

High-Pressure Synthesis of PbCrO_3

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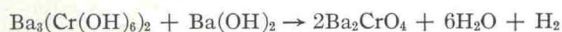
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A new compound with the composition PbCrO_3 , with Cr in the valence state of 4, was synthesized at high pressures above a pressure-temperature line extending from about 50 kbars at 750°C to 60 kbars at 1450°C. PbCrO_3 can be quenched and retained 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 $\text{PbO}:\text{CrO}_2$ 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 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, 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.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 Jaunarajs² studied Cr^{5+} analogs of phosphates (apatites). Scholder and Klemm³ reported the synthesis of Cr^{4+} oxides such as Ba_2CrO_4 and Ba_3CrO_5 and 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 Ba_2CrO_4 and in $\text{Ba}_3(\text{CrO}_4)_2$ was 2.82 and 1.71 μ_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 Klemm³ attempted to prepare BaCrO_3 by similar methods at 1 atm but were unsuccessful. Since CrO_2 can be retained to temperatures as high as 1500°C at

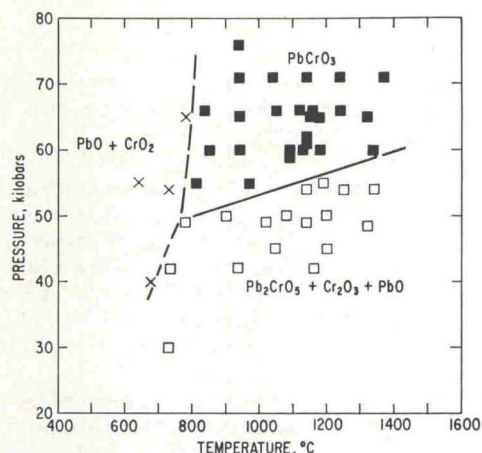


Fig. 1. Pressure-temperature diagram defining region from which PbCrO_3 can be quenched as determined from $\text{PbO}:\text{CrO}_2$ mixtures.

50 kbars for at least 0.5 hr in the high-pressure "belt" apparatus,⁴ it was feasible to try the direct reaction of metal oxides with 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 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 CrO_2 . The CrO_2 was made by decomposing 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. (°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	$2Pb_2O_4:3Cr_2O_3$	1:1:2.83	b	65	1150	25	$PbCrO_3$, PbO , X, Cr_2O_3
8	$91PbO:3Pb_2O_4:100CrO_2$	1:1:3.03	c	65	1150	21	$PbCrO_3$, Pb_2CrO_5 , X
9	$Pb_2O_4:3CrO_2$	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.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 $PbCrO_3$ 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-

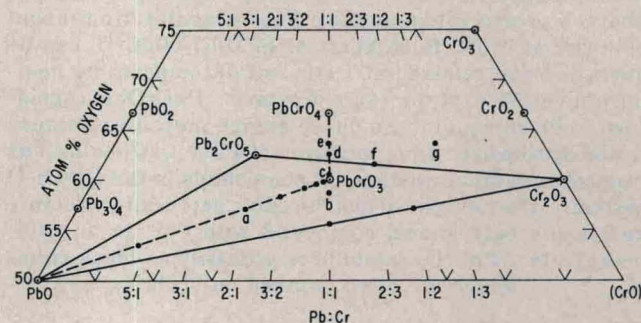


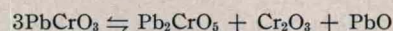
Fig. 2. Portion of system Pb-Cr-O showing compositions studied and pertinent compounds in the system. Lines of constant Pb/Cr ratio are defined by marks at top and bottom. Atom % oxygen is defined by lines parallel to base. Data on lettered dots are given in Table I. Unlabelled dots between $PbCrO_3$ 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°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 $PbCrO_3$

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

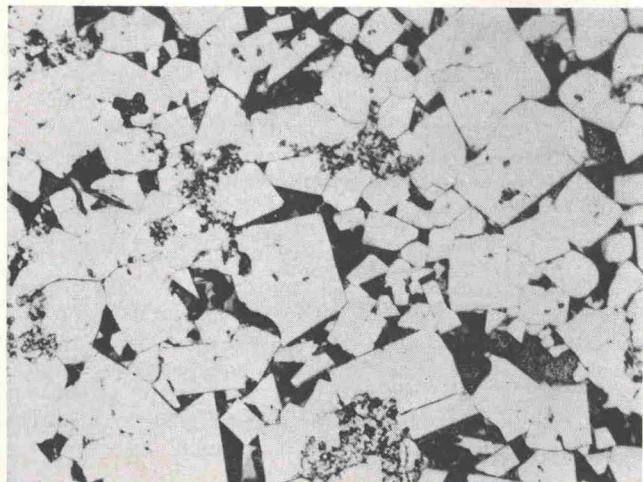


Fig. 3. Polycrystalline aggregate of PbCrO_3 . Impurity phases are visible as speckled areas among the light gray crystals. Black areas are pore spaces due primarily to pull-outs. (Bright field, as-polished; $\times 500$.)

most readily identifiable in the early stages of decomposition, and the presence of this phase was regarded as delineating a point in the decomposition region even though the reaction may not always have gone to completion during the run.

