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Cation ordering and order–disorder phase transition in Co-substituted $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinels

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In this paper we present the results of the synthesis, crystal structure investigations and *in situ* X-ray diffraction studies of the order–disorder phase transition in cobalt substituted lithium titanate oxide spinels, $\text{Li}_{1.33x}\text{Co}_{2-2x}\text{Ti}_{1+0.67x}\text{O}_4$ ($0 \leq x \leq 1$). Depending on the chemical composition the samples crystallize in two

space groups (S.G.): $\text{Fd}\bar{3}\text{m}$ ($0 \leq x \leq 0.40$ and $x = 1$) and $\text{P}4_3\text{2}$ ($0.50 \leq x \leq 0.875$). Samples crystallizing in the S.G. $\text{P}4_3\text{2}$ are ordered spinels with a cation ordering of the $1\bar{3}$ type at octahedral 4b and 12d sites.

The cation ordering in octahedral sites is full in the sample with $x = 0.75$ (Li and Ti occupy 4b and 12d sites, respectively) and decreases for samples with higher/smaller x . Changes of the extinction conditions and nonlinearities in the concentration dependence of the lattice parameter in the regions $0.40 < x < 0.50$

and $0.875 < x < 1$ indicate changes of the crystal symmetry ($\text{Fd}\bar{3}\text{m} \leftrightarrow \text{P}4_3\text{2}$). The partially ordered spinel $x = 0.50$ has a convergent, reversible, order–disorder phase transition at $T_c = (1083 \pm 10)$ K. Samples with $x = 0.875$ and 0.75 have an order–disorder phase transition out of our experimental ranges with $T_c(x = 0.875) < 973$ K and $T_c(x = 0.75) > 1173$ K. The mechanism of the phase transition is based on cation migration.

1 Introduction

Lithium titanate oxide spinel, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, has been intensively investigated in order to be used as an anode material in lithium rechargeable batteries [1, 2]. From that reason its synthesis, structure, and electrochemical properties were quite well investigated recently. It crystallizes in a spinel type structure of the

space group $\text{Fd}\bar{3}\text{m}$. Li^+ and Ti^{4+} cations occupy two nonequivalent crystallographic sites, tetrahedral ($8a$ or A) and octahedral ($16d$ or B), where the cation distribution is given by $(\text{Li})_{8a}[\text{Li}_{1/3}\text{Ti}_{5/3}]_{16d}$ [2]. Likewise, the other structure type was referred, with Li^+ and Ti^{4+} ordering at the octahedral sites [3]. The spinel structure with its empty octahedral $16c$ and both tetrahedral $8b$ and $48f$ cationic sites is suitable for lithium insertion and extraction.

In the binary spinel with the general formulae AB_2O_4 the cation distribution at room temperature may be: $(\text{A})_{8a}[\text{B}_2]_{16d}$ (normal), $(\text{B})_{8a}[\text{AB}]_{16d}$ (inverse), $(\text{A}_{1-x}\text{B}_x)_{8a}[\text{A}_x\text{B}_{2-x}]_{16d}$ (intermediate) or $(\text{A}_{1/2}\text{B}_{2/3})_{8a}[\text{A}_{2/3}\text{B}_{4/3}]_{16d}$ (random). It is determined by the individual cation site preferences. At elevated temperatures a cation

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redistribution is possible, with (convergent) or without changes in the lattice symmetry (non-convergent phase transition). The state at room temperature is denoted as order and the former as disorder [4]. This type of order–disorder transition is truly studied experimentally and theoretically within the Landau theory, e.g., by Carpenter et al. [5].

Some spinels possess an ordered structure with a cation ordering at tetrahedral or/and octahedral sites, where this ordering causes the formation of two new sublattices in one (or both) A/B sublattice [6, 7]. The occupancy ratio of the Wyckoff's positions of cations in the A/B sublattice is entitled “type of order-

ing”. These spinels become disordered (S.G. $\overline{\text{Fd}3\text{m}}$) by a cation substitution and/or by a thermal treatment (heating or cooling) [8, 9].

Ternary samples $\text{Li}_{1.33x}\text{Co}_{2-2x}\text{Ti}_{1+0.67x}\text{O}_4$ ($0 < x < 1$) were obtained by a partial cation substitution, $\text{Li}^+ + \text{Ti}^{4+} \rightarrow 5/2 \text{Co}^{2+}$ in the parent diamagnetic compound $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Co_2TiO_4 ($x = 0$) is a magnetic

spinel compound (S.G. $\overline{\text{Fd}3\text{m}}$) with complex magnetic behavior [10, 11]. From the magnetic point of view, the synthesized ternary samples are diluted magnetics.

The goals of this work are manifold: first, to synthesize ternary spinels in a wide concentration range; second, to find a relationship between crystal structure and chemical composition; third, to determinate the cation distribution both in order and disorder spinels, and finally, to study the order–disorder phase transition by *in situ* X-ray diffraction.

Ternary spinels can possess different physical properties influenced by the cation substitution in host binary spinels, which is important in material application. Changes of the physical properties induced by the cation substitution and the cation distribution could be controlled during the synthesis.

