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POLYCRYSTALLINE SPINEL FROM POWDERS PREPARED BY FREEZE DRYING TECHNIQUE

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POLYCRYSTALLINE SPINEL FROM POWDERS PREPARED BY FREEZE DRYING TECHNIQUE

Chi-Shine Cliff Tao
(M.S. Thesis)

June 1972

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POLYCRYSTALLINE SPINEL FROM POWDERS PREPARED
BY FREEZE DRYING TECHNIQUE

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POLYCRYSTALLINE SPINEL FROM POWDERS PREPARED BY FREEZE DRYING TECHNIQUE

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June 1972

ABSTRACT

Stoichiometric spinel \((\text{MgAl}_2\text{O}_4)\) powder was prepared by calcining freeze dried powders formed from an aqueous solution of magnesium sulfate hydrate and aluminum sulfate hydrate.

The freeze dried powder was characterized by X-ray diffraction analysis, size distribution analysis and scanning electron microscopy. Thermal reactions of the freeze dried powder were studied by using differential thermal analysis, thermogravimetric analysis and X-ray diffraction. The formation of spinel was postulated to be an aluminum sulfate decomposition activated reaction. These postulated reactions were verified by calculations of their free energy change.

The reactivity of the freeze dried powder to form spinel on calcination depended upon the freeze drying temperature and the starting solution concentration. Freeze dried powder prepared from a starting solution containing 12% by weight of anhydrous magnesium and aluminum sulfates and dried at 25°C was found to be the most satisfactory.

Spinel powders developed from the freeze drying technique consisted of submicron size powders and large aggregates of 5 to 50 micron in size. The large aggregates have a lower sinterability in comparison with the submicron size powders, resulting in the formation of a nonhomogeneous
microstructure on sintering.
I. INTRODUCTION

Spinel (MgAl₂O₄) has excellent properties as a refractory ceramic: high melting point, high resistance to chemical attack, and relatively high strength at elevated temperatures. The traditional method of processing first involves the preparation of spinel powders by calcining a powder mixture of MgO and Al₂O₃ at temperatures of 1600 to 1800°C, followed by crushing and milling.¹ The spinel powders prepared in this manner are then sintered, but they are not sufficiently reactive to form high density bodies.

The development of microstructure in sintered ceramics is highly dependent on the starting material. Ultrafine homogeneous powders normally have high sinterability and thus achieve high density and fine grain size at lower firing temperatures.

Different methods have been used for the preparation of reactive spinel powder: calcination of a powder mixture of magnesium carbonate and reactive grade alumina,² reaction of alumina trihydrate with magnesium hydroxide,³ coprecipitation of magnesium and aluminum hydroxides followed by calcination,⁴ spray drying of an aqueous solution of magnesium sulfate and aluminum sulfate followed by calcination,⁵ co-crystallization of a saturated aqueous solution of hydrated magnesium sulfate and hydrated aluminum sulfate followed by calcination,⁶ boiling off the solvent of a magnesium carbonate, aluminum sulfate solution followed by calcination,⁷ boiling off the excess water from a magnesium sulfate hydrate, ammonia-aluminum alum aqueous solution followed by calcination,⁸ and freeze drying of the aqueous solution of magnesium.
sulfate and aluminum sulfate and followed by calcination.

The objectives of this research are:

(a) To prepare ultrafine homogeneous stoichiometric spinel powder by freeze drying of aqueous solution of magnesium sulfate and aluminum sulfate and followed by calcination,

(b) To characterize the freeze dried powder and to determine its thermal behavior, and

(c) To characterize the spinel powders and to relate their characters to their sintered microstructure.
II. BACKGROUND OF FREEZE DRYING TECHNIQUE
FOR PREPARATION OF INORGANIC MATERIALS

The freeze drying technique, which involves removal of water while
in the frozen state, was first developed to preserve biological speci-
mens which suffer severe shrinkage and change of chemical properties
through ordinary drying. Freeze drying has been successful in maintain-
ing the important chemical and physical properties of the specimen. For
instance, the morphology, chemical integrity and solubility are well
maintained for most specimens. Coffee is prepared in this way in order
to keep its original flavor.

Recently, freeze drying has been utilized to prepare ultrafine
powders of inorganic materials, because this method offers promise of
achieving an intimate molecular mixing of materials with a complex com-
position. Tungsten and tungsten-rhenium alloy ultrafine powders were
prepared by Langsberg and Cambell.\textsuperscript{10} Freeze dried Cd doped AgCl powders
were shown to have intimate mixing on a molecular scale by A. C. C.
Tseung and Bevan.\textsuperscript{11} Extensive work was done at Bell Laboratories to
prepare and characterize oxide powders by the freeze drying method.\textsuperscript{9,12-15}

Oxide powders prepared by use of the freeze drying technique have
been shown to have a homogeneous composition. They were submicron in
size with a high surface area resulting in high sinterability. Furthermore,
the powders were as pure as the starting material since no other
additives or mechanical grinding were needed during the processing.

