New Phase in the Lead Chromate–Lead Molybdate System

J.E. BISHOP and A.R. HANKE
Pigments Department, E.I. du Pont de Nemours & Co., Inc., Newark, N. J.

IN THE PURE STATE, lead molybdate is white or colorless, whereas lead chromate is yellow or orange. Single-phase products of intermediate composition exist in the system lead chromate-lead molybdate. Such products vary in color, but are generally orange or red-orange.

As early as 1863, Schultze (*10*) had noticed and commented on the fact that sometimes the mineral wulfenite ($PbMoO_4$) was colored strongly red when it occurred near the mineral crocoite ($PbCrO_4$). Working from melts in the laboratory, Schultze reported that up to 42% lead chromate could dissolve in molten lead molybdate and on cooling crystallize as a single-phase homogeneous salt having the tetragonal phase of lead molybdate. These homogeneous salts were colored a dark, deep red, much darker than he was able to obtain from pure lead chromate.

Later, in 1921, Jeager and Germs (*4*) reported mixed crystals containing about 44% lead chromate.

In 1932, Wagner, Haug, and Zipfel (*11*) reported on polymorphism in the lead chromate system. They described only three phases, which they list as: (1) monoclinic, (2) orthorhombic, and (3) tetragonal.

They state that the orthorhombic phase is metastable and that the tetragonal phase found by Jeager and Germs exists at high temperatures and is stable only above 783° C. Recently, Collotti, Conti, and Zocchi (*2*) have reported on the structure of orthorhombic lead chromate.

Starting with Lederle and Grimm (*5*) in 1933, there have been many contributions concerning the lead chromate-lead molybdate system, as it deals with the commercial pigment, Molybdate Orange (*1, 3, 6,–9*). These deal, for the most part, with processes for manufacture of and pigment properties of Molybdate Orange. Some suggestions are made regarding the structure of Molybdate Orange, but little evidence is given in support of the suggestions.

The object of the present work was to study the system lead chromate-lead molybdate and the type of distortion necessary to produce the intermediate phases.

EXPERIMENTAL

All samples were prepared by aqueous precipitation. Solutions of sodium molybdate and sodium chromate were premixed and added in the appropriate proportions to a solution of lead nitrate. Samples were prepared at 14 different compositions ranging from 100% lead chromate to 100% lead molybdate. In terms of mole per cent chromate, these were 0, 5, 10, 20, 30, 40, 50, 60, 75, 80, 85, 90, 95, and 100.

Specific Example. To the solution of 87 grams of lead nitrate crystals in 1200 ml. of water at 18° C., add in 25 minutes a solution containing 48.11 grams of sodium chromate ($Na_2CrO_4 \cdot 4\ H_2O$) and 5.88 grams of sodium molybdate ($NaMoO_4 \cdot 2\,H_2O$) in 1 liter of water at 18° C. to give a solution of pH 7.5. Following addition of the chromate-molybdate solution, add a solution of 27 grams of NaCl and 0.75 gram of HCl in 150 ml. of water. Stir 15 minutes and add 2.6 grams of sodium carbonate in 25 ml. of water to obtain a final pH of 5.8 to 6.0. Filter, wash, and dry at 60° C. The low temperature, NaCl addition, and pH control are to help stabilize the metastable Molybdate Orange phase, preventing it from converting to the stable monoclinic lead chromate phase.

All samples were examined by x-ray diffraction methods using a North American Philips wide-range x-ray diffractometer, nickel-filtered copper radiation, and standard powder techniques for sample mounting.

X-ray diffraction diagrams show that the tetragonal structure of lead molybdate persists up to the 60% $PbCrO_4$–40% $PbMoO_4$ sample. There is a shift of peaks which is uniform and continuous with change in composition, indicating a solid solution of lead chromate in lead molybdate. During this change, the lattice dimensions change from a = 5.41 A., c = 12.08 A. for pure $PbMoO_4$ to a = 5.27 A., c = 12.33 A. for the sample containing 60% $PbCrO_4$. Between 60 and 75% $PbCrO_4$, a new phase is indicated by the x-ray patterns.

The phase change observed by the x-ray diffraction patterns is also evident in the color of the samples prepared. As little as 5% of lead chromate coprecipitated with the lead molybdate gives a marked yellow-orange color. Increasing amounts of lead chromate give increasing redness up to somewhere within the range 60 to 75%.

At this point, a sudden change in hue indicates the beginning of the new phase. As the per cent lead chromate is increased further, the hue becomes still redder, reaching a maximum at around 90% lead chromate. Beyond this percentage, the redness rapidly decreases and at 100% lead chromate, the color is that of yellow monoclinic lead chromate.

CRYSTAL STRUCTURE OF 90/10 PHASE

The x-ray diffraction pattern of the 90/10 phase ($PbCrO_4/PbMoO_4$) is very similar to that of tetragonal $PbMoO_4$, except that several peaks which appear as singlets in the $PbMoO_4$ phase are split into doublets, as shown in the x-ray patterns of the two phases (Figure 1). This similarity suggests that the structure of the 90/10 phase does not differ greatly from that of tetragonal $PbMoO_4$. Efforts to index the pattern on the basis of a tetragonal or orthorhombic cell or as a two-phase system were unsuccessful. It was possible to index the pattern on the basis of a single-phase body-centered monoclinic unit cell which is simply related to the tetragonal $PbMoO_4$ cell.

Dimensions of the unit cells of the different phases of lead chromate and lead molybdate are given in Table I for comparison.

