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Dedicated to Professor Lisa Heller-Kallai on the occasion of her 65th birthday

FORMATION OF PARTIALLY INVERSE Mg–Al SPINEL BY GRINDING MgO WITH γ-Al_2O_3

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Abstract

Spinel ($MgAl_2O_4$) was synthesized mechanochemically (MC) by grinding MgO with γ-Al_2O_3 up to 10 hours. Examination of the MC product by neutron diffraction and infrared spectroscopy showed that it has a higher degree of inversion than its thermally produced counterpart – 47% as against 10% respectively. X-ray studies showed that $MgAl_2O_4$ crystallites grow equidimensionally at a much higher rate than in the case of α-Al_2O_3. The higher degree of inversion and higher formation rate when γ-Al_2O_3 is used, is attributed to similarities in oxygen framework of MgO, Al_2O_3 and spinel and to the higher retention of the cations coordination number. The equidimensional growth is attributed to the presence of multiple soft modes, the {111} planes.

Keywords: Mg-Al spinel

Introduction

The term 'spinel' covers the mineral $MgAl_2O_4$ and, in the plural, a group of minerals with the general composition AB_2O_4, similar in structure to the formed. Some spinels with anions other than O^{2-} are also know to exist [1].

The oxygen ions are arranged in a cubic close-packed structure (C.C.P.). A unit cell contains 8 chemical formula subunits, with 64 tetrahedral (coordination number 4) and 32 octahedral (coordination number 6) sites available for the metallic cations between the oxygens, of which 8 tetrahedral and 16 octahe-

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* Deceased.

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dral sites are usually occupied. The site occupation patterns are as follows: in normal spinels – *A*-type cations in the tetrahedrals, *B*-type in the octahedrals; in inversed spinel – *A*-type in the octahedrals, *B*-type distributed equally between the two groups; in random spinel (also known as mixed or partially inversed), both types distributed between the two groups, the general crystallochemical formula being 1. $(A_1\text{-}xBx)[AxB_2\text{-}x]O_4$ (or 2. $(A_1\text{-}xBx)_8[AxB_2\text{-}x]_8\ O_{32}$ in terms of the unit cell), the round and square brackets denoting the tetrahedral and octahedral sites respectively. *A*-type cations are usually divalent, *B*-type trivalent.

A list of spinels classified according to their degree of inversion is given in [2]. However, Datta and Roy [3–5] showed that preparation conditions may act upon metallic cations' distribution for instance for $NiAl_2O_4$ prepared at 600°C and 1550°C, the formulas being: $(Al_{1.0})[Ni_{1.0}Al_{1.0}]O_4$ and $(Ni_{0.25}Al_{0.75})[Ni_{0.75}Al_{1.25}]O_4$ respectively, so that the classification is somewhat ambiguous.

Spinels are produced by heating together the appropriate raw materials, for instance a mixture of MgO and Al_2O_3 for $MgAl_2O_4$. Mechanochemical (MC) synthesis were also reported, mostly in attempts to produce ferrites (Fe^{3+} spinels) Inter alia, Singh *et al.* [6] ground zinc hydroxy carbonate with Fe_2O_3 gels for 90 minutes and claimed (on the basis of thermal analysis) that some zinc ferrite $ZnFe_2O_4$ was formed. They used the term 'zinc ferrite precursor' to describe their product. Lefelshtel *et al.* [7], through prolonged grinding of α-Fe_2O_3 with ZnO or $ZnCO_3$, obtained zinc ferrite which was also detectable by X.R.D. Other attempts to prepare $NiFe_2O_4$ from NiO + αFe_2O_3 by same experimental conditions proved unsuccessful. Some of their arguments are cited in the discussion section of this text.

In this work, MC synthesis of $MgAl_2O_4$ by grinding mixtures of MgO and γ-Al_2O_3 was studied.