2 Experimental

2.1 Sample preparation

The samples $\text{Li}_{1.33x}\text{Co}_{2-2x}\text{Ti}_{1+0.67x}\text{O}_4$ ($0 \leq x \leq 1$) were synthesized by classical ceramic technology. The starting compounds Li_2CO_3 , TiO_2 , and Co_3O_4 were mixed in appropriate stoichiometric ratios. Then, the mixtures were heated at 920 K in air for 12 h. The samples were slowly cooled down to room temperature. Green colored samples were obtained except for the white $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample. The elemental analyses were performed by inductively coupled plasma optical emission spectroscopy (Spectroflame ICP, 2.5 kW, 27 MHz) and DC argon-stabilized plasma arc emission spectroscopy. The found cation ratio corresponds to the one given via x in formula units within the experimental error. The results obtained by both devices are in good agreement. The crystal structures were checked by X-ray diffraction technique.

The result was as follows: i) samples with $0 \leq x \leq 0.40$ and $x = 1$ crystallize in a space group $\overline{\text{Fd}3\text{m}}$ and ii) samples with $0.50 \leq x \leq 0.875$ crystallize in a space group $\text{P}4_332$.

2.2 Collection of X-ray diffraction data

The X-ray powder diffraction (XRPD) investigations were done on a high-resolution prototype two-axis goniometer [12]. The goniometer was equipped with an 18 kW Rigaku X-ray source with rotating anode operating at 50 kV and 300 mA. A graphite monochromator for CuK_α radiation was used. The high temperature XRPD measurements were performed in a Meric cryofurnace with a temperature stability better than 0.5 K. Data for Rietveld refinements were collected in different 2θ -steps and number of accumulations in two different 2θ -regions. A typical data collection scheme is given in Table 1. Estimated standard deviations (e.s.d.) of the XRPD intensities, recorded at room temperature in different 2θ -regions, are presented. The good statistical accuracy of the measurements and the high resolution of the diffractometer allowed us to obtain precise structural data. X-ray data between 10° and the first reflection

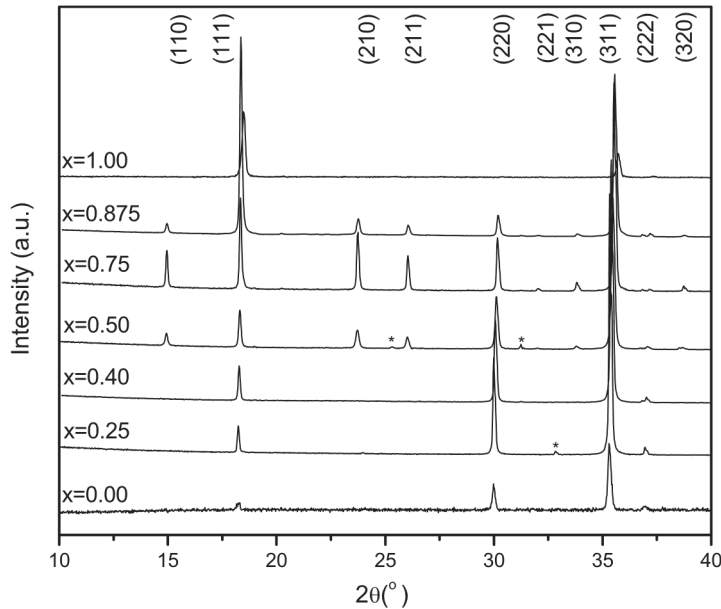
were excluded during the refinement procedure. The ordered spinel samples were heated and the data were collected from 973 K up to 1273 K in steps of 20 K. At each temperature, the samples were annealed for 20 min. X-ray monitoring was done in the 2θ -range from 10° to 90° with steps of 0.02° and an

Table 1 Data collection scheme for the Rietveld refinement of ternary sample spinels. Some values at room temperature for the sample with $x = 0.40$ are given. $2\theta_i$, y_i , and σ_i are angle of diffraction, diffracted intensity, and estimated standard deviation of diffracted intensity, respectively.

2θ region ($^\circ$)	2θ step ($^\circ$)	number of records	t (s)	$2\theta_i$ ($^\circ$)	y_i (counts)	σ_i (counts)
10–50	0.02	2	10	16.1978	51.70	2.27
				24.6658	28.70	1.69
				35.3204	2608.20	16.15
				49.0742	23.60	1.54
50–110	0.08	6	10	50.0932	12.90	0.66
				66.4110	11.00	0.61
				83.8486	8.83	0.54
				108.2550	8.40	0.53

exposition time of 4 s/step. X-ray data for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Co_2TiO_4 were collected at a Philips 1010 diffractometer ($\text{CuK}\alpha$) in the 2θ -range from 10° to 90° with a step scan of 0.02° and a scanning time of 5 s per step.

