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Abstract. The cationic distribution and some structure parameters of mixed spinels with a general formula $Zn_xCo_{3-x}O_4$, $0.5 < x < 1$, prepared by thermal decomposition of corresponding zinc-cobalt nitrate precursors, have been studied by means of neutron powder diffraction technique. A partially inverse structure has been determined in all cases with Zn^{2+} cations occupying preferentially the tetrahedral positions.

1. Introduction

Among the factors which condition the wide range of properties of the oxide spinels at a given chemical composition it is the cationic distribution over the spinel lattice sites that plays a substantial role, especially in clarifying the electric and magnetic properties. Recently, several authors (see, e.g. [1–3] and the citations therein) have demonstrated that polycrystalline binary oxide spinels $M_xCo_{3-x}O_4$ (M = Cu, Mg, Zn) can be obtained using starting compounds with preset composition and a specific layered structure. Direct methods by solid state reaction of oxides were found not suitable for preparation of such single phase cobalt based spinels due to the low thermal stability of the final product so that alternative techniques have been developed. We present here neutron diffraction data of the structural parameters of $Zn_xCo_{3-x}O_4$ with the aim to help the understanding of the mechanism of their formation and peculiarities of their properties. Results from similar studies on $Cu_xCo_{3-x}O_4$ [4] and $Mg_xCo_{3-x}O_4$ [5] have been published earlier.

2. Experiment

2.1. Samples

The method described in [1] was used for preparation of the appropriate precursor precipitates with general formula $Zn_yCo_{2-y}(OH)_3NO_3$. Bulk spinel samples $Zn_xCo_{3-x}O_4$ with different x were obtained by thermal decomposition of the precursors with an appropriate Zn/Co atomic ratio, n, in the interval $0.15 < n < 0.5$, for which the process was reported [6] to result in a single-phase product, at temperatures ranging from 350 °C to 450 °C in air. X-ray diffraction analyses were carried out for phase control of the precursors and final products. The content of zinc and cobalt in the resulting single-phase black substances were determined by complexometric and atomic emission methods (Spectroflame spectrometer Germany) as well as x-ray fluorescence.

2.2. Time-of-flight measurements and raw data corrections

Neutron diffraction measurements were performed by the time-of-flight (TOF) method on the high-intensity diffractometer DN-2 placed at the mirror guide tube at beam 6B of the pulsed reactor IBR-2 of JINR, Dubna [7]. The instrument was equipped with a linear position-sensitive detector (PSD) which covers a $10°$ angular sector of the reciprocal plane at once and two ^{3}He detectors. A thin-walled cylindrical vanadium container for the powder samples was used. The zinc cobalt oxides are in paramagnetic state at room temperature and their diffraction patterns (see figure 1) consist of Bragg peaks (due to nuclear coherent scattering) in positions specified by the spinel structure only and of a smooth background. The integrated intensity of a Bragg reflection is given [8] by

$$I_{obs} \sim \frac{F_{hkl}^2 \lambda^4}{\sin^2 \theta} N(\lambda) \qquad (1)$$

where $N(\lambda)$ is the spectrum of the white neutron beam incident upon the sample. Due to the mirror guide the incident spectrum has a cut-off at $\lambda \sim 1$ Å, reaches a maximum at $\lambda \sim 2$ Å and decreases in the long wavelength side approximately as λ^{-4}. Therefore the experimental sensitivity to the structure factor F_{hkl}^2 is nearly uniform in the region $8 > \lambda > 2$ Å where the upper limit is set by the need to have sufficient neutron intensity for a reasonable statistics of counting. The normalization of the diffraction patterns for the spectrum of the incident neutron beam is performed dividing them by a previously measured diffraction pattern of vanadium. The spectrum is also corrected for the wavelength dependent absorption [9]. With detectors centred in position $2\theta = 125°$ (PSD), $2\theta = 90°$ (detector A) and $2\theta = 146°$ (detector B) the range of λ from 2 Å to 8 Å corresponds to interplanar spacings $d = 1.05$–5.7 Å which was the actual range of our investigation. The angular positions and flightpath lengths of the three detectors were determined by measuring and refining a spectrum of a standard sample of Al_2O_3.

