INFLUENCE OF THERMAL TREATMENT ON THE CRYSTALLO-GRAPHIC STRUCTURE OF A SERIES OF $Li_2O(5-2t)Fe_2O_3tCr_2O_3$ FERRITES

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In a series of mixed lithium chromites-ferrites with spinel structure, Li_2O $(5-2t)$ $Fe_2O_32tCr_2O_3$, where the parameter t ranges from 0.00 to 1.70 the occurrence of three regions with different type of arrangement of cations has been found.

Limiting compositions for these types of arrangement have been determined. The lattice constant a, the oxygen parameter u and inversion parameter x, have been determined in the entire range of the parameter t. Three samples representing the particular regions of cation arrangement were subject to thermal treatment. For two out of these three samples the transition order-disorder has been investigated and the transition temperature approximately determined. In addition in all investigated samples the character of the ion diffusion was found to be the same.

1. Introduction

A series of mixed lithium chromites-ferrites samples with spinel structure has been obtained by gradual substitution of iron ions in lithium ferrite Li_2O $(5Fe_2O_3)$ by chromium ions.

In the paper of Gorter [1] concerning this series of ferrites the information on the crystallographic structure is unfortunately not quite complete. There are virtually no data on the influence of thermal treatment on this structure. It seemed thus useful to determine the structure of lithium chromites-ferrites in a wide range of the parameter t, to study the influence of thermal treatment on the structural parameters, and to find the influence of the quenching process on the character of ion diffusion in samples with both low and high chromium contents.

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Samples with the following values of the parameter t have been prepared: $t = 0$, 0.10, 0.30, 0.35, 0.40, 0.50, 0.70, 0.95, 1.00, 1.15, 1.25, 1.45, 1.50, 1.55, 1.60, 1.70, and 1.75.

The methods used for the solution of the above-mentioned problems were X-ray diffraction and neutronographic method.

2. Preparation of samples and analysis of their quality

The materials used for the production of samples were pure grade Fe_2O_3 (produced in USSR) and pure Cr_2O_3 and Li_2CO_3 (produced by CIECH, Poland).

Semiquantitative spectral analysis permitted the determination of trace contaminations by Ni (0.004%), Mg (0.008%), Fe (0.05%) and Si (0.03%).

The samples were prepared using the following simple ceramical method:

a) the stock materials were mixed in suitable proportion,

b) the mixture was pressed into pellets,

c) it was subject to preliminary sintering at 1000°C in air atmosphere for six hours and then again at 1150°C for three hours,

d) the samples were cooled at the rate of about 15°C/hour,

e) the pellets were powdered to the grain size of about 60 μm,

f) mechanical stress in grains produced during the grinding process was eliminated by soaking at 200°C for several hours,

g) the samples quenched from corresponding temperatures were prepared by soaking at the temperatures 600, 700, 800, and 1000°C for six hours and then sudden cooling in ice-water mixture,

h) the preparation of powder and the elimination of stress in quenched samples were carried out in the same manner as in case of samples in initial state (not quenched).

After this procedure the samples were subjected to quantitative chemical analysis as well as to phase analysis by means of X-ray method. The contents of the particular elements were determined using the following methods: lithium by flame photometry [2] iron by complexometry [3], and chromium by the biamperometric method [4]. The results of the chemical analysis were consistent with the assumed chemical compositions.

X-ray phase analysis of samples both in initial state and quenched from the particular temperatures has shown pure spinel phase without any admixtures of the initial material which had not entered into the chemical reaction. The X-ray analysis was carried out using a GDR-produced HZG-1 counter goniometer. Samples with low chromium contents were analysed using the K_α line of ^{60}Co ($\lambda = 1.7902$ Å) while those with high chromium contents using the K_α line of Cr ($\lambda = 2.20092$ Å). This procedure permitted the background due to fluorescence to be decreased.

