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Microstructure studies on Ti^{4+}- and Zr^{4+}-substituted Li–Zn ferrites

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Abstract. XRD and microstructure studies were carried out on Ti^{4+} and Zr^{4+}-substituted Li–Zn ferrites prepared by standard ceramic technique. All the ferrite compositions exhibit single phase formation. The lattice parameter *a* increases linearly with the content of $Zn^{2+}Zr^{4+}$ and $Zn^{2+}Ti^{4+}$, which is attributed to the ionic volumes of the cations involved. With substitution by Zr^{4+} the average size decreases, while with substitution by Ti^{4+} the grain size increases. In both the series grain size varies with the composition. Excess substitution of Zr^{4+} ($x > 0{\cdot}4$) leads to the formation of secondary images and discontinuous grain growth. Both Zr^{4+} and Ti^{4+} compositions obey Kurtz theory.

Keywords. Microstructure; grain size.

1. Introduction

Understanding and control of microstructure in ferrites is important because many properties such as mechanical strength, electrical conductivity, magnetic susceptibility, optical transmission, etc. are strong functions of microstructure (Yan *et al* 1976; Postupolski 1989).

For specimens of the same composition, the dielectric permittivity of ferrites is related to the average grain size (Mioshkin *et al* 1981).

For polycrystalline ferrites microstructure means porosity, grain structure and phases detectable by micrographic analysis. In this communication we report the grain size and spatial features of granular structure of Ti^{4+}- and Zr^{4+}-substituted Li–Zn ferrite.

2. Experimental

Ferrites of the composition $Li_{0{\cdot}5}Zn_xZr_xFe_{2{\cdot}5-2x}O_4$ ($x = 0, 0{\cdot}1, 0{\cdot}2, 0{\cdot}3, 0{\cdot}4, 0{\cdot}5$) and $Li_{0{\cdot}5}Zn_xTi_xFe_{2{\cdot}5-2x}O_4$ ($x = 0, 0{\cdot}1, 0{\cdot}2, 0{\cdot}3, 0{\cdot}4, 0{\cdot}5$) were prepared by the standard ceramic method using AR grade oxides of Li_2CO_3, ZrO_2, TiO_2, ZnO and Fe_2O_3. Pre-sintering of powders was carried out for 8 h at 725°C, while the final sintering was done at 1100°C. The compositions were cooled in the furnace at 80°C/h. X-ray diffraction studies were carried out with a Philips PW 1820 diffractometer using Fe K_α radiation.

In order to determine the average grain size, SEM micrographs of all compositions were taken using a well-polished pellet surface. The average grain size has been evaluated by using the method already described (Ishikawas *et al* 1989). About 10 SEM micrographs for each composition were used to compute average grain size and spatial features of granular structure.

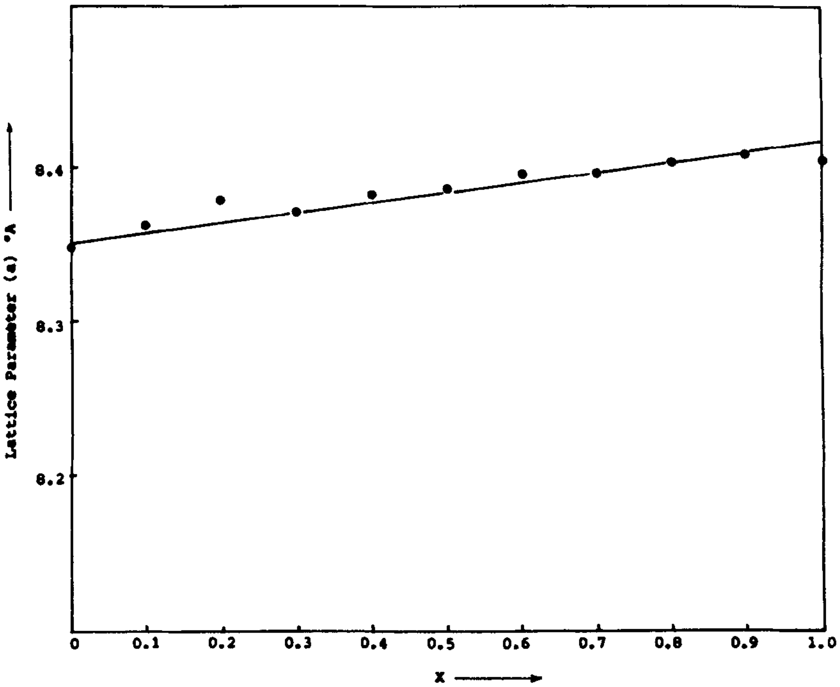


Figure 1. Compositional variation of the lattice parameter for the series $Li_{0.5}Zn_xTi_x \cdot Fe_{2.5-2x}O_4$.