2.3. Structure refinement

Since the intensity of neutron diffraction lines is related with the square of the coherent neutron scattering amplitude which reflects the isotope concentration alone and is independent of the atomic valence state of the scatterer, the zinc cobalt oxides should be considered as containing only two cationic components and the cationic distribution over the two spinel sites is expressed by the formula

$$Zn_{x-\alpha}Co_{1-x+\alpha}\left[Co_{2-\alpha}Zn_\alpha\right]O_4 \qquad (2)$$

where α depends on x and denotes the degree of inversion defined as the fraction of octahedral sites occupied by Zn^{2+} ions, and the cations in B-sites are given in brackets. Of special note is the completely random cationic distribution described by $\alpha = (2/3)x$. The average scatterer amplitudes b_A and b_B of the effective scatterers in the tetrahedral (A) and the octahedral (B) sites of the spinel structure are given by

$$\begin{aligned} b_A &= (x - \alpha)b_{Zn} + (1 - x + \alpha)b_{Co} \\ 2b_B &= (2 - \alpha)b_{Co} + \alpha b_{Zn} \end{aligned} \qquad (3)$$

where b_{Co} and b_{Zn} are the tabulated neutron scattering lengths of cobalt and zinc, e.g. in [10]. From (3) it follows that the relation

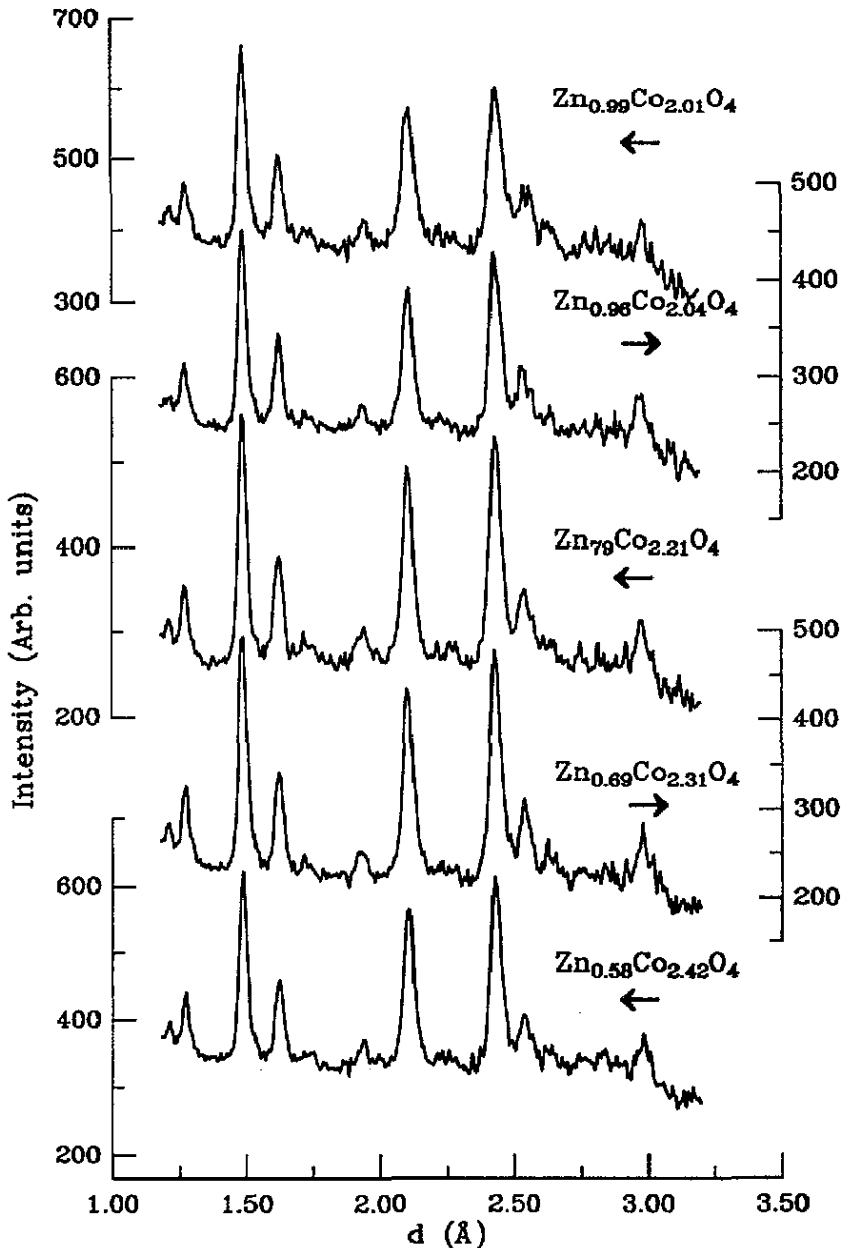$$b_A + 2b_B = xb_{Zn} + (3 - x)b_{Co} \qquad (4)$$

