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Cation distribution in the tetragonal spinel $MgMn_2O_4$

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Auszug

Im tetragonalen Spinell $MgMn_2O_4$ wurden mittels Elektronenbeugung die Parameter der Sauerstoffatome und die Verteilung der Kationen bestimmt. Die Ionenabstände wurden berechnet. Der Anteil von inversem Spinell beträgt ca. 20%.

Abstract

The cation distribution in the tetragonal spinel magnesium manganite has been determined by neutron diffraction. The degree of inversion has been found to be about 20 per cent. The values of the oxygen parameters as well as the interionic distances have also been calculated.

Introduction

The electrical and magnetic properties of the spinel-like manganites are sensitive to the cation distribution. Magnesium manganite crystallizes with the hausmannite structure in which the metal ions are distributed over the (distorted) tetrahedral and the (distorted) octahedral sites in the oxygen-anion lattice as represented by $(A_mB_{1-m})_{tetr}\,[A_{1-m}B_{1+m}]_{oct}O_4$. The distortion of the cubic structure to a tetragonal symmetry has been thought of as due to the presence of the Jahn-Teller ions $Mn^{3+}(3d^4)$ at the octahedral sites.

The crystallographic properties of $MgMn_2O_4$ have been studied by SINHA *et al.* (1957) by the x-ray diffraction method. According to them the compound possesses approximately a normal distribution

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of the metal ions ($m = 1$). However, the studies on the structural and magnetic properties of the compound by MURAMORI and MIYAHARA (1960) indicate that the compound is inverted to the extent of 20 per cent. It is seen that the cation distribution is also sensitive to the preparative conditions.

In the structural investigations of these mixed metal oxides, wherein x-rays are used as the probe, the data do not often lead to unambiguous determination of the degree of inversion (the value of m) and the oxygen parameters because of the similarity of the x-ray scattering amplitudes of the metal ions, and the low scattering power of the oxygen ions. On the other hand, the neutron-diffraction technique can be effectively used as manganese has a negative scattering amplitude (-0.36×10^{-12} cm) for neutrons and thereby facilitating a precise determination of the structural features of these compounds.

Experimental

The compound was prepared from pure (G. R. grade chemicals) MgO and Mn_2O_3 by the standard ceramic sintering technique. The reaction was carried out at 950 °C for a period of 48 hours. The product was then brought to room temperature by controlled cooling at the rate of 2 °C per minute. For neutron-diffraction experiments the sample was shaped into the form of circular pellets of 18 mm diameter and 2—3 mm thick and was encased in a thin aluminium foil. Diffraction patterns were taken using unpolarized neutrons of wavelength, $\lambda = 1.24$ Å.

Results and discussion

The neutron-diffraction patterns of the compound showed in each case the existence of a single tetragonal phase unattended by any parasitic phases. From the observed d values the cell constants were calculated by the method of least-squares.

Analysis of the neutron-diffraction patterns of the compound yielded the cation distribution and the values of the oxygen parameters. The reflection 202 was found to be the strongest and hence was used for the normalization of the intensities of other reflections. The absorption factor, being insignificant, was neglected in the calculations. The refinement was carried out with the aid of a CDC-3600 computer program. The program obtains a best least-squares fit by

varying independently the oxygen parameters, the degree of inversion and the isotropic temperature factor. The R value, defined as,

$$R = \frac{\Sigma |\sqrt{I_{obs}} - \sqrt{I_{calc}}|}{\Sigma \sqrt{I_{obs}}} \times 100$$

associated with the refinement process was found to be 1.97 per cent. A comparison of the observed and calculated intensity ratios is presented in Table 1.

Table 1. *Comparison between the calculated and observed neutron intensity ratios for* $MgMn_2O_4$

$h\,k\,l$	I_{calc}	I_{obs}
1 0 1	8	8
1 1 2	2	2
2 0 0	1	0
1 0 3	0	0
2 1 1	0	0
2 0 2	100	100
0 0 4	5	6
2 2 0, 1 1 4, 2 1 3	16	15
3 0 1	4	3
2 0 4, 1 0 5	1	1
3 1 2, 3 0 3, 3 2 1	2	2
2 1 5, 2 2 4	21	20
4 0 0, 3 1 4, 1 1 6, 3 2 3	10	9
4 1 1, 3 0 5, 4 0 2, 2 0 6	30	29
3 3 2, 1 0 7, 4 1 3, 4 2 0	2	1
4 2 2, 4 0 4, 3 2 5	50	48

Table 2. *Crystallographic data for the compound* $MgMn_2O_4$

Parameters			Results
a			8.070 ± 0.003 Å
c			9.281 ± 0.003 Å
c/a			1.15
Degree of inversion			20.1 %
Cation distribution			$(Mg_{0.8}Mn_{0.2})_{tetr}\,[Mg_{0.2}Mn_{1.8}]_{oct}$
Oxygen parameters:	x		0.240
	z		0.380
Thermal factor, B			0.72 Å^2
R value			1.97 %
Bond lengths	M_{oct}—O	(long)	2.28 Å
	M_{oct}—O	(short)	1.98
	M_{tetr}—O		1.91

The crystallographic data for $MgMn_2O_4$ obtained from the present work are given in Table 2. The data indicate that the compound is about 20 per cent inverted.

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