

# High-Pressure Synthesis of $\text{PbCrO}_3$

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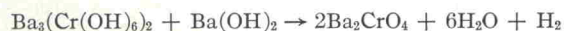
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A new compound with the composition  $\text{PbCrO}_3$ , with Cr in the valence state of 4, was synthesized at high pressures above a pressure-temperature line extending from about 50 kbars at 750°C to 60 kbars at 1450°C.  $\text{PbCrO}_3$  can be quenched and retained at 1 atm but decomposes on heating above 275°C at the same pressure.  $\text{PbCrO}_3$  is considered to be an equilibrium phase at high pressures because it was synthesized from mixtures of  $\text{PbO}:\text{CrO}_2$  as well as from several other mixtures of compounds in the Pb-Cr-O system. The new phase has the cubic perovskite structure and is the only known compound with  $\text{Cr}^{4+}$  in an octahedral site.  $\text{PbCrO}_3$  crystallizes primarily as black cubes which are often twinned on (111).

## Introduction

A NEW compound with the perovskite structure,  $\text{PbCrO}_3$ , was synthesized from mixtures in the system Pb-Cr-O using high-pressure techniques. Neutron diffraction and magnetic studies of this new compound were previously reported.<sup>1</sup> Because it has not been possible to produce pure samples in sufficient quantity for chemical analysis and characterization, some of the diffraction results are cited here when necessary to establish the composition and valence state of the new compound. The synthesis is of general interest in its use of high-pressure apparatus for studying reactions involving valence states which may be unstable or metastable at 1 atm.

Although we know of no other perovskite with  $\text{Cr}^{4+}$  in the octahedral site, synthesis of other compounds with Cr valence states between 3 and 6 is known. Banks and Jaunarajs<sup>2</sup> studied  $\text{Cr}^{5+}$  analogs of phosphates (apatites). Scholder and Klemm<sup>3</sup> reported the synthesis of  $\text{Cr}^{4+}$  oxides such as  $\text{Ba}_2\text{CrO}_4$  and  $\text{Ba}_3\text{CrO}_5$  and  $\text{Cr}^{5+}$  oxides such as  $\text{Ba}_3(\text{CrO}_4)_2$  by reactions of the type:



All these reactions were in pure nitrogen at 1 atm. The effective magnetic moment of Cr in  $\text{Ba}_2\text{CrO}_4$  and in  $\text{Ba}_3(\text{CrO}_4)_2$  was 2.82 and 1.71  $\mu_B$ , respectively, compared to the calculated values of 2.83 and 1.73 for the spin-only contributions of  $\text{Cr}^{4+}$  ( $d^2$ ) and  $\text{Cr}^{5+}$  ( $d^1$ ).

Scholder and Klemm<sup>3</sup> attempted to prepare  $\text{BaCrO}_3$  by similar methods at 1 atm but were unsuccessful. Since  $\text{CrO}_2$  can be retained to temperatures as high as 1500°C at

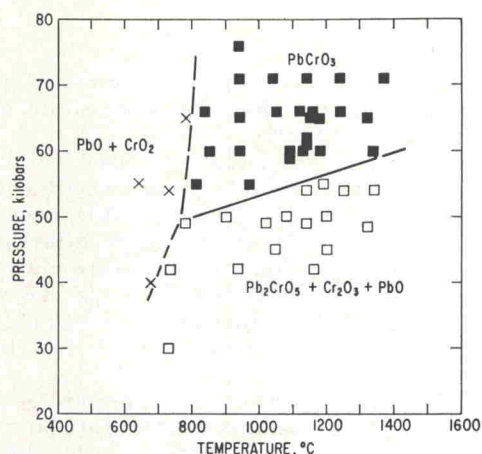


Fig. 1. Pressure-temperature diagram defining region from which  $\text{PbCrO}_3$  can be quenched as determined from  $\text{PbO}:\text{CrO}_2$  mixtures.

50 kbars for at least 0.5 hr in the high-pressure "belt" apparatus,<sup>4</sup> it was feasible to try the direct reaction of metal oxides with  $\text{CrO}_2$  to form new compounds. The system  $\text{PbO}-\text{CrO}_2$  was chosen because of the probability of forming a perovskite phase and because the lower melting point of  $\text{PbO}$ , compared to other divalent oxides, might allow the reaction to proceed at a moderate temperature.

