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PREPARATION AND CRYSTAL DATA OF THE SPINEL SERIES $Co_{1+2s}Cr_{2-3s}Sb_sO_4$ $(0 \leqslant s \leqslant \frac{2}{3})$

P. GARCÍA CASADO
Facultad de Farmacia, Universidad de Navarra, E-31080 Pamplona, Spain

and

I. RASINES*
Instituto Elhúyar, Serrano 113, E-28006 Madrid, Spain

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Abstract—Eight polycrystalline materials of the new spinel series $Co_{1+2s}Cr_{2-3s}Sb_sO_4$ ($s = 0$, 0.10 ... 0.60 or 0.67) have been prepared and studied by X-ray powder diffraction. The series goes from $CoCr_2O_4$ ($s = 0$) to $Co_{7/3}Sb_{2/3}O_4$ ($s = \frac{2}{3}$), with a gradually increasing from 8,3346(3) ($s = 0$) to 8.5330(6) Å ($s = \frac{2}{3}$), and u slightly decreasing from 0.261 ($s = 0$) to 0.258 ($s = \frac{2}{3}$). Interatomic distances are given. The series may be thought as the result of progressive substitution of Cr^{3+} by $\frac{2}{3}Co^{2+} + \frac{1}{3}Sb^{5+}$ in the normal spinel $CoCr_2O_4$. This substitution can be total, so that $CoCr_2O_4$ *becomes* $Co_{7/3}Sb_{2/3}O_4$.

Recently the authors have suggested[1,2] that an oxide spinel constituted by three equal or different metals, M, M′ and M″, in oxidation states m, m' and m'', can be a member of the series $M_sM'_dM''_eO_4$, where $d = (8-3m''-ms+m''s)/(m'-m'')$ and $e = (3m'-8+ms-m's)/(m'-m'')$, s, d and e being positive. This suggestion has been confirmed for the series $Co_{3-s}Al_sO_4$ $(0 \leqslant s \leqslant 2)$,[1] and $Mn_{1+s}Cr_{2-3s}Sb_sO_4$ $(0.05 \leqslant s \leqslant 0.30)$.[2] This second series may be conceived of as the result of partial substitution of Cr^{3+} by $\frac{2}{3}Mn^{2+} + \frac{1}{3}Sb^{5+}$ in the normal spinel $MnCr_2O_4$. At first sight the mentioned substitution could be performed for s values up to $\frac{2}{3}$, but in fact it could not be accomplished for $s > \frac{1}{3}$, because in these cases a mixture of phases was found.[2]

The hypothetical series $M(II)_{1+2s}Cr_{2-3s}Sb_sO_4$ is limited by two compounds: for $s = 0$, the *chromite* MCr_2O_4; for $s = \frac{2}{3}$, the oxide $M_{7/3}Sb_{2/3}O_4$. Whereas all the *chromites* are spinels, only two $M_{7/3}Sb_{2/3}O_4$ compounds with spinel structure are known,[3] those of Co and Zn. Thus, in these two cases it seems feasible to prepare the complete series $M_{1+2s}Cr_{2-3s}Sb_sO_4$, i.e. for s values from zero up to $\frac{2}{3}$. In fact, the oxide for which M = Co and $s = 0.50$ has been described[4] as a spinel with $a = 8.499$ Å.

This paper aims to report how the series $Co_{1+2s}Cr_{2-3s}Sb_sO_4$ was prepared and the X-ray diffraction data for eight samples ($s = 0, 0.10 \ldots 0.60$ or 0.67) of the series. These data are relevant especially for the first and last members, because dark green $CoCr_2O_4$ has been known since 1927, but it has not been completely studied: according to the last investigation[5] its lattice constant a was 8.332 ± 0.005 Å, but the oxygen positional parameter (u) was not determined. On the other hand, for black $Co_{7/3}Sb_{2/3}O_4$, $a = 9.523$ Å; and $u = 0.255 \pm 0.005$, origin at center, ($\bar{3}m$), was determined[6] from the intensity ratios of some reflections.