Experimental

Materials

The materials used were Merck 1077 alumina and Merck 5866 magnesia. The alumina was identified as γ-Al_2O_3 by comparing its X.R.D. pattern to those reported by Burleson [8], except where otherwise stated. This alumina served for all grinding experiments. The magnesia powder was tested for iodine number (I.N.) and activity in citric acid (C.A.A.), the respective results being 33 and 3–4 min – an indication of more-than-moderate, albeit not very high, activity.

Grinding

10 grams of mixtures, with MgO/Al_2O_3 molar ratio 1:1, were ground in a centrifugal ball mill (speed 400 r.p.m.) charged with seven tungsten carbide (WC) balls $\Phi = 20$ mm. Grinding was interrupted once every hour, the container was opened, the powder adhering to the balls or the container wall was removed by scraping, and the container placed in a dessicator which had been connected for 30 minutes to a vacuum pump, in order to ensure complete removal of water absorbed from the air during the scraping intermission. After that the grinding operation was resumed.

Instrumentation

X-ray powder diffractograms were taken with a Philips PW 1050/25 unit, using CuK_α radiation. Samples were scanned at 1° 2θ/min for identification purposes, and at 0.25° 2θ/min for determination of peak width.

Neutron diffraction studies were carried out with 2.47 Å neutrons, with pyrotilic graphite as monochromator. Scanning was carried out in 0.05° steps which, in view of the fluctuations in the neutron flux, were spaced at equal numbers of neutron hits rather than at equal time intervals. For this purpose a normalizing detector was placed before the sample, covering 1% of its area, and – since the flux at the sample is proportional to that in the detector – ensuring the desired spacing of the steps. Each step lasted 2–3 minutes and 2–4 days were required for one complete examination.

IR absorption spectra were obtained using KBr or CsI pellets. Samples were run on a Perkin-Elmer 457 spectrophotometer.

Results

Formation of MC spinel: When γ-Al_2O_3 is ground with MgO, spinel formation sets in almost immediately. In fact, weak X.R.D. reflections of spinel were detectable already after 15 minutes grinding. On the other hand, weak MgO (periclase) lines could be observed after 10 grinding hours (Fig. 1); it is believed that the reaction is slowed down by adherence of particles to one another and to the grinding balls. Otherwise, less than 10 h would be sufficient for completion of the MC synthesis. Accumulation of contaminates made further grinding impracticable.

The picture changed drastically when α-Al_2O_3 was used instead of γ-Al_2O_3; after 10 grinding hours, only traces of spinel could be detected (Fig. 1).

