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 alkali oxides of respective composition. By synthesis and investigation of new silver(I)-borates we can demonstrate that these findings hold for the pairs Na₂B₃O₆/Ag₂B₃O₆ and NaB₀₂/AgB₀₂ too.

Ag₂B₃O₆ (Jansen, Scheld, Z.Anorg.Allg.Chem., in press) is dimorphic (Jansen, Brochtel, to be published). Both modifications as well as AgB₀₂ (Brochtel, Jansen, Z.Anorg.Allg.Chem., in press) have been prepared by solid state reaction of the binary components using elevated oxygen pressures (p(O₂) > 1500 bar). The crystal structures of Ag₂B₃O₆(I) and Ag₂B₃O₆(II) are identical with respect to the silver partial structures, whereas the linkages of AgO₆- and B₂O₅-polyhedra is completely different. AgB₀₂ contains instead of the expected cyclo-trimetaborate-anions a B₂O₅-isopolyanion with boron coordinated trigonal-prion in equal parts tetrahedrally and trigonal-planar by oxygen.

The title compound, prepared at 1300°C and 60-65 kbar by reaction of Cr₂O₃ and Ba₂CrO₆ as one of a mixture of products, crystallizes in space group P6₃/mmc, a = 5.649 ± 0.002 Å, c = 32.461 ± 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 BaO₂ layers in Zhdanov notation is [2(1)2(2)3(2)]. All O₆ 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 K₃NiF₅-type 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 1000-1680°C for several periods of time, in air atmosphere.

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

Four new compounds (Sr₂Nb₂O₇, Sr₂Ni₂O₇, Sr₂Ta₂O₇, and Sr₂Nb₂CoO₇) were identified. All of them are unstable, and decompose above 1680°C. In some cases (Co compounds), intermediate structures between perovskite and K₃NiF₅-structures appeared in the whole temperature range studied.

The crystal structures of the compounds were determined by X-ray diffraction at room temperature. The powder-diffraction patterns were indexed, and the lattice constants for the different synthesized compounds were calculated. The structures of the compounds were refined by least squares to a conventional R of 4.1%.