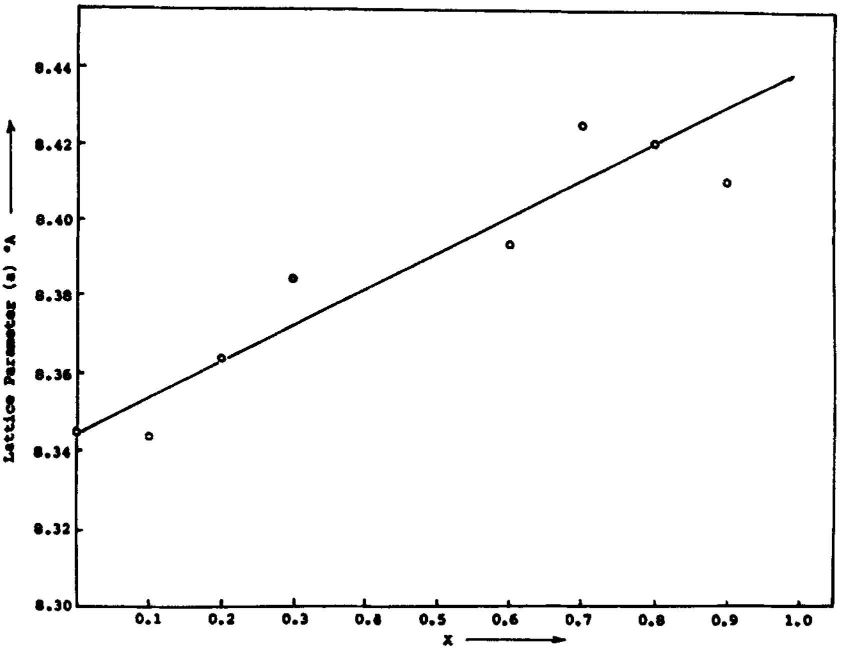


Figure 2. Compositional variation of the lattice parameter for the series $Li_{0.5}Zn_xZr_x \cdot Fe_{2.5-2x}O_4$.

3. Results and discussion

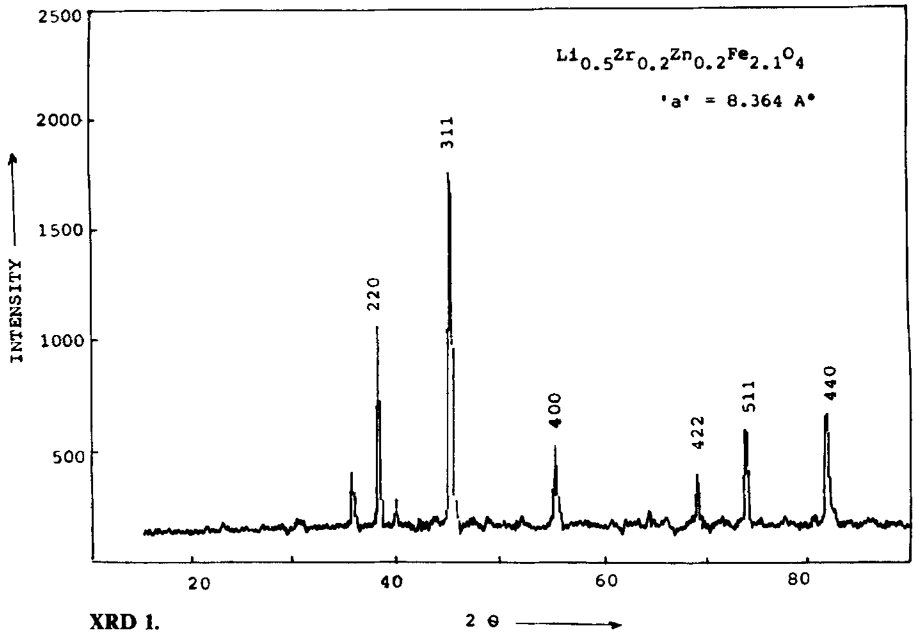
In figure 1 variation of the lattice parameter *a* (Å) with the content of TiZn, i.e. *x* for the series $Li_{0\cdot5}Ti_xZn_xFe_{2\cdot5-2x}O_4$ ($x = 0$, 0·1, 0·2,…, 1), is given. Concentration of Li^{1+} ions (0·6 Å) is kept constant. An increase of Zn^{2+} (0·74 Å) and Ti^{4+} (0·68 Å) reduces the Fe^{3+} (0·67 Å) concentration. Thus an increase of *a* with increase of *x* is due to ionic volumes of Ti^{4+} and Zn^{2+}.