The operations in the preparation of oxide powders by freeze drying
are solution mixing, quick freezing, sublimation, and calcination. Con-
sidering these four operations, the starting salts are limited since an
aqueous solution is normally preferable because of its relatively high freezing point. Salts that are mutually soluble in water are required, and they should preferably have the same anion group to avoid any undesirable chemical reactions from taking place in solution. They should also maintain their stability up to the decomposition reaction temperatures. For example, salts that melt before they reach their decomposition temperature are not applicable to this process. Also, the decomposition temperatures of the salts should not be too high in order to avoid extensive crystal growth during calcination. For a multisalt system, it is more favorable to have the individual decomposition temperatures not too different from each other. Furthermore, it is better if the gas evolved on calcination is nontoxic and has a low solubility in the product oxide at the calcination temperature.

1) Solution Mixing

Homogeneous mixing on an atomic scale of several chemical species can be achieved when they are mutually dissolved in a solution. Solutions of individual salts can be prepared with a fixed concentration and chemically analyzed. Several solutions can then be easily mixed by weight or volume to give the exact desired composition.

2) Quick Freezing

The purpose of quick freezing is to solidify the mixed solution without phase separation. In general, salt solutions upon freezing under equilibrium conditions form hydrates which are immiscible in ice. As an example, upon slow cooling a solution represented by the $\text{Al}_2(\text{SO}_4)_3$-$\text{H}_2\text{O}$ system, Fig. 1, either the hydrated salt or ice will separate out from the solution whose composition then follows the corresponding
Figure 1. Temperature, concentration relations in the system 
$\text{Al}_2(\text{SO}_4)_3-\text{H}_2\text{O}$
liquidus line of the phase diagram. Upon reaching the eutectic, further cooling will completely solidify the remaining solution as an eutectic mixture. Unfortunately, ternary phase diagrams having water as one component that would show cooling paths for more complex compositions are rarely available. In quick freezing separation and segregation of the salts as described is minimized by rapid cooling from the liquidus to the solidus temperatures.

Quick freezing can be done by pouring a small amount of solution into a cold liquid bath,\textsuperscript{10} spraying the solution onto a precooled plate,\textsuperscript{16} introducing the solution into precooled hexane as a fine stream,\textsuperscript{9} or spraying the solution into a cool volatile liquid such as freon-12 or liquid nitrogen.

Liquid nitrogen, however, has not been found to be a satisfactory cooling medium. Pouring the solution into such a bath does result in unavoidable segregation. Spraying the solution has the problem that the solution mist actually starts to freeze as it reaches the cold region above the liquid nitrogen surface; thus, there is no assurance that the freezing is rapid enough throughout the droplet to avoid segregation.

An interesting possibility that has not been tried for the preparation of inorganic materials is evaporative freezing which consists of spraying the solution into an adiabatic vacuum chamber.\textsuperscript{17} The principle of this method is that the latent heat consumed by the evaporation of water causes the solution droplets to freeze. This technique can be carried out automatically and continuously on a large production scale.
(3) **Sublimation**

The purpose of the sublimation step is to remove the frozen water without any remelting in order to prevent any separation of phases that may arise due to vaporization of remelted ice. A pressure-temperature phase diagram for pure water and a salt solution is shown in Fig. 2. At point 0, the three phases of water coexist in equilibrium at 0.0075°C and 4.58 torr. As salt is added to the water, the freezing point is lowered according to the molal freezing-point lowering. The solid lines in the diagram represent the equilibrium conditions for a solution of a certain fixed composition. Point Q, which is the invariant point for the solution, is called the cryohydric point. At pressures below that of the cryohydric point, ice in the frozen solution can be removed by sublimation. Because the ice is removed without passing through the liquid state, the finely divided salt crystallites maintain their mixedness or structure present in the frozen pellets throughout the drying process.

An effective sublimation process requires thermal energy for sublimation and the removal of sublimated water molecules. In vacuum freeze drying, the pressure is kept below the cryohydric point, and the vaporized water molecules are transferred to the condenser.

