

Lawrence Berkeley National Laboratory

Recent Work

Title

STRUCTURAL PHASE TRANSITION IN THE SPINEL $MgAl_2O_4$.

Permalink

<https://escholarship.org/uc/item/2wn8p5sc>

Author

Mishra, R.K.

Publication Date

1977-11-01

0 3 4 6 0 7 4 3 2

Submitted to Acta Crystallographica

LBL-5702
Preprint c.1

STRUCTURAL PHASE TRANSITION IN THE SPINEL $MgAl_2O_4$

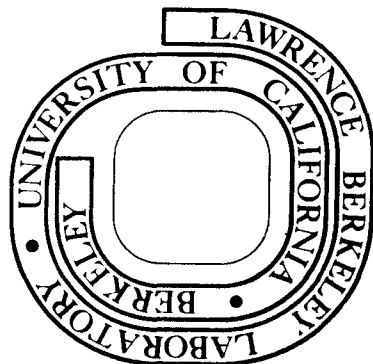
R. K. Mishra and G. Thomas

January 1977

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

For Reference

Not to be taken from this room



LBL-5702
c.1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

STRUCTURAL PHASE TRANSITION IN THE SPINEL MgAl_2O_4

R.K. Mishra and G. Thomas

Department of Materials Science and Engineering and
 Materials and Molecular Research Division
 Lawrence Berkeley Laboratory
 University of California
 Berkeley, California 94720

ABSTRACT

A new crystallographic phase transformation in MgAl_2O_4 is reported in which the low temperature low symmetry space group of MgAl_2O_4 transforms to the "Spinel" space group $\text{Fd}\bar{3}\text{m}$ at $\sim 450^\circ\text{C}$. The in situ electron diffraction experiments suggest that this is a second order phase transformation.

Grime's (1972, 1973) suggestion that the space group of the spinel structure may not be $\text{Fd}\bar{3}\text{m}$ but $\text{F}\bar{4}3\text{m}$ has been supported by recent electron and x-ray diffraction evidence, in which, the presence of hko reflections with $h+k=4n+2$ in MgAl_2O_4 (Hwang, Heuer and Mitchell, 1973) and some thiospinels, (Higgins, Speer and Craig, 1975) have been found at room temperature. However, in other compounds with the spinel structure, such as LiFe_5O_8 , the room temperature electron diffraction patterns of the $\langle 100 \rangle$ reciprocal lattice sections (Figure 1) do not exhibit these forbidden reflections, suggesting that the structure has the originally proposed

space group Fd3m (Bragg, 1915). Neutron diffraction experiments from magnetite by Samuelson (1974) and x-ray diffraction from $\text{Cu Co}_2 \text{S}_4$ by Williamson and Grimes (1974), also support the result that the space group of Fe_3O_4 or CuCo_2S_4 is Fd3m at room temperature. The purpose of this communication is to report the observation of a structural phase transition in MgAl_2O_4 that transforms its space group to Fd3m at high temperature.

Figure 1a and 1b show the symmetrical $\langle 100 \rangle$ selected area electron diffraction pattern from a stoichiometric MgAl_2O_4 spinel single crystal grown by the Czochralski method. The electron transparent specimen was prepared from the bulk crystal by ion thinning and examined in the Phillips EM301 transmission electron microscope operating at 100 kV. Figure 1a shows the presence of hko spots with $h+k=4n+2$ (i.e. 200, 420 etc). The integrated intensity of the 200 spots as measured from microdensitometer traces is less than (1/1000)th of that of the 400 spots. This is consistent with the estimation by Heuer and Mitchel (1975). On heating the specimen in the hot stage of the electron microscope to a temperature close to 450°C , the "forbidden" spots disappear, as is evident in figure 1b taken from the same area of the foil ($\sim 2 \mu\text{m}$ in diameter). In order to prove that the extra reflections are representative of structural changes and not double diffraction or other effects, figures 2a-d show selected area diffraction patterns taken from the foil near $\langle 100 \rangle$ orientation tilted so as to excite the $\langle 400 \rangle$ reflection after the temperature changes as shown. The heating sequence fig. 2a-c shows the disappearance of the 200 reflection near 450°C , and the reflection subsequently reappears upon cooling, as in figure 2d. Close examination of the corresponding images both in bright field and dark field using the 200 and 400 reflections does not show any changes in microstructure or morphological features.

This strongly suggests that the observed symmetry change is not accompanied by a solid state phase transition involving nucleation and growth, by which two phases can coexist.