The chemical homogeneity of samples was checked by determining the distribution of iron and chromium in the grains with the use of a CAMECA microprobe. The chemical homogeneity of the samples turned out to be good thus confirming the validity of the adapted technology.

3. Crystallographic structure of samples in initial state

a. Cation arrangement

The distribution of cations in the investigated series of samples can be described by means of the formula

$$Fe_x Li_{1-x}(Li_{x-0.5}Fe_{2.5-x-t}(Cr_t)O_4$$
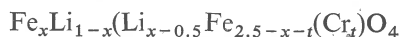
where the cations located in the tetrahedric sublattice are written before and those located in the octahedric lattice inside the brackets. These two types of sublattice are denoted in the further text by A and B, respectively.

When the ratio of the number of iron and chromium to that of lithium ions in sublattice B is close to 3.00, the arrangement of cations established in the sublattice is of the type $1:3$. In such a case the distribution of ion in the spinel lattice is described by the space group $P4_332$ (No 208 in Ref. [5]).

The permissible positions of ions in this space group are the following:

Sublattice A:

Fe in 8(c) x, x, x, $x = 0 + \varDelta_5$

Sublattice B:

B_1 Li in 4(b) $5(8,5(8,5)8$,

B_2(Fe, Cr) in 12(d) $1/2 + x'$ $1/4 + x', 7/8$ $x' = 3/8 + \varDelta_6$

Oxygen sublattice:

O_1 in 8(c) $x'' x'', x''$ $x'' = 3/8 + \varDelta_1$

O_2 in 24(e) x''', y, z $x''' = 3/8 + \varDelta_2$

$y = 1/8 - \varDelta_3$

$z = 1/8 - \varDelta_4$

where $\varDelta_1, \varDelta_2, \varDelta_3, \varDelta_4, \varDelta_5, \varDelta_6$ are variable parameters.

The extinction conditions for this group are listed in International Tables for X-Ray Crystallography [5] and permit super-structure patterns e. g. (210) and (211).

If, however, the ratio of the number of iron and lithium ions to that of iron in tetrahedric sublattice is close to 2.00, then the arrangement of cations becomes of the type $1:1$ in this sublattice which is described by the space group $F\bar{4}3m$ (No 216 in Ref. [5]). The positions of ions in this group are the following: origin at $43m$ and translation FC $(0, 0, 0; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0)$.

Sublattice A:

A_1 Fe in 4(a) $(0, 0, 0)$

A_2 (Li, Fe) in 4(c) $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$

Sublattice B:

(Li, Fe, Cr) in 16(a) $r, r, r;$ $r, \bar{r}, \bar{r};$ $\bar{r}, r, \bar{r};$ $\bar{r}, \bar{r}, r$

Oxygen sublattice:

O_1 in 16(c) $u, u, u;$ $u, \bar{u}, \bar{u};$ $\bar{u}, u, \bar{u};$ $u, \bar{u}, u;$

O_2 in 16(c) $v, v, v;$ $v, \bar{v}, \bar{v};$ $\bar{v}, v, \bar{v};$ $\bar{v}, \bar{v}, v;$

The extinction conditions in the $F\bar{4}3m$ group allow the existence of the superstructure pattern (200). If the above ratios of the ion contents deviate from 3.00 in the octahedric and 2.00 in the tetrahedric sublattice, then the orderly arrangement of cations decays and their distribution in the spinel lattice is described by the space group $Fd3m$ (No 227 in Ref. [5]).

