Stability of Two Cobalt Titanate Defect Spinels

JOHN P. SHARPLES AND ALEXANDRA NAVROTSKY*
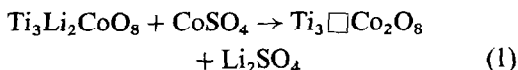
Department of Chemistry, Arizona State University, Tempe, Arizona 85281

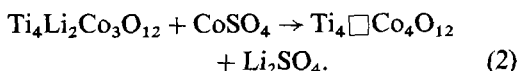Preparation of the defect spinels $Ti_3\square Co_2O_8$ and $Ti_4\square Co_4O_{12}$ was attempted by solid state exchange reactions. $Ti_4\square Co_4O_{12}$ was successfully synthesized but attempts at preparing pure $Ti_3\square Co_2O_8$ were unsuccessful, The enthalpy of transformation of $\frac{1}{4}Ti_4\square Co_4O_{12}$ to $CoTiO_3$ (ilmenite) was determined by calorimetry, $\Delta H^\circ_{298} = -1.7 \pm 1.0$ kcal/mole.

1. Introduction

It has been shown that nonstoichiometric spinels with ordered vacancies can be synthesized by solid state exchange reactions between lithium-containing spinels and salts containing a dipositive cation (*1*), for example

$$Ti_3Li_2CoO_8 + CoSO_4 \rightarrow Ti_3\square Co_2O_8$$
$$+ Li_2SO_4 \qquad (1)$$

or

$$Ti_4Li_2Co_3O_{12} + CoSO_4 \rightarrow Ti_4\square Co_4O_{12}$$
$$+ Li_2SO_4. \qquad (2)$$

The defect spinels form only in a narrow temperature range and decompose exothermically to more stable phase assemblages at higher temperatures. The purpose of this study was to attempt to prepare the two spinels above and to measure their enthalpies of transformation to the stable ilmenite-containing assemblages

$$Ti_3\square Co_2O_8 \rightarrow 2\, CoTiO_3 + TiO_2 \qquad (3)$$
$$Ti_4\square Co_3O_{12} \rightarrow 4\, CoTiO_3 \qquad (4)$$

by high temperature calorimetry.

2. Experimental

2.1. Preparation of Starting Spinels

The spinels $Ti_3Li_2CoO_8$ and $Ti_4Li_2Co_3O_{12}$ were prepared from stoichiometric mixtures

* To whom all correspondence should be addressed.

of dried Co_3O_4, Li_2CO_3, and TiO_2, ground together under acetone, and heated in a platinum crucible in a muffle furnace, first for three days at 900°C and then for three days at 1000°C. This heat treatment minimized vaporization loss of unreacted lithium oxide and produced single phase spinels, as shown by X-ray powder diffraction of both samples.

2.2. Preparation of Defect Spinels

The method described by Joubert (*1*) was followed. Each starting spinel was ground together with $CoSO_4 \cdot 7H_2O$ in a 1:10 weight ratio. The mixture was pressed into pellets (using a pressure of ~2000 lbs/in.² = 138 bars) to increase contact between grains, and the pellets were placed in a quartz crucible in a cold furnace. The furnace was gradually heated to the desired temperature and the sample allowed to remain for a specified time. The temperatures and times used are shown in Table I. The results of early runs were used to optimize conditions in later experiments.

Upon completion of the reaction period, the product was washed thoroughly with distilled water to remove Li_2SO_4 and $CoSO_4$. Washing was continued until the filtrate tested free of Li and Co. In general, this procedure included an overnight leaching with distilled water. The sample was filtered and analyzed by X-ray diffraction to establish whether the spinel structure had been retained

