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Precision cell dimensions of manganese-doped nickel ferrites. By K. N. SUBRAMANYAM and L. R. KHARE,
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In the spinel $\text{NiFe}_{2-x}\text{Mn}_x\text{O}_4$, doping of Mn in place of Fe to a value of $x = 0.02$ preserves unchanged the unit cell of the ferrite, while $x = 0.05$ of manganese significantly enlarges the unit cell.

Introduction

The general strategy in precision measurements of cell dimensions of polycrystalline substances by photographic methods has been extensively described by Parrish & Wilson (1959), Lipson & Steeple (1968), and many others. In the present work, spectroscopically pure Ni, Fe and Mn oxides were mixed in the proportions to produce Mn-doped Ni ferrites of the following compositions: $\text{NiFe}_{1.98}\text{Mn}_{0.02}\text{O}_4$ and $\text{NiFe}_{1.95}\text{Mn}_{0.05}\text{O}_4$. Initially, the oxides were mixed and thoroughly ground in a pestle and mortar. The mixture was then pre-fired at 600°C for 12 h and again ground to produce particles of the order of $1\ \mu\text{m}$ diameter. The resulting powder was then mixed with a few drops of distilled water before being compressed in a die at a pressure of $1.303 \times 10^8\ \text{N m}^{-2}$ to produce cylindrical pellets. These specimens were again pre-fired and were finally sintered for 10 h at 1200°C in an oxygen atmosphere of $1.013 \times 10^5\ \text{N m}^{-2}$. The samples were then slowly cooled until the temperature had reached 600°C , when the specimens were allowed to cool rapidly to room temperature. The above samples were adapted for X-ray work as follows. The sample was broken into small pieces and pulverized into particles of the size of a few μm . Long and narrow cylindrical specimens were made by coating a mixture of the powder sample with 'gum tragacanth' on a Lindemann-glass fibre. The X-ray powder photographs of the two samples were taken with filtered Co radiation of wavelengths $K\alpha_1 - 1.7889$ and $K\alpha_2 - 1.7928\ \text{\AA}$. The routine indexing of the photographs showed that the unit cell of the two samples is of the f.c.c. type. Other relevant details of experimental procedure, film measurement and corrections are exactly the same as outlined by Subramanyam (1971a). The results of film measurements on

several high-angle reflections were used in a computer program from which Tables 1 and 2 containing the d spacings and their corresponding cell edges a were obtained. In turn, the several values of a were plotted against the Nelson–Riley function:

$$f(\theta) = \frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$$

to obtain the extrapolated value of a corresponding to $2\theta = 180^\circ$.

Discussion

The chemical analyses of the content of the samples showed that they were within 10% of ideal. Repeated measurements on the same film show negligible scatter in the measured value of the cell dimension a . The differences in cell dimensions between the two specimens are definitely outside the limits of experimental error, as determined by the method of least squares with a computer program.

According to Subramanyam (1971b), the measured oxygen U parameter values for the present samples with $x = 0.02$ and $x = 0.05$ Mn are (0.381 ± 0.001) and (0.384 ± 0.001) respectively. These values, coupled with the a cell dimensions have been used for the following discussion. Smit & Wijn (1959) show that, for small displacements, the radii of the spheres in both types of interstitial site are given by:

$$r_A = [(U - \frac{1}{4})a\sqrt{3} - R_O],$$

$$r_B = [(\frac{3}{8} - U)a - R_O],$$

Table 1. hkl reflections and their corresponding d and a spacings for $\text{NiFe}_{1.98}\text{Mn}_{0.02}\text{O}_4$ sintered at 1200°C under $1.013 \times 10^5\ \text{N m}^{-2}$ oxygen

Film shrinkage = 1.001.