The lattice parameter *a* in figure 2 increases with content of ZrZn. Concentration of Li^{1+} ions (0·60 Å) is kept constant. An increase of Zn^{2+} (0·74 Å) and Zr^{4+} (0·80 Å) reduces the Fe^{3+} (0·67 Å) concentration. Thus an increase of *a* with increase of *x* is due to ionic volumes of Zr^{4+} and Zn^{2+}. The completion of the solid state reaction and single phase formation of the composition have been confirmed from X-ray diffraction patterns as shown below (XRDs 1 and 2).

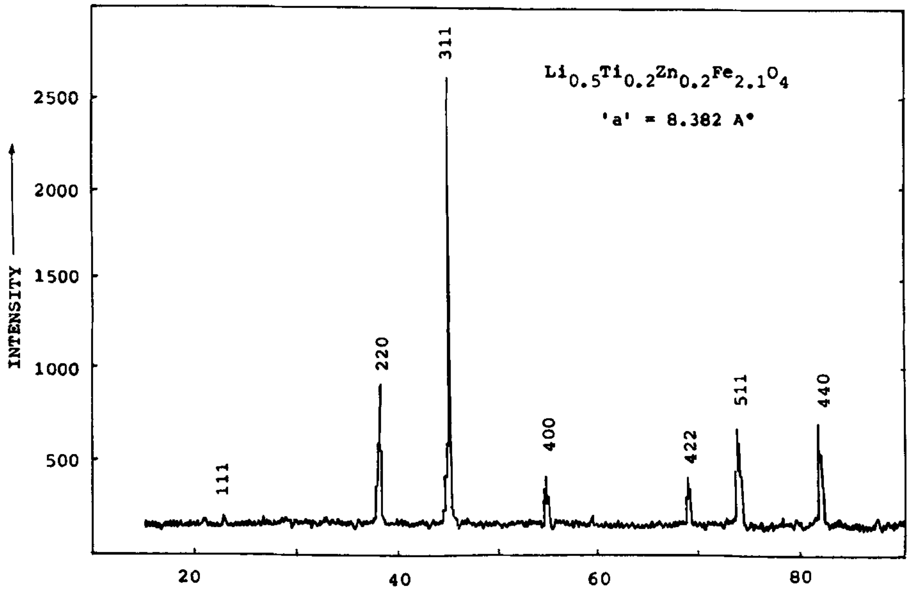
From SEM photographs shown in figures 3 and 4 the grain size *Dm* is calculated by (i) drawing a diagonal on the photograph, (ii) measuring the maximum unidirectional particle size in the vertical direction against the diagonal, and (iii) averaging the maximum unidirectional particle size.

In table 1 the data on grain size of various compositions is given.

From table 1 it is seen that for the system $Li_{0\cdot5}Ti_xZn_xFe_{2\cdot5-2x}O_4$, with the addition of Ti_xZn_x the average grain diameter *Dm* (μm) increases up to $x = 0\cdot3$ and decreases for $x > 0\cdot3$. However, the grain size of all the substituted ferrites is greater than that of unsubstituted ferrite, i.e. Li ferrite. From the photographs (figure 3) some observations have been made: (i) the grain growth is continuous and there are no exaggerated grains, (ii) secondary electron images do not appear in any of the micrographs, and (iii) the pore size does not show any regular trend with increase of TiZn concentration. In all the cases pore size is between 0·5 and 1 μm.



