

Investigation on lattice constants of Mg-Al spinels

JING SHOU-YONG

Chengdu Fine Optical Engineering Centre, Chengdu 610041, People's Republic of China
E-mail: jingshouyong@hotmail.com

LIN LI-BIN, HUANG NING-KANG

Irradiation Phys. and Tech. Open Lab., Sichuan University, Chengdu 610064, People's Republic of China

ZHANG JIN

Department of Physics, Yunnan University, Kunming 650091, People's Republic of China

LU YONG

Department of Physics, Yunnan University, Kunming 650091, People's Republic of China

Mg-Al spinel is the most typical material in the family of chemical compounds with spinel crystalline structure that exhibits many applications [1, 2]. In general, it can be noted as $MgO \cdot n \cdot Al_2O_3$.

$MgAl_2O_4$ spinel is an fcc structure of oxygen ions with a lattice parameter of 0.808 nm. There are eight molecules in its unit cell, in which there are 64 tetrahedral symmetry sites and 32 octahedral ones. In the perfect case, magnesium ions occupy 8 tetrahedral positions and aluminum ions occupy 16 octahedral sites [3]. In many cases, this $MgO \cdot n \cdot Al_2O_3$ compound is non-stoichiometric, n is not equal to 1. From 1 up to 7.3, the excess Al^{3+} ions occupying tetrahedral sites, substitute for Mg^{2+} ions [4]. This causes a proportional decrease of lattice parameter with the amount of excess Al^{3+} due to a smaller diameter of Al^{3+} than that of Mg^{2+} .

In the present paper, we show the result of the unit cell parameters of Mg-Al spinels solid solutions with XRD and provide a formula for calculating the lattice parameter of such Mg-Al spinel compounds, which has a good physical meaning compared with that given by Sigalovsky *et al.* [5].

In our experiments ultra-fine powders of Mg-Al spinel were prepared with a method of high temperature solid reaction. Reagent grade $AlNH_4(SO_4)_2 \cdot 12H_2O$ and $MgSO_4 \cdot 7H_2O$ were mixed based on different n in de-ionized water. These solutions were calcimined at 1080 °C for 4–5 h to obtain a single spinel phase powder with being high pure, good disperse and homogeneous. The obtained powders were measured by XRD using Cu- K_α radiation on a D/max *ra* diffractometer.

The XRD patterns of the obtained powder samples are given in Fig. 1. The stoichiometric spinel XRD pattern (a pattern labelled $n = 1.0$) is the same as the standard powder XRD pattern [6]. For the non-stoichiometric spinel samples, the peaks shift to the direction in higher values of 2θ as n increases. That means the distance of (hkl) plane d_{hkl} became smaller according to the following expression:

$$a(n) - a_0 = \sqrt{h^2 + k^2 + l^2} \times \Delta d_{hkl}$$

where $a(n)$ stands for the lattice constant of non-stoichiometric spinel at different n , a_0 is the lattice constant of $MgAl_2O_4$ spinel, i.e. $n = 1.0$. Δd_{hkl} is the difference of distance of plane with lattice constants between $a(n)$ and $a(1)$. For a certain value of n , the calculated $a(n)$ is not changed at different hkl , this means that the non-stoichiometric powders were also a face-center-cubic spinel structure. The lattice constants can