The mechanism of vacuum freeze drying can be discussed in greater detail. The heat of melting of ice is 1.44 Kcal/mole, and heat of vaporization of water is 9.72 Kcal/mole. A controlled amount of heat thus has to be added in order to maintain a reasonable drying rate without any melting of the frozen solution. The temperature of the drying specimen is therefore selfdetermined by the rate of heat input,
Figure 2. Temperature, pressure relations in a salt-water system. (Ref. 9)
composition of the drying layer, and the rate of removal of water molecules from the drying layer. As the drying process proceeds, an increasing shell thickness of dried material develops. All the water vapor formed by sublimation at the drying boundary must diffuse through the dried shell. Other investigations showed that a layer of dried material will significantly reduce the sublimation rate. The driving force for the diffusion of water molecules from the drying layer to the surface is the water vapor pressure gradient. A high vacuum system enhances the pressure gradient and facilitates the transferring of water vapor to the condenser.

The prevention of remelting of the frozen specimen is the most critical factor in the drying process. The temperature-pressure relationship for ice is shown in Fig. 3. The critical pressure is not that of the vacuum chamber but the vapor pressure at the drying boundary inside the specimen. As heat is supplied at a constant rate to the specimen, the water vapor has to be removed sufficiently rapidly to maintain the pressure at the drying boundary below the cryohydrionic pressure. The pressure in the vacuum chamber thus has to be kept at a much lower level.

An ideal freeze drier would have the specimen hanging freely in the center of a vacuum chamber surrounded by a heating system and condenser. In practice, the thermal energy for sublimation is supplied mainly by conduction and partly by radiation. The vacuum obtained with a mechanical pump is kept in the range of 5 to 20 micron Hg. Either a dessicant or chilled tubes can be used as a condenser. The drying rate is determined by the external, internal heat transfer and external,
Figure 3. Temperature, vapor pressure relation for ice.
internal water vapor transfer.

Freeze drying can also be done without vacuum by keeping the specimen temperature below its melting point and at the same time blowing a sufficient amount of dry air over the specimen to remove the water vapor.

Freeze drying without vacuum has only been tried with biological material and natural food. Meryman had the specimen hung in a cold zone and blew dry air over the specimen to remove the water vapor. This method consumes a huge amount of dry air and is not economical for the preparation of inorganic materials. King and Clark improved the method using convective heat and mass transfer by combining the frozen food and dessicant into mixed beds, through which gas was circulated as a medium for the heat and mass transfer. The question of whether or not this convective transfer method is applicable to the freeze drying of inorganic materials is still a research problem.

Calcination

The freeze dried powder aggregates have a sponge-like morphology and a size range from 10 to 300 microns. Upon calcination, the large freeze dried powder aggregates break down to fine powders through the dehydration and decomposition reactions. A freeze dried powder containing only one salt, upon calcination, simply decomposes to form its corresponding oxide. The steps of decomposition and formation of a homogeneous complex oxide compound from a freeze dried powder consisting of more than one salt are more complex and will be discussed in the discussion section.
III. EXPERIMENTAL PROCEDURE

The experimental part of this research is divided into: (1) preparation of the freeze dried powders and their characterization, (2) calcination of the freeze dried powders and characterization of the calcined spinel powders, and (3) densification of the spinel powders.

A. Freeze Dried Powders

(1) Preparation

Baker reagent grade magnesium sulfate hydrate (MgSO₄·7H₂O) and aluminum sulfate hydrate (Al₂(SO₄)₃·16H₂O or Al₂(SO₄)₃·18H₂O) were used as starting materials. Aqueous solutions of each salt were prepared and the exact molarity of the solutions was determined by chemical analysis. The magnesium sulfate solution was determined titrimetrically with E.D.T.A. reagent, and aluminum sulfate solution was determined gravimetrically by precipitation with 8-hydroxyquinoline (Appendix 1). The two solutions with known molarity were then apportioned by volume to provide the exact ratio of magnesium and aluminum.

The mixed solution under an argon pressure of 40 psi was atomized onto the surface of liquid freon-12 through a pneumatic jet, Fig. 4. The small droplets of the mixed solution were frozen into small icy pellets as they hit the freon-12, which has a boiling point at -28°C. The size of the frozen pellets depended on the argon pressure and the jet size. Higher pressure usually produced finer droplets which were considered to be more favorable. The frozen pellets were collected by a kitchen strainer and stored in a prechilled stainless steel pan. Before drying, the frozen pellets were evacuated overnight to remove the residue freon-12.
Figure 4. Laboratory arrangement of setup for quick freezing of aqueous solution of mixed salts.
Two freeze dryers have been used in this project: a laboratory-built model, Fig. 5, and a model 10-800 freeze drier from Virtis Company, Fig. 6. In Fig. 5, the freeze drier consists of a vacuum chamber connected with a 15 cfm vacuum pump with an intermediate condenser. The vacuum chamber can be prechilled by dry ice and then heated up to 140°C. The operating pressure of this freeze drier was about 0.2 to 0.05 torr.