EXPERIMENTAL

The samples were prepared from mixtures of analytical grade Co_3O_4, Cr_2O_3 and Sb_2O_3, of molar ratios Co : Cr : Sb = $(1+2s):(2-3s):s$ ($s = 0, 0.10 \ldots 0.60$ or 0.67), which were heated in air at 953, 1173, 1273, 1473 and 1500 K during 1 day. After each thermal treatment the materials were quenched and ground. Additional experimental details were as indicated elsewhere.[7] The unit-cell parameters, a,

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* Author to whom correspondence should be addressed.

were refined from the 2θ values of at least eight of the last 12 reflections using the program PARAM.[8] The intensities were calculated with the program LAZY-PULVERIX,[9] using scattering factors for neutral atoms, Debye–Waller, Lorentz and polarization factors, and correction for anomalous dispersion. The arbitrarily chosen Debye–Waller factors, B_j, for the calculation of the intensities were 0.30 and 0.80 Å^2 for Sb and oxygen atoms respectively; the values 0.60 and 0.63 Å^2 for Co and Cr, respectively, were obtained from these two by interpolation of the respective atomic masses between those of oxygen and Sb. Intensities were calculated for u equal to 0.255, 0.256 ... 0.263, origin at centre, $(\bar{3}m)$, and assuming tetrahedral (a) sites occupied by Co atoms for all the samples. The disrepancy factor between observed and calculated intensities:

$$R = (\sum |I_o^{1/2} - I_c^{1/2}|)/\sum I_o^{1/2}$$

was computed after making $\sum I_o$ equal to $\sum I_c$, and taking into account all the reflections with $I_o > 5$. For each member of the series, the u value taken as observed was that leading to the smallest R.

RESULTS AND DISCUSSION

The eight samples of composition $Co_{1+2s}Cr_{2-3s}Sb_sO_4$ ($0 \leqslant s \leqslant \frac{2}{3}$) were obtained as powders coloured from dark grey blue ($s = 0$), blackish blue ($s = 0.10$ and 0.20) to black ($s = 0.30$, 0.40 ... 0.67), which gave good X-ray diffraction patterns* characteristic of spinels. The a values showed a gradual variation, confirming the existence of the series. Thus, $Co_{1+2s}Cr_{2-3s}Sb_sO_4$ ($0 \leqslant s \leqslant \frac{2}{3}$) is a series of cubic spinels, space group $Fd\bar{3}m$ (No. 227), $Z = 8$, with the a and observed u_o values which are shown in Table 1. For $CoCr_2O_4$, $Co_2Cr_{0.5}Sb_{0.5}O_4$, and $Co_{7/3}Sb_{2/3}O_4$, the observed unit-cell parameters compare with those previously determined.[4–6] Calculated intensities,* I_c, were obtained for the distribution of cations and u_o values of Table 1, where the best R factors are also shown.

Observed u_o values can be compared with those calculated, u_c, using the expression $u_c = 3r^2 + (33r^2-8)^{1/2} - 8/24(r^2-1)$, where r is the ratio of the octahedral, d_o, to the tetrahedral, d_t, M—O distances. This expression is deduced taking into account that $d_o = a(3u^2-2u+3/8)^{1/2}$, and $d_t = a3^{1/2}(u-1/8)$. Assuming the distribution of cations indicated in the supplementary material,* and the corresponding ionic radii[10] (Å), values for d_o, d_t, r and u_c are obtained.* The u_c agree acceptably with the u_o.

Table 1. Crystal data for the spinels $Co_{1+2s}Cr_{2-3s}Sb_sO_4$, with ESDs in parentheses

s	a (Å)	u_o	u_c	R
0.00	8.3346(3)	0.261	0.261	0.042
0.10	8.3461(4)	0.260	0.260	0.030
0.20	8.3783(3)	0.260	0.260	0.029
0.30	8.4187(5)	0.260	0.259	0.025
0.40	8.4577(3)	0.260	0.259	0.027
0.50	8.4909(4)	0.259	0.258	0.031
0.60	8.5185(4)	0.259	0.258	0.031
0.67	8.5330(6)	0.258	0.257	0.043

