X-Ray Studies on Some Mixed Oxide Systems of Pseudobrookite Structure

GUDRUN ÅSBRINK and ARNE MAGNÉLI

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

Trititanium pentoxide, when in a pure state, shows a rapid, reversible phase transformation at about 120°C. The structure of the low temperature modification has been reported by S. Åsbrink and Magnéli.[1] Detailed investigations of the high temperature form, shortly to be described elsewhere,[2] have shown this structure to be of a monoclinic, slightly distorted pseudobrookite type. The structure of the mineral pseudobrookite (Fe_2TiO_5) is orthorhombic and was determined in 1930 by Pauling.[3] Quite low contents of iron increase the stability range of the high temperature form of Ti_3O_5. Thus the latter exists at room temperature, when only a few per cent of iron are substituted for titanium. This observation formed the starting-point for the present investigation, which so far includes studies on the pseudobinary systems high-Ti_3O_5-Fe_2TiO_5, high-Ti_3O_5-Al_2TiO_5 and high-Ti_3O_5-$MgTi_2O_5$. Al_2TiO_5 and $MgTi_2O_5$ are both isomorphous with Fe_2TiO_5.[4]

High purity preparations of TiO_2, Ti_2O_3, Fe_2O_3, Al_2O_3, and MgO were used as starting materials to press pellets, which were heated either in an electric arc furnace in an argon atmosphere or in evacuated, sealed silica tubes. The latter samples had to be heated for considerable periods of time at about 1150°C in order to reach equilibrium. The preparations thus obtained were investigated by taking X-ray powder photographs in a Guinier type camera. The powder patterns could be interpreted in terms of pseudobrookite structures, orthorhombic or, close to Ti_3O_5, monoclinic. For the Ti_3O_5-Al_2TiO_5 system the unit cell dimensions change smoothly with the composition. The changes are considerably less for the Ti_3O_5-$MgTi_2O_5$ system, but also here they seem to be continuous. The picture is quite different with the Ti_3O_5-Fe_2TiO_5 system, which shows marked discontinuities of the unit cell parameters around the composition $FeTi_2O_5$. This is illustrated in Fig. 1, which indicates the *c* cell parameter *versus* composition behaviour. Discontinuities, although less marked, also occur in the *a* and *b* parameters of the system with iron. It seems natural to assume that the discontinuities around $FeTi_2O_5$ are associated with the distribution and valence states of the metal atoms. Further studies on this matter are in progress including detailed X-ray investigations and applications of various physical techniques, in the first place Mössbauer spectroscopy.

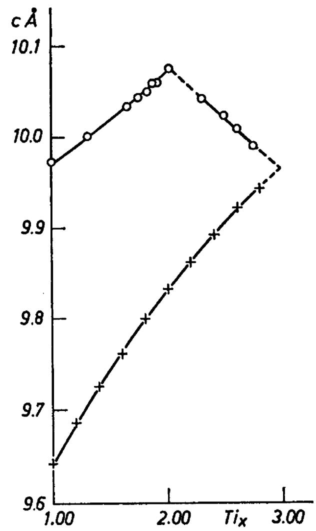

Fig. 1. O represents $Fe_{3-x}Ti_xO_5$ $1 \leq x \leq 3$. + represents $Al_{3-x}Ti_xO_5$ $1 \leq x \leq 3$. By extrapolation the curves intersect at $x = 3$ (*i.e.* Ti_3O_5) and a value of *c* equal to the one observed for high-Ti_3O_5 (at 120°C).

This study forms part of a research program on the structural chemistry of trimetal pentoxides, which is supported by the *Swedish Natural Science Research Council*.

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Received August 11, 1967.