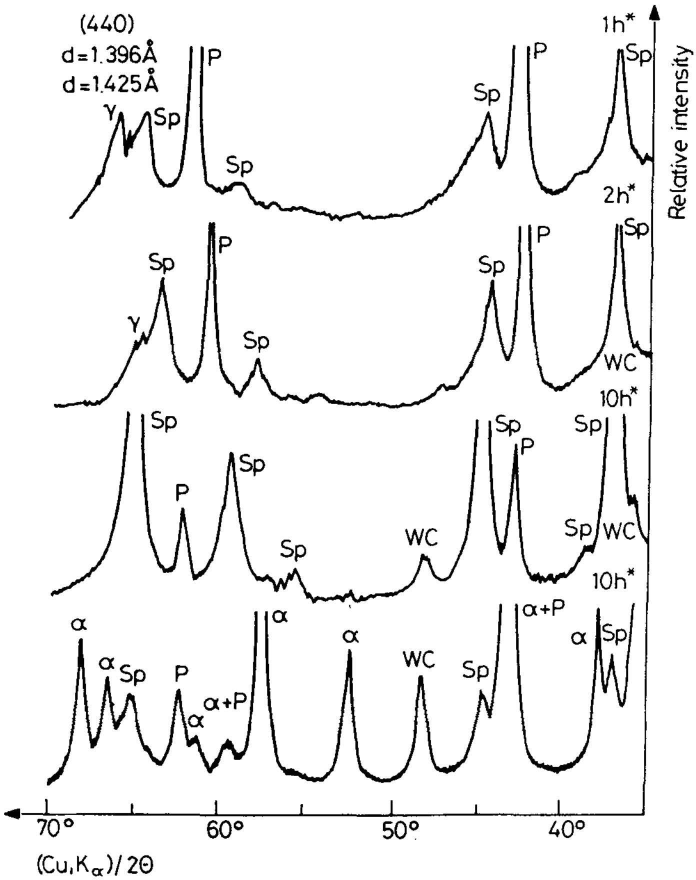

Fig. 1 X.R.D. patterns of grinding products - magnesia and gamma alumina. * - Magnesia and alpha-alumina; Sp - Spinel; P. - Periclase; WC - Tungsten carbide

Crystallite size and the microstrain level of the MC-formed spinel were determined by the X-ray line broadening method [9]. Two relationships were examined:

(a) $\beta\cos\theta = K\lambda/L + 2\Delta\varepsilon \sin\theta$

(b) $\beta^2\cos^2\theta = K^2\lambda^2/L^2 + 4(\Delta\varepsilon)^2 \sin^2\theta$

where

β - net peak width at half-height
θ - Bragg angle
K - coefficient usually taken as 0.9
L - crystallite dimension in perpendicular direction to reflection planes
$\Delta\varepsilon$ - microstrain level

For equidimensional crystallites βcosθ plotted against sinθ, or $\beta^2\cos^2\theta$ against $\sin^2\theta$, yields a straight line. In non-equidimensional cases, the points of the graphs are scattered.

Peak widths of six reflections: (111) (220) (311) (400) (511) (440) – were measured in samples obtained after 4 and 6 grinding h; in a 2-h sample only the 3 first peaks could be measured with any accuracy. The linear regression coefficient for the βcosθ *vs.* sinθ curve exceeds 0.95 (Table 1). For the $\beta^2\cos^2\theta$ *vs.* $\sin^2\theta$ it is somewhat lower, about 0.9, but still high enough to conclude that the MC crystallites grow equidimensionally.

Table 1 Crystallite size and microstrains in MC spinel

	2 h		4 h		6 h	
	β	β^2	β	β^2	β	β^2
L /Å	240	140	267	142	283	146
Δε%	0.46	0.84	0.84	0.65	0.67	0.97
regression coefficient	1.00*	1.00*	0.96	0.9	0.97	0.91

*Only 3 points

Crystallite dimensions obtained from the first-power equation were almost double those from its second-power counterpart – 240–280 Å against 140–150 Å. This discrepancy is too large for a clean cut choice, and the best that can be concluded is that the crystallites fall within the 140–280 Å range.

The microstrain levels fall in the 0.5–1% range. These values are higher than those reported in the author's earlier work [10] for the hard mineral α-Al_2O_3 obtained by the MC transformation from γ-Al_2O_3, but still attain the same range and even lower than those found for softer minerals (3–5 Mohs scale). For instance, Gammage and Glasson [11] found about 1.5% lattice strain in ground calcite.

Distribution of Mg and Al atoms between tetra- and octahedral sites: while the scattering coefficients of Mg and Al atoms for X-rays are too close, those for neutrons differ sufficiently for the neutron diffraction method (N.D.) to be suitable for determining the position of the atoms in the spinel structure. N.D. method for examining $MgAl_2O_4$ spinel, was applied by Bacon [12] and Stall *et al.* [13], the former finding that the degree of inversion is about 10%. In the present study, three spinel samples were examined by N.D.:

(a) MC spinel prepared by 10 h grinding and then heating at 400°C for 2 h (see below).

(b) Ditto, after additional heating at 1200°C for 12 h.

(c) Thermal spinel, prepared by heating an unground mixture of MgO and γ-Al_2O_3.

