08.2-03 NEW SILVER(I)-BORATES. By <u>Martin Jansen</u>, Justus Liebig-Universität, 6300 Gießen, Heinrich-Buff-Ring 58, FRG.

Silver(I)-oxides with a high ratio cations/oxygen show unusual structural features with respect to the arrangement of Ag⁺. The positively charged silver particles aggregate to form cluster-like agglomerates with Ag-Ag distances in the same order of magnitude as those in metallic silver (Jansen, J.Less-Common Metals, 1980, 76, 285). This tendency causes formation of special crystal structures which are not isostructural to those of ternary alkalioxides of respective composition. By synthesis and investigation of new silver(I)-borates we can demonstrate that these findings hold for the pairs Na_3B0_3/Ag_3B0_3 and $NaB0_2/AgB0_2$ too.

Ag_BO₂ (Jansen, Scheld, Z.Anorg.Allg.Chem., in press) is dimorphic (Jansen, Brachtel, to be published). Both modifications as well as AgBO₂ (Brachtel, Jansen, Z.Anorg.Allg.Chem., in press) have been prepared by solid state reaction of the binary components using elevated oxygen pressures ($p(O_2) > 1500$ bar). The crystal structures of Ag_BO₃(I) and Ag_BO₃(II) are identical with respect to the silver partial structures, whereas the linkage of AgO₂- and BO₃-polyhedra is completely different. AgBO₂ contains instead of the expected cyclo-trimetaborate-anions a $\frac{1}{40}$ BO₂-isopolyanion with boron coordinated in equal parts tetrahedrally and trigonal-planar by oxygen.

The title compound, prepared at 1300°C and 60-65 kbar by reaction of CrO_2 and Ba_2CrO_L as one of a mixture of products, crystallizes in space group $P6_3/mmc$, <u>a</u> = 5.649 \pm 0.002, <u>c</u> = 32.461 \pm 0.005 Å. The structure was determined from 346 independent, observed, reflections collected by automated counter methods and refined by least squares to a conventional R of 4.1%. The fourteen layer stacking sequence of close packed Ba0₃ layers in Zhdanov notation is |2(3)2|2(3)2|. All 0_6 octahedral sites are occupied by Cr. Despite the different repeat distances, the fourteen layer is structurally closely related to the four, six, and twenty-seven layer polytypes, and all are stoichiometric. These polytypes differ from the twelve layer barium chromium oxide in both structural features and composition.

The three-oxide compounds with perovskite structure have been studied in many works. In these compounds B' and B" are two cations with small ionic radii and different valence states.

In the present work three-oxide compounds with K_2NiF_* , structure (derived from perovskite structure) were synthesized. The cations were pentavalent Nb and Ta, and divalent Ni and Co. The starting raw materials were high-purity oxides and carbonates. The compounds were prepared by solid-state reaction of the appropriate components. The temperature range was 1000-1400°C for several periods of time, in air atmosphere.

The samples were examined by X-ray diffraction at room temperature. The powder diffraction patterns were indexed, and the lattice constants for the different synthesized compounds were calculated.

Four new compounds $(Sr_6Nb_2NiO_{12}, Sr_6Nb_2CoO_{12}, Sr_6Ta_2NiO_{12}, and Sr_6Ta_2CoO_{12})$ were identified. All of them are unstable, and decompose above $1400^{\circ}C$. In some cases (Co compounds), intermediate structures between perovskite and K_2NiF_4 -structures appeared in the whole temperature range studied.

(5) Å, $D_x = 3.80$, $D_m = 3.84$ Mg m⁻³, Z = 2. The final R is 0.059 for 139 visually estimated reflections. Mn ions are octahedrally coordinated by Br ions. Each MnBr octahedron shares five vertices with the neighbouring octahedra to form layers of perovskite-type structure, two unit-cells thick, parallel to (100), alternate layers being displaced by a distance $a/\sqrt{2}$ in the [100] direction. Br ions at the unshared vertices are linked to the Br⁻ ions in the adjacent layer of perovskite structure such that each Rb(1) ion is coordinated by nine Br⁻ ions. The Rb(2) ions lie within the layers and each is coordinated by 12 Br⁻ ions. The structure is strictly isomorphous with that of Sr₃Ti₂O₇.