By making use of the appearance of super structure patterns of the type (210) and (211) in the group $P4_332$, and (200) in the group $F\bar{4}3m$ it was possible to determine the limiting values of composition at which an arrangement of a given type occurs. Fig. 1
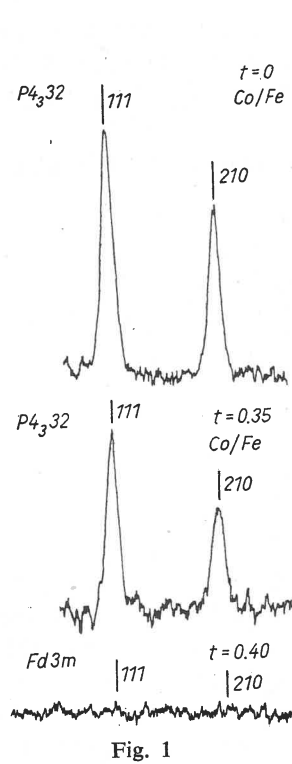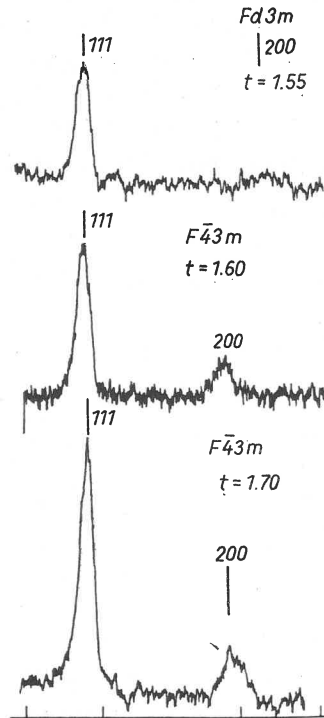

Fig. 1

Fig. 2

Fig. 1. Determination of the limiting composition t for the $P4_332$ group by means of the X-ray diffraction method

Fig. 2. Determination of the limiting composition t for the $F\bar{4}3m$ group by means of the X-ray diffraction method

shows some X-ray diffraction patterns for compositions representing the transition from the group $P4_332$ to $Fd3m$, while Fig. 2 illustrates the determination of the limiting composition of the $F\bar{4}3m$ group.

It follows from Figs 1 and 2 that the samples with t-parameter ranging from 0.40 to 1.55 exhibit no cation arrangement in any sublattice which means that the distribution in such samples is described by the space group $Fd3m$.

The permissible positions of ions in this group are the following: origin at $\bar{4}3m$ and translation FC $(0, 0, 0;\ 0,\ \frac{1}{2},\ \frac{1}{2};\ \frac{1}{2},\ 0,\ \frac{1}{2};\ \frac{1}{2},\ \frac{1}{2},\ 0)$.

Sublattice A:

(Fe, Li) in 8(a) $0, 0, 0$ $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$;

Sublattice B:

(Li, Fe, Cr)   16(a) $\frac{5}{8}, \frac{5}{8}, \frac{5}{8}$; $\frac{5}{8}, \frac{7}{8}, \frac{7}{8}$; $\frac{7}{8}, \frac{5}{8}, \frac{7}{8}$; $\frac{7}{8}, \frac{7}{8}, \frac{5}{8}$;

Oxygen sublattice:

O in 32(e) u, u, u; $u, \bar{u}, \bar{u}$; $\frac{1}{4}-u, \frac{1}{4}-u, \frac{1}{4}-u$; $\frac{1}{4}-u, \frac{1}{4}+u, \frac{1}{4}+u$;

$\bar{u}, u, u$; $\bar{u}, \bar{u}, u$; $\frac{1}{4}+u, \frac{1}{4}-u, \frac{1}{4}+u$; $\frac{1}{4}+u, \frac{1}{4}+u, \frac{1}{4}-u$.