(3) Characterization of PbCrO_3

The material quenched from the PbCrO_3 stability region is a fine-grained, sintered compact (see Fig. 3) whose X-ray powder diagram is primarily that of a perovskite-type phase with a cubic lattice parameter of 4.00 Å.¹ Impurity second phases are present in amounts of about 5%. These phases can be seen as fine-grained material scattered among the larger crystals of the principal phase in Fig. 3. Although the X-ray patterns of the impurity phase assemblage were somewhat broad and diffuse, the best interpretation of both X-ray data and microscopic observations from experiments designed to produce increasing amounts of the undesired phases indicates the presence of poorly crystallized high-pressure decomposition products of PbCrO_3 . These impurities were almost completely eliminated by adding a few percent excess PbO , but under these conditions the excess PbO is the contaminant.

The impurity phases appear to result from slight local compositional changes such as might come from loss of oxygen. The role of excess PbO in reducing the amount of PbCrO_3 decomposition products may be associated with either (1) enhancement of kinetics of conversion of PbO and CrO_2 to PbCrO_3 via a liquid phase, or (2) smoothing out of pressure gradients which can lead to local inhomogeneities in the reaction vessel.

The purest sample obtainable (i.e. containing about 5% impurity phases) was analyzed for Pb and Cr with oxygen content being established by difference. Although this is not a very satisfactory analytical situation, the results were compatible with the composition PbCrO_3 . We believe the agreement between the intensity calculated for a perovskite, PbCrO_3 , and intensities measured on single crystals by X-ray diffraction and on powder by neutron diffraction (Table II) is good evidence for the composition of PbCrO_3 . The slight discrepancies of the weaker neutron intensities are probably due to small displacement of the oxygen atoms from the ideal sites in the perovskite arrangement.

As previously reported, the valence state of Cr was established by neutron diffraction. Below 250°K, PbCrO_3 is an antiferromagnet in which the atomic spins on each Cr are antiparallel to those on the six nearest neighbors. A moment

Table II. Intensities of PbCrO_3 Diffraction Patterns

hkl	X-ray*		Neutron†	
	Calc.‡	Obs.§	Calc.‡	Obs.§
100	168	S	0	2
110	421	VS	34	38
111	206	S	153	154
200	375	VS	142	136
210	71	W	0	8
211	188	M	21	8
220	232	M	129	111
221	58	VW	0	2
300				
310	160	W	11	0
311			105	104
222			53	63

* Single crystal, Mo $K\alpha$ precession photograph.

† Polycrystalline; $\lambda_n = 1.013$ Å.

‡ Calculated for nuclear scattering from ideal perovskite structure.

§ Room-temperature data.

of $1.9\mu_B$ per chromium atom was deduced from the magnetic intensities measured at 4.2°K.¹ Since $2\mu_B$ is the spin-only value expected for two unpaired electrons, we conclude that the average valence state is $\text{Cr}^{4+}(3d^2)$. A d^2 electronic configuration also is consistent with the temperature dependence of the magnetic susceptibility measured above the Néel temperature.¹ The neutron data serve as a physicochemical analysis for the tetravalent state of Cr and hence support the composition PbCrO_3 . Such an analysis would be extremely difficult by normal chemical methods.

(4) Evidence for Equilibrium

Although the impurity problem is only partly solved, the perovskite phase predominates and forms reproducibly from the P - T region defined in Fig. 1. There is no doubt that it is an equilibrium phase in the system at high pressures and temperatures. Table I shows that essentially identical results were obtained from three oxide mixtures which are chemically equivalent to PbCrO_3 . Furthermore, if the high-pressure decomposition products of PbCrO_3 (e.g. a run at 1160°C and 42 kbars) are quenched, examined to be sure decomposition is complete, and reheated in the PbCrO_3 stability range, almost complete conversion to PbCrO_3 is achieved (see No. 4, Table I). Similar reproducibility of results with different mixtures of $\text{Pb}:\text{Cr}=2:1$ and with mixtures between PbCrO_3 and PbCrO_4 also attest to a close approach to equilibrium in parts of the Pb-Cr-O system at high pressures.