Trial No.	hkl	$\theta(^\circ)$	$d(\text{\AA})$	$a(\text{\AA})$	$a(2\theta = 180^\circ)(\text{\AA})$
1	$\alpha_2\ 5\ 5\ 5$	68.664	0.96236	8.33427	$8.3378 \pm 3 \times 10^{-4}$
	$\alpha_1\ 6\ 6\ 2$	69.327	0.95600	8.33425	
	$\alpha_2\ 6\ 6\ 2$	69.655	0.95604	8.33455	
	$\alpha_1\ 8\ 0\ 0$	73.707	0.93187	8.33492	
	$\alpha_2\ 8\ 0\ 0$	74.113	0.93200	8.33605	
	$\alpha_1\ 9\ 1\ 1$	77.804	0.91510	8.33698	
2	$\alpha_2\ 5\ 5\ 5$	68.669	0.96233	8.33399	$8.3380 \pm 3 \times 10^{-4}$
	$\alpha_1\ 6\ 6\ 2$	69.327	0.95600	8.33425	
	$\alpha_2\ 6\ 6\ 2$	69.655	0.95604	8.33455	
	$\alpha_1\ 8\ 0\ 0$	73.700	0.93191	8.33524	
	$\alpha_2\ 8\ 0\ 0$	74.116	0.93199	8.33595	
	$\alpha_1\ 9\ 1\ 1$	77.804	0.91510	8.33698	

Table 2. *hkl* reflections and their corresponding *d* and *a* spacings for NiFe_{1.95}Mn_{0.05}O₄ sintered at 1200°C under 1.013 × 10⁵ N m⁻² oxygen

Film shrinkage = 1.0003.

Trial No.	<i>hkl</i>	θ (°)	<i>d</i> (Å)	<i>a</i> (Å)	<i>a</i> (2θ = 180°) (Å)
1	α_2 5 5 5	68.298	0.96268	8.33707	8.3417 ± 3 × 10 ⁻⁴
	α_1 6 6 2	69.269	0.95637	8.33748	
	α_2 6 6 2	69.594	0.95642	8.33788	
	α_1 8 0 0	73.613	0.93232	8.33897	
	α_2 8 0 0	74.060	0.93224	8.33824	
	α_1 9 1 1	77.694	0.91549	8.34047	
2	α_2 5 5 5	68.281	0.96280	8.33809	8.3412 ± 2 × 10 ⁻⁴
	α_1 6 6 2	69.254	0.95647	8.33830	
	α_2 6 6 2	69.581	0.95650	8.33856	
	α_1 8 0 0	73.605	0.93236	8.33929	
	α_2 8 0 0	74.070	0.93220	8.33783	
	α_1 9 1 1	77.691	0.91549	8.34055	

where r_A , r_B and R_O stand for the radius of the *A* site, the *B* site and the *O* ion, respectively, and *a* and *U* have the usual significance. In the case of the sample with $x = 0.05$ Mn, as well as having a larger *U* parameter, it also has a larger lattice constant *a*. Such a combined effect can arise from an enlargement of the *A* sites of this sample. In the case of the sample with $x = 0.02$ Mn, the results lead us to suppose that the impurity in the sample may not be wholly incorporated in the lattice. It seems likely that the impurity remains at the grain boundary. Electron-probe investigations might help to clarify studies on the grain boundaries of such a sample.

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Die Strukturbestimmung der Isomaltulose, C₁₂H₂₂O₁₁·H₂O: errata. Von WOLFGANG DREISSIG und PETER LUGER, *Institut für Kristallographie der Freien Universität Berlin, Takustrasse 6, 1 Berlin 33, Bundesrepublik Deutschland*

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The following corrections are made to the data given in the paper by Dreissig & Luger [*Acta Cryst.* (1973), B29, 514–521]. The positional parameters (×10³) in Table 3 should read: H(6): $x = 171$ (5), $y = 172$ (4); H(9): $x = 238$ (4). The bond angles in Fig. 3 should read C(10)–C(11)–C(12) 111.5, C(2)–C(3)–C(4) 103.0°.

Alle Daten sind in der Zusammenfassung gegeben.