b. Determination of structural parameters

For the whole investigated composition range the authors have determined the lattice constant, the inversion parameter, and the oxygen parameter. The measurement of the lattice constant was made using a counter goniometer (HZG-1).
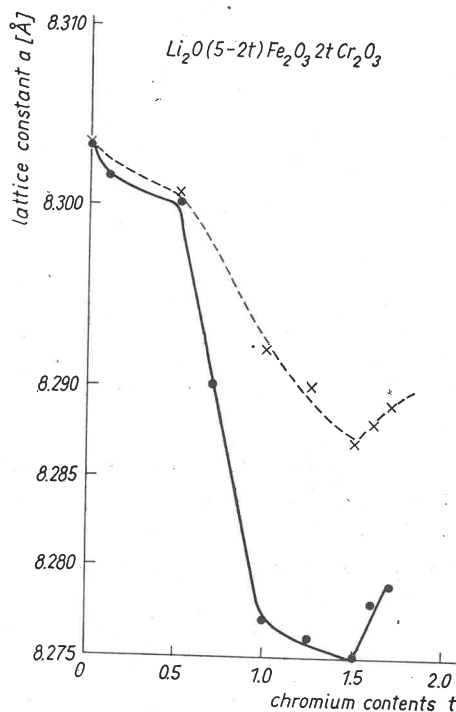

Fig. 3. Dependence of the lattice constant on chromium contents in a series of lithium ferrites-chromites. ———— present work, – – – – Gorter's work [1]

Fig. 3 shows the comparison of the dependence of the lattice constant on the composition according to our data and those of Gorter [1]. It can be seen that there is qualitative agreement between the results of these two papers; the quantitative differences may be due to differences in the technology of the preparation of samples.

The measurement of other structural parameters, *i. e.*, the inversion parameter and the oxygen parameter *u* have been made using the neutron diffraction method. Unfortunately the iron and chromium ions cannot be distinguished in *X*-ray analysis owing to very close atomic numbers. On the other hand the amplitudes for neutron scattering on these two nuclei differ considerably ($b_{Fe} = 0.96 \cdot 10^{-12}$ cm^{-1} and $b_{Cr} = 0.35 \cdot 10^{-12}$ cm^{-1}), which permits accurate determination of the position of iron, the *x*-parameter and the oxygen parameter *u*. A detailed description of the method of determination of these two parameters is given in Ref. [6]. For samples with cation arrangement described by the group $F\overline{4}\,3m$ the values of the oxygen parameter, the inversion parameter, the Debye-
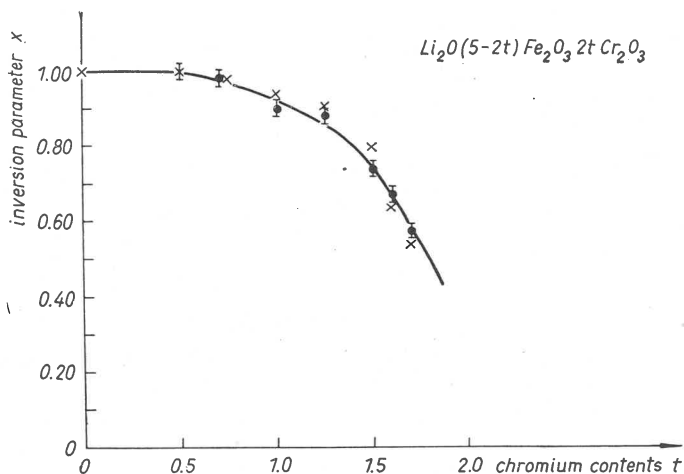

Fig. 4. Dependence of the inversion parameter on chromium contents in a series of lithium ferrites--chromites. ● present work, × Gorter's work [1]

Waller factor and the parameter *r* which is free in this group have been determined with the help of the UMC-1 computer. The accuracy of these quantities has been computed on the basis of statistical errors.

The measure of the goodness of the fit was the *R*-index defined as follows:

$$ R = \frac{\sum |I_{exp} - I_{calc}|}{\sum I_{calc}} $$

The results of the fits for the particular samples in initial state are given in Table I. The compositions *t* for which the values of the parameters have been fitted by the computer are marked by asterisks.

The dependence of the inversion parameter on the composition is shown in Fig. 4. For the sake of comparison the results of Gorter [1] have also been plotted in the figure.