3 Results and discussion



3.1 Refinement of the crystal structure of $\text{Li}_{1.33x}\text{Co}_{2-2x}\text{Ti}_{1+0.67x}\text{O}_4$ spinels by the Rietveld method

Parts of the X-ray diffraction patterns for ternary samples are given in Fig. 1. It can be noticed that all

samples show reflections characteristic for a spinel type structure, S.G. $\text{Fd}\bar{3}m$. For a higher cation ratio x ($x \geq 0.50$), additional reflections which characterize the ordered spinel phase with the $\text{P}4_3\bar{3}2$ space group were detected. These reflections are (110), (210), (211), etc. Hence, with a change of the cation ratio in mixed samples (x from 0 to 1), changes in the crystal structure were obtained, $\text{fcc} \rightarrow \text{P}$

fcc. The border

concentrations for the order–disorder transition ($\text{Fd}\bar{3}m \leftrightarrow \text{P}4_3\bar{3}2$) were $0.4 < x'_1 < 0.5$ and $0.875 < x'_2 < 1$. The intensities of the reflections (210) and (211) for $x = 0.75$ are higher than those in samples with a

Fig. 1 X-ray diffraction patterns of disordered and ordered spinels from the $\text{Li}_{1.33x}\text{Co}_{2-2x}\text{Ti}_{1+0.67x}\text{O}_4$ series ($0.25 < x < 0.875$); * denotes about 1–2% of impurity phase.

Table 2 Refined parameters, cation–anion distances (d), and corresponding agreement factors for $\text{Li}_{1.33x}\text{Co}_{2-2x}\text{Ti}_{1+0.67x}\text{O}_4$ ($x = 0.50, 0.75, \text{ and } 0.875$). M denotes cations in 12d site (M is Co, Ti for $x = 0.50$ and $x = 0.75$ and Li, Ti for $x = 0.875$). Parameters ^a and ^b correspond to the used method for the calculation of the cation–anion distances (see text).

crystal system: primitive cubic	space group	P4 ₃ 2 (212)	
concentration x	0.50	0.75	0.875
lattice parameter a (Å)	8.3882 (4)	8.3747 (2)	8.3687(4)
cation–anion distances d (Å)			
d_{8c-O}^a	1.954(6) × 3	1.954(4) × 3	1.962(7) × 3
	1.982(7) × 1	2.007(4) × 1	2.008(7) × 1
$\langle d_{a8c-O} \rangle$	1.961(6)	1.967(4)	1.974(8)
d_{8c-O}^b	1.963	1.965	1.968
d_{4b-O}^a	2.094(6) × 6	2.115(3) × 6	2.054(5) × 6
d_{4b-O}^b	2.091	2.133	2.074
d_{a12d-O}	1.950(7) × 2	1.991(7)	1.901(3) × 2
	× 2	2.046(4) × 2	2.008(5) × 2
	2.043(7) × 2	1.993(4) × 2	2.022(5) × 2
$\langle d_{12d-O}^a \rangle$	1.995(7)	1.980(4)	1.991(5)
d_{b12d-O}	1.999	1.986	1.998
fractional coordinates			
M _{12d}	y	0.3696 (2)	0.3677 (1)
(Co, Li) _{8c}	x	0.9992 (3)	0.9990 (3)
O _{8c}	x	0.3872 (8)	0.3889 (5)
	O _{24c}	x	0.1120 (8)
	y	z	0.1240
			(5)
			0.1084 (5)
			0.1266
			(4)
			0.3883 (5)
			0.3884 (4)
			0.3860 (6)
overall temperature factor B_{ov} (Å ²)	0.62 (4)	0.74 (4)	0.72 (4)
population parameters (P)			
$P(\text{Co})_{8c}$	1.381(5)	0.619(5)	0.986(4)
$P(\text{Li})_{8c}$	0.247(3)		1.014(4)
$P(\text{Co})_{4b}$			0.00
$P(\text{Li})_{4b}$	0.743(3)		0.945(3)
$P(\text{Ti})_{4b}$	0.00		0.056(3)
$P(\text{Co})_{12d}$	0.343(3)		0.00
$P(\text{Li})_{12d}$	0.00		2.945(3)
$P(\text{Ti})_{12d}$	2.670		0.248(6)
			2.752(6)
agreement factors			
R_p (%)	12.7	11.0	8.0
R_{wp} (%)	13.9	13.6	10.7
R_B (%)	4.5	4.2	3.9
χ^2	7.3	4.75	4.8
D	0.59	0.63	0.38

smaller/higher x (Fig. 1), what will be discussed in the further text. It was obtained, that the binary sam-

ples $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Co_2TiO_4 crystallize in the $\text{Fd}\bar{3}\text{m}$ space group, what is in accordance with earlier data [1, 10].

