0.2	0.0	3.9769(3)	9.064(2)
0.25	0.0	3.966(2)	9.070(3)
0.3	0.0	3.9693(3)	8.992(2)
0.4	0.0	3.9614(3)	8.889(3)
0.5	0.0	3.9543(6)	8.817(5)
0.6	0.0	3.9460(5)	8.730(4)
0.75	0.0	3.9362(6)	8.453(9)
0.8	0.0	3.9328(4)	8.378(5)
0.9	0.0	3.9275(4)	8.244(2)
1.0	0.0	3.9221(7)	8.113(4)
0.2	0.25	3.9504(5)	8.937(8)
0.35	0.40	3.918(3)	8.45(2)

mixture, and d indicates R_σ for pure diluent powder. S is the scattering power of the diluent from E. M. Patterson, *et al.* [18]. (The values given there are $S/2$.) P is the packing fraction, assumed equal for mixture and pure diluent. It was measured to be 0.485. The term v_p is the volume fraction of the colored pigment in the mix. It was calculated from the mass fraction, c_p, as

$$v_p = P\left[1 + \left(\frac{1 - c_p}{c_p}\right)\frac{\rho_p}{\rho_d}\right]^{-1}, \qquad (3)$$

where ρ_p is the intrinsic density of the colored pigment and ρ_d is the intrinsic density of the diluent ($\sim$4.5 g/cm^3).

RESULTS AND DISCUSSION

Table 3 and Fig. 2 show that $BiOI_{1-x}Br_x$ forms a complete solid solution series. Very little change occurs in a, whereas significant change occurs in c; similar behavior was reported for LaOCl, LaOBr and LaOI [13]. The Bi_2O_2 layer probably remains rigid while most of the expansion occurs in the (Br, I) double layer. This would allow the Bi-O distances to remain almost the same and the Bi-X distances to increase significantly.

Correlating roughly with the change in c, the color of these solid solutions varies from yellow ($x \cong 0.75$) to orange ($x \cong 0.4$–0.6) to red-orange ($x \cong 0.25$). The colors are intense and have good fade resistance in ultraviolet light.

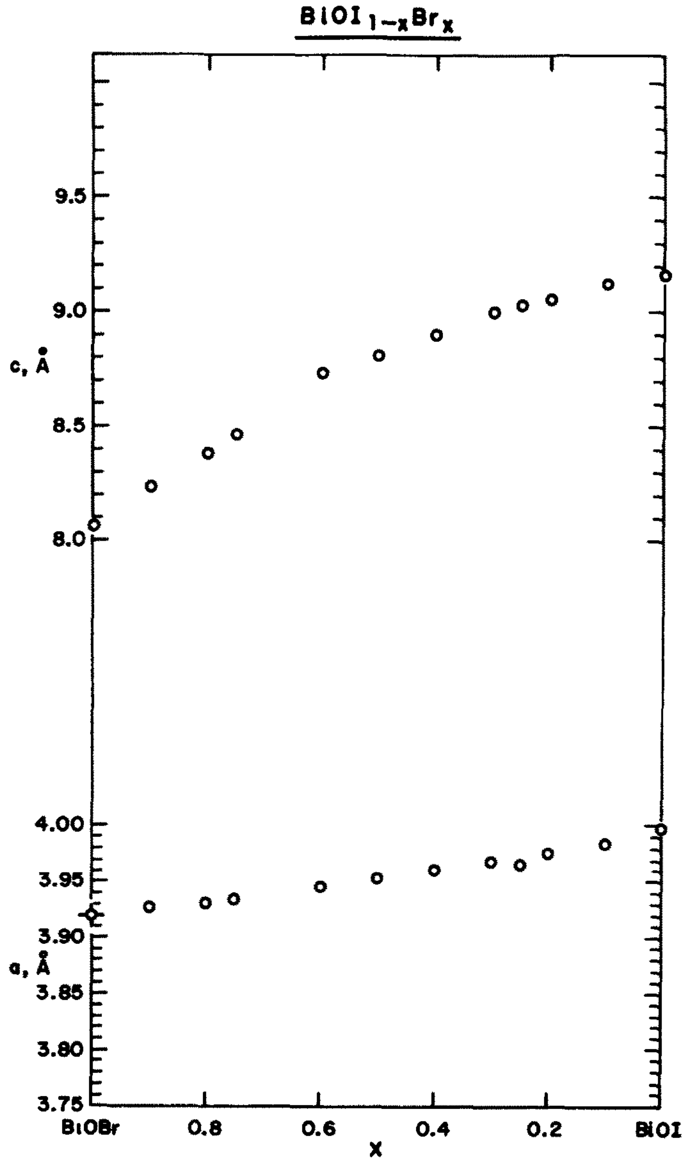

Fig. 2. Unit cell dimensions versus x for tetragonal $BiOI_{1-x}Br_x$. The smooth progression indicates that no phase change occurs over the range $0 < x < 1$.

Table 4 Color properties of masstone (100%) $BiOI_{1-x}Br_x$ drawdowns

x	c, Å	hue $\tan^{-1}(b/a)$	S/S'	L
0.75	8.453	1.36	0.568	85.0
0.60	8.730	1.36	0.530	86.2
0.50	8.817	1.09	0.519	74.1
0.40	8.889	1.11	0.489	77.4
0.0	9.155	0.74	0.355	57.5
$PbCrO_4$		1.36	0.637	85.4

Diffuse reflectance spectra of masstone drawdowns are shown in Fig. 3. The absorption edge shifts to longer wavelength with increasing I/Br ratio Band theory calculations [19] indicate that the band gap does decrease as the size of the halogen increases (Cl-Br-I) and the interlayer spacing, *c*, increases. The gap decrease results largely from increase in the energy of halogen *p* states involved in formation of the valence band.