XRD 1.



XRD 2.

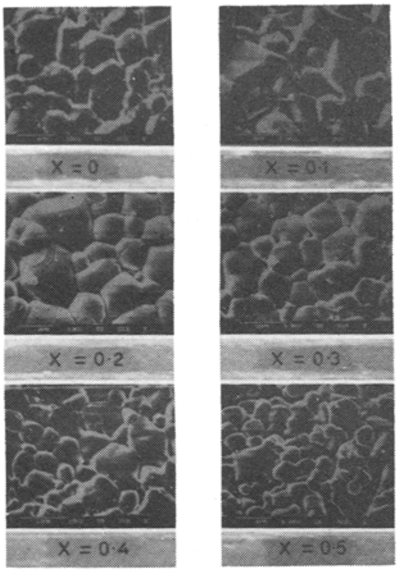


Figure 3. Microstructure photographs for the compositions $Li_{0.5}Zn_xTi_xFe_{2.5-2x}O_4$.

In order to adequately characterize this structure, the spatial dimensions and shapes of grains of which the polycrystalline material is built should be determined first. This should be of statistical character because the grains forming the real polycrystalline material are differentiated in size and shape. The microstructural examinations of the opaque granular solids are formed mainly for two-dimensional images of the

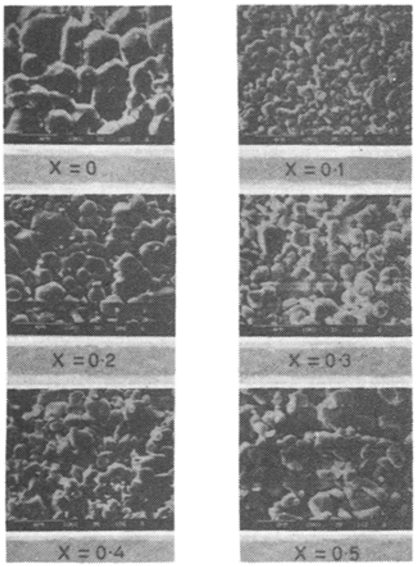


Figure 4. Microstructure photographs for the compositions $Li_{0\cdot5}Zn_xZr_xFe_{2\cdot5-2x}O_4$.

Table 1. Composition and grain size.

$Li_{0\cdot5}Zr_xZn_xFe_{2\cdot5-2x}O_4$ Composition x	Grain size $Dm(\mu m)$	$Li_{0\cdot5}Ti_xZn_xFe_{2\cdot5-2x}O_4$ Composition x	Grain size $Dm(\mu m)$
0·0	2·74	0·0	2·74
0·1	0·93	0·1	2·81
0·2	1·63	0·2	4·01
0·3	1·70	0·3	6·00
0·4	1·15	0·4	4·69
0·5	0·81	0·5	2·86

granular structure. Such images are obtained by the random plane cross-section of a sample. For each planar image the size *Dm* and number of sides *n* have been determined for each individual grain cross-section (having a polygon shape). Independently, the coordination number k_n (number of nearest neighbours) for each grain cross-section have also been determined. The grain cross-section size *Dm* is the planar granulometric parameter, the number *n* and k_n are the planar topological parameters of the plane image of granular structure (figures 5 and 6).

The main results of the analysis are as follows: The number of neighbours k_n of the planar grain cross-section (being a polygon) is statistical, equal to the number of its sides *n*.

The number of sides *n* of the polygon, being a result of averaging the statistically large number of random planar intersections of one polyhedron, is linked with the number of faces *F* of this polyhedron by the following topological relationship