The crystal structures of ternary samples $\text{Li}_{1.33x}\text{Co}_{2-2x}\text{Ti}_{1+0.67x}\text{O}_4$ for $x = 0.25, 0.40, 0.50, 0.75,$ and 0.875 were refined from X-ray diffraction data by the Rietveld method, using the software package Fullprof [13]. For ordered spinel samples, the starting model was the same as for $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ crystallizing in the space group $\text{P}4_3\bar{3}2$ [14]. The cations occupy tetrahedral 8c and octahedral 4b and 12d sites. Oxygen ions are placed in 8c and 24e sites. During the refinement procedure, the following atomic and crystal parameters were varied: six fractional coordinates, lattice parameter (a), overall isotropic temperature factor (B_{ov}) and population parameters (P). The remaining parameters were five polynomial coefficients for background, scale factor, zero point, three half-width parameters, asymmetry, and mixing parameters. A pseudo-Voigt peak shape was used in the refinement. The samples with $x = 0.50$ and 0.875 are analyzed at two ways: (i) as a single phase (S.G. $\text{P}4_3\bar{3}2$) and (ii) as a two phases system, i.e., a mixture of two phases, S.G. $\text{P}4_3\bar{3}2$ and S.G. $\text{Fd}\bar{3}\text{m}$. The obtained R factors were slightly smaller for the two phases Rietveld refinement, but the quantity of both phases and the values of the refined parameters indicate that two samples ($x = 0.50$ and 0.875) should be treated as single phases (S.G. $\text{P}4_3\bar{3}2$). The results of the refinement are given in Table 2. The diffraction pattern for the sample with $x = 0.75$ is shown in Fig. 2a.

Samples with $x = 0.25$ and 0.40 were refined in the space group $\text{Fd}\bar{3}\text{m}$ (origin at center $-\bar{3}$). The refined atomic and crystal parameters were the oxygen parameter (u), the isotropic temperature factors (B), the lattice parameter (a), and the population parameters (P). The profile refined parameters were the same as in the case of ordered spinels. The obtained atomic and crystal values are given in Table 3 and the diffraction pattern for the sample with $x = 0.40$ is shown in Fig. 2b.

We point up at the values of the statistical factors χ^2 and D in the Tables 2 and 3. There are some differences than usually obtained in a good refinement. This is caused by the method of X-ray diffraction data collection, see Table 1. A repetition of recording leads to smaller standard deviations of intensities, what causes more accuracy of the refined parameters as well as a higher χ^2 and a smaller D due to the weighted scheme $w = 1/y_i$ and not $w = 1/\sigma^2(y_i)$, where y_i is the measured intensity and $\sigma(y_i)$ is the e.s.d. of y_i at the i -th point.

The starting model for the determination of the cation distribution in ordered spinels was based on site preferences for cation sites in the spinel structure. Li^+ and Co^{2+} have no preferences and could occupy each of the three different cation sites [14, 15]. The Ti^{4+} ions preferentially occupy octahedrallycoordinated sites [14, 16] and in the starting model they are placed at both octahedral 4b and 12d sites.

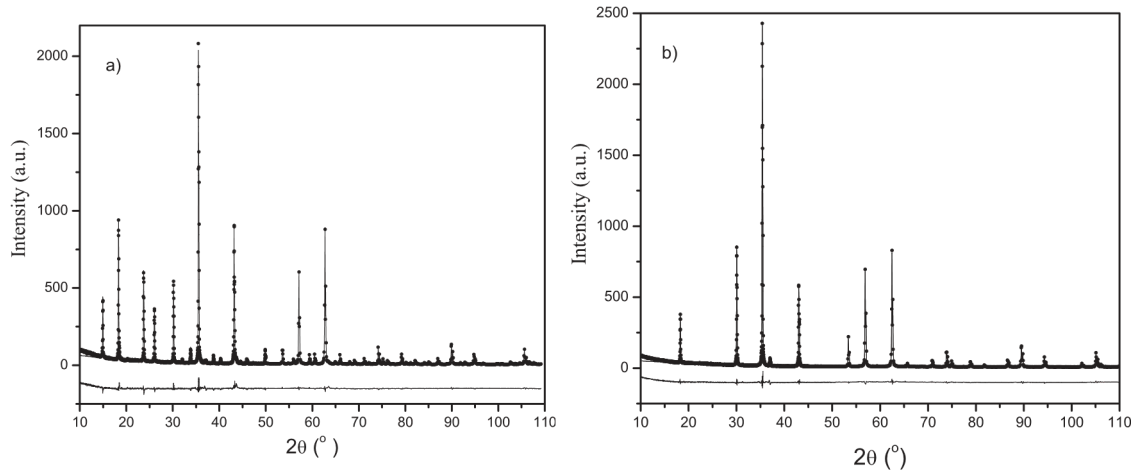


Fig. 2 X-ray diffraction patterns of a) $\text{LiCo}_{0.50}\text{Ti}_{1.50}\text{O}_4$ (S.G. $\text{P}4_3\bar{3}2$) and b) $\text{Li}_{0.53}\text{Co}_{1.20}\text{Ti}_{1.27}\text{O}_4$ (S.G. $\text{Fd}\bar{3}\text{m}$). Dots denote experimental values, the line represents calculated values. The differences between experimental and calculated values are given at the bottom.