The original MC spinel was also examined by N.D., but the cumulative counts proved too low for reliable statistics. This lack of sensitivity results from the basic limitations of N.D. methods, enhanced in this case by the defective structure of the material – which, by contrast, yielded a clear X-ray pattern. In order to remedy this situation, the sample was heated at 400°C to cure lattice defects and reexamined as sample 'a'.

The experimental and calculated intensities for normal and inversed $MgAl_2O_4$ spinel are compared. The calculation was confined to the peaks which could be measured. As technical limitations prevented measurements of the 440 peak which is supposed to be the strongest, the intensity of the 400 peak – next in order – was taken as 100. The degree of inversion was determined as follows. The theoretical peak intensities were calculated for the 0–100% inversion range in small steps, after which the value with the best fit between the experimental and calculated results was found by the least-squares method.

The calculated degree of inversion for samples 'a' was 47%, while those of samples 'b' and 'c' were almost the same – about 10% – and similar to Bacon's [12] results. The formulas of MC and thermal spinel should therefore read, respectively, as:

3. $(Mg_{0.53}Al_{0.47})[Mg_{0.47}Al_{1.53}]O_4$

4. $(Mg_{0.9}Al_{0.1})[Mg_{0.1}Al_{1.9}]O_4$

The near coincidence of samples b and c indicates, that during heating of MC spinel the Mg and Al cations are redistributed according to their natural equilibrium positions.

Some clues to the inversion process may also be found in the IR absorption spectrum, in which four stretching bands, designated V_1, V_2, V_3, V_4 are expected. The last two are usually weak or undetectable and the first two are assigned to Al–O stretching. The frequencies for Al atoms at tetrahedral sites are higher than for their counterparts at octahedral ones. Datta and Roy [3] used the location of the absorption bands in following changes in the degree of inversion.

The results of IR studies are listed in Table 2 and plotted in Fig. 2. The frequencies of the V_1, V_2 bands of the MC spinel obtained after 10 h grinding decreased on heating at 1200°C from 717 and 553 cm^{-1} to 699 and 545 cm^{-1} respectively. This supports the hypothesis that the percentage of Al atoms at tetrahedral sites is higher in the unheated MC material than in its heated counterpart; still, the latter frequencies are higher than those in thermal spinel, for which there is no explanation so far. The V_3 band was detected in heated samples only, its frequency being 307 cm^{-1} – close to the value cited in literature.