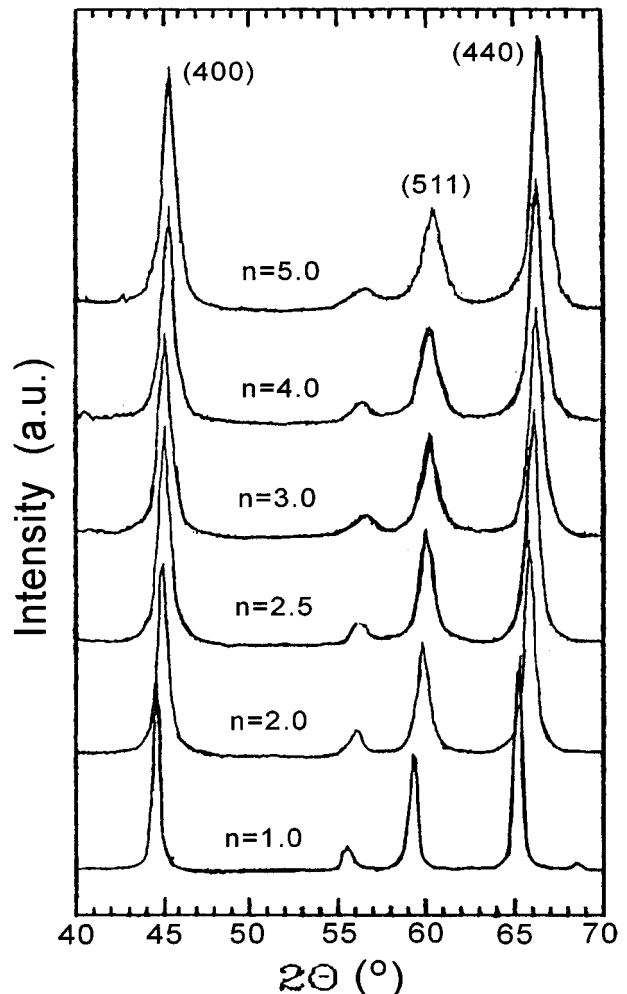


Figure 1 XRD patterns of Mg-Al spinel.

TABLE I The data of XRD experiments

	n					
	1.0	2.0	2.5	3.0	4.0	5.0
2θ (°)	44.80	45.20	45.30	45.35	45.45	45.55
d (400) (nm)	0.2022	0.2004	0.2000	0.1998	0.1994	0.1990
$a(n)$ (nm)	0.8085	0.8017	0.8000	0.7992	0.7971	0.7961

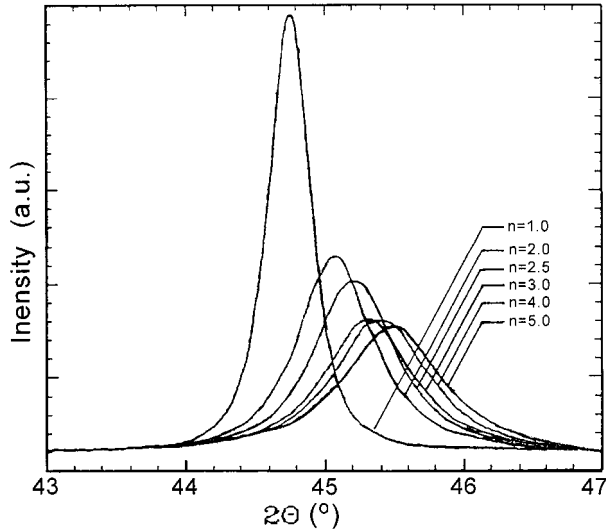


Figure 2 XRD patterns of Mg-Al spinel near (400) plane.

be calculated with following formula:

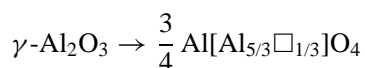
$$a(n) = \sqrt{h^2 + k^2 + l^2} \times d_{hkl}$$

The experimental results are summarized in Table I.

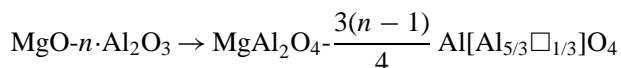
For clarification, XRD patterns at a peak of (400) with different n are given in Fig. 2. We can also regard $\text{MgO} \cdot n \cdot \text{Al}_2\text{O}_3$ as a solid solution of MgAl_2O_4 and Al_2O_3 , Al_2O_3 in it is $\gamma\text{-Al}_2\text{O}_3$ of a spinel phase with a lattice constant of 0.729 nm, which is dissolved to MgAl_2O_4 . This results in the substitution of the Mg^{2+} by the Al^{3+} ions in the tetrahedral site with the formation of supplementary cation vacancies in the octahedral site [3]. The solid solution of Mg-Al spinel can be regarded as the following scheme:



and also [4]



then



where \square stands for a vacancy at an octahedral site. So the lattice constant of $\text{MgO} \cdot n \cdot \text{Al}_2\text{O}_3$ can be as a weight average value of those for MgAl_2O_4 and