It follows from Fig. 4 that the ferrites of the investigated series of samples are completely inversed up to $t = 0.70$, and become slowly normal with increasing chromium content. The oxygen parameter for these ferrites has been determined for the first time in the

TABLE I

Parameters defining the structure of lithium ferrites-chromites in initial state. The values given at the particular hkl correspond to the intensities

$$jF^2 \exp\left(-\frac{2W\sin^2\theta}{\lambda^2}\right)$$

Composition t	0.50 $Fd3m$		0.70 $Fd3m$		1.00 $Fd3m$		1.25 $Fd3m$		1.50 $Fd3m$		1.60* $F\bar{4}3m$		1.70* $F\bar{4}3m$	
hkl	I_{calc}	I_{meas}	I_{calc}	I_{meas}	I_{calc}	I_{meas}	I_{calc}	I_{meas}	I_{calc}	I_{meas}	I_{calc}	I_{meas}	I_{calc}	I_{meas}
111	1.10	1.00	1.00	0.90	1.50	3.00	2.00	0	1.60	0	53.42	66.68	88.23	99.56
200	—	—	—	—	—	—	—	—	—	—	46.45	61.68	93.93	110.82
220	717.12	680.20	693.12	668.07	575.96	600.38	552.00	606.19	374.28	379.74	302.21	318.71	192.65	242.04
311	2107.92	2050.10	1761.36	1741.19	1461.29	1528.74	1147.20	1280.89	931.92	913.22	896.05	920.45	877.75	844.35
222	803.20	801.84	921.20	881.36	1040.80	1120.50	1284.00	1291.50	1243.44	1202.26	1228.59	1170.62	1225.92	1258.87
400	1350.00	1349.50	1713.60	1716.00	2053.20	2030.10	1728.00	1735.89	2043.06	1982.14	2194.57	2198.15	2561.44	2517.22
331, 420	144.00	151.38	252.60	259.04	268.70	321.20	468.80	478.27	251.76	268.01	576.58	587.04	621.89	800.28
422	1379.28	1255.51	1311.84	1321.37	1055.04	1100.13	979.20	953.54	653.76	773.86	469.69	592.74	312.64	332.70
511, 333	3507.52	3495.75	3471.12	3387.70	3072.32	2845.57	2844.00	2670.81	2409.76	2515.15	2713.34	2589.98	2310.87	2331.04
440	14125.20	13391.85	13157.28	13130.21	11924.40	11556.12	10620.00	10547.08	10015.56	9940.00	9389.23	9367.28	9322.85	9072.85
R-index	4.2%		1.00%		4.20%		2.50%		2.30%		2.30%		3.62%	
Inversion parameter	1.00±0.02		0.98±0.02		0.90±0.02		0.88±0.02		0.74±0.02		0.675±0.005		0.575±0.005	
Oxygen parameters uvw and r parameter	0.379±0.002		0.381±0.002		0.382±0.002		0.383±0.002		0.384±0.002		0.385±0.002 0.864±0.002 0.626±0.001		0.383±0.002 0.867±0.002 0.624±0.001	
Debye-Waller factor W (Å⁻²)	0.90		0.85		0.86		0.74		0.82		0.76		0.86	

present paper. Using the determined distribution of cations and the ionic valence which is known, we have determined the average charge in the tetrahedric sublattice. The knowledge of this charge permits the check of the applicability of the semiempirical formula for oxygen parameter. According to Ref. [7] this formula has the following form:

$$u = 0.407 - 0.012\, q_A \pm 10^{-3}\, q_A^2$$

where q_A is the average charge.

A comparison of the value of the oxygen parameter measured with those calculated by means of the above formula is shown in Table II.

