

## PRECISE LATTICE PARAMETER DETERMINATION OF SPINEL $\text{MgAl}_2\text{O}_4$ FROM X-RAY POWDER DIFFRACTION PATTERNS

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### Abstract

A very precise knowledge of the lattice parameters of materials is important in solid-state investigations. In order to achieve high precision in lattice parameters measurements one can use the popular methods based on plotting the lattice parameter as a function of some extrapolation functions (Bradley-Jay, Nelson-Riley, etc) or applying the analytical Cohen method. Some new methods based on the Rietveld-type pattern-fitting approaches can also be used. In this paper we present a comparative study of these lattice parameter evaluation procedures. Diffraction data was recorded by Bragg-Brentano X-ray diffractometry, using a set of  $\text{MgAl}_2\text{O}_4$  powder samples presenting different crystallinities. For the Rietveld-type analysis we used the FullProf programs package. Our results are important for the studies involving systems of particles in the medium range diffraction angles ( $2\theta$  between  $10^\circ - 90^\circ$ ).

**Keywords:** lattice parameter, powder diffraction.

### 1. Introduction

In the last few years, the continuously growing demand for new and advanced materials with well-defined structures and properties has brought into light new and improved methods for quantitative analysis of X-Ray diffraction patterns.

The subject of the present work is the precise determination of the lattice parameter for the cubic spinel structure of  $\text{MgAl}_2\text{O}_4$  using different methods: one using an extrapolation function, another using the Cohen method and the third is the Rietveld method for whole pattern fitting.

### 2. Lattice parameter determination methods

For the extrapolation method [1] the lattice parameter,  $a_o$ , is computed for each line of the pattern and is plotted against a so called “extrapolation function”. A straight line should

result and the true value of the lattice parameter can be found by extrapolating this line to  $\theta=90^\circ$ . This so called extrapolation functions are functions of  $\theta$ , like  $\cos^2\theta$ ,  $\sin^2\theta$ ,  $\cos^2\theta/\sin\theta$ ,  $k(\cos^2\theta/\sin\theta+\cos^2\theta/\theta)$ .

The Cohen method [1] consist from two sets of equations,

$$\begin{aligned} A\sum\alpha^2 + C\sum\alpha\delta &= \sum\alpha\sin^2\theta \\ A\sum\alpha\delta + C\sum\delta^2 &= \sum\delta\sin^2\theta \end{aligned} \quad (1)$$

where  $A = \lambda^2 / 4a_0^2$ ,  $\alpha = (h^2 + k^2 + l^2)$  and  $\delta = 10\sin^2 2\theta$ . With the two sets of equations we can find the  $A$  and  $C$  values. Once the value of  $A$  is found,  $a_0$  can be calculated. The constant  $C$  is related to the amount of systematic error involved.

The Rietveld method [2] is more complicated and sometimes difficult to use but, as our comparative study is about to show, it yields the best results. The method is a profile fitting technique involving the simulation of the diffraction pattern, based on a structural model. The calculated intensities are fitted to the observed intensities, which is achieved by minimization of the sum of the squares

$$\sum_i [(I_i)_{obs} - (I_i)_{calc} - (I_i)_b]^2 \quad (2)$$

Although the principles behind the Rietveld profile refinement method are rather simple, the use of the technique requires some expertise.

### 3. Experimental and results

Diffraction data were recorded in the medium range diffraction angles ( $2\theta$  between  $10^\circ$  –  $90^\circ$ ) by Bragg-Brentano X-Ray diffractometry, using a Bruker D8 Advance equipment (CuK $\alpha$  radiation, 40 kV, 30 mA, Ni filter or graphite monochromator).

The Diffrac<sup>Plus</sup> software package was used for data acquisition and peak search. Two home-made computer programs were used for the determination of the lattice parameter by the extrapolation and Cohen methods, respectively. For the Rietveld-type analysis we used the FullProf programs package [4].

