

BRIEF COMMUNICATIONS

The Series of Spinel $\text{Co}_{3-s}\text{Al}_s\text{O}_4$ ($0 < s < 2$): Study of Co_2AlO_4

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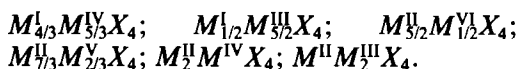
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Co(III) of Co_3O_4 can be gradually replaced by Al to produce the series of spinels $\text{Co}_{3-s}\text{Al}_s\text{O}_4$ ($0 < s < 2$), S.G. *Fd3m* (No. 227), $Z = 8$. For Co_2AlO_4 ($s = 1$), $a = 8.086(1)\text{Å}$, $U = 528.7(2)\text{Å}^3$, $D_x = 5.25\text{Mgm}^{-3}$, $u = 0.264$, and 27% of Al in 8(a) positions, $R = 0.031$. The frequencies of the observed ir absorption bands of Co_2AlO_4 are also presented.

Introduction

The spinels are crystalline solids well known to mineralogists, chemists, and solid-state physicists. The most abundant spinel groups, of stoichiometry AB_2X_4 , are those formed by some metals in oxidation states II-III and II-IV. X usually stands for oxygen or one chalcogen. Stoichiometries as $\text{Co}_{7/3}\text{Sb}_{2/3}\text{O}_4$, $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$, $\text{Cu}_{1/2}\text{Fe}_{5/2}\text{O}_4$, LiAlSiO_4 , LiZnSbO_4 , CrMnNiO_4 , are also known. All these compounds can be represented by M_3X_4 , M denoting the same or different metals. For a nondeficient spinel containing two metals, M , M' , in oxidation states m , m' , respectively, and divalent X anions, the formula $\text{M}_b\text{M}'_c\text{X}_4$, wherein $b = (3m' - 8)/(m' - m)$; $c = (8 - 3m)/(m' - m)$; includes all the possible stoichiometries, i.e., $\text{M}_2^{\text{I}}\text{M}'^{\text{VI}}\text{X}_4$; $\text{M}_{7/4}^{\text{I}}\text{M}'_{5/4}\text{X}_4$;



b and c values are obtained if electroneutrality is assumed and by requiring that the sum of b and c has to be equal to three. For three metals, M , M' , M'' , in oxidation states m , m' , m'' , the series $\text{M}_s\text{M}'_d\text{M}''_e\text{X}_4$, where $d = (8 - 3m'' - ms + m's)/(m' - m'')$; $e = (3m' - 8 + ms - m's)/(m' - m'')$ is encountered with s , d , and e positive.

The spinel CoAl_2O_4 , the so-called *Thénard blue*, has been known for a long time and has been extensively studied (1, 2). It may be considered as derived from $\text{Co}^{\text{II}}\text{Co}_2^{\text{III}}\text{O}_4$ by replacing all the Co^{III} with Al. This paper deals with the $\text{Co}^{\text{II}}\text{Co}_{2-s}^{\text{III}}\text{Al}_s\text{O}_4$ ($0 < s < 2$) series, which arises when the above-mentioned substitution is carried out in steps. The spinel structure type, M_3X_4 , is based on a cubic closest-packed array of X^{2-} ions, with the M ions occupying one-eighth of the tetrahedral and

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one-half of the octahedral sites, $M_x[M_{3-x}]$. The brackets represent octahedral site occupations and M may represent as before, either one or several metals. In a spinel MM'_2X_4 two extreme distributions of the cations among the available sites are possible: the so-called normal, $M[M'_2]X_4$, and the inverse distribution, $M'[MM']X_4$. Intermediate cation distributions, $M_{1-x}M'_x[M_xM'_{2-x}]$, are also possible. Here x is the degree of inversion, equal to zero and unity for the normal and inverse arrangements, respectively. When referred to space group $Fd\bar{3}m$, $Z = 8$, and origin at center, ($\bar{3}m$), the 24 cations occupy 8 tetrahedral (a) positions, 1/8, 1/8, 1/8, and 16 octahedral (d) positions, 1/2, 1/2, 1/2; and the anions are located on 32(e) positions, u, u, u . Therefore, letting a be the unit-cell parameter, the significant distances in the spinel unit-cell are