Assuming that the space group of MgAl_2O_4 at room temperature is $\overline{F}43m$ as suggested by Grimes (1972,1973), this experimental result suggests that the nonequivalent octahedral sites of the room temperature $\overline{F}43m$ phase become statistically equivalent at higher temperature due to thermal vibration. The transformation can be accomplished without any long range diffusion. Application of Landau's theory of a second order phase transition shows that it is possible for the transition $\overline{F}43m \rightleftharpoons Fd3m$ to occur by either a first or a second order transformation (Haas, 1965). However, the experimental evidence that no microstructural changes are resolved within the limits of this experimental technique, suggests that the transformation is actually one of second order. It is possible that the other spinel structure compounds that do not give rise to hko reflections with $h+k=4n+2$ at room temperature may also transform and show these reflections at lower temperatures. Hence it may be that this transformation could be a general one for oxide spinels and thiospinels.

ACKNOWLEDGMENT

This research was supported by the Energy Research and Development Administration through the Materials and Molecular Research Division of the Lawrence Berkeley Laboratory.

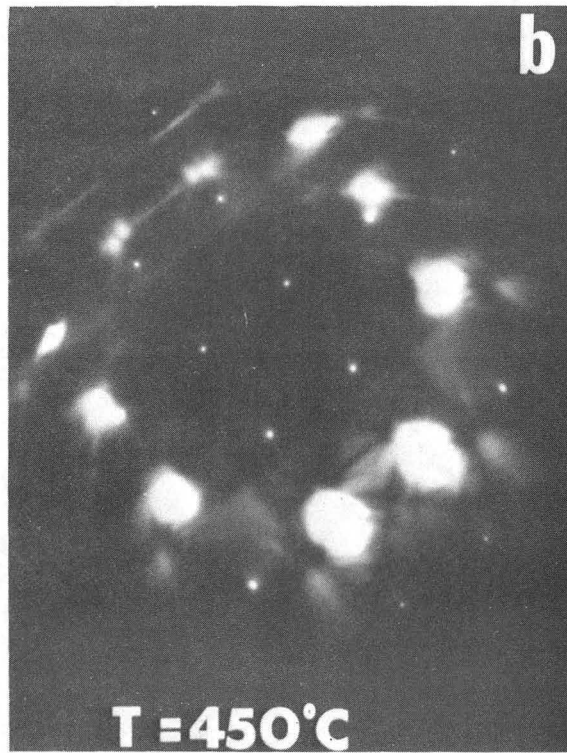
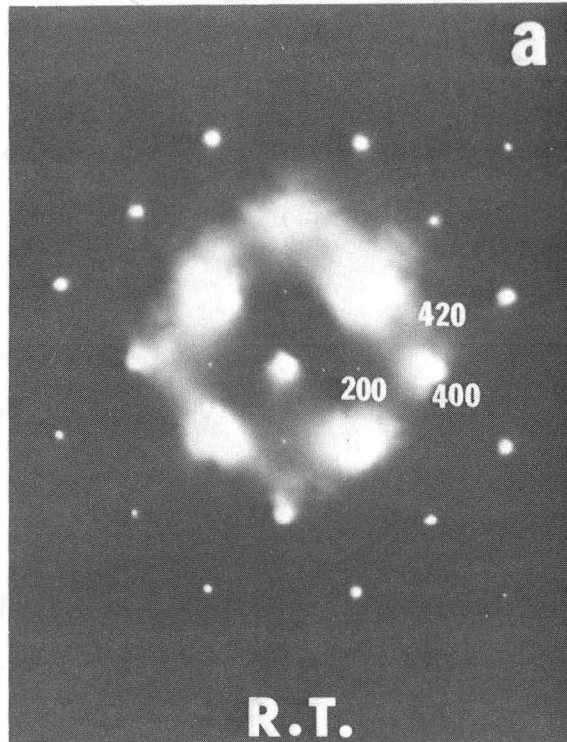
REFERENCES