As the temperature in the vacuum chamber was raised, the ice sublimation rate of the frozen pellets increased. It was very difficult, however, to keep the operating pressure below the cryohydric pressure. The flow condition of water vapor through the pumping line can be considered as a continuous, compressible flow. As the pressure was reduced at one end of the pumping line, the gas speed increased and reached sonic speed, which is called the choking condition. At this point, the flow rate through a constant cross section area reached a maximum. Friction between the water vapor molecules and the tube wall resulted in an effect corresponding to the reduction of the flow cross section area. As the sublimation rate of ice increased, the pressure in the vacuum chamber built up and finally caused the melting of the icy pellets. The increasing pressure indicated that the maximum flow rate of the water vapor through a 3/8 inch I.D. pumping line is smaller than that of the sublimation rate of the ice at that temperature. This problem of controlling an increasing water vapor pressure was solved by placing some dessicants in the vacuum chamber to serve as a built in condenser. Linde type 4A molecular sieves were used as the dessicant because they are available in a clean and durable form and can be easily regenerated by heating to about 250°C.
Figure 5. The laboratory-built freeze drier.
Figure 6. Virtis model 10-800 freeze drier.
The Vitris 10-800 model freeze drier, shown in Fig. 6, has a vacuum chamber with a built-in condenser. The sample plate can be operated in the temperature range from -40 to 120°C. The chamber pressure as measured by a McLeod vacuum gauge operates below 20 micron Hg. A radiant heating plate at about 35°C can be put on top of the frozen material to supply the heat of sublimation. This drier provided a higher condensing capacity and better control of the pressure and temperature and was consequently used for all subsequent experiments after its arrival.

The sample plate in the freeze drier was precooled to -40°C before loading the frozen powder. A stabilized pressure under 20 micron Hg in the chamber was appropriate before heating was employed to expedite the drying rate. The end point of drying was considered to have been reached when the chamber pressure was below 5 micron Hg and the sample temperature was the same as that of the sample plate. The freeze drying time depended on the amount of material and on the freeze drying temperature, e.g. three days were needed for drying one and a half liters of frozen solution at 25°C.

Samples of the same frozen powder were dried at 25, 50, 80, 100, 120 and 140°C, respectively, to determine the effect of freeze drying temperature on subsequent calcining of the powders.

Mixed magnesium sulfate hydrate and aluminum hydrate solutions of stoichiometric spinel composition but of four different concentrations based on the weight of total anhydrous salts were freeze dried at 25°C for three days to determine the effect of solution concentration on the calcination reaction to form the oxide compound.
(2) Characterization

X-ray diffraction patterns for the different freeze dried powders were obtained. The results and analysis will be covered in the section on Results and Discussion.

The data for the size distribution were obtained by sieve analysis. Sieves with openings of 37, 53, 74, 104, 208 and 295 micron meter were used. Cumulative weight percentage of the sized powder was plotted against their sizes. The spray freezing condition was kept the same for different batches which resulted in reproducible size distribution.

A Jeolco scanning electron microscope was used to investigate physical morphology of the freeze dried powders. The topographical details of a rough surface can be brought out by the large depth of focus of the scanning electron microscope. To prepare a specimen, a dilute isopropyl alcohol dispersion of the powders was dropped onto a well polished brass sample holder, the isopropyl alcohol was evaporated, and the powders were then coated with a thin layer of Pt-Pd alloy to form a conducting surface.

B. Calcination of Freeze Dried Powders

(1) Determination of Reactions

(a) Differential Thermal Analysis. Differential thermal analyses were made for the freeze dried powders, and the magnesium and aluminum sulfate hydrates. The heating rate was programmed at 12°C per minute. In order to identify the thermal effects indicated by the D.T.A. curve, the freeze dried powders were isothermally calcined at a series of temperatures in a vertical wire-wound resistance tube furnace. One gram of freeze dried powders was calcined in air at 190, 350, 450, 690, 800,
900, 925, and 950°C for one hour. The calcined powders were then examined by X-ray diffraction.

(b) Thermogravimetric Analysis. A vacuum thermogravimetric analysis was made of the freeze dried powders at an ambient pressure of about 0.05 torr. The powders were placed in a platinum crucible which was suspended from an Ainsworth microbalance that was also within the vacuum system. The heating rate was programmed at 12°C per minute. The result was plotted as cumulative percent weight loss versus temperature.