The dimensions of the 90/10 unit cell refer to one whose space group is $I2/c$. The choice of cell axes leading to

Table I. Cell Dimensions

	Unit Cell Dimension, A.				Cell
	a	b	c	β Angle,°	Volume, Cu. A.
$PbMoO_4$ (tetragonal)	5.41	5.41	12.08	90.0	353.6
60/40 $PbCrO_4/PbMoO_4$ (tetragonal)	5.27	5.27	12.33	90.0	342.4
90/10 $PbCrO_4/PbMoO_4$ $I2/c$	5.34	5.09	12.46	92.5	338.4
$PbCrO_4$ (orthorhombic)	8.67	5.59	7.13	90.0	345.6
$PbCrO_4$ (monoclinic)	6.82	7.48	7.16	102.5	356.6

Table II. *HKL* Indices

2θ Cu$K\alpha$	d, A.	Rel. Int.[a]	$\sin^2\theta$ Obsd.	$\sin^2\theta$ Calcd.	*HKL* $I2/c$	*HKL* $C2/c$
18.12	4.891	32	0.0248	0.0247	(110)	(110)
18.80	4.716	28	0.0267	0.0267	(011)	$(11\bar{1})$
20.48($PbCrO_4$)	4.333	6	. . .	. . .	. . .	. . .
25.85($PbCrO_4$)	3.444	7	. . .	. . .	. . .	. . .
27.64	3.224	100	0.0571	0.0571(0.0572)	$(12\bar{1})$(031)?	$(22\bar{1})(13\bar{1})$
28.62	3.116	93	0.0611	0.0610(0.0612)	(121)(040)?	(021)(040)
29.7 ($PbCrO_4$)	3.005	8	. . .	. . .	. . .	. . .
33.56	2.668	19	0.0832	0.0832	(200)	(200)
35.2	2.547	14	0.0914	0.0914	(002)	$(20\bar{2})$
37.4	2.402	6	0.1028	0.1029	$(14\bar{1})$	$(24\bar{1})$
38.0	2.366	6	0.1060	0.1062	$(21\bar{1})$	$(31\bar{1})$
38.2	2.354	3	0.1070	0.1068	(141)	(041)
39.16	2.298	21	0.1123	0.1121	$(11\bar{2})$	$(31\bar{2})$
39.4	2.285	21	0.1136	0.1140	(211)	(111)
39.96	2.254	21	0.1168	0.1165	(150)	(150)
40.3	2.236	3	0.1187	0.1184	(051)	$(15\bar{1})$
40.5	2.225	4	0.1200	0.1201	(112)	$(11\bar{2})$
43.4	2.083	7	0.1367	0.1365	$(23\bar{1})$	$(33\bar{1})$
44.4	2.039	3	0.1428	0.1428	$(13\bar{2})$	$(33\bar{2})$
44.7	2.026	25	0.1446	0.1446(0.1446)	(240)(231)	(240)(131)
45.7	1.984	8	0.1508	0.1507	(132)	$(13\bar{2})$
45.95	1.973	21	0.1523	0.1526	(042)	$(24\bar{2})$
48.22	1.886	7	0.1669	0.1669	$(20\bar{2})$	$(40\bar{2})$
50.15	1.817	5	0.1796	0.1794	$(16\bar{1})$	$(26\bar{1})$
50.3	1.812	21	0.1806			
50.7	1.799	24	0.1833	0.1833(0.1827)	(161)(202)	(061)(002)

[a] Relative to that of 26.64° peak, arbitrarily set at 100.

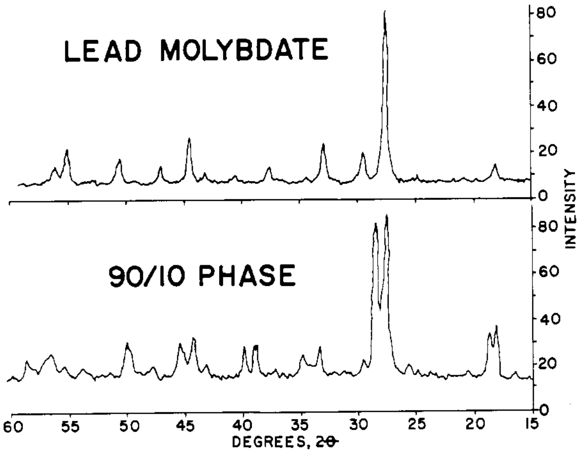

Figure 1. X-ray patterns of lead molybdate and 90/10 phase

Table I was prompted by a desire to show the structural similarity between this cell and the tetragonal prototype. This type of cell is described more usually in terms of space group $C2/c$, and *HKL* indices for both space groups are included in Table II. The dimensions of the $C2/c$ unit cell are:

a = 5.09 A. c = 7.22 A.
b = 12.46 A. β = 132.5°

Space groups Cc and $C2/c$ are both consistent with the available x-ray diffraction data. An effort was made to distinguish between the polar Cc and the centrosymmetric $C2/c$ structure by piezoelectric measurements. No response was observed and $C2/c$ was, therefore, considered to be the more probable space group.

SUMMARY

Solubility of lead chromate in the tetragonal lead molybdate lattice is within the range of 60 to 70 mole % rather than the 44% previously reported (2).

A previously unreported phase, the 90/10 phase, reaching its maximum purity at around 90 mole % chromate, has been found and its crystal structure determined.

The unit cell of the 90/10 phase is monoclinic, space group $C2/c$, and there are four molecules per unit cell. This monoclinic cell is a slightly distorted version of the tetragonal lead molybdate cell. X-ray diffraction peak intensities of the new 90/10 phase indicate that the structure is essentially similar to that of tetragonal lead molybdate.

The color of the lead chromate-lead molybdate system can be used to indicate the phase boundaries. There is a sharp change in hue at the beginning of the 90/10 phase. Maximum redness is obtained at the point of maximum 90/10 phase.

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