X-Ray Studies on Some Alkali Titanates, $Li_xTi_{4-x/4}O_8$, Rb_xTiO_2 and Cs_xTiO_2

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In the systems A_2O-TiO_2 where A is Na, K or Rb, the crystal structures of several titanates formed in the solid state have been reported.[1-3] When $Na_2Ti_3O_7$ and $K_2Ti_2O_5$ were reduced in hydrogen at 950°C, two different bronzes $Na_xTi_4O_8$ and K_xTiO_2 were formed.[4,5]

In the TiO_2-rich part of the Li_2O-TiO_2 system, one compound, $Li_2Ti_3O_7$, has been reported by Jonker.[6] No structural information was, however, given. In order to complete the picture of the chemistry of the alkali titanates, studies on this compound and also on the reduced titanates of rubidium and cesium were taken up by us.

Li_2CO_3 and TiO_2 were mixed in the mole ratio 1:3, fused and then heated at 1050°C for three days. By means of single crystal studies it was found that the structure of the prepared oxide was of the well known ramsdellite type.[7,8] The following orthorhombic unit cell dimensions were obtained from the Guinier powder pattern. Lines not belonging to the ramsdellite type pattern could not be detected even after strong exposure

$$a = 5.011 \text{ Å}$$
$$b = 9.549 \text{ Å}$$
$$c = 2.948 \text{ Å}$$
$$V = 141.1 \text{ Å}^3$$

The ramsdellite structure type contains eight oxygen and four metal atoms in the unit cell. The structure has tunnels which could accommodate some or all of the lithium atoms.[8] The crystals are colourless, indicating that the titanium atoms have to be in the tetravalent state. This gives the following general composition:

$$Li_xTi_{4-x/4}O_8$$

With the experimentally obtained unit cell volume, densities have been calculated for different integer numbers of x.

X	formula	d_{calc}
1	$LiTi_{3.75}O_8$	3.70
2	$Li_2Ti_{3.5}O_8$	3.64
3	$Li_3Ti_{3.25}O_8$	3.58

Jonker's composition $Li_2Ti_3O_7$ with $x = 16/7$ falls between $Li_2Ti_{3.5}O_8$ and $Li_3Ti_{3.25}O_8$ and gives a calculated density of 3.62 in fair agreement with the observed value of 3.57. A careful study of the stoichiometry of this oxide will be started.

The results of reducing $Rb_2Ti_2O_5$ and $Cs_2Ti_2O_5$ in hydrogen at 900°C for a few hours were analogous to those obtained earlier with $K_2Ti_2O_5$.[5] The colours of the oxides were intensely blue black.

The unit cell dimensions of Cs_xTiO_2, Rb_xTiO_2 and also K_xTiO_2[4] are given below:

K_xTiO_2	$a = 10.17$ Å	$c = 2.85$ Å
Rb_xTiO_2	$a = 10.19$ Å	$c = 2.96$ Å
Cs_xTiO_2	$a = 10.28$ Å	$c = 2.97$ Å

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