(2) Characterization of the Calcined Spinel Powders

One gram portions of the freeze dried powders were calcined in air for one hour at 850, 900, 915, 925, 950, 1000, 1100, 1225 and 1300°C to study their crystallite growth and the completeness of the decomposition reaction. X-ray diffraction patterns were obtained of these calcined powders. The powders were packed in the X-ray diffraction sample holder so as to obtain the same packing density. The half peak width and the area under the curve were measured at 20 equals to 31.3° and 59.4°, which correspond to d spacing values of 2.86 and 2.02 Å, respectively. The calculated average crystallite size was plotted versus the temperature. The percentage completion of the sulfate decomposition as measured by the integrated intensity of the diffraction peaks was also plotted on the same figure.

Calcined spinel powders were viewed by the scanning electron microscope. The sample preparation was the same as that for the freeze dried powders.

In addition, the starting materials of Baker reagent grade MgSO₄·7H₂O and Al₂(SO₄)₃·18 H₂O, the freeze dried powders, and calcined
spinel powders of the same batch were spectrographically analyzed to check the possibility of picking up impurities during processing. The analyses are listed in Table I.

C. Densification of Spinell Powders

The spinel powders used for densification studies were prepared by calcining freeze dried powders at 950 and 1150°C in vacuum for one and two hours. The freeze dried powders were formed by drying frozen solutions containing 12% by weight of anhydrous salts at 25°C. The crystal-lite sizes of the four calcined powders were measured by the X-ray line broadening technique.

A horizontal vacuum tube furnace that was available in the laboratory was used for vacuum calcining, Fig. 7. This furnace has a Kanthal resistance heating wire wound on a mullite tube with glass fittings joined to both ends of the tube. One of the glass joints is connected to a mechanical pump which controls the pressure in the furnace at about 0.04 torr. The present set up, however, does not have the oxygen probe lead indicated in the figure. Two alumina tubes are thus used to support the platinum heat shields and to introduce the thermocouples. A platinum boat for the powder calcination was set on top of the alumina dee.

In order to eliminate processing variables in attempting to correlate the different microstructures with the spinel powders, the green pellets were made with the same density and fired under identical

### Table I. Semi-quantitative spectrographic analysis *

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<tr>
<th></th>
<th>MgSO₄·7H₂O</th>
<th>Al₂(SO₄)₃·18H₂O</th>
<th>Freeze Dried Powder</th>
<th>Calcined Spinel Powder</th>
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<td>20. %</td>
<td>40. %</td>
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<td>Pt</td>
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*This work was done by American Spectrographic Laboratories.*
Figure 7. Vacuum calcination furnace.
conditions. To obtain the same green density for the different bodies, equal weights of the different powders and a spacer to control the plunger movement inside the die were used. The green densities were determined by weighing and dimensional measuring of the compacts. The compacts were dried at 170°C for one day before sintering and sintered together in air in a MoSi₂ resistance heating vertical furnace. The specimens were heated at a rate of about 8°C per minute to 1550°C, held for three hours, and furnace cooled. Polished specimens were etched with H₃PO₄ at 210°C for seven minutes and examined with a scanning electron microscope.
IV. RESULTS AND DISCUSSIONS

Initial solution concentrations were determined by the low condensing capacity of the laboratory constructed freeze drier. The preliminary powders used for characterization and reaction studies were thus prepared from solutions containing 19% by weight of the anhydrous salts and freeze-dried by raising the temperature gradually to 120°C. After acquisition of the Virtis freeze drier, the starting solution concentration and the freeze drying temperature were varied in order to study their effect on the calcining behavior of the freeze dried powders. As a result of these experiments, the spinel powders for the sintering study were made from a starting solution containing 12% by weight of the anhydrous salts and freeze dried at 25°C.

Al₂(SO₄)₃·18H₂O and MgSO₄·7H₂O were used as the starting materials in the preparation of freeze-dried powders for the characterization study. Because of subsequent unavailability of Al₂(SO₄)₃·18H₂O, Al₂(SO₄)₃·16H₂O was then used for the solution concentration, freeze drying temperature and sintering experiments. Since both aluminum sulfate hydrates are mutually soluble with magnesium sulfate heptahydrate, there should have been no difference in the freeze dried powders because of the different Al₂(SO₄)₃ hydrates.