(5) Evidence for Other Equilibrium Assemblages

Although the primary purpose of this study was the synthesis of PbCrO_3 and the delineation of its P - T stability region, some of the data permit definition of other equilibrium relations besides the high-pressure decomposition of PbCrO_3 .

PbCrO_3 and PbCrO_4 appear to be compatible phases under the conditions defined for runs on mixtures 9, 10, and 12 (Fig. 2 and Table I) and also from the mixtures of $\text{Pb}_2\text{CrO}_5 + \text{Cr}_2\text{O}_3$ made from a $2\text{PbO}:\text{Cr}_2\text{O}_3$ melt at 1 atm (No. 13). Mixtures 7, 8, 11, and 14 (Table I) all indicate other possible phase assemblages, the definition of which requires more investigation.

Contrary to results of reacting PbO and Cr_2O_3 in air at 1 atm where other phases on the $\text{PbO-Cr}_2\text{O}_3$ system can be formed,⁶ at 65 kbars and up to at least 1160°C for 30 min, PbO and Cr_2O_3 coexist without reaction. This probably is due to the absence of excess oxygen in the cell and the role of pressure per se in maintaining the low volume phases.

From points 5 and 6 of Table I and from other mixtures of PbO and CrO_2 between PbO and PbCrO_3 , it was firmly established that PbO and PbCrO_3 can coexist below the decom-

position curve of $PbCrO_3$ and that a Pb_2CrO_4 phase does not form at high pressures. It is interesting to compare this result with the 1 atm synthesis of Ba_2CrO_4 .³ As stated earlier, Scholder and Klemm³ made this and other Cr^{4+} -containing-compounds by a reaction similar to the foregoing. However, their attempted synthesis of $BaCrO_3$ was unsuccessful. That Pb_2CrO_4 did not form at high pressures* in the present study is not unreasonable if one accepts a structural argument based on data for Ba_2TiO_4 , with which Ba_2CrO_4 is said to be isomorphous.³

The structure of Ba_2TiO_4 is based on distorted TiO_4 groups in which the Ti—O bonding has considerable covalent character, the structure being analogous to Ba_2SiO_4 .⁷ The density of Ba_2TiO_4 is 5.16 g/cm³ indicating that the structure based on fourfold coordination of Ti^{4+} is quite open.⁷ The density of $BaTiO_3$ with Ti^{4+} in sixfold coordination is 6.01,⁸ and the molar volume of the phase assemblage of BaO (density 5.72)⁹ plus $BaTiO_3$ is almost 15% less than that of Ba_2TiO_4 . Thus the latter would not be expected to be favored at high pressures. Similarly it is reasonable that the more dense phase assemblage of yellow PbO (density, 9.642)¹⁰ and $PbCrO_3$ (calculated density, 7.98) would be more stable at high pressures than Pb_2CrO_4 . The synthesis of $PbCrO_3$ thus far only at high pressures suggests that in addition to a high oxygen pressure to maintain Cr^{4+} at high temperatures, pressure per se is required to stabilize the sixfold coordination. This argument provides a structural explanation for the failure of the attempted synthesis of $BaCrO_3$ at 1 atm.

(6) Growth of Crystals of $PbCrO_3$

To increase the size of the crystals above the maximum of about 30μ found in the average run, we tried growing crystals in a larger cell where a temperature gradient can be established. In this way crystals up to 0.1 mm and a few flat plates nearly 0.25 mm in the largest dimension were grown and used for the X-ray measurements. These crystals, which are black, very brittle, and frequently twinned on (111), show cube face development more often than octahedral faces. The crystals are badly strained, and X-ray photographs exhibited considerable asterism. Crystal perfection and size can probably be improved by combining controlled temperature gradients, cooling rate, and composition variation just

* Synthesis of Pb_2CrO_4 at low pressures by the method of Scholder and Klemm³ for Ba_2CrO_4 is not possible because of the ease of reduction of the lead compounds under the same conditions.

as one might do for any solution growth, because we believe the $PbCrO_3$ crystals may grow from molten PbO. From the data of Tomonari¹¹ the fusion curve of PbO as a function of pressure crosses the stability region of $PbCrO_3$ at almost a constant temperature of 1060° to 1070°C. Because $PbCrO_3$ and PbO are the only phases found in compositions between these two components, growth of $PbCrO_3$ from excess PbO should occur.

IV. Summary and Conclusions

$PbCrO_3$ is a stable phase in the system Pb-Cr-O at high temperatures and pressures. The equilibrium nature of the phase was established by using mixtures of different oxides in the system. Pressure per se appears to be necessary to form the perovskite phase in this system. The magnetic moment as determined from neutron diffraction studies is consistent with a chromium valence of 4 in this material.

Acknowledgments

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