Table 2 shows the observed M—O and O—O distances at tetrahedral (a) and octahedral (d) sites. The O—O distances have been calculated from the following expressions: at tetrahedral sites, O—O = $a2^{1/2}(2u-\frac{1}{4})$; for octahedral positions, O—O = $a2^{1/2}(\frac{3}{4}-2u)$; O—O′ = $a(4u^2-2u+\frac{3}{8})^{1/2}$. As can be deduced from Table 2, the distances M—O and O—O for tetrahedral positions remain unaltered along the series, equal 1.967(9) and 3.212(14) Å, respectively. The ESD obtained for these distances illustrate the precision of the method, which consists in establishing u_o and, as a function of a and u_o, the M—O and O—O distances. The mentioned ESD are those calculated for a u_o absolute error of 0.0006 units. Assuming this u_o error, from the expressions which give the distances M—O, O—O and O—O′ for octahedral sites as a function of a and u_o the following ESDs are deduced for these distances: 0.005, 0.014 and 0.0006 Å respectively.

Table 2. Observed interatomic distances (Å) in the spinels $Co_{1+2s}Cr_{2-3s}Sb_sO_4$ ($0 \leqslant s \leqslant \frac{2}{3}$).

	Tetrahedral (a) sites		Octahedral (d) sites		
s	M—O	O—O	M—O	O—O	O—O′
0.00	1.963	3.206	1.996	2.687	2.952
0.10	1.952	3.187	2.007	2.715	2.956
0.20	1.959	3.199	2.014	2.725	2.967
0.30	1.969	3.215	2.024	2.738	2.981
0.40	1.978	3.320	2.033	2.751	2.995
0.50	1.971	3.218	2.049	2.786	3.006
0.60	1.977	3.229	2.056	2.795	3.016
0.67	1.966	3.210	2.067	2.824	3.020

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* The data have been deposited with the Editor and are available on request.

Table 2 shows how the tetrahedral M—O bond lengths are constant along the series, whereas the octahedral M—O distances increase with s. These results could be anticipated, because the series $Co_{1+2s}Cr_{2-3s}Sb_sO_4$ ($0 \leq s \leq \frac{2}{3}$) can be thought of as derived from the normal spinel $CoCr_2O_4$ through progressive substitution of two Cr^{3+} by two of the more voluminous cations, $\frac{2}{3}Mn^{2+} + \frac{1}{3}Sb^{5+}$. This substitution takes place at the octahedral sublattice, whereas the tetrahedral sites remain unaltered, occupied by Co^{2+} ions. Hence, the mentioned substitution has to be accomplished keeping unchanged the tetrahedral M—O distances and progressively increasing the octahedral ones.

From these results and those of the previous paper,[2] it is concluded that in the series $M_{1+2s}Cr_{2-3s}Sb_sO_4$, limited by the oxides MCr_2O_4 ($s = 0$) and $M_{7/3}Sb_{2/3}O_4$ ($s = \frac{2}{3}$), when both of these oxides are spinels, s can adopt all the values from zero to $\frac{2}{3}$, i.e. all the $\lambda +$ chromium of MCr_2O_4 can be substituted by $\frac{2}{3}M\frac{1}{3}Sb$. On the other hand, when the oxide $M_{7/3}Sb_{2/3}O_4$ is not a spinel, only half the chromium in MCr_2O_4 can be substituted, and s can vary only up to $\frac{1}{3}$.

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REFERENCES

1. P. García Casado and I. Rasines, *J. Solid State Chem.* 1984, **52**, 187.
2. P. García Casado and I. Rasines, *Polyhedron* 1985, **4**, 517.
3. R. J. Hill, J. R. Craig and G. V. Gibbs, *Phys. Chem. Miner.* 1979, **4**, 317.
4. P. Tarte and J. Preudhomme, *J. Solid State Chem.* 1979, **29**, 273.
5. E. Whipple and A. Wold, *J. Inorg. Nucl. Chem.* 1962, **24**, 23.
6. J. Dulac and A. Durif, *C. R. Acad. Sci.* 1960, **251**, 747.
7. P. García Casado and I. Rasines, *Z. Krist.* 1982, **160**, 34.
8. M. Martínez Ripoll, PARAM. Refinamiento por mínimos cuadrados de parámetros. Instituto Rocasolano, C.S.I.C., Madrid.
9. R. Yvon, W. Jeitschko and E. Parthé, *J. Appl. Cryst.* 1977, **10**, 73.
10. R. D. Shannon, *Acta Cryst.* 1976, **A32**, 751.