Table 3 Crystal data and corresponding agreement factors for $\text{Li}_{1.33x}\text{Co}_{2-2x}\text{Ti}_{1+0.67x}\text{O}_4$ ($x = 0.25$ and $x = 0.40$). M denotes Li, Co and Li, Co, Ti cations in 8a and 16d sites, respectively. The parameters ^a and ^b correspond to the used method for the calculation of the cation–anion distances (see text).

	space	
	group	\bar{m}
crystal system: face centered cubic		Fd3m (227)
concentration x	0.25	0.40
lattice parameter a (Å)	8.4176(3)	8.4046(2)
cation–anion distances d (Å)		
$d^a(\text{M}_{8a}-\text{O})$	1.968(4)	1.970(3)
	× 4	× 4
$d^b(\text{M}_{8a}-\text{O})$	1.961	1.962
$d_a(\text{M}_{16d}-\text{O})$	2.019(5)	2.018(3)
	× 6	× 6
$d_b(\text{M}_{16d}-\text{O})$	2.016	2.018
oxygen parameter u	0.2602(6)	0.2603(4)
temperature factors B (Å ²)		
B_{8a}	0.74(9)	0.81(8)
B_{16d}	0.72(8)	0.68(7)
B_{32e}	0.8(1)	0.7(1)
population parameters (P)		
$P(\text{Co})_{8a}$	0.913(6)	0.806(4)
$P(\text{Li})_{8a}$)	0.194(4)
$P(\text{Co})_{16d}$	0.087(6)	0.336(4)
$P(\text{Li})_{16d}$)	0.394(4)
$P(\text{Ti})_{16d}$	0.243(6)	1.27
)	
	0.587(6)	
	1.17	
agreement factors		
R_p (%)	16	12.9
R_{wp} (%)	16.7	13.7
R_B (%)	4	2.9
χ^2	6.8	7.8
D	1.54	0.36

Hence, we used a step-by-step method to refine eight population parameters. At the start of the refinement procedure, we coupled occupancies of Li^+ and Co^{2+} ions at tetrahedral and both octahedral sites keeping the stoichiometric ratio. The occupation numbers for Ti^{4+} in 4b and 12d sites were coupled and varied by one codeword. After that, Li^+ and Co^{2+} in octahedral sites were coupled and varied by one codeword and the same ions in a tetrahedral site by another one. Ti^{4+} was varied by the same way as previously. During the refinement of occupancies, it was obtained that some occupancies were zero or negative. In the last cycle of refinement six occupancies were varied by two codewords, the first one was coupling tetrahedral ion occupancies and the other octahedral ones.

–

For samples crystallizing in the space group Fd3m, occupancies of Li⁺ and Co²⁺ in tetrahedral 8a and octahedral 16b sites were coupled and varied by one codeword. It was found that Ti⁴⁺ ions exclusively occupy octahedral 16d sites and in the last cycle of the refinement, its occupancy was not varied.

The refined values of occupancies for all samples are given in the Tables 2 and 3. Using a step-by-step method of refinement for ordered samples, we obtained that the sum of occupancies for each site agrees with the expected value within the experimental error, see Tables 2 and 3. From the values of occupancies some conclusions can be done. The sample with $x = 0.75$ is a fully ordered spinel (within experimental error) with an ordering of 1:3 type at octahedral sites, Li⁺(4b) and Ti⁴⁺(12d). This was already shown by Blasse [6]. For higher x ($x = 0.875$) Ti⁴⁺ ions migrate from 12d to 4b sites (and Li⁺ vice versa), inducing a fast change in ordering and causing a visible decrease of the reflection intensities, which characterize the ordered phase, as shown in Fig. 1. For lower x ($x = 0.50$) Ti⁴⁺ exclusively occupy the 12d site, while Co²⁺ ions are at both octahedral sites. Cation migration leads to a lowering of the ordering, from full ($x = 0.75$) to partial ($x = 0.50$ and $x = 0.875$). The intensities of the reflections (210) and (211) are lower for the concentration $x = 0.875$ than for $x = 0.50$. Consequently, it seems that the migration of Ti⁴⁺ between two octahedral sites is the main reason for the ordering change in octahedral sites (from order to disorder state). Samples with $x \leq 0.40$ show a random cation distribution at octahedral 16d sites

in space group Fd3m, see Table 3. The given cation distributions for binary samples are taken from [2, 10]. Considering each kind of cation we obtained the following results: i) the percentage of Li⁺ in tetrahedral 8a or 8c sites increases, when x increases from 0 to 1, ii) in an ordered spinel Ti⁴⁺ ions dominantly occupy octahedral sites of lower symmetry (12d), and iii) the percentage of Co²⁺ in tetrahedral sites is higher than in octahedral ones, see Tables 2 and 3.

The migration of the cations (Li⁺, Co²⁺, and Ti⁴⁺) influences the changing of the crystal symmetry with concentration, x . The phase transition Fd3m \leftrightarrow P4₃32 at a concentration x_c below $x = 0.5$ is dominantly caused by a Li⁺ preference to an octahedral coordination and a Co²⁺ preference to a tetrahedral ones. The

phase transition P4₃32 \leftrightarrow Fd3m over $x = 0.875$ is induced by the migration of Li⁺, Co²⁺, and Ti⁴⁺. The migration of Ti⁴⁺ from 12d to 4b sites increase, when x changes towards x_c ($0.875 < x_c < 1.00$).