Figure 1. Normalized neutron diffraction spectra of $Zn_xCo_{3-x}O_4$ at room temperature. The range of lattice distances $1.15 \leqslant d_{hkl} \leqslant 3.20$ Å is shown wherein 15 reflections contribute to the measured profile.

may be used either as a constraint during the crystal structure refinement or, when the parameters are refined as independent variables, the chemical composition and the stoichiometry of the sample under study may be checked.

The neutron diffraction patterns were analysed by the full profile powder method of Rietveldt [11] implemented in the computer code MRIA [12]. The instrument dependent

parameters in the analysis were the coefficients of the polynomial (maximum order 5) accounting for the background, the delay of the start of the time analyser (the 'zero' channel), the coefficients of the linear dependence of the peak width on channel number [12] and the factor of proportionality. The structural parameters that varied during the refinement were the effective scattering amplitudes b_A and b_B, the oxygen parameter u, and the lattice constant a_0. The temperature factors strongly correlated with some structurally independent parameters and were left out of consideration. The conventional profile reliability factors R and R_w together with χ^2 values were used as a criterion for the convergence of the theoretically calculated profile to the experimental one. For the structure factor calculations the origin of the spinel unit cell was taken at the point $\bar{4}3m$, the tetrahedral, octahedral and oxygen sites being in $8(a)$, $16(d)$ and $32(e)$ positions, respectively, of the space group $Fd3m$, number 227 in the *International Tables*.

3. Results and discussion

First refinements were carried out separately on the individual diffraction profiles recorded by the corresponding detector. Thus, a set of instrument dependent refinement parameters associated with a given detector was specified. Rather good profile reliability factors of the order of 1.9–2.5 % and χ^2 values ranging from 1.2 to 2.5 resulted for all samples investigated, but the structural parameters were found detector dependent although the corresponding values were close to each other. Final refinements were performed simultaneously on the set of three diffraction patterns of each composition. Figure 2 shows the neutron diffraction pattern of the sample with composition $x = 0.576$ as a typical illustration of the final result of refinement procedures with or without imposed constraints. The values of the refined structure parameters are presented in table 1.

Table 1. Dependences of the lattice cell parameter, a_0, oxygen parameter, u, tetrahedral (A) and octahedral (B) site occupancies of $Zn_xCo_{3-x}O_4$ spinels on the zinc content, x, in the formula unit. Conventional profile reliability factors R and R_w are shown[a].

x	a_0 (Å)	u	Occupancies, A			Occupancies, B		R (%)	R_w (%)	Ref.
			Zn^{2+}	Co^{3+}	Co^{2+}	Zn^{2+}	Co^{3+}			
0.0	8.0835(6)	0.389(1)			1.00		2.00			[13]
	8.065	0.388			1.00		2.00			[15]
	8.0819(3)	0.388(1)			1.00		2.00			[16]
0.576(6)	8.0881(7)	0.3886(1)	0.53(1)	0.04(1)	0.42(1)	0.04(1)	1.96(1)	2.3	2.3	
0.686(8)	8.0926(7)	0.3884(1)	0.62(1)	0.06(1)	0.31(1)	0.06(1)	1.94(1)	2.5	2.5	
0.79(1)	8.0944(7)	0.3883(1)	0.68(1)	0.11(1)	0.21(1)	0.11(1)	1.89(1)	2.3	2.4	
0.964(9)	8.1007(7)	0.3882(1)	0.80(1)	0.16(1)	0.04(1)	0.16(1)	1.84(1)	2.3	2.4	
0.99(1)	8.1019(7)	0.3881(1)	0.79(1)	0.20(1)	0.01(1)	0.20(1)	1.80(1)	2.3	2.3	