TABLE II[1]

Composition t	x	q_A	u_{calc}	u_{meas}
0	1.00	3.00	0.380	0.379
0.50	1.00	3.00	0.380	0.379
0.70	0.98	2.96	0.380	0.381
1.00	0.90	2.80	0.381	0.382
1.25	0.88	2.76	0.382	0.383
1.50	0.74	2.48	0.383	0.384
1.60	0.68	2.35	0.384	0.385
1.70	0.58	2.15	0.386	0.383

[1] Error of oxygen parameter measurement ± 0.002.

It can be seen from Table II that the agreement of the calculated values of u with experiment is good.

4. The crystallographic structure of quenched samples

a. Study of the order-disorder transformation

The thermal treatment consisted in quenching samples of some chosen composition from the temperatures 600°C, 700°C, 800°C, and 1000°C.

Three compositions representing three different types of cation arrangement were subject to quenching:

$t = 0.10$ (arrangement $1:3$ in octahedrons described by the $P4_332$ group)

$t = 0.70$ (no arrangement in any sublattice described by the $Fd3m$ group)

$t = 1.60$ (arrangement of the type $1:1$ in tetrahedrons described by the $F\bar{4}3m$ group).

The influence of the quenching process on the crystallographic structure of samples with the above-listed compositions was investigated using mainly the X-ray diffraction method. The signal for the occurrence of arrangement of a specific type was the appearance of additional patterns which are extincted in the $Fd3m$ group, $e. g.$ the (210 peak in the $P4_332$ group and (200) peak in the $F\bar{4}3m$ group. X-ray measurements made, have shown that long range cation order in both sublattices decreases with increasing quench-

ing temperature. It was found that for the composition $t = 0.10$ the temperature of the order-disorder transformation was about 800°C and for the composition $t = 1.60$ the corresponding temperature amounted to 1000°C. The measurements for $t = 1.70$ with a sample quenched from 1000°C have shown that long range order in the tetrahedric lattice remained. For this particular t-value we have observed, however, a considerable weakening of superstructure patterns in quenched samples, in comparison with those
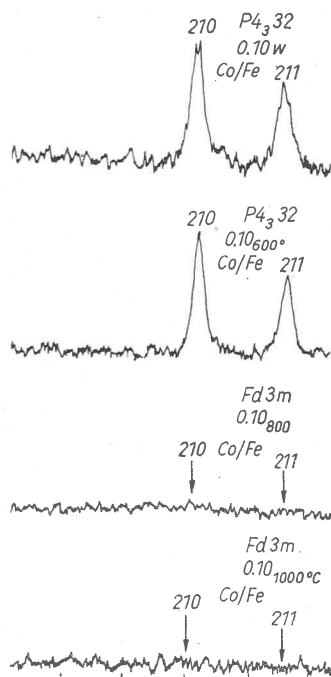

Fig. 5

Fig. 6

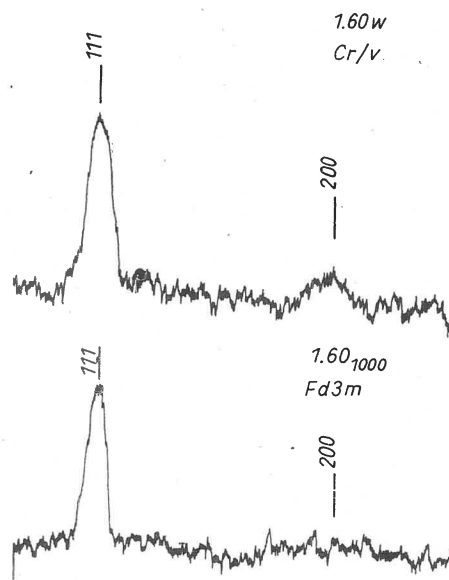Fig. 5. Sample with $t = 0.10$. Transformation from the $P4_332$ group to $Fd3m$ due to thermal treatment

Fig. 6. Sample with $t = 1.60$. Transformation from the $F\bar{4}3m$ group to $Fd3m$ due to thermal treatment

in initial state. This would mean that the orderly arrangement phase is considerably diminished for the former. These facts permit the conclusion to be drawn that the temperature of order-disorder transformation increases with increasing chromium contents.