At tetrahedral (a) positions:

$$M-X = a^{3/2}(u - 1/8)$$

$$X-X = a^{2/2}(2u - 1/4)$$

At octahedral (d) positions:

$$M-X = a(3u^2 - 2u + 3/8)^{1/2}$$

$$X-X = a^{2/2}(3/4 - 2u)$$

$$X-X' = a(4u^2 - 2u + 3/8)^{1/2}$$

Variations in u reflect the adjustment of the structure to accommodate differences in the relative radii of the cations in the tetrahedral and octahedral sites. When $u = 0.250$, the X anions are arranged in an ideal cubic closest-packing arrangement. This particular situation and the cases $u < 0.250$ are rarely realized; more often u value lies in the range 0.251 to 0.269.

In order to study a particular spinel, three variables have to be established: the cell dimension, a ; the positional parameter, u , for oxygen atoms; and the distribution of cations, x , between tetrahedral and octahedral sites. It is the aim of this paper to establish these parameters for $\text{Co}^{\text{II}}\text{Co}^{\text{III}}\text{AlO}_4$, middle term of the above-mentioned spinel series.

Experimental

Mixtures of analytical grade Co_3O_4 and $\gamma\text{-Al}_2\text{O}_3$ in the molar ratios $\text{Co}_3\text{O}_4 : \text{Al}_2\text{O}_3 = (6 - 2s) : 3s$ ($s = 0.25, 0.50 \dots 1.75$), were heated in air at 1073 K for 24 hr, to obtain seven samples of the series $\text{Co}_{3-s}\text{Al}_s\text{O}_4$. Experimental conditions and details on the analysis of the X-ray diffraction data have been described elsewhere (3). The unit-cell parameter of Co_2AlO_4 was refined from the 2θ values of the last eight reflections; the arbitrarily chosen Debye-Waller factors, B_j , for the calculation of the intensities, were 0.80 and 0.60 \AA^2 for the oxygen and Co atoms, respectively; the value, 0.75 \AA^2 , for Al was obtained from these two by interpolation of the atomic mass of Al between those of Co and O. The intensities were calculated in two stages. First, six runs including 36 jobs were performed for $u = 0.250, 0.255, 0.260, 0.2625, 0.265, 0.270$ and $x = 0, 10, 20, 30, 33, 40$. The second stage included 54 jobs for the following u and x values: $u = 0.261, 0.262, 0.2625, 0.263, 0.264, 0.265, 0.266, 0.267, 0.268$; $x = 25, 26, 27, 28, 29, 30$. Infrared spectra were recorded using a Perkin-Elmer 325 spectrophotometer, KBr disks and Nujol oil mulls.

Results

The seven samples were obtained as blackish blue powders, which produced good X-ray diffraction patterns characteristic of spinels, space group $Fd\bar{3}m$ (No. 227). The a values exhibited slight variations, confirming the existence of the $\text{Co}^{\text{II}}\text{Co}^{\text{III}}_{2-s}\text{Al}_s\text{O}_4$ ($0 < s < 2$) series. The observed and calculated interplanar spacings, d_o and d_c , for Co_2AlO_4 , the middle term of the series, are included in Table I. Thus, Co_2AlO_4 is a spinel, with $a = 8.086(1) \text{\AA}$, $U = 528.7(2) \text{\AA}^3$, $Z = 8$, and $D_x = 5.25 \text{Mgm}^{-3}$. The observed, I_o , and calculated, I_c , inten-