[a]Data refined using the following neutron nuclear scattering amplitudes: $b_{Co} = 0.249$, $b_{Zn} = 0.5680$, $b_O = 0.5805$ $(10^{-12}$ cm) [10]. Standard deviations referred to the last significant digit are given in parentheses.

$$R = \frac{\sum_i |I_i^{exp} - I_i^{calc}|}{\sum_i I_i^{exp}} \qquad R_w = \left(\frac{\sum_i w_i (I_i^{exp} - I_i^{calc})^2}{\sum_i w_i (I_i^{exp})^2} \right)^{1/2}$$
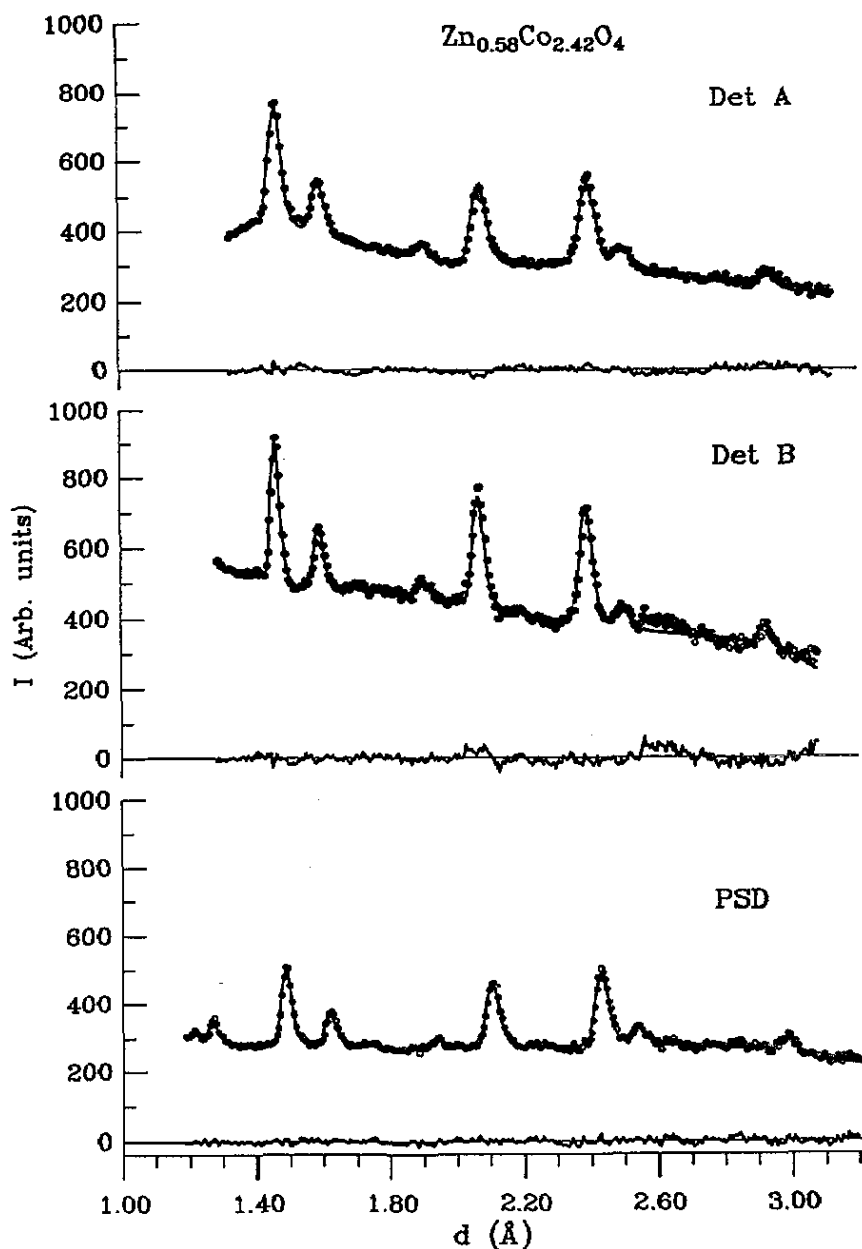
Figure 2. Neutron TOF scattering profiles of the sample with composition $x = 0.576$ recorded by the three independent detectors set at different scattering angles (see text). Circles are observations and the full curve shows the calculated profile. The difference between observed and calculated profiles is given below the corresponding pattern.