Figs 5 and 6 show X-ray diffraction patterns of samples with $t = 0.10$ and $t = 1.60$ illustrating the transformation from the $P4_332$ group to $Fd3m$, and from $F\bar{4}3m$ to $Fd3m$.

b. Determination of structural parameters of quenched samples

For three representative compositions of samples quenched from the temperatures 600, 700, 800 and 1000°C we have determined the lattice constant, the inversion parameter and the oxygen parameter. The method of the determination of the lattice con-

stant was the same as in case of samples in initial state. The estimated error of this constant does not exceed 0.001 Å.

The two remainig structural parameters were fitted using the ODRA 1303-computer. The R-index of the structure did not exceed 7% in any sample.

For samples with the t-values 0.70 and 1.60 quenched from 1000°C neutronographic measurements have been made in order to investigate whether the ions migrating between the A and B sublattices are Li and Fe or Li, Fe, and Cr. The suggestion of Ref. [8] is that both processes are possible. The results of the fits for the particular compositions are listed in Table III.

TABLE III

Parameters defining the structure of lithium ferrites-chromites quenched from 1000°C. $Li_{1-x}Fe_{x-y}Cr_y$ $(Li_{x-0.5}Fe_{2.5-x+y-t}Cr_{t-y})O_4$. The values given at the particular hkl correspond to the intensities

$$jF^2 \exp = \left(- \frac{2W \sin^2\theta}{\lambda^2} \right)$$

Composition t	0.70		1.60	
hkl	I_{calc}	I_{meas}	I_{calc}	I_{meas}
111	0.72	0	27.68	20.10
220	747.00	740.00	282.24	279.15
311	1854.24	1820.00	752.62	756.50
222	1987.20	1960.10	1152.00	1130.00
400	2009.40	2100.20	2281.20	2275.10
331	361.20	350.10	244.32	234.15
422	1296.48	1276.00	411.36	405.10
511.333	2780.80	2800.00	2757.92	2740.82
440	13548.10	13510.00	7440.00	7415.10
R	1.50%		1.00%	
x	0.94 ± 0.02		0.65 ± 0.02	
y	0 ± 0.02		0.01 ± 0.02	
u	0.385 ± 0.002		0.386 ± 0.002	
W	0.92		0.88	

The data contained in Table III indicate that in samples with both high and low t-values only the Li^+ and Fe^{3+} ions migrate between the two sublattices. This is consistent with the fact that the chromium ions have a rather high binding energy to octahedric coordination.

Figs 7, 8, and 9 shows the dependence of the inversion parameter in the quenching temperature and of the lattice constant on the inversion parameter for t-values: 0.10, 0.70, and 1.60. The errors of the parameters are indicated in the figures.

The results indicate that thermal treatment exerts similar influence on the structural parameters in the whole investigated t-range. Below 600°C the diffusion of ions is insignificant. As the temperature increases the diffusion rate becomes higher. On the other hand the inversion parameter decreases with increasing temperature, and the ferrites become more normal.
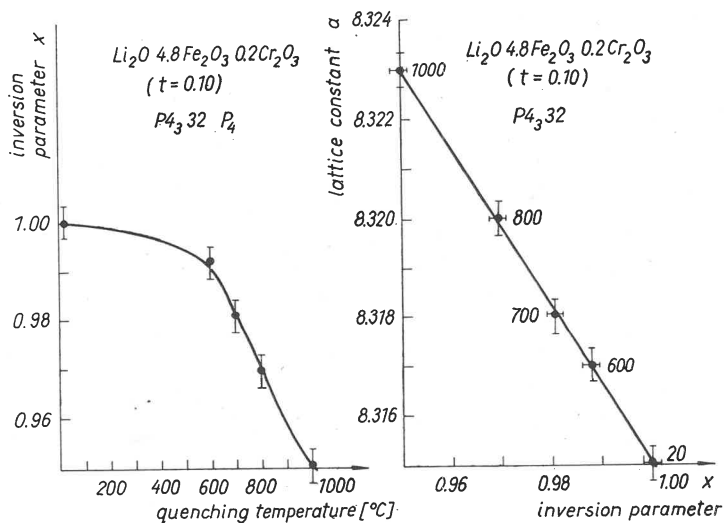