Cation-anion bond lengths for the first coordination spheres were calculated in two ways: a) from the refined values of lattice parameters and fraction coordinates, d^a , and b) by using the obtained cationic distribution and Shannon ionic radii, d^b (Tables 2 and 3). In ordered spinels, cations in 4b sites have six equidistant oxygen ions. Tetrahedrally and octahedrally (12d) coordinated cations have oxygen at different distances, three + one and two + two + two, respectively. The average values are given in brackets, see Tables 2 and 3. The values of d^a and d^b are equal within 2 e.s.d. or better, except for the 4b site, where the differences are from 1 e.s.d. ($x = 0.50$) to 6 e.s.d. ($x = 0.75$). The octahedral 4b sites are preferentially occupied by Li⁺ ions. Thus, the number of electrons per site is small (i.e. 2.7 for the sample with $x = 0.75$) and the accuracy in the determination of the cation-anion distances is smaller. The differences are smaller in disordered samples, see Table 3. The satisfactory agreement between d^a and d^b is a confirmation, that the values of occupation are good enough in all refined samples.

The refined values of the lattice parameter a versus the concentration x are shown in Fig. 3. With increasing x in the formula unit, the parameter a decreases in the full concentration region. In the spinel

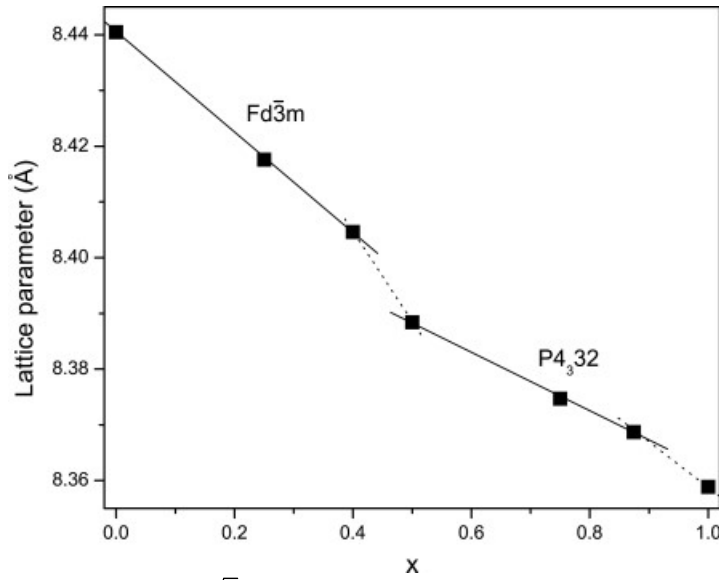


Fig. 3 Lattice parameter versus x for $\text{Li}_{1.33x}\text{Co}_{2-2x}\text{Ti}_{1+0.67x}\text{O}_4$.

structure $a = 8/9(\sqrt{3}d_T + 3d_O)$, where d_T and d_O are the tetrahedral and octahedral cation-anion bond lengths, respectively. The ionic radii are different for the coordination four and six, and are: $r^{\text{IV}}(\text{Li}^+) = 0.73 \text{ \AA}$, $r^{\text{VI}}(\text{Li}^+) = 0.90 \text{ \AA}$, $r^{\text{IV}}(\text{Co}^{2+}) = 0.72 \text{ \AA}$, $r^{\text{VI}}(\text{Co}^{2+}) = 0.79 \text{ \AA}$, $r^{\text{IV}}(\text{Ti}^{4+}) = 0.56 \text{ \AA}$, $r^{\text{VI}}(\text{Ti}^{4+}) = 0.745 \text{ \AA}$, where $r^{\text{IV}}(\text{O}^{2-}) = 1.24 \text{ \AA}$ [17]. Hence, the cation-anion bond lengths are determined by occupancies of the cation sites, and then the obtained $a(x)$ dependence is a consequence of the cation distribution and cation ordering.

The linear dependence of the lattice parameter on the concentration for $0.00 < x < 0.40$ and $0.50 < x < 0.875$ indicates the same structure type and confirms the Vegard's rule validation for these solid solutions. This dependence also shows two nonlinearities (given by the dashed line in Fig. 3), caused by changes in the crystal structure. At concentrations $0.40 < x < 0.50$ and $0.875 < x < 1.00$ there is

a change of the crystal structure, $\text{P4}_332 \leftrightarrow \text{Fd}\bar{3}m$. Around these concentrations there are two phase re-

gions (nonhomogeneity): $\text{P4}_332 + \text{Fd}\bar{3}m$. Probably, long-range cation ordering progressively disappears and the region (cluster) of ordered phase becomes smaller and smaller with decreasing x below 0.50 (or increasing over 0.875). It means that in this case the regions of coherent scattering are smaller and the reflections of the ordered phase are broader, as was shown in Ref. [14]. In a two phase refinement for the samples with $x = 0.50$ and $x = 0.875$ we obtained that the lattice parameters of two phases are the same

within two e.s.d. If the two mentioned samples are nonhomogeneous ($\text{P4}_332 + \text{Fd}\bar{3}m$), a displacement in $a(x)$ should be seen, especially for the samples with $x = 0.50$ (reflection splitting at high angles of diffraction), see Fig. 3. Hence, all investigated samples are single phase. Unfortunately, we have no additional samples with a different concentration near the critical one to give a more precise conclusion.