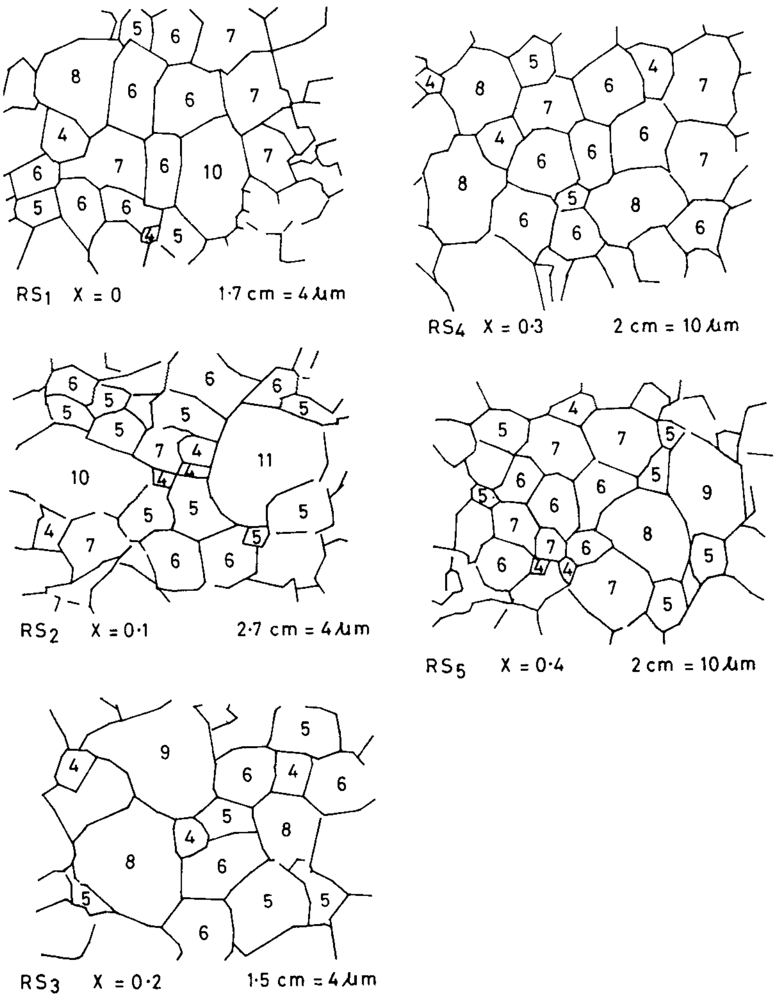


Figure 5. Fragment of the drawn contours of planar grain cross-section with marked numbers of nearest neighbour (coordination numbers) for ZnTi system.

(Postupolski *et al* 1988):

$$n = (\pi/2)\sqrt{F}. \tag{1}$$

As it has been reported (Hald 1952) this formula is valid not only for regular polyhedra with regular faces but also for the irregular polyhedra with various faces.

As the relationship between n and F is known, the type of distribution of number of grain faces F, $G(F)$ can be obtained starting from the known distribution function of $n, g(n)$. Using a transformation formula,

$$G(F) = g(n)\frac{\mathrm{d}n}{\mathrm{d}F}, \tag{2}$$

for

$$n = f(F) = 0{\cdot}5\pi\sqrt{F}. \tag{3}$$

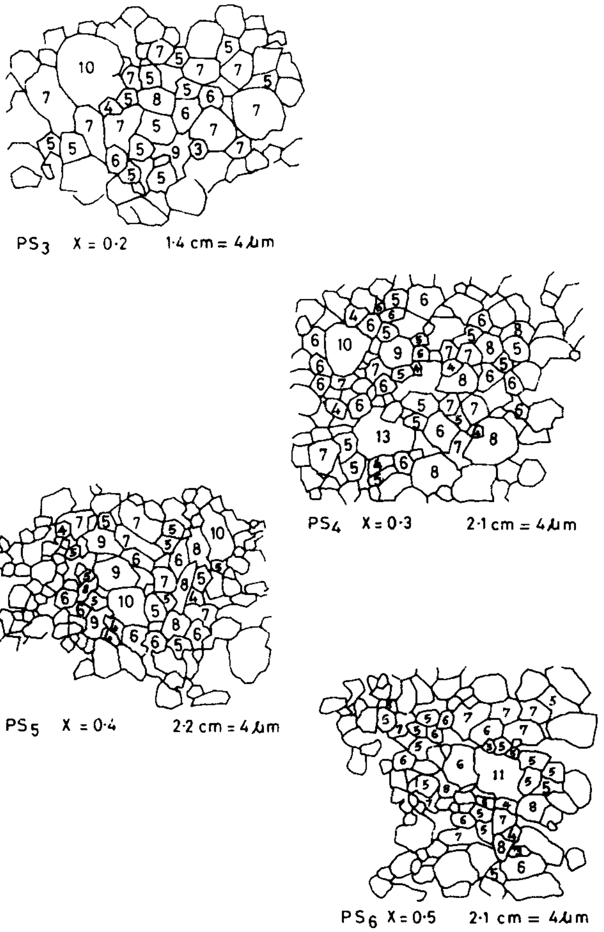


Figure 6. Fragment of the drawn contours of planar grain cross-section with marked numbers of nearest neighbours (coordination numbers) for ZnZr system.