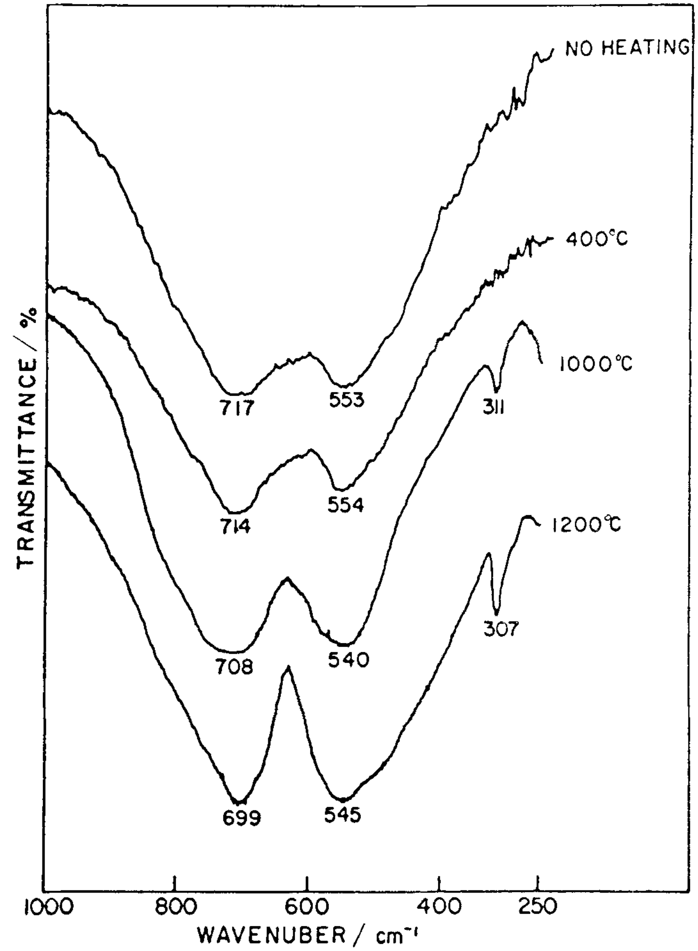

Fig. 2 IR spectra of spinel obtained from oxides by grinding and heating. 10 h grinding

Discussion

(a) Importance of structure similarities

The structure of normal spinel, viewed perpendicular to the oxygen layers, is shown schematically in Fig. 3.

The oxygen layers alternate with arrays of metallic cations, in which layers with all cations occupying octahedral sites alternate with others with a distribution of 2/3 tetrahedral and 1/3 octahedral cation-occupied sites. In γ-Al_2O_3, whose structure is similar to spinel, Al cations are distributed between octa-

Table 2 Location of IR absorption bands of different spinels

Source	Grinding time / h	Heating temp./ °C	Band cm $^{-1}$ V_1	V_2	V_3	Remarks
Natural spinel			688	522	309	Ref. [14]
Natural spinel			685	521		Ref. [15]
Synthetic spinel			690	538		Ref. [15]
Thermal spinel			687	521	305	
MC Spinel	6	-	717	552		V_2 is spread
MC Spinel	6	1000	709	540	312	
MC Spinel	10	-	717	553		
MC Spinel	10	400	714	554		
MC Spinel	10	1000	708	540	311	
MC Spinel	10	1200	699	545	315	

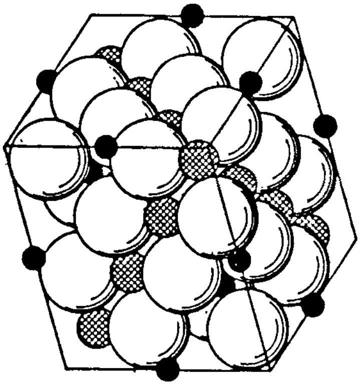

Fig. 3 Spinel structure. Blank spheres represent oxygen black spheres 4-fold atoms (A), corss-hatched spheres represent 6-fold atoms (B) [16]

and tetrahedral sites 62.5% to 37.5%. The formula should be written as 5. $(Al)[Al_{5/3}\square_{1/3}]O_4$, □ designating vacancies. In MgO all Mg atoms occupy octahedral sites. Both in γ-Al_2O_3 and MgO the oxygens are arranged in a framework of cubic close packing (C.C.P.).

The importance of similarities between the coordination numbers of metal cations in oxides and their products in mechanochemical synthesis was discussed by Lefelshtel *et al.* [7]. These authors obtained zinc ferrite ($ZnFe_2O_4$) by prolonged grinding of ZnO + αFe_2O_3 or $ZnCO_3$ + αFe_2O_3 but failed to obtain nickel ferrite ($NiFe_2O_4$) under similar experimental conditions, which failure they attributed to the need in the case of nickel, unlike that of zinc, for shifting half of the Fe cations from an octa- to a tetrahedral site. A similar argument may apply for $MgAl_2O_4$. Assuming formulas 3, 4, 5 for MC-spinel, thermal spinel and γ-Al_2O_3 respectively, and since all Mg cations in MgO are at octahedral sites, it can be shown by simple calculation that during thermal synthesis 90% of the Mg and 32.5% of the Al cations have to be shifted, as against only 53% of the Mg and 14% of the Al cations in MC synthesis.