The dependence of the unit cell parameter a_0 on the zinc content x in the formula unit satisfactorily obeys the simple Vegard's law. A straight line with a slope of 0.032(2) and a correlation coefficient $r = 0.995$ can be fitted to the experimental data. The intercept 0.8070(1) nm is consistent with literature data on the lattice constant of Co_3O_4

which is a normal spinel. It should be noted that nearly the same estimate of a_0 has been found from the intercept of analogous straight lines drawn in the case of $Cu_xCo_{3-x}O_4$ [4] and $Mg_xCo_{3-x}O_4$ [5] spinels obtained by the same technique of preparation.

The data (see table 1) show that all zinc-cobalt oxides investigated are partially inverse spinels with oxygen parameter close to that of the normal spinel Co_3O_4 $u = 0.389(1)$ [13]. Again linear regression analysis shows that a straight line (correlation coefficient $r = 0.97$) with an intercept $u = 0.3892(1)$ can describe the slight decrease of u with increasing x.

If the solid solutions obtained were statistical solid solutions, the probability of occupation of the two cationic positions in the spinel structure by Zn or Co should not depend on the cationic species. However, it is well known from the literature that in oxide spinels, ferrites in particular, the Zn^{2+} ions exhibit a strong preference to occupy tetrahedral positions. As seen from table 1 and figure 3 this is true for the cobaltites under study, too.
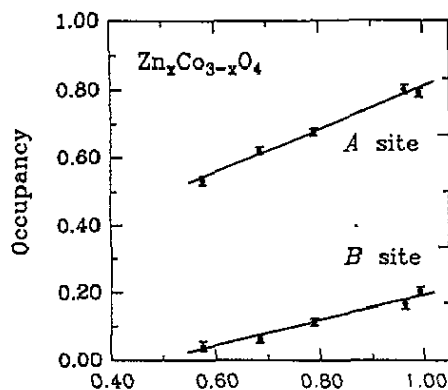

Figure 3. Dependence of the fraction of Zn ions in tetrahedral (A) sites and octahedral (B) sites on the total Zn content, x, per formula unit $Zn_xCo_{3-x}O_4$.

The variation of the amount of Zn^{2+} in octahedral lattice sites, α, and in tetrahedral sites, $x - \alpha$, with composition x fit straight lines with correlation coefficients near unity

$$
\begin{aligned}
x - \alpha &= 0.18 + 0.63x \qquad r = 0.94 \\
\alpha &= -0.18 + 0.37x \qquad r = 0.983.
\end{aligned}
\tag{5}
$$

At a given x the partially inverse distribution found in all cases studied is consistent with the ionic formula

$$
Zn^{2+}_{x-\alpha}Co^{2+}_{1-x}Co^{3+}_{\alpha}[Co^{3+}_{2-\alpha}Zn^{2+}_{\alpha}]O^{2-}_4
\tag{6}
$$

which accounts for the formal valence of the cations and the condition for electrical neutrality. The resulting occupancies by the different cationic species according to (6) presented in table 1 are calculated using the refined values of the average scattering amplitudes b_A and b_B.