TABLE I

RESULTS OF EXCHANGE REACTIONS

Initial composition	T (°C)	Time (days)	Phases present	Analysis	
				Initial wt % Li	Final wt % Li
$Ti_3Li_2CoO_8$	473	10	$CoTiO_3$		
	441	4	$CoTiO_3$		
	380	4	$CoTiO_3$		
	367	2	Spinel	3.70	1.20
	359	14	Spinel	3.70	1.32
	348	4	Spinel	3.70	1.02
	323	6	Spinel	3.70	1.17
$Ti_4Li_2Co_3O_{12}$ (a)	417	14	$(Ti_4Co\square)Co_3O_{12}$	2.42	0.00
$Ti_4Li_2Co_3O_{12}$ (b)	386	14	$(Ti_4Co\square)Co_3O_{12}$	2.42	0.00
$Ti_4Li_2Co_3O_{12}$ (c)	433	14	$(Ti_4Co\square)Co_3O_{12}$	2.42	0.00

during the reaction or if decomposition had occurred. Flame emission analysis was employed to determine the extent to which the lithium present in the starting spinel had been displaced during the reaction. The flame analysis was carried out on a 0.35 mm monochromator (Heath Kit EU-701-30) spectrophotometer, using the 670.8 nm Li line. In addition, a semiquantitative atomic absorption cobalt analysis established an increase in cobalt during the reaction. This increase paralleled the loss of lithium.

2.3. Calorimetry

The high temperature Calvet-type twin microcalorimeter used has been described previously (2). Experiments were of the "transposed-temperature-drop" type (3), that is, samples were dropped from room temperature into the calorimeter by 810°C. Each calorimetric sample consisted of about 100 mg of defect spinel encapsulated in about 150 mg of platinum. The first time a sample was dropped, it transformed to the more stable assemblage in the calorimeter. The measured heat effect consisted of the heat content of the defect spinel and of the platinum, plus the enthalpy of the transition. The second time a capsule was dropped, the heat absorbed consisted of the heat content of the transformed material (ilmenite) and of the platinum

capsule. From the difference between the average values obtained in drops of the first and second type, the enthalpy of the transition at room temperature (See Table III) was calculated. The total heat effect measured in each experiment was about 20 cal. Calibration of the calorimeter was achieved by dropping pieces of platinum wire of known weight into the calorimeter, and using the heat content equation of Kelley (4) to calculate the heat effects obtained.

3. Results and Discussion

A. Initial Composition $Ti_3Li_2CoO_8$

The results of exchange experiments are shown in Table I. Although samples run below about 380°C retained the spinel structure and lost some lithium, the final product $Ti_3\square Co_2O_8$, which would contain no lithium, was never obtained. Indeed, all the samples, regardless of the temperature of reaction (323–367°C) or time of reaction (2–14 days) showed surprisingly comparable amounts of residual lithium, namely about one-fourth of that initially present. These results are at variance with those of Joubert (1) in two respects. First, he reports that the defect spinel can be prepared at 480°C, whereas we observe decomposition to ilmenite above 370°C. Such differences may

well be attributed to differences in particle size and impurity contents of the samples, although, see below, we had no difficulty duplicating his reported $CoTiO_3$ preparation with our starting materials. Secondly, Joubert does not report any lithium analyses on his samples, but relies on reaching a constant X-ray intensity ratio to indicate complete reactions. Our X-ray intensities (see Table II) agree with his fairly well, but our analyses show lithium. We interpret our results to mean that the "pure" defect spinel $(Ti_3\square$-$Co_2O_8)$ probably cannot be made, and we question whether Joubert's spinel was really lithium-free. A structural reason for the instability of $(Ti_3\square Co_2O_8)$ is not readily apparent.

We believe that the lithium found in the analysis truly is in the spinel phase (rather than adsorbed on it) for several reasons. The washing procedure used was quite elaborate and no difficulty was obtained with the other preparation. The amount of lithium in the defect spinel is large, of the order of one-fourth of the initial amount, and no other phases are visible, either in the X-ray patterns or in grain mounts under the microscope. The semiquantitative cobalt analysis suggested that the amount of cobalt in the sample was less than that required for complete substitution.