From the steepness of the absorption edge we may infer that the color purity, or saturation, of the bismuth oxyhalides is less than that of $PbCrO_4$. This difference in absorption edge steepness may be similar to that observed between $PbCrO_4$ and CdS containing crystal defects [20]. In $PbCrO_4$, the highly localized nature of the chromophore protects it from the Urbach-type broadening that results from local electric field anomalies surrounding defects in the more covalent CdS lattice.

In Table 4, the color properties of the drawdowns are quantified in the CIE 1976 (L*a*b*) system (abbreviated as CIELAB) [21]. CIELAB uses a right-handed orthogonal color space in which the *x* or red-green axis is labeled a*; the *y* or yellow-blue axis is labeled *b**, and the *z* or "lightness" axis is labeled *L**. Lightness is a measure of the fraction of a white illuminant light that is reflected The color appearance of a surface is represented by a point in the space. The coordinates of the point can be calculated from the absolute reflectance spectrum of the surface The azimuth of the representative point is the hue, *h* The colors available from the bismuth oxyhalides are all represented by points in the red-yellow positive first quadrant, $h = 0$ to $\pi/2$ radians. The horizontal distance from the L (*z*) axis to the representative point is a measure of the saturation (*S*). But the maximum possible saturation (*S'*) is a function of hue Hence, we have given the relative saturation, *S*/*S'*. This is the ratio of the saturation, calculated from the experimental spectrum of a pigment drawdown to that calculated from a hypothetical spectrum of maximum saturation at the same hue.

From Table 4, we see again how as I content and *c* lattice dimension increase, hue trends from yellow toward red, and the relative saturation and lightness move to lower values. We also confirm that the color saturation of $PbCrO_4$ is superior to that of the bismuth oxyhalide of the same hue. These conclusions quantify what is expected from observation of the colors and inspection of the spectra.

Intrinsic absorption spectra of bismuth oxyhalides, calculated from the diffuse reflectance spectra of dilute mixtures with $BaSO_4$, are given on Fig. 4. While all are not as strong as $PbCrO_4$, α greatly exceeds 10^4 cm^{-1} in the visible.

Figure 5 indicates the nearly null effect on the $BiOI_{0.5}Br_{0.5}$ absorption spectrum of partial Cl substitution for Br. The difference in the *c* dimension of

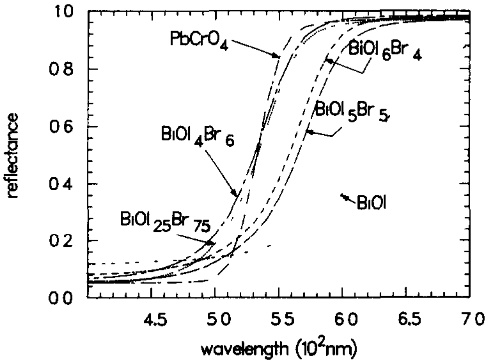

Fig. 3 Diffuse reflectance spectra of $BiOI_{1-x}Br_x$ pigment drawdowns backed by a thick pellet of $BaSO_4$ $PbCrO_4$ is shown for comparison

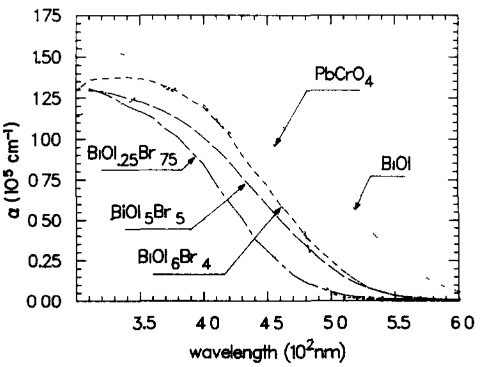

Fig 4 Intrinsic absorption coefficient spectra of $BiOI_{1-x}Br_x$ pigments. $PbCrO_4$ is shown for comparison

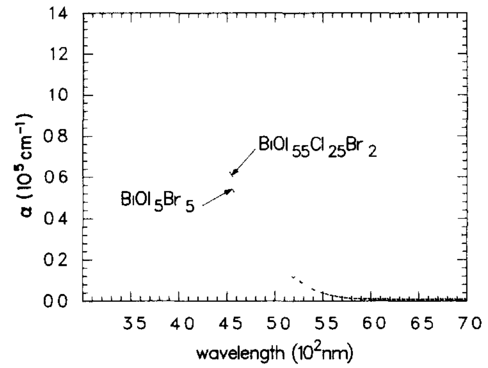

Fig 5 Intrinsic absorption coefficient spectra of $BiOI_{0\ 5}Br_{0\ 5}$ and $BiOI_{0\ 55}Cl_{0\ 25}Br_{0\ 2}$ showing relative insensitivity to Cl Br ratio

the unit cells for the two compounds (Table 3) shows again that color change in this series only approximately follows the c dimension change

SUMMARY

The compounds $BiOI_{1-x}Br_x$ form a complete solid solution series and all crystallize in a layered tetragonal matlockite structure They vary in color from yellow through red-orange to coral red as x decreases from 0 75 to 0, and the interlayer spacing increases from 8 45 to 9 16 Å. The compounds $BrOI_{1-x-y}Br_xCl_y$ where $x = 0.2$, $y = 0.25$ and $x = 0\ 35$, $y = 0\ 4$ crystallize similarly, but color is largely determined by $x + y$ The color strength of bismuth oxyhalide pigments is comparable to that of $PbCrO_4$ ($\alpha > 10^5$ cm^{-1}); but quantified color purity, while in a useful range, does not equal that of $PbCrO_4$. The pigment colors are light-fast

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