Taking into account the octahedral Zn^{2+} and Co^{3+} ionic radii ($r_{Zn^{2+}} = 0.74$ Å, $r_{Co^{3+}} = 0.61$ Å in the high-spin state or $r_{Co^{3+}} = 0.545$ Å in the low-spin state [14]) an increase in the average distance from the metal in the B site to oxygen, L_{BO}, with increasing content of zinc can be expected. On the other hand, in accordance with requirements concerning electroneutrality, part of the smaller Co^{3+} ions should replace the larger Co^{2+} ions ($r_{Co^{2+}} = 0.58$ Å) in the A sites. A slight decrease in the average

distance from the metal in the A site to oxygen, L_{AO}, should result since the effective ionic radii of tetrahedrally coordinated Zn^{2+} and Co^{2+} are nearly equal ($r_{Zn^{2+}} = 0.60\,\text{Å}$).

These expectations can be related to the determined structural parameters because knowing the values of the unit cell parameter a_0 and the oxygen parameter u one can calculate the tetrahedral L_{AO} and octahedral L_{BO} bond lengths using the formulae relevant for the spinel lattice

$$L_{AO} = (u - 1/4)a_0\sqrt{3}$$
$$L_{BO} = a_0[(5/8 - u)^2 + 2(3/8 - u)^2]^{1/2}$$

(7)

The results of the calculations plotted in figure 4 show that with increasing x the L_{BO} distance increases, whereas L_{AO} decreases as expected.
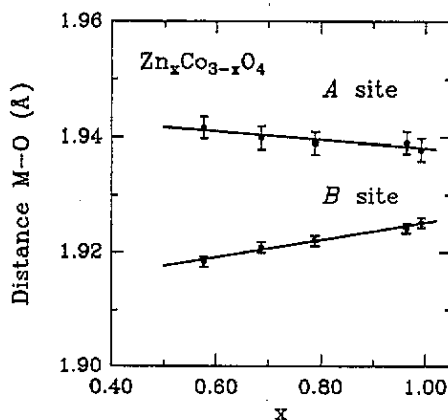

Figure 4. Dependence of the average distances between oxygen and the metal cation in tetrahedral (A) sites and octahedral (B) sites on composition x. The solid lines are drawn to guide the eye.

In conclusion, for the mixed spinel system $Zn_xCo_{3-x}O_4$ it was found that the fraction of the octahedral sites occupied by zinc does not exceed 0.2 indicating that the zinc cobaltites under study are rather normal than inverted.

Acknowledgments

References

[1] Petrov K, Markov L, Ioncheva R, and Rachev P 1988 *J. Mater. Sci.* **23** 181
[2] Markov L, Petrov K and Ioncheva R 1985 *Zh. Neorg. Khim.* **30** 3023 .
[3] Peshev P, Toshev A and Gyurov G 1989 *Mater. Res. Bull.* **24** 33
[4] Petrov K, Krezhov K and Konstantinov P 1989 *J. Phys. Chem. Solids* **50** 577
[5] Krezhov K and Konstantinov P 1992 J. Phys.: Condens. Matter **4** L543
[6] Petrov K, Markov L and Ioncheva R 1985 *J. Mater. Sci.* **4** 711
[7] 1992 *Neutron Experimental Facilities at JINR, Dubna. User's Guide* ed Yu V Taran (Dubna: Joint Institute for Nuclear Research)

[8] Bacon G E 1975 *Neutron Diffraction* (Oxford: Clarendon Press) p 152

[9] Windsor C G 1981 *Pulsed Neutron Scattering* (London: Taylor and Francis) p 273

[10] Koester L, Rauch H and Seymann E 1992 *Neutron News* **3** 38 Fold-out table of neutron scattering lengths

[11] Rietveldt H M 1969 *J. Appl. Crystallogr.* **2** 65

[12] Zlokazov V B and Chernyshov V V *Communications of JINR 1990* **P10–90–315** Dubna, Russia

[13] Knop O, Ried K I G, Sutarno and Nakagawa I 1968 *Can. J. Chem.* **46** 3463

[14] Shannon R 1976 *Acta Crystallogr.* **A32** 751

[15] Roth W L 1964 *J. Phys. Chem. Solids* **25** 1

[16] Petrov K, Karamaneva T, Angelov S and Mechandjiev D 1983 *Mater. Res. Bull.* **18** 637