B. Initial Composition $Ti_4Li_2Co_3O_{12}$

This preparation presented no difficulty under the conditions given by Joubert (1). The X-ray powder pattern of the spinel is shown in Table II. No lithium could be detected in this spinel; the limit of detectability, based on a 10 mg sample, being 2×10^{-4} ppm lithium in solution which corresponds to $1 \times 10^{-4}\%$ by weight Li in the spinel.

The calorimetric results are shown in Table III.

The heat content data show a substantially larger standard deviation for the first group of experiments (starting with untransformed defect spinel) than for the second group (dropping sample already transformed to the ilmenite structure). Three separate preparations of the defect spinel were used for calorimetry, with no systematic difference among

TABLE II

COMPARISON OF X-RAY PATTERNS

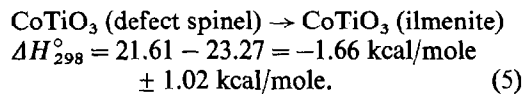|		Sharples		Joubert	
		$Ti_3\square Co_2O_8$			
$h\,k\,l$		d_{obs}	I_{obs}	d_{obs}	I_{obs}
1 1 0		—	—	5.96	23
1 1 1		—	—	4.85	4
2 1 0		3.77	15	3.76	19
2 1 1		3.45	12	3.43	15
2 2 0		2.98	40	2.97	50
2 2 1			0	2.80	3
3 1 0		2.66	5	2.66	5
3 1 1		2.54	100	2.53	100
2 2 2			0	2.42	1
3 2 0		2.34	3	2.33	3
3 2 1		2.25	2	2.24	2
4 0 0		2.10	27	2.10	16
4 1 0, 3 2 2		2.04	2	2.03	1
4 1 1, 3 3 0		1.985	2	1.977	1
3 3 1		1.933	2	1.927	1
4 2 0			0		0
4 2 1		1.841	7	1.829	6
3 3 2			0		0
4 2 2		1.722	16	1.709	18
4 3 0		1.689	1	1.674	1
5 1 0, 4 3 1		1.656	2	1.642	1
5 1 1, 3 3 3		1.621	40	1.612	42
5 2 0, 4 3 2		1.565	4	1.555	4
5 2 1		1.537	6	1.529	5
4 4 0		1.486	50	1.481	51
		$Ti_4\square Co_4O_{12}$			
1 1 0		—	—		
1 1 1		—	—		
2 1 0		3.81	16		
2 1 1		3.48	14		
2 2 0		3.01	41		
2 2 1		2.89	5		
3 1 0		2.68	4		
3 1 1		2.56	100		
2 2 2		2.46	11		
3 2 0		2.36	4		
3 2 1		2.26	2		
4 0 0		2.12	15		
4 1 0, 3 2 2		2.04	3		
4 1 1, 3 3 0		1.997	2		
3 1 1		1.941	2		
4 2 0			0		
4 2 1		1.844	7		
3 3 2			0		
4 2 2		1.724	17		
4 3 0		1.692	1		
5 1 0, 4 3 1		1.658	1		
5 1 1, 3 3 3		1.626	32		
5 2 0, 4 3 2		1.575	5		
5 2 1		1.541	5		
4 4 0		1.492	43		

TABLE III

CALORIMETRIC RESULTS

Preparation	Sample wt (mg) Defect spinel	Pt wt (mg)	Total calories $\frac{1}{4}Ti_4\square Co_4O_{12}$	Calories absorbed by sample	ΔH (kcal/mole)
a	108.10	169.30	20.205	15.706	22.502
a	99.60	179.10	19.478	14.726	22.895
a	99.20	156.00	18.418	14.275	22.291
b	100.81	159.53	18.894	14.680	22.548
b	105.70	181.22	19.205	14.411	21.110
b	107.77	177.63	19.561	14.868	21.361
b	110.00	183.26	19.011	14.171	19.947
b	105.39	190.27	19.465	14.440	21.215
b	103.89	186.03	19.188	14.274	21.273
b	103.05	191.99	19.079	14.009	21.048
b	101.53	191.23	19.317	14.267	21.757
c	107.42	168.71	18.935	14.371	20.713
c	101.32	181.17	19.293	14.397	22.001
c	102.39	159.61	17.932	13.593	20.555
c	109.12	162.08	20.590	16.186	22.967

average = 21.61 ± 0.90 (15)[a]