A. Freeze Drying

(1) Phase Transformations

The MgSO₄-Al₂(SO₄)₃-H₂O system was studied by Bassett and Watt at 25°C; their 25°C isothermal section is shown in Fig. 8. The double salt MgAl₂(SO₄)₄·22H₂O was considered to be an equilibrium solid phase
Figure 8. $25^\circ$C isotherm of system $\text{MgSO}_4-\text{Al}_2(\text{SO}_4)_3-H_2O$ plotted in weight percentage (ref. 22).
(point D containing 54 weight percent of the anhydrous salts). The aqueous solutions used in this study lie on the $\text{H}_2\text{O-MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ join; the solutions with 12 and 19 weight percent of anhydrous salts are represented by points A and B, respectively.

If a solution is dried at 25°C under equilibrium conditions, $\text{H}_2\text{O}$ will leave the system by vaporization and the solution composition will move away from the $\text{H}_2\text{O}$ end of the join, at 71 weight percent of $\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ will start precipitating and will continue to precipitate with further loss of $\text{H}_2\text{O}$. When the $\text{H}_2\text{O}$ content drops below 65 weight percent, the $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ will react peritectically with the remaining solution to form $\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$, which would become the entire product when the overall $\text{H}_2\text{O}$ concentration became 46%. This peritectic reaction would have difficulty in maintaining equilibrium because of the need of material transport by diffusion through the reaction product layer. The final dried material would then consist of a heterogeneous mixture of $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$, $\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ and magnesium sulfate hydrate.

If the solution is frozen without loss of $\text{H}_2\text{O}$ under equilibrium conditions and if the diagram of Fig. 8 is used as an approximation for the phase diagram (which is not available for this system), on cooling, pure ice will crystallize first followed by $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$. On reaching the peritectic temperature, $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ will react with the remaining solution to form $\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$, the final products then being this salt and ice. Again, the peritectic reaction would probably prevent achievement of equilibrium, resulting in a heterogeneous solid mixture of $\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$, ice, unreacted $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ and some
salts containing magnesium sulfate.

If the solution is frozen or cooled under non-equilibrium conditions the \( \text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O} \) does not have time to separate extensively and the peritectic reaction is essentially bypassed. If the freezing is fast enough, an intimate amorphous solid mixture is formed which more or less retains the structure of the solution. An amorphous structure is then essentially retained if the removal of the ice by sublimation is achieved under conditions which prevent any remelting of the ice.

(2) Characterization of Freeze Dried Powders

The freeze dried powders prepared from the two different starting solutions showed an amorphous X-ray diffraction pattern with two diffuse peaks at 2θ values equal to approximately 15° and 25°, corresponding to \( d \) spacings of 5.90 Å and 3.56 Å, respectively. With increasing sublimation temperature, these two peaks increased in intensity which was probably due to the growth of the salts' crystallite size. The powders have a sponge-like structure and are highly hydroscopic. When the powders are allowed to absorb moisture from the air, the X-ray diffraction pattern shows many peaks that have not been identified.

The X-ray amorphous nature of the freeze dried powders must be associated with lack of crystalline structure which is due to the rapid freezing of the solutions. Luyet\(^{23}\) studied the phase transformations of dilute aqueous solutions on freezing with emphasis on their cooling rate. He postulated that increasing the freezing velocity will result in varieties of different crystalline structures. He found that different types of ice crystals occurred and with increased cooling rates incomplete crystallization of ice resulted, as verified by X-ray
analysis by Meryman. In this study the freezing conditions consisted of a fine spray of magnesium aluminum sulfate aqueous solution striking the surface of liquid freon-12 at -28°C. After the crystallization of part of the water, the rest of the solution apparently formed an intimate solid mixture of hydrated salts and ice. Upon sublimation of the ice, the amount of hydration water remaining was about 15 weight percent which is considerably less than the 46 weight percent of H₂O in the stable double salt of MgAl₂(SO₄)₄·22H₂O. The X-ray amorphous nature of the freeze dried powders is then probably due to the non-crystalline arrangement of atoms caused by the rapid freezing and relatively small amount of water or due to the very small crystallite size of an intimate mixture of salt hydrates.

The size distribution of two batches of freeze dried powders obtained under the same drying conditions were analyzed, and reproducible data were obtained. Figure 9 shows the fractional weight distribution over the size ranges. If the droplets leaving the nozzle are of uniform size, formation of different sized freeze-dried particles may be due to two reasons. First, coalescence of the fine droplets in the mist may have occurred while they travelled from the pneumatic jet to the surface of freon-12; these particles should be essentially spherical in shape. Secondly, growth may occur by collision of the fine mist with the frozen particles on the freon-12 surface; these should have irregular shapes. The seven different sizes of freeze-dried powders were viewed by a scanning electron microscope. The powders are generally of spherical or flaky morphology, as seen in Figs. 10 and 11. The particles are not
Figure 9. Size distribution of freeze dried powder.
Figure 10. A particle from freeze dried powder from the size fraction smaller than 37μ. This powder was prepared from the starting solution containing 12% by weight of magnesium sulfate and aluminum sulfate and dried at 120°C.