The slope in the $a(x)$ dependence is more pronounced in the region $0.40 < x < 0.50$, than the one in the region $0.875 < x < 1.00$, see Fig. 3. In ordered samples the lattice parameter depends on three types of cation-anion bond lengths, which are dependent on the cation distribution. Probably, the mentioned difference is caused by the different velocity of cation reordering.

Considering conclusions reported at a similar system $\text{La}_2\text{O}-\text{TiO}_2-\text{Fe}_2\text{O}_3$ [14], we could suggest a

mechanism of changing the crystal symmetry with concentration x ($\text{P4}_332 \leftrightarrow \text{Fd}\bar{3}m$). It is based on the formation of a nucleus (cluster) of a new phase near bordering concentrations. The change in symmetry leads to no change in the coordination spheres but there is a change in the local site symmetry, where $8c(3)$, $4b(32)$, $12d(2)$ is for the order and $8a(-43m)$, $16d(-3m)$ is for the disorder state.

3.2 In-situ X-ray diffraction study of phase transition, $P4_332 \leftrightarrow Fd\bar{3}m$,

in $Li_{1.33x}Co_{2-2x}Ti_{1+0.67x}O_4$

The phase transition and the thermal expansion of ordered and partially ordered spinel samples ($x = 0.50, 0.75, \text{ and } 0.875$) were studied by *in situ* X-ray diffraction technique by following the disappearing of ordered phase reflections. Presence and disappearing of reflections can be used to choose one of the space groups. From X-ray diffraction data at elevated temperatures the lattice parameters are determined. The temperature dependence of the lattice parameters is approximated with a polynomial function, $a(T) = a_0 + a_1T + a_2T^2 + a_3T^3 + \dots$, where the a_i coefficients were fitting parameters. The degree of polynomial was chosen by the following criteria: a) to choose the polynomial of the smallest degree, obtaining the lattice parameter error Δa , less or equal to the experimental one, and b) a further increase of the polynomial degree does not give a considerably smaller error than the previous one [18].

The lattice parameter versus temperature for the sample with $x = 0.50$ is shown in Fig. 4. Two regions are visible, from 973–1073 K and from 1093–1253 K. In the lower temperature region the $a(T)$ dependence is fitted to a linear function and the obtained coefficients were $a_0 = 8.387(5)$ and $a_1 = 1.12(7) \times 10^{-4}$. For the higher temperature region, the third degree polynomial was employed without linear and square parts (a_1 and a_2 are 0). The fitting parameters were $a_0 = 8.4537(9)$ and $a_3 = 5.0(1) \times 10^{-11}$. In the $a(T)$ dependence a change in the lattice symmetry is visible. Namely, at $T_C = (1083 \pm 10)$ K, the spinel from

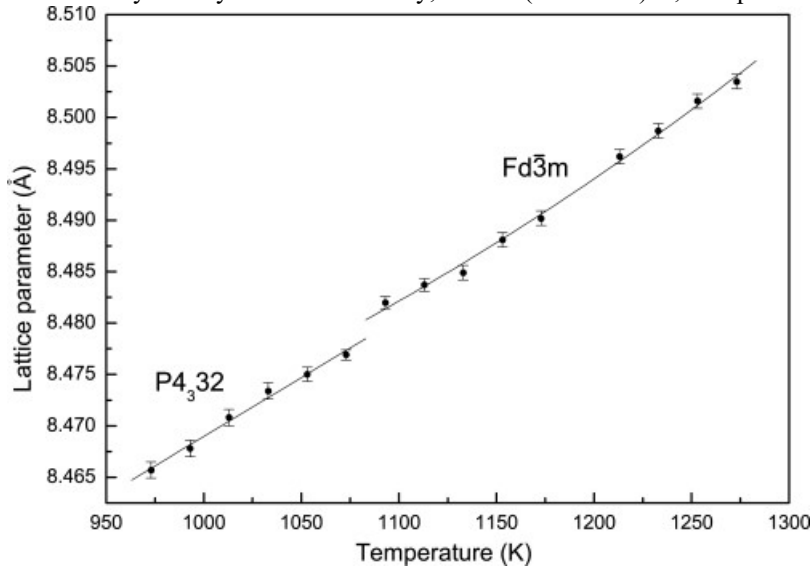


Fig. 4 Temperature dependence of the lattice parameter for $Li_{0.665}CoTi_{1.335}O_4$ ($x = 0.50$).

the ordered state goes to a disordered one, $P4_332 \leftrightarrow Fd\bar{3}m$. At 1253 K, a reflection at $2\theta = 39.57^\circ$ ($d = 2.27 \text{ \AA}$) originating from an unidentified phase appeared. It becomes more intensive at 1273 K ($I/I_{\max} = 0.29$).