Ilmenite CoTiO₃

	107.50	160.70	20.847	16.574	23.872
	68.90	142.50	13.892	10.107	22.713
	105.90	136.40	19.901	16.278	23.803
	108.80	179.725	21.725	16.958	24.133
	105.30	179.80	20.568	15.793	23.221
	108.19	178.18	20.727	16.021	22.928
	103.21	164.58	19.855	15.508	23.264
	108.30	145.27	20.002	16.165	23.111
	102.23	181.67	20.401	15.604	23.633
	113.80	184.73	21.810	16.931	23.037
	104.93	176.91	20.159	15.487	22.852
	105.60	155.86	19.665	15.464	22.673

average = 23.27 ± 0.48 (12)

[a] Error estimated is standard deviation, number in parenthesis is number of experiments done.

them, but the observed scatter was seen in each case. The reason for this is not clear; possibilities include (1) inhomogeneity of the defect spinel, (2) some variation in the completeness of cation and vacancy ordering, and (3) incomplete transformation to ilmenite during the drop experiment. The last seems unlikely since a sample held at 800° for 5 min showed no trace of spinel in its diffraction pattern. The estimated error in the reported enthalpy of transformation reflects this problem.

For the reaction

CoTiO₃ (defect spinel) → CoTiO₃ (ilmenite)

$$\Delta H^\circ_{298} = 21.61 - 23.27 = -1.66 \text{ kcal/mole}$$
$$\pm 1.02 \text{ kcal/mole.} \quad (5)$$

The fairly small exothermic heat of decomposition indicates that although this defect spinel is indeed metastable with respect to the ilmenite structure, it is not very metastable. One can compare its enthalpy of transformation with that for the $\gamma \to \alpha$ transition

in Al_2O_3 and Fe_2O_3, $\Delta H^{\circ}_{298} - 5.3$ kcal/mole (5), and -3.3 kcal/mole (6), respectively.

In all three of these transitions, the basic structural change is from cubic to hexagonal close packed oxygens, with a redistribution of cations. The ilmenite structure is, of course, related to the corundum structure by the ordered replacements of $2M^{3+}$ by M^{2+} and M^{4+}. Although the defect structures of γ-Al_2O_3 and γ-Fe_2O_3 are not known with complete certainty (7, 8), the structural and calorimetric data suggest that the defect spinel becomes less metastable with increasing ordering of the vacancies (a better developed superstructure), that is, in the series Al_2O_3, Fe_2O_3, $CoTiO_3$.

Acknowledgments

References

1. J. C. JOUBERT, G. BERTHET, AND E. F. BERTAUT, Bull. Soc. Franc. Mineral. Crist. 90, 589 (1967).
2. A. NAVROTSKY AND O. J. KLEPPA, J. Inorg. Nucl. Chem. 30, 479 (1968).
3. J. L. HOLM, O. J. KLEPPA, AND E. F. WESTRUM, SR., Geochim. Cosmochim. Acta 31, 2289 (1967).
4. K. K. KELLEY, U.S. Bur. Mines Bull. 584 (1960).
5. T. YOKOKAWA AND O. J. KLEPPA, J. Phys. Chem. 68, 3246 (1964).
6. ALBERT FERRIER, C.R. Acad Sci. Paris, C 264, 819 (1967).
7. K. P. SINHA AND A. P. B. SINHA, J. Phys. Chem. (London) 61, 758 (1957).
8. G. W. VAN OOSTERHOUT AND C. J. M. ROOYMANS, Nature (London) 181, 44 (1958).