TABLE I
X-RAY POWDER DIFFRACTION DATA FOR Co_2AlO_4

<i>hkl</i>	d_o	d_c	I_o	I_c
111	4.670	4.669	147	149
220	2.860	2.859	352	348
311	2.439	2.438	1,052	1,000
222	2.3337	2.3342	64	48
400	2.0214	2.0215	207	235
422	1.6505	1.6505	95	96
511,333	1.5568	1.5562	356	362
440	1.4294	1.4294	420	431
531	1.3668	1.3668	10	13
600,442	—	1.3477	—	1
620	1.2784	1.2785	25	30
533	1.2331	1.2331	86	84
622	1.2189	1.2190	33	33
444	1.1672	1.1671	23	26
711,551	—	1.1323	—	10
642	1.0806	1.0805	34	45
731,553	1.0528	1.0527	124	124
800	1.0107	1.0108	48	52
733	—	0.9879	—	1
822,660	0.9530	0.9529	24	25
751,555	0.9336	0.9337	92	91
662	0.9275	0.9275	24	20
840	0.9041	0.9040	35	34
911,753	—	0.8876	—	6
842	—	0.8823	—	1
664	—	0.8620	—	9
931	0.8476	0.8476	104	106
844	0.8254	0.8253	219	201
933,771,755	—	0.8127	—	5
10.20,862	0.7930	0.7929	66	70
951,773	0.7817	0.7817	306	326

sities which gave the best discrepancy factor, $R = (\sum |I_o^{1/2} - I_c^{1/2}|) / \sum I_o^{1/2} = 0.031$, are also included in Table I, and were obtained for $u = 0.264$, with the origin at center, $(\bar{3}m)$, and $x = 27\%$ of Al atoms in tetrahedral (*a*) sites. The M–O and O–O distances for $\text{Al}_{0.27}\text{Co}_{0.73}[\text{Al}_{0.73}\text{Co}_{1.27}]\text{O}_4$ were: for tetrahedral (*a*) sites, M–O = 1.947 Å, O–O = 3.179 Å; and for octahedral (*d*) sites, M–O = 1.915 Å, O–O = 2.539 Å, O–O' = 2.868 Å.

Table II includes the frequencies (cm^{-1}) of the observed infrared absorption bands

TABLE II
FREQUENCIES (cm^{-1}) OF THE IR ABSORPTION BANDS OBSERVED FOR Co_2AlO_4 , AS COMPARED WITH THOSE REPORTED^a FOR Co_3O_4 AND CoAl_2O_4

Compound	ν_1	ν_2	ν_3	ν_4
Co_2AlO_4	656	564	383	217
Co_3O_4	672	590	392	220
CoAl_2O_4	684	563	523	237

^a J. Preudhomme and P. Tarte, Ref. (4).

for Co_2AlO_4 as well as those for Co_3O_4 and CoAl_2O_4 measured by Preudhomme and Tarte (4). These authors studied the infrared spectra of normal $A^{II}[B_2^{III}]$ spinels ($x = 0$) in which four bands, corresponding to the four infrared-active modes T_{1u} , are observed. They showed that the two ν_1 and ν_2 bands are related to the vibrations of the lattice of octahedral groups, and that two low-frequency bands, ν_3 and ν_4 , correspond to complex vibrations involving the participation of both the tetrahedral and the octahedral cations. These assignments were deduced for the normal cation distributions and cannot be applied to inverse spinels. More recently, Toriumi and co-workers (5) have shown that CoAl_2O_4 is not a normal spinel ($x = 0.155$). The assignments proposed by Preudhomme and Tarte (4) thus are not applicable to CoAl_2O_4 . This is also the case for Co_2AlO_4 . Nevertheless, the partial substitution of Co^{III} from Co_3O_4 by Al to give Co_2AlO_4 is accompanied by a rather slight lowering of the four frequencies. By contrast, CoAl_2O_4 exhibits an erratic variation of these frequencies which is especially pronounced for ν_3 .

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