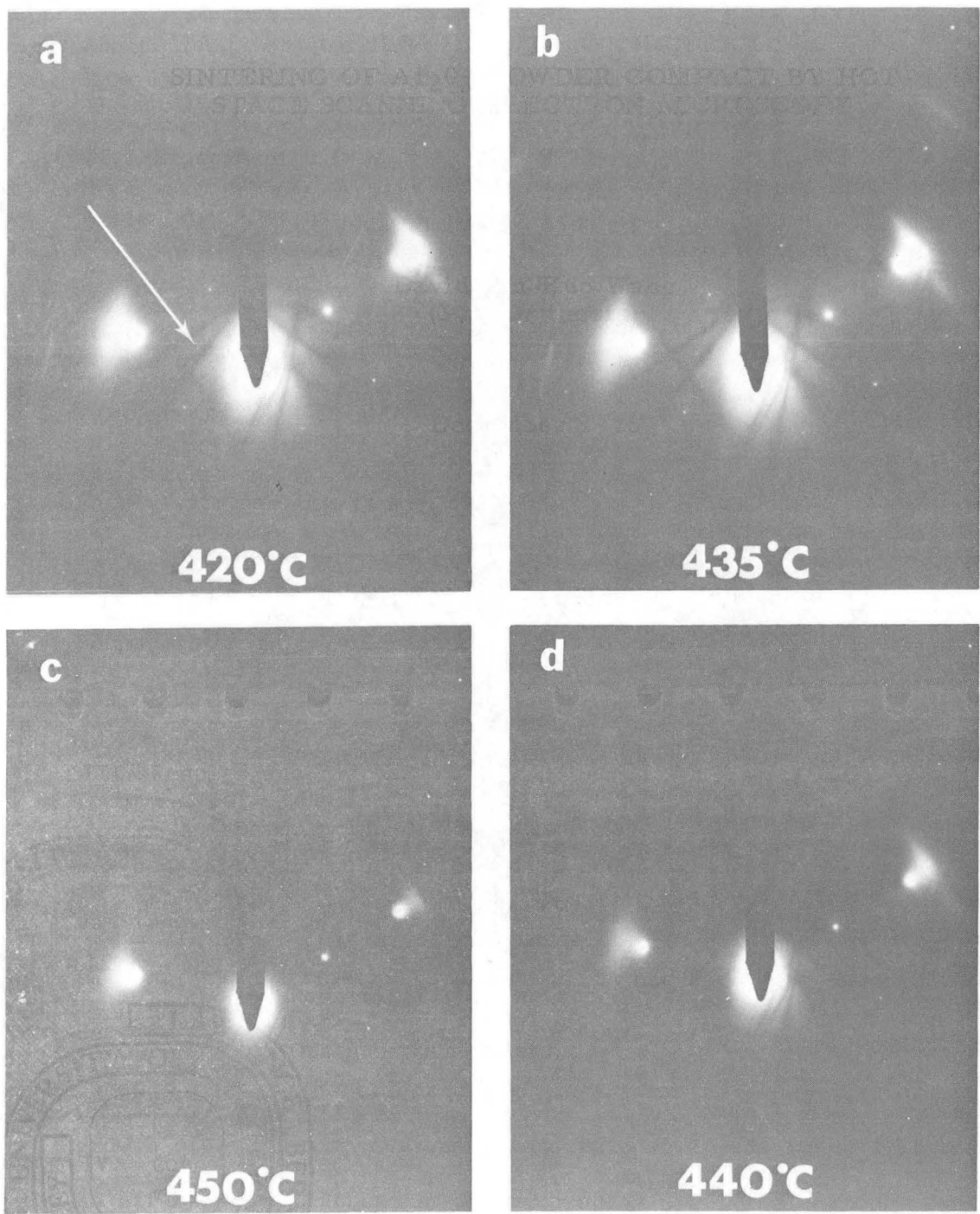
- BRAGG, W.H. (1915). Nature, Lond. 95, 561, Phil. Mag. 30 305-315
- GRIMES, N.W. (1972). Phil. Mag. 26, 1217-1226; (1973) J. Phys. C, 6
L78-79.
- WILLIAMSON, D.P. and GRIMES, H.W. (1974). J. Phys. D, 7, 1-6
- HAAS, C. (1965). J. Phys. Chem. Sol., 26, 1225-1232.
- HEUER, A. H. and Mitchell, T. E. (1975), J. Phys. C., 8, L541-3 (1975).
- HIGGINS, J.J., SPEER, J.A. and CRAIG, J.R. (1975). Phil. Mag., 30 683-685.
- HWANG, L., HEUER, A.H. and MITCHELL, T.E. (1973). Phil. Mag., 28 241-243
- SAMUELSON, E. (1974), J. Phys. C, 7, L115-117.

FIGURE CAPTIONS

Figure 1. Selected area electron diffraction patterns from MgAl_2O_4 in $\langle 100 \rangle$ orientation; (a) taken at room temperature showing 200, 420, type spots, (b) taken at $\sim 450^\circ\text{C}$ from the same area where these reflections have disappeared. The slight shift in the Kikuchi pattern is due to a slight buckling of the foil upon heating.

Figure 2. SAD from MgAl_2O_4 oriented near $\langle 100 \rangle$ to excite the (400) systematic row. (a-c) taken at the temperatures shown during a heating sequence, and (d) taken after cooling the specimen to 440°C . Note the disappearance of the 200 spot marked by an arrow in (a) upon heating to 450°C and its reappearance in (d) upon cooling.





XBB 767-5948

FIG. 2

This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720