Research on the Crystal Structure of R_3O_5 Type Oxides and Classification of sixfold co-ordinated Oxide Crystals

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Introduction

The data of crystal structure of pseudo-brookite ($Fe_2O_3 \cdot TiO_2$), a natural mineral, is as follows.(1)

Pseudo-brookite $Fe_2O_3 \cdot TiO_2$ Orthorhombic

V_h^{17} = Bbmm $a = 9.79$ kX

$Z = 4$ $b = 9.93$ kX

$c = 3.725$ kX

In the previous paper,(2) the author found that $Al_2O_3 \cdot TiO_2$ and $MgO \cdot 2TiO_2$ have the same crystal structure as $Fe_2O_3 \cdot TiO_2$ (R_3O_5 type) and

(1) W. L. Bragg, "Atomic structure of minerals", (1937).
(2) G. Yamaguchi, *J. Ceram. Assoc. Japan*, **55**, 94, (1947).

Table 1

Expected Formula	Mixing Molar Ratio of Powdered Oxides	Sintering Temp. (°C.)	Time (h)	Result*
$Fe_2O_3 \cdot TiO_2$	1 : 1	1250	1	○
$Fe_2O_3SnO_2$	1 : 1	1000, 1250	1	×
$Al_2O_3 \cdot TiO_2$	1 : 1	1250, 1400	1	○
$Al_2O_3 \cdot SnO_2$	1 : 1	1000, 1250	1	×
$MgO \cdot 2TiO_2$	1 : 2	1400	1	○
$MgO \cdot 2SnO_2$	1 : 2	1250	1	×
$CoO \cdot 2TiO_2$	1 : 2	1250, 1400	1	○
$NiO \cdot 2TiO_2$	1 : 2	1250, 1400	1	×
$ZnO \cdot 2TiO_2$	1 : 2	1250	1	○
$ZnO \cdot 2SnO_2$	1 : 2	1250	1	×

* ○…the R_3O_5 type is found by X-rays.
×…the R_3O_5 type is not found.

described a clasification of sixfold coordinated oxide crystals, but, in this paper, other R_3O_5 type oxides and many examples of crystals fitted and not fitted in this classification, shall be described.

Synthetic experiment of R_3O_5 type oxides

Powdered simple oxides were mixed in a definite ratio and sintered at a constant temperature. After cooling, the sintered products were analyzed by X-ray method and their crystal structure was determined. Conditions of synthesis and the results are shown in Table 1, but these conditions are only typical examples of synthesis.

Values of latice constants

Obtained latice constants are shown in Table 2.

Table 2

	Experimental Data (spacing in kX)				Calculated Latice Const		
	d_{002}	d_{430}	d_{322}	d_{320}	a	b	c
$Fe_2O_3\cdot TiO_2$	1.866	1.969	1.541	2.727	9.80	9.93	3.733
$Al_2O_3\cdot TiO_2$	1.798	1.905	1.485	2.641	9.46	9.58	3.596
$MgO\cdot 2TiO_2$	1.867	1.978	1.543	2.739	9.84	9.98	3.734
$CoO\cdot 2TiO_2$	1.862	1.960	1.536	2.713	9.75	9.88	3.724
$ZnO\cdot 2TiO_2$	1.867	1.965	1.540	2.723	9.78	9.90	3.734