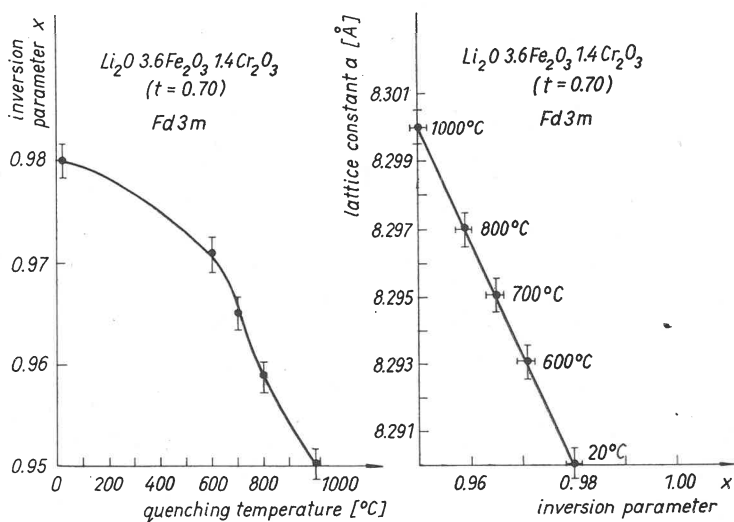Fig. 7. Sample with $t = 0.10$. Change of structural parameters due to thermal treatment

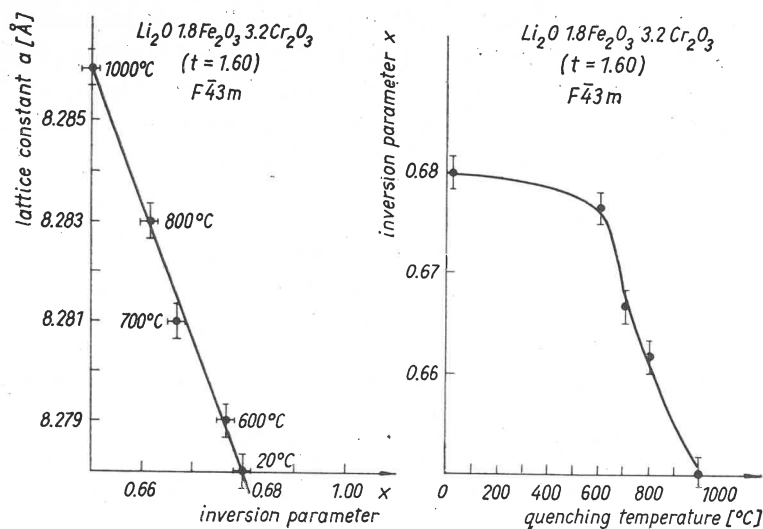Fig. 8. Sample $t = 0.70$. Change of structural parameters due to thermal treatment

Fig. 9. Sample with $t = 1.60$. Change of structural parameters due to thermal treatment

5. Conclusions

In the investigated series of ferrites there are three t-regions with different types of arrangement of cations: X-ray diffraction measurements permitted the limiting compositions to be determined for the particular types of arrangement. The quenching of samples from the particular temperatures gives rise to phase transformation from order to disorder. It was found that for any t-value the character of the diffusion of ions between A and B sites is the same and consists in the dislocation of Fe and Li ions only, whereas the Cr-ions are completely fixed at their octahedric sites.

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