TABLE II The lattice constants of Mg-Al spinel

	Crystal Const. (nm)	
	Exp.	Cal.
Our work		
$n = 1.0$	0.8055	0.8086
$n = 2.0$	0.8017	0.8016
$n = 2.5$	0.8000	0.7999
$n = 3.0$	0.7992	0.7987
$n = 4.0$	0.7971	0.7972
$n = 5.0$	0.7961	0.7963
Navrotsky's work		
$n = 1.000$	0.8084	0.8084
$n = 1.148$	0.8068	0.8069
$n = 1.333$	0.8049	0.8048
$n = 1.571$	0.8031	0.8032
$n = 1.889$	0.8013	0.8014
$n = 2.333$	0.7996	0.7995

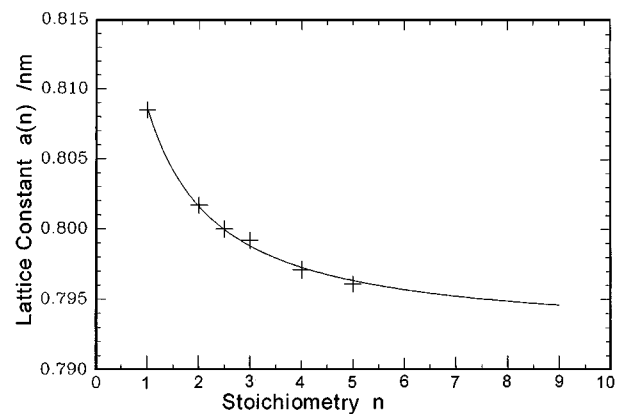


Figure 3 The fitting curve of lattice constants.

$\text{Al}[\text{Al}_{5/3}\square_{1/3}]\text{O}_4$, hence

$$a(n) = \frac{a_0 + 3(n-1)a_1/4}{1 + 3(n-1)/4}$$

where a_1 stands for the lattice constant of $\text{Al}[\text{Al}_{5/3}\square_{1/3}]\text{O}_4$. The data by fitting the above formula with our experiment given in Table I, we have the results of $a_0 = 0.8086$ nm and $a_1 = 0.7922$ nm, corresponding to the constants of MgAl_2O_4 and $\gamma\text{-Al}_2\text{O}_3$ respectively (fitting curve can be seen in Fig. 3).

Navrotsky's experimental data were also used to fit the formula, and got a satisfying result, too ($a_0 = 0.8084$ nm and $a_1 = 0.7911$ nm).

For comparison these $a(n)$ values using the fitting parameters a_0 and a_1 also are given in the Table II. It is found that the results calculated from our formula are good coincident with that from experiments.

Acknowledgments

The first author gratefully thanks the scholarship supports of Donggang group (China).

References

1. T. R. YANG and H. E. HORNG, *Physica C* **235-240** (1994) 1445.

2. H. CYNNE, S. K. SHARMA, T. F. COOHEY and M. NICOL, *Phys. Rev. B* **45**(1) (1992) 500.
3. T. J. GRAY, in "High Temperature Oxides," Part IV (Academic Press, INC Ltd, London, 1971) p. 77.
4. C. GARAPAN, H. MANAA and R. MONCORGE, *J. of Chem. Phys.* **95**(8) (1991) 5501.
5. J. SIGALOVSKY, J. S. HAGGERTY and J. E. SHEEHAN, *J. of Crystal Growth* **134** (1993) 313.
6. *JCPDS* **10** (1960) 425; *ibid.* **21** (1971) 1152; *ibid.* **29** (1979) 63.

*Received 21 July
and accepted 22 July 1999*