## II. Experimental Procedure

Most of the data are from runs made on equimolar mixtures of cp  $\text{PbO}$  (yellow form) and  $\text{CrO}_2$ . The  $\text{CrO}_2$  was made by decomposing  $\text{CrO}_3$  at 425°C and about 0.25 kbars oxygen pressure. The perovskite stability region shown in Fig. 1 was established with about 130 runs on the  $\text{PbO}:\text{CrO}_2$  mixtures. The equilibrium nature of the phase was

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Table I. Summary of Data on Mixtures Other than  $PbO:CrO_2$ 

Serial No.	Point on initial composition	Pb:Cr:O	Point on Fig. 2	Pressure (kbars)	Temp. ( $^{\circ}C$ )	Time (min)	Phases present*
1	$PbO:CrO_2$	1:1:3	$PbCrO_3$	65	1150	30	$PbCrO_3$ , X†
2	$2PbO:PbCrO_4:Cr_2O_3$	1:1:3	$PbCrO_3$	65	1150	30	$PbCrO_3$ , X
3	$PbO:Pb_2CrO_5:Cr_2O_3$	1:1:3	$PbCrO_3$	64	1120	30	$PbCrO_3$ , X, tr. $PbO$ , tr. $Cr_2O_3$
4	Product of decomposition of $PbCrO_3$ at high pressure	1:1:3	$PbCrO_3$	65	1250	16	$PbCrO_3$ , tr. $Cr_2O_3$ , $PbO$ ?
5	$5PbO:PbCrO_4:Cr_2O_3$	2:1:4	a	65	1150	30	$PbCrO_3$ , $PbO$
6	$2PbO:CrO_2$	2:1:4	a	65	1150	23	$PbCrO_3$ , $PbO$
7	$2Pb_3O_4:3Cr_2O_3$	1:1:2.83	b	65	1150	25	$PbCrO_3$ , $PbO$ , X, $Cr_2O_3$
8	$91PbO:3Pb_3O_4:100CrO_2$	1:1:3.03	c	65	1150	21	$PbCrO_3$ , $Pb_2CrO_5$ , X
9	$Pb_3O_4:3CrO_2$	1:1:3.33	d	65	1150	20	$PbCrO_3$ , $PbCrO_4$
10	$2PbO_2:Cr_2O_3$	1:1:3.5	e	65	1150	22	$PbCrO_3$ , $PbCrO_4$
11	$2PbO:3CrO_2$	2:3:8	f	65	1130	22	$PbCrO_3$ , $PbCrO_4$ , $PbO$ , $CrO_2$
12	$Pb_2CrO_5:Cr_2O_3$	2:3:8	f	65	1150	21	$PbCrO_3$ , $PbCrO_4$ , X
13	$Pb_2CrO_5 + Cr_2O_3$ (from $2PbO:Cr_2O_3$ melt)			65	1150	21	$PbCrO_3$ , $PbCrO_4$
14	$PbCrO_4:Cr_2O_3$	1:3:7	g	64	1130	25	$PbCrO_4$ , $PbO$ , $CrO_2$
15	$PbCrO_4$	1:1:4	$PbCrO_4$	60	1300	16	$PbCrO_3$ , $PbO$ , $Pb_2CrO_5$ , $Cr_2O_3$
16	$Pb_2CrO_5$	2:1:5	$Pb_2CrO_5$	65	1150	31	$Pb_2CrO_5$
				50	1200	35	$Pb_2CrO_5$

\* For every initial composition except g and  $Pb_2CrO_5$ ,  $PbCrO_3$  was the major reaction product.

† X = unidentified phase, considered to be poorly crystallized; high pressure decomposition products of  $PbCrO_3$  (see text); tr. = trace.

confirmed by synthesis from other combinations of oxides in the Pb-Cr-O system; these compositions are listed in Table I and plotted in Fig. 2.

After the desired proportions were weighed out, the oxide powders were mixed mechanically in plastic bottles by motor driven mixing machines. Cylindrical pellets were pressed from the powders and slipped into tight-fitting platinum tubes made from 0.001 in. foil. The ends were crimped shut, thus eliminating reaction with material of the high-pressure cell. The wrapped sample was inserted into the belt apparatus in an internally heated cell similar to that described by Hanneman and Strong.<sup>5</sup>

The procedure during a run was: (1) Pressure was raised to the desired value; (2) temperature was raised at a programmed rate of  $200^{\circ}C/min$ ; (3) the sample was held at temperature for 20 to 30 min; (4) the sample was quenched at about  $400^{\circ}C/sec$  by turning off the power to the cell with the pressure still applied; and (5) the pressure was released and the sample removed for examination.