Figure 11. Two magnifications of the same freeze dried powder as described in Fig. 10, but from the size fraction of +74 -104μ.
solid and undoubtedly reflect the structure of the frozen particles before drying.

The different size fractions were calcined at 915°C for one hour. X-ray diffraction patterns showed identical spinel crystalline peaks which indicates that all of the powders were aggregates composed of crystallites of the same average size. These powders were also viewed with a scanning electron microscope. The fraction above 208 μm showed a large number of large aggregates; since this fraction constituted only 15 weight percent of the total amount, it was discarded from the calcined powders used in subsequent sintering studies. Generally, the powders formed by calcining -208 μm freeze dried powders consist of submicron particles, as seen in Fig. 12. Some aggregates in the size range of 5 to 50 μm, however, were observed among the fine submicron particles, Fig. 13. Two types of structures were exhibited by the large aggregates: a beehive-like structure shown in Fig. 14, and a dense sponge-like structure shown in Fig. 15.

B. Thermal Reactions

(1) Differential Thermal Analysis

Differential thermal analysis and X-ray diffraction analysis were used to investigate the reactions and phase transformations that occur during calcining of the freeze dried powders, MgSO₄·7H₂O and Al₂(SO₄)·18H₂O. The latter salts were heated in vacuum at 120°C to drive off part of their hydrated water in order to have comparable conditions to the freeze dried powder which was dried at 120°C and to reduce the magnitude of the endothermic dehydration reactions. The X-ray diffractions of the two partially dehydrated salts showed amorphous
Figure 12. Three magnifications of the spinel powder prepared by calcining the freeze dried powder described in Fig. 10 for 4 hours at 915°C.
Figure 13. Three magnifications of the spinel powder prepared by calcining the freeze dried powder described in Fig. 10 for 1 hour at 915°C. A large aggregate of spinel is shown in the photographs.
Figure 14. Two magnifications of the beehive-like aggregate which was found in the batch of calcined spinel powder shown in Fig. 12.
Figure 15. Four magnifications of sponge-like aggregates which were found in the batch of calcined spinel powder shown in Fig. 12.
patterns. The three thermograms are plotted in Fig. 16.

$\text{Al}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ loses water in a continuous way up to about 370°C, resulting in an extended endothermic peak. Anhydrous aluminum sulfate then starts to decompose to $\gamma$-$\text{Al}_2\text{O}_3$, $\text{SO}_2$ and $\text{O}_2$ at about 700°C. The $\gamma$-$\text{Al}_2\text{O}_3$ formed upon decomposition has poor crystallinity as shown by X-ray diffraction analysis. At about 1300°C, $\gamma$-$\text{Al}_2\text{O}_3$ transforms to $\alpha$-$\text{Al}_2\text{O}_3$ indicated by an exothermic peak and X-ray analysis. The temperature at which $\gamma$-$\text{Al}_2\text{O}_3$ transforms to $\alpha$-$\text{Al}_2\text{O}_3$ is influenced by impurities and particle size.

$\text{MgSO}_4 \cdot n\text{H}_2\text{O}$ undergoes a dehydration reaction, as $\text{Al}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$, as represented by the first endothermic peak. An exothermic peak is superimposed at about 300°C, which was also observed by Schnettler, Monforte and Rhodes, who identified it as a transformation of the poorly crystalline low temperature modification to the crystalline high temperature modification of magnesium sulfate. This analysis was verified in this study. Three endothermic peaks are shown in the high temperature region. The peak from 1100 to 1180°C is caused by the decomposition of $\text{MgSO}_4$. Two more D.T.A. runs were made to identify the other two endothermic peaks; one was stopped at 1110°C and the other at 1240°C. A phase change of $\text{MgSO}_4$ at 1010°C has been reported; the X-ray diffraction pattern for the specimen quenched at 1110°C showed major peaks similar to those for $\text{MgSO}_4$ at a lower temperature, but minor changes were observed in some of the weaker peaks. Melting was observed in the specimen quenched at 1240°C, because the melting point for $\text{MgSO}_4$ was reached before it was completely decomposed. The last endothermic peak therefore corresponds to the melting of $\text{MgSO}_4$ and the base line drifting
Figure 16. D.T.A. thermograms of aluminum sulfate, freeze dried magnesium aluminum sulfate and magnesium sulfate, obtained at a heating rate of 12°C/min. in air.
indicates a better heat transfer to the differential temperature couple.

