



Fig. 3. Polycrystalline aggregate of  $\text{PbCrO}_3$ . 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 $\text{PbCrO}_3$

The material quenched from the  $\text{PbCrO}_3$  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.<sup>1</sup> 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  $\text{PbCrO}_3$ . 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  $\text{PbCrO}_3$  decomposition products may be associated with either (1) enhancement of kinetics of conversion of PbO and  $\text{CrO}_2$  to  $\text{PbCrO}_3$  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  $\text{PbCrO}_3$ . We believe the agreement between the intensity calculated for a perovskite,  $\text{PbCrO}_3$ , 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  $\text{PbCrO}_3$ . 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,  $\text{PbCrO}_3$  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  $\text{PbCrO}_3$  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.<sup>1</sup> 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.<sup>1</sup> The neutron data serve as a physicochemical analysis for the tetravalent state of Cr and hence support the composition  $\text{PbCrO}_3$ . 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  $\text{PbCrO}_3$ . Furthermore, if the high-pressure decomposition products of  $\text{PbCrO}_3$  (e.g. a run at 1160°C and 42 kbars) are quenched, examined to be sure decomposition is complete, and reheated in the  $\text{PbCrO}_3$  stability range, almost complete conversion to  $\text{PbCrO}_3$  is achieved (see No. 4, Table I). Similar reproducibility of results with different mixtures of Pb:Cr=2:1 and with mixtures between  $\text{PbCrO}_3$  and  $\text{PbCrO}_4$  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  $\text{PbCrO}_3$  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  $\text{PbCrO}_3$ .

$\text{PbCrO}_3$  and  $\text{PbCrO}_4$  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  $\text{Cr}_2\text{O}_3$  in air at 1 atm where other phases on the PbO- $\text{Cr}_2\text{O}_3$  system can be formed,<sup>6</sup> at 65 kbars and up to at least 1160°C for 30 min, PbO and  $\text{Cr}_2\text{O}_3$  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  $\text{CrO}_2$  between PbO and  $\text{PbCrO}_3$ , it was firmly established that PbO and  $\text{PbCrO}_3$  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  $Ba_2CrO_4$ .<sup>3</sup> As stated earlier, Scholder and Klemm<sup>3</sup> 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.<sup>3</sup>

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  $Ba_2SiO_4$ .<sup>7</sup> The density of  $Ba_2TiO_4$  is 5.16 g/cm<sup>3</sup> indicating that the structure based on fourfold coordination of  $Ti^{4+}$  is quite open.<sup>7</sup> The density of  $BaTiO_3$  with  $Ti^{4+}$  in sixfold coordination is 6.01,<sup>8</sup> and the molar volume of the phase assemblage of BaO (density 5.72)<sup>9</sup> 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)<sup>10</sup> 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  $30\mu$  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 Klemm<sup>3</sup> 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 Tomonari<sup>11</sup> 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

The authors gratefully acknowledge the contributions of Edith Raviola (metallography); L. Osika, D. Ochar, and R. Romanczuk (X-ray diffraction); and G. Smith (chemical analysis). George Dinsmore made the high-pressure cells and contributed freely from years of experience with high-pressure equipment. We especially thank T. Negas and R. Roth of the National Bureau of Standards for providing X-ray patterns of  $Pb_2CrO_5$ ,  $Pb_5CrO_8$ , and  $Pb_2CrO_6$ . During the early stage of this study there were many helpful and encouraging discussions with D. Wilkins.

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