The sample with $x = 0.875$ has an order–disorder transition at a temperature less than 973 K. The sample with $x = 0.75$ remains in an ordered state up to 1133 K. But with increasing temperature the reflection intensities (210) and (211) become smaller: $I(210)|_{T=1133}/I(210)|_{T=973} = 0.54$ and $I(211)|_{T=973}/I(211)|_{T=1133} = 0.55$. The temperature dependences of the lattice parameters are shown in Fig. 5. They

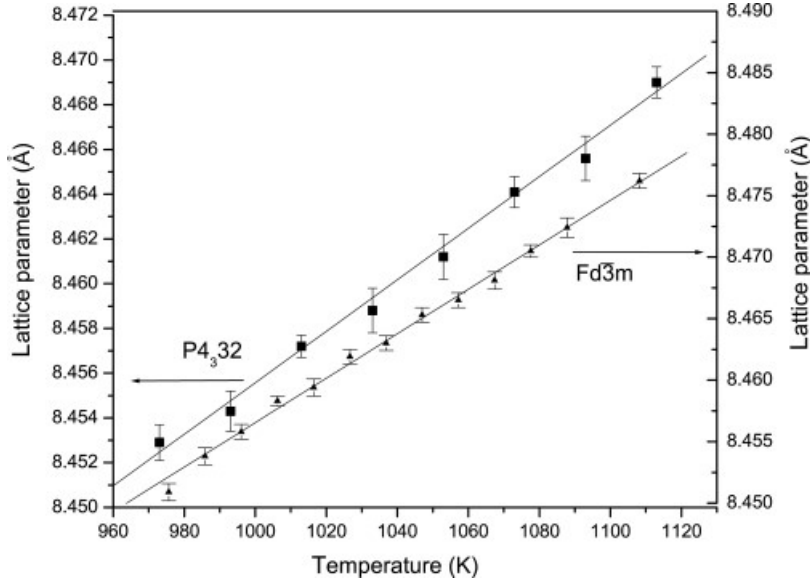


Fig. 5 Temperature dependence of the lattice parameter for $\text{LiCo}_{0.5}\text{Ti}_{1.5}\text{O}_4$ ($x = 0.75$, S.G. $P4_332$) and $\text{Li}_{1.167}\text{Co}_{0.25}\text{Ti}_{1.583}\text{O}_4$ ($x = 0.875$, S.G. $Fd3m$). were approximated by the first order polynomial $a(T)|_{x=0.75} = 8.341(4) + 1.14(4) \times 10^{-4} T$ and $a(T)|_{x=0.875} = 8.331(2) + 1.24(2) \times 10^{-4} T$. The corresponding linear coefficients of the thermal expansion are $\alpha|_{x=0.75} = 13.67 \times 10^{-6} \text{ K}^{-1}$ and $\alpha|_{x=0.875} = 14.88 \times 10^{-6} \text{ K}^{-1}$. In an ordered state the $a(T)$ dependences for $x = 0.50$ and $x = 0.75$ were approximated by linear functions. The obtained α values for both samples were similar ($\alpha|_{x=0.50} = 13.5 \times 10^{-6} \text{ K}^{-1}$). Hence, thermal expansion is higher when samples are in the disordered than in the ordered state, within the same temperature region. The phase transition could be characterized with the point of changing of the crystal symmetry.

Hence, because of the changing of the space group with temperature, $P4_332 \leftrightarrow Fd3m$, is a convergent one. Changes of the reflection intensities of the ordered phase indicate some structural changes, associated with a changing in the cation ordering. Cation migration, as a mechanism of the changes, leads to a decrease of the ordering and a more randomly cation distribution appears, when the temperature goes to the critical one. In a spinel with an 1:3 order at octahedral sites only a first order transition was possible according to the prediction based on Landau's theory of phase transitions [7]. This can suggest the same mechanism for the phase transition with temperature as one mentioned for changing the crystal symmetry with concentration. Thus, near the temperature of the phase transition T_C probably there is a region of

a mixed two phase system, $P4_332 + Fd3m$ and the phase transition goes such as $P4_332 \leftrightarrow P4_332 + Fd3m \leftrightarrow Fd3m$.

4 Conclusion

Lithium oxides with transition metal ions crystallizing in the spinel (i.e. LiMn_2O_4 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$) and layered structures (i.e. LiCoO_2 , LiMnO_2) can reversibly intercalate mobile Li ions in their structure. These materials are intensively investigated as potential electrode materials in lithium ion batteries. We synthesized Co-substituted $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in the full concentration range. It was found that the crystal structure of the samples displays the concentration dependence. Cation ordering at the octahedral sites causes reducing

of the crystal symmetry from S.G. Fd3m to S.G. P4₃32. The change of the crystal structure by varying the chemical composition can improve the electrical properties of the electrode materials, which is important in view of their application.

From a magnetic point of view, the investigated samples are diluted magnetics. The magnetic Co²⁺ ion distribution determines the magnetic behavior and could cause magnetic phenomena related to diluted magnetic systems such as clusterization, spin glass transition, etc.

The order-disorder phase transition was studied by *in situ* X-ray diffraction. A change of the crystal symmetry in samples with partial cation ordering for $x = 0.50$ and $x = 0.875$ was found. In an ordered sample ($x = 0.75$) there is no order-disorder transition up to 1253 K. It was found that the thermal expansion is higher for samples in the disordered state within the same temperature region.

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