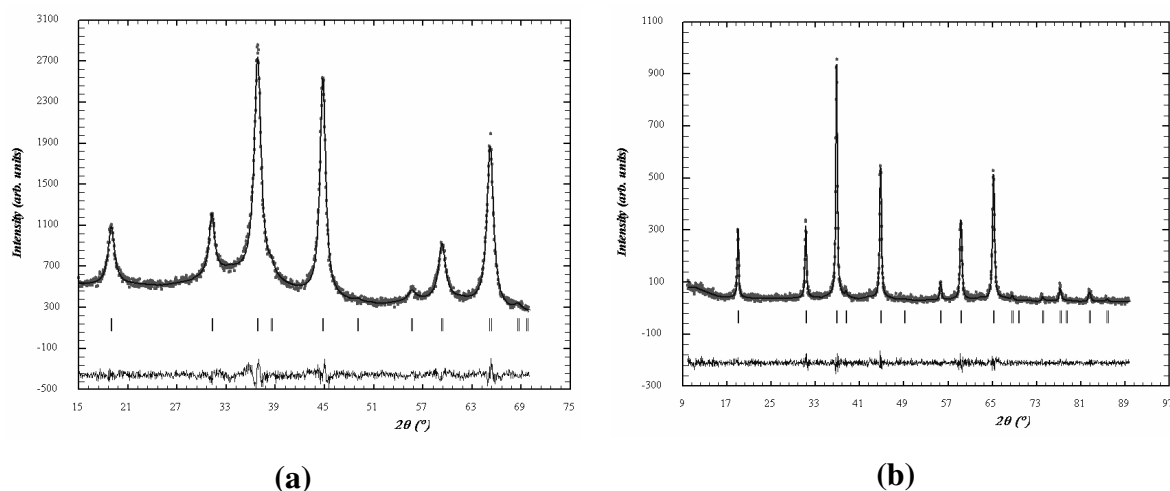
A set of MgAl<sub>2</sub>O<sub>4</sub> powder samples presenting different crystallinities was used. They were prepared by three different methods [3]: sol-gel, combustion, and thermal conversion, respectively.

The average size of the cell parameter for these samples is presented in Table 1. Although the calculated values are quite similar to those from the references for well crystallized spinel ( $a_0=8.0831$  Å, JCPDS file 21-1152), it is obvious that the extrapolation and

Rietveld methods give better results, with a plus of reproducibility and precision for the last one.

**Table 1.** Lattice parameter calculated for the  $MgAl_2O_4$  powders, using different methods

Sample	Lattice parameter $a_{med}$ (Å)			
	Cohen		Extrapolation $\cos^2\theta/\sin\theta$	Rietveld
	$a_{med}$	$C$		
1a	8,121	0,003	$8,086 \pm 0,002$	$8,0939 \pm 0,0005$
2	8,112	0,000165	$8,101 \pm 0,037$	$8,0772 \pm 0,0021$
3	8,097	0,000054	$8,086 \pm 0,004$	$8,0909 \pm 0,0007$
3bis	8,088	0,000095	$8,092 \pm 0,002$	$8,0935 \pm 0,0005$
4	8,054	0,000262	$8,093 \pm 0,020$	$8,0972 \pm 0,0026$
6	8,093	0,000033	$8,082 \pm 0,005$	$8,0951 \pm 0,0008$
52	8,124	0,0003	$8,089 \pm 0,001$	$8,0926 \pm 0,0004$



**Fig. 1** Rietveld refinement results for samples 6 (a) and 52 (b) respectively (see text and Table 1 for details).

As an example of the Rietveld method, in the figures 1.a-b we present the graphics resulted after refinement with Fullprof software package of the powder diffraction patterns for the samples 6 and 52. In these figures the grey dots represent the experimental data points, the black line between those points represents the calculated pattern using a model provided by user, the black lines under the peaks represent the calculated Bragg positions and the dark-grey line under the two patterns represents the difference between calculated and observed patterns.

The correlation between the synthesis method and the lattice parameter for the spinel samples will be presented elsewhere.

#### **4. Conclusions**

Using the Rietveld method in the medium range diffraction angles ( $2\theta$  between  $10^\circ$  and  $90^\circ$ ) the results obtained for the lattice parameter determination are the best. The error calculated is lower and, as we have observed, the reproducibility of the results is also increased using the Rietveld method. Good results are also obtained using the extrapolation method.

#### **References:**

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- [4] <http://www-llb.cea.fr/fullweb/fp2k/fp2k.htm>