The pressure of the cell was calibrated at room temperature at the 25.5 and 27.0 kbar transformation of Bi and at the 58.0 kbar transformation of Ba. Temperature was determined from a watts versus temperature plot which had previously been established by measuring cell temperatures with a Pt-Pt10Rh thermocouple inserted into the cell on each of several runs. Since the electrical characteristics of the cells are highly reproducible, this secondary calibration method is trustworthy and time-saving.

The phases formed were identified primarily by X-ray powder diffraction. Optical examination with transmitted light was useful for noting the presence of some impurity phases. Because of their opacity,  $PbCrO_3$  and  $CrO_2$  can be identified with reflected light microscopy.

### III. Results and Discussion

The results of the high-pressure synthesis of  $PbCrO_3$  from  $PbO:CrO_2$  are seen in Fig. 1, which shows the  $P$ - $T$  range from which  $PbCrO_3$  can be quenched to room temperature and pressure. Several points relative to the significance of the interpretation shown need discussion.

#### (1) Formation of $PbCrO_3$ from $PbO$ and $CrO_2$

The dashed line separating the  $PbO$  and  $CrO_2$  region from  $PbCrO_3$  is somewhat uncertain because the rate of reaction was not studied extensively. With longer runs this boundary may be moved to lower temperatures; however, some observations suggest that the boundary is approximately cor-

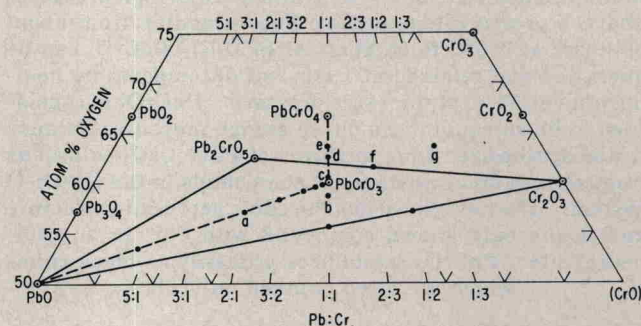


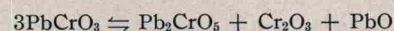
Fig. 2. Portion of system Pb-Cr-O showing compositions studied and pertinent compounds in the system. Lines of constant Pb/Cr ratio are defined by marks at top and bottom. Atom % oxygen is defined by lines parallel to base. Data on lettered dots are given in Table I. Unlabelled dots between  $PbCrO_3$  and  $PbO$  and between  $PbO$  and  $Cr_2O_3$  represent mixtures between the respective end-members. Solid triangle  $Pb_2CrO_5$ - $PbO$ - $Cr_2O_3$  represents equilibrium assemblage for decomposition of  $PbCrO_3$ . Dashed lines from  $PbO$  to  $PbCrO_3$  and from  $PbCrO_3$  to  $PbCrO_4$  represent equilibrium assemblages below  $PbCrO_3$  decomposition.

rect. A run at 65 kbars and  $780^{\circ}C$  for 45 min produced no  $PbCrO_3$ , whereas in a run at 55 kbars and  $810^{\circ}C$  for 15 min, some  $PbCrO_3$  could be detected with X-ray diffraction. Both of these temperatures are about  $3/4$  of the melting point of  $PbO$  at these pressures.

A series of runs 5, 10, 20, and 40 min long at  $1150^{\circ}C$  and 65 kbars established that the reaction to form  $PbCrO_3$  from  $PbO$  and  $CrO_2$  was essentially complete after 10 min. The  $P$ - $T$ - $t$  conditions chosen as the standard for synthesis of  $PbCrO_3$  were 65 kbars,  $1150^{\circ}C$ , and 20 min. The trend of the reaction was clear in 5 to 10 min for all runs at  $900^{\circ}C$  and above.

#### (2) Decomposition of $PbCrO_3$

The curve separating the phase region of  $PbCrO_3$  from its decomposition products at high temperatures and pressures represents the reaction:



as determined by identification of these quenched phases by X-ray diffraction. This equilibrium reaction is indicated by a solid triangle in Fig. 2. The  $Pb_2CrO_5$  pattern is the