Another structural factor which accelerates MC synthesis is the positional similarity of the oxygen ions, which are arranged in a C.C.P. framework in MgO and γ-Al_2O_3 as well as in the spinel. By contrast, in α-Al_2O_3 the oxygens are arranged in hexagonal close packing (H.C.P.). As has been shown previously, the formation rate of MC spinel from α-Al_2O_3 is much slower than from γ-Al_2O_3. The inversion degree of the former is not known. Assuming the same degree as obtained experimentally with γ-Al_2O_3 no significant differences is found in the calculated relative amount of cation to be shifted; 53% Mg and 14% Al in MC synthesis from γ-Al_2O_3, as against 53% Mg and 23.5% Al in MC synthesis from α-Al_2O_3. This means that besides the similarity in the cations coordination numbers, similarity in the arrangement of the oxygens also plays an important rule.

(b) Softmodes

In the presence of a low shear constant in several directions, fracturing may, in some minerals, proceed along preferred crystallographic planes, referred to by mineralogists as 'cleavage planes', and by Lin and Nadiv [17] as 'soft modes'. The weakest planes in spinel are the (111)'s [18]. In γ-Al_2O_3, which is structurally related to spinel, those planes are also weakened by vacancies at some octahedral sites, and it is suggested that initially γ-Al_2O_3 fractures along them, and Mg cations are incorporated there at the octahedral vacancies, without change in the cations' coordination numbers, shifting of Mg or Al cations to their final sites requires an energy input for overcoming the energy barrier which hinders their movement in the framework of the oxygens. At high temperatures this energy is of thermal origin; in mechanochemical synthesis, where spinel is formed at ambient temperature, the source is the accumulated strain energy characteristic of the highly-strained and defective crystalline structure [19]; only part of this energy is drawn upon, the remainder being retained by the MC spinel, whose crystalline structure is still defective.

The presence of soft modes may also account for the equidimensional growth of spinel crystallites: due to the high symmetry of the spinel structure, the multiplicity factor of the {111} planes is 8; this means that γ-Al_2O_3 may fracture along 8 types of {111} planes, on which Mg cations are then incorporated.

(c) Liberation of heat

It is known that heat liberation is involved with the mechanochemical process. It is possible that some phenomena which are interpreted as mechanochemical are actually thermal.

Heat liberation was discussed by Boldyrev & Avvakumov in their review [20]. It is assumed that the temperature may rise up to 1000°C in locally restricted points on the surface in the order of 10^{-4} second. The main bulk of the substance remains cold. However, non of the phenomena described in this work can be explained just as a result of thermal action only. The spinel which has been obtained by grinding, or by grinding followed by heating at 400°C, shows to be different from the spinel obtained by further heating at 1200°C or from thermal spinel. If the phenomena of sharp local temperature rise exists in these experiments, it acts mainly upon increasing the spinel's rate formation with negligible influence on its structure.

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Zusammenfassung — Spinell ($MgAl_2O_4$) wurde mechanochemisch (MC) durch 10 Stunden langes Zusammenmahlen von MgO mit γ-Al_2O_3 hergestellt. Eine Untersuchung des MC-Produktes mittels Neutronendiffraktion und IR-Spektroskopie zeigte, daß es einen höheren Umsatzgrad (47%) aufweist, als sein thermisch hergestelltes Gegenstück (10%). Röntgendiffraktionsuntersuchungen ergeben, daß die $MgAl_2O_4$ Kristallite äquidimensional mit wesentlich höherer Geschwindigkeit wachsen als im Falle von α–Al_2O_3. Der höhere Umsetzungsgrad und die Höhere Bildungsrate bei Verwendung von γ-Al_2O_3 wird der Ähnlichkeit des Sauerstoffgitters von MgO, Al_2O_3 und Spinell und der stärkeren Beibehaltung der Kationen-Koordinationszahl zugeschrieben. Das äquidimensionale Wachstum wird der Gegenwart von {111} Ebenen zugeschrieben.