It is observed that for all the compositions

$$n_{av} = 6{\cdot}1 \text{ and } F(n_{av}) = 15,$$

$$n_{max} = 12 \text{ and } F(n_{max}) = 60.$$

From the data on grain size *Dm* for $Li_{0\cdot5}Zr_xZn_xFe_{2\cdot5-2x}O_4$ series given in table 2, the following observations have been made:

(i) With the addition of ZnZr in the system the grain size *Dm* decreases. Grain size of $Li_{0\cdot5}Fe_{2\cdot5}O_4$ sample is greater than that of all the substituted samples.

(ii) The grain size *Dm* initially decreases on addition of ZnZr, then it increases and reaches a value 1·70 µm for the sample with $x = 0{\cdot}3$, and for further increase of x *Dm* shows a decreasing trend.

(iii) From the micrographs of the samples (figure 4) it is seen that the average pore size for all the samples varies from 0·5 µm to 0·88 µm. However there is no systematic variation of pore size and content of ZnZr, i.e. x.

(iv) For $x > 0{\cdot}4$ secondary images tend to appear. These images become distinct in the sample with $x = 0{\cdot}5$. Thus the secondary images appear to be composition-sensitive. The average size of the secondary image is 0·31 μm.

(v) It is also seen that grain growth tends to be discontinuous with addition of ZnZr, promoting exaggerated grain growth.

Table 2. Data on dc resistivity ρ_{dc} for the series $Li_{0{\cdot}5}Zn_xZr_x{\cdot}Fe_{2{\cdot}5-2x}O_4$.

Composition (x)	dc × 10^5 (Ωm)
0·0	3
0·1	25
0·2	33
0·3	62
0·4	98

Table 3. Grain size and frequency.

Neighbours (n)	Grain size Dm(μm)	Frequency
3	1·65	1
4	1·45	4
	1·86	3
	0·72	8
5	2·18	6
	6·00	3
	3·00	3
	4·30	5
	0·92	42
6	1·77	4
	3·75	9
	6·00	10
	1·14	26
7	3·50	5
	7·00	9
	1·33	27
8	4·00	1
	6·60	1
	8·50	3
	1·71	11
9	5·80	1
	1·43	4
10	3·26	1
	4·23	1
	2·10	4
11	2·28	1
	3·26	1
12	—	—
13	3·1	1

Discontinuous grain growth is expected to increase the intergranular porosity of the matrix resulting in increase of ρ_{dc} as seen from table 2.

On comparing grain sizes of $Li_{0\cdot5}Ti_xZn_xFe_{2\cdot5-2x}O_4$ and $Li_{0\cdot5}Zr_xZn_xFe_{2\cdot5-2x}O_4$ compositions, it is seen that the average grain size of all compositions of $Li_{0\cdot5}Zr_x\cdot Zn_xFe_{2\cdot5-2x}O_4$ is smaller. The smaller grain size resulted in X-ray line broadening in XRD.

The formula $n = 0{\cdot}5\pi\sqrt{F}$ is used to fix sides of polyhedron, and the observations are similar to the previous one, i.e.

$$n_{av} = 6{\cdot}1 \text{ and } F(n_{av}) = 15,$$

$$n_{max} = 12 \text{ and } F(n_{max}) = 60.$$

These values agree closely with the corresponding values of n_{av} and n_{max} reported for samples of Ni–Zn and Mn–Zn ferrites (Postupolski 1989).

An interesting result that follows from theory developed by Kurtz and Carpay (1980) is that maximum to median grain size should be constant at a value $D_{max}/D_{med} = e$.

In TiZn-substituted series that ratio is about 1·5 while in ZrZn-substituted system it is 1·6.

In table 3 data on number of nearest neighbours (n), frequency and average grain size obtained from the SEM photographs of all compositions are given.

From table 3 it is clear that the tendency to show maximum coordination number is with $n = 5$, 6 and 7.

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