High-Pressure Synthesis of PbCrO₃
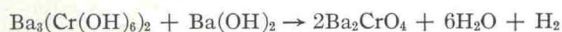
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A new compound with the composition $PbCrO_3$, with Cr in the valence state of 4, was synthesized at high pressures above a pressure-temperature line extending from about 50 kbars at 750°C to 60 kbars at 1450°C. $PbCrO_3$ can be quenched and retained at 1 atm but decomposes on heating above 275°C at the same pressure. $PbCrO_3$ is considered to be an equilibrium phase at high pressures because it was synthesized from mixtures of $PbO:CrO_2$ 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 Cr^{4+} in an octahedral site. $PbCrO_3$ crystallizes primarily as black cubes which are often twinned on (111).

Introduction

A NEW compound with the perovskite structure, Pb-CrO₃, 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.[1] 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 Cr^{4+} in the octahedral site, synthesis of other compounds with Cr valence states between 3 and 6 is known. Banks and Jaunarajs[2] studied Cr^{5+} analogs of phosphates (apatites). Scholder and Klemm[3] reported the synthesis of Cr^{4+} oxides such as Ba_2CrO_4 and Ba_3CrO_5 and Cr^{5+} oxides such as $Ba_3(CrO_4)_2$ by reactions of the type:

$$Ba_3(Cr(OH)_6)_2 + Ba(OH)_2 \rightarrow 2Ba_2CrO_4 + 6H_2O + H_2$$

$$BaCrO_4 + Cr_2O_3 + 5Ba(OH)_2 \rightarrow 3Ba_2CrO_4 + 5H_2O$$

$$2BaCrO_4 + BaCO_3 \rightarrow Ba_3(CrO_4)_2 + CO_2 + {}^1/_2 O_2$$

All these reactions were in pure nitrogen at 1 atm. The effective magnetic moment of Cr in Ba_2CrO_4 and in $Ba_3(CrO_4)_2$ was 2.82 and 1.71μ_B, respectively, compared to the calculated values of 2.83 and 1.73 for the spin-only contributions of Cr^{4+} (d^2) and Cr^{5+} (d^1).

Scholder and Klemm[3] attempted to prepare BaCrO₃ by similar methods at 1 atm but were unsuccessful. Since CrO₂ can be retained to temperatures as high as 1500°C at
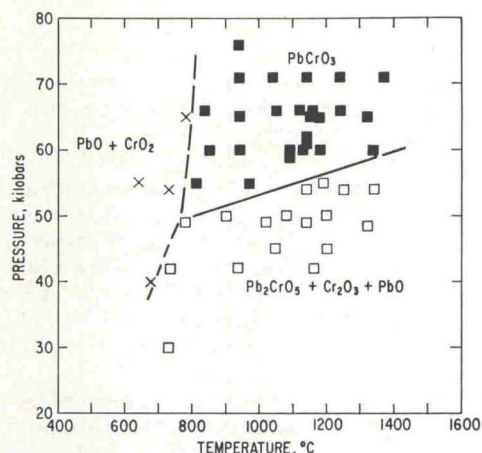

Fig. 1. Pressure-temperature diagram defining region from which PbCrO₃ can be quenched as determined from PbO:–CrO₂ mixtures.

50 kbars for at least 0.5 hr in the high-pressure "belt" apparatus,[4] it was feasible to try the direct reaction of metal oxides with CrO₂ to form new compounds. The system PbO-CrO₂ was chosen because of the probability of forming a perovskite phase and because the lower melting point of 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 PbO (yellow form) and CrO₂. The CrO₂ was made by decomposing CrO₃ 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 PbO: CrO₂ mixtures. The equilibrium nature of the phase was

Table I. Summary of Data on Mixtures Other than PbO:CrO₂

Serial No.	Point on initial composition	Pb:Cr:O	Point on Fig. 2	Pressure (kbars)	Temp. (°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 PbCrO₃ 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 cp 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.[5]

The procedure during a run was: (1) Pressure was raised to the desired value; (2) temperature was raised at a programmed rate of 200°C/min; (3) the sample was held at temperature for 20 to 30 min; (4) the sample was quenched at about 400°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 PbCrO₃ from PbO and CrO₂

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-
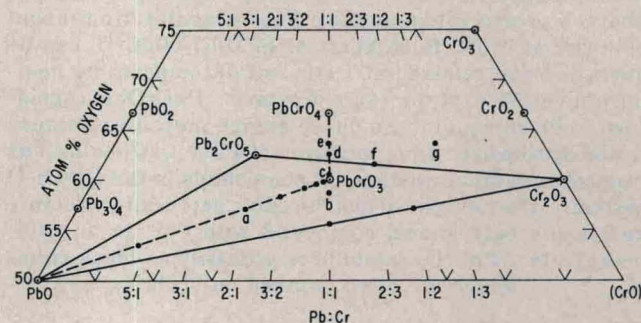

Fig. 2. Portion of system Pb-Cr-O showing compositions studied and pertinent compounds in the system. Lines of constant Pb/Cr ratio are defined by marks at top and bottom. Atom% oxygen is defined by lines parallel to base. Data on lettered dots are given in Table I. *Unlabelled dots* between $PbCrO_3$ 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°C for 45 min produced no $PbCrO_3$, whereas in a run at 55 kbars and 810°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°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°C, and 20 min. The trend of the reaction was clear in 5 to 10 min for all runs at 900°C and above.

(2) Decomposition of PbCrO₃

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

$$3PbCrO_3 \rightleftharpoons Pb_2CrO_5 + Cr_2O_3 + PbO$$
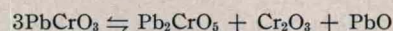
as determined by identification of these quenched phases by X-ray diffraction. This equilibrium reaction is indicated by a solid triangle in Fig. 2. The Pb_2CrO_5 pattern is the