Table 3

Type	Positive Results	Negative Results.
RO (NaCl or MgO type)	$Li_2O\cdot Fe_2O_3$ (800) *, $Li_2O\cdot Al_2O_3$ (800), $Li_2O\cdot TiO_2$ (1000)	$Li_2O\cdot Cr_2O_3$, $Li_2O\cdot SnO_2$
R_3O_4 (spinel type)	Al_3O_4 (fused),[3] $MgO\cdot Al_2O_3$ (1250), $CoO\cdot Al_2O_3$ (1200) $NiO\cdot Al_2O_3$ (1100), $CuO\cdot Al_2O_3$ (1100), $ZnO\cdot Al_2O_3$ (1100) $MnO\cdot Al_2O_3$ (1100), $MgO\cdot Fe_2O_3$ (1250), $CoO\cdot Fe_2O_3$ (1250) $NiO\cdot Fe_2O_3$ (1250), $Li_2O\cdot 5Al_2O_3$ (800), $Li_2O\cdot 5Fe_2O_3$ (800), $MgO\cdot Cr_2O_3$ (1250), $2MgO\cdot TiO_2$ (1250), $2ZnO\cdot TiO_2$ (1250), $2MgO\cdot SnO_2$ (1250), $2ZnO\cdot SnO_2$ (1250), $2CoO\cdot SnO_2$ (1250), $CoO\cdot MgO\cdot TiO_2$ (1250) [8.43]†, $CoO\cdot ZnO\cdot TiO_2$ (1250) [8.44], $CoO\cdot MgO\cdot SnO_2$ (1250) [8.57], $CoO\cdot ZnO\cdot SnO_2$ (1250) [8.58], $NiO\cdot CoO\cdot TiO_2$ (1250) [8.40], $NiO\cdot ZnO\cdot TiO_2$ (1250) [8.40], $NiO\cdot MgO\cdot SnO_2$ (1250) [8.54], $NiO\cdot ZnO\cdot SnO_2$ (1250) [8.53], $CuO\cdot MgO\cdot TiO_2$ (1100) [8.43], $CuO\cdot CoO\cdot TiO_2$ (1100) [8.43], $CuO\cdot ZnO\cdot TiO_2$ (1000) [8.44], $MnO\cdot MgO\cdot TiO_2$ (1100) [8.46], $MnO\cdot CoO\cdot TiO_2$ (1100) [8.47], $MnO\cdot MgO\cdot SnO_2$ (1250) [8.64], $MnO\cdot CoO\cdot SnO_2$ (1250) [8.66]	$Li_2O\cdot 5Cr_2O_3$, $2NiO\cdot TiO_2$, $2NiO\cdot SnO_2$, $NiO\cdot MgO\cdot TiO_2$, $NiO\cdot CuO\cdot SnO_2$, $CuO\cdot MgO\cdot SnO_2$(?)**, $CuO\cdot CoO\cdot SnO_2$(?), $CuO\cdot ZnO\cdot SnO_2$, $2CuO\cdot TiO_2$, $2CuO\cdot SnO_2$, $MnO\cdot ZnO\cdot TiO_2$, $MnO\cdot ZnO\cdot SnO_2$, $2MnO\cdot TiO_2$,†† $2MnO\cdot SnO_2$
$RO_{4/3\sim 3/2}$ (imperfect spinel type)	$MgO\cdot xAl_2O_3$ (sintered or fused), $CoO\cdot xAl_2O_3$ (sintered), $x > 1$ $NiO\cdot xAl_2O_3$ (sintered), $Li_2O\cdot yAl_2O_3$ (Sintered) $y > 5$	
R_2O_3 (Cr_2O_3 type)	$MgO\cdot TiO_2$ (1250), $CoO\cdot TiO_2$ (1250), $NiO\cdot TiO_2$ (1250), $(0.8NiO\cdot 0.2CoO)\cdot TiO_2$ (1250), $(0.9NiO\cdot 0.1CoO)\cdot TiO_2$ (1250)	$CuO\cdot TiO_2$, $MgO\cdot SnO_2$, $NiO\cdot SnO_2$
R_3O_5 ($Fe_2O_3\cdot TiO_2$ type)	$Fe_2O_3\cdot TiO_2$ (1400), $Al_2O_3\cdot TiO_2$ (1400), $MgO\cdot 2TiO_2$ (1400), $CoO\cdot 2TiO_2$ (1400), $ZnO\cdot 2TiO_2$ (1400)	$Al_2O_3\cdot SnO_2$, $MgO\cdot 2TiO_2$, $Fe_2O_3\cdot SnO_2$, $MgO\cdot 2SnO_2$,
RO_2 (SnO_2 type)	TiO_2, SnO_2	$CoO\cdot 2SnO_2$, $ZnO\cdot 2SnO_2$

* ( )……one example of sintering temp. (°C) in author's experiment.

† [ ]……latice constant (kX) of spinel which is not listed in "Crystal Structure, Vol. 2" by Wyckoff.

** (?)……doubtful.

†† $2MnO\cdot TiO_2$ is listed as spinel in the Wyckoff's book.

(3) "Aluminium suboxide" G. Yamaguchi, *J. Electrochem. Assoc. Japan*, **14**, 106 (1946); *J. Ceram. Assoc. Japan*, **55**, 42 (1947). *Bull. Chem. Soc. Japan*, **23**, 90 (1952)

Classification of sixfold coordinated oxide crystals and results of synthesis.—Four types of the oxide crystals (RO, R_3O_4, R_2O_3, RO_2) are known, but the author proposes to add the new type, R_3O_5, according to the results of this paper, and the imperfect spinel type ($RO_{4/3\sim3/2}$). The author's extended classification with examples of positive and negative results is as Table 3.

Result

1. Latice constants of R_3O_5 type crystals ($Fe_2O_3 \cdot TiO_2$, $Al_2O_3 \cdot TiO_2$, $MgO \cdot 2TiO_2$, $CoO \cdot 2TiO_2$, $ZnO \cdot 2TiO_2$) are determined.

2. Crystal structures of interoxide compounds of metals, whose coordination number of oxygen is six, are classified into six types; RO(NaCl or MgO type), R_3O_4 (spinel type), $RO_{4/3\sim3/2}$ (imperfect spinel type), R_2O_3 (Cr_2O_3 type), R_3O_5($Fe_2O_3 \cdot TiO_2$ type), RO_2(SnO_2 type). Between interoxide compounds of the same type, formation of solid solution is expected.

3. SnO_2 fits into this theory only in the case of spinel formation.

4. NiO and CuO have almost no acidic property, so that in the cases of formation of R_3O_4 and R_3O_5, they act peculiarly.

5. The author proposes to give the name of "definite ratio solid solution" to crystals of those interoxide compounds when metal atoms are distributed at random at latice points.

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