In the freeze dried powder D.T.A., the endothermic peak at about 150°C is due to the removal of absorbed water and the one at about 350°C is associated with the removal of hydrated water. One gram portions of the freeze dried powder were calcined isothermally for one hour at 190, 350, 450 and 690°C and examined by X-ray diffraction in order to help identify the thermal effects. At 190°C, the powders were still amorphous. Calcined at 350°C, the X-ray diffraction pattern showed weak peaks for both the anhydrous magnesium sulfate and aluminum sulfate; at 450°C, X-ray diffraction peaks were much stronger; and at 690°C, the peaks were even sharper, indicating increasing crystallinity and growth of the individual sulfate crystallites. The large endothermic peak corresponds to the decomposition of sulfate starting at about 700°C, which is similar to the temperature at which decomposition of aluminum sulfate starts. This seems to indicate that the decomposition of magnesium sulfate and simultaneous formation of spinel are dependent on the aluminum sulfate decomposition reaction. X-ray diffraction pattern of powder calcined at 940°C showed all spinel diffraction peaks; calcination at 750°C for three days also resulted in an X-ray pattern mainly with spinel diffraction peaks but with some minor peaks common to both magnesium and aluminum sulfates.

(2) Thermogravimetric Analysis

A thermogravimetric analysis of the same specimen used for D.T.A. was made at a heating rate of 12°C per minute under an ambient pressure of about 0.05 torr. The results are plotted as percent weight of freeze dried powder versus temperature in Fig. 17. After application of the
Figure 17. T.G.A. thermogram of the freeze dried powder, obtained at heating rate of 12°C/min. in vacuum.
vacuum, and prior to any heating, four to five percent weight loss occurred due to the loss of physically absorbed water which is not shown in the figure. With heating, about fifteen percent of weight loss occurred gradually up to 625°C; this loss was associated with the dehydration reaction of the freeze dried salts. The additional 45% weight loss is due to the sulfate decomposition which started at about 625°C and was completed at about 850°C. This experiment supports the D.T.A. results and also indicates the dependence of the decomposition temperature on the ambient pressure.

(3) Thermodynamic Considerations

Experimentally it has been seen that the decomposition and reaction of the freeze dried powders starts at the same temperature as the decomposition for aluminum sulfate. The overall spinel reaction can be written as:

\[ \text{MgSO}_4(s) + \text{Al}_2(\text{SO}_4)_3(s) = \text{MgAl}_2\text{O}_4(s) + 4\text{SO}_2(g) + \text{O}_2(g) \]

which can be postulated as consisting of the step reactions:

\[ \text{Al}_2(\text{SO}_4)_3(s) = \gamma\text{-Al}_2\text{O}_3(s)_{\text{amorphous}} + 3\text{SO}_2(g) + 3/2 \text{O}_2(g) \]

\[ \gamma\text{-Al}_2\text{O}_3(s)_{\text{amorphous}} + \text{MgSO}_4(s) = \text{MgAl}_2\text{O}_4(s) + \text{SO}_2(g) + 1/2 \text{O}_2(g) \]

The free energy change for the overall reaction is the sum of the free energy changes of the step reactions; the values over the
temperature range from 650 to 1150°C are plotted in Fig. 18. Free energy function data for aluminum sulfate above 1100°C was obtained by extrapolation of lower temperature data. Curve II is based on the results obtained by using alpha alumina as the intermediate compound, and indicates that the reaction becomes thermodynamically feasible at 820°C. Estimating the difference of standard entropy for alpha alumina and amorphous gamma alumina to be 5.5 cal/mole°K, and assuming $H^0_t$ and $S^0_t$ to be the same for crystalline $\alpha$-Al$_2$O$_3$ and amorphous $\gamma$-Al$_2$O$_3$ in the free energy function at high temperatures, the free energy change using amorphous gamma alumina as the intermediate compound is plotted as curve I. It is seen that the overall reaction then becomes thermodynamically feasible at 775°C which is close to the experimental results. These calculations are based on one atmosphere as the standard state for the gaseous products. The gaseous products in actual reactions have partial pressures less than one atmosphere which will result in the reaction taking place at a lower temperature.

The reaction analysis indicates that each crystallite of aluminum sulfate decomposes and reacts with its neighboring magnesium sulfate crystallite to form spinel. If any local segregation of the two salts occurs during heating, the overall reaction, if not carried to equilibrium, would result in either localized nonstoichiometric spinel or the presence of residue sulfates. Therefore, the intimate mixing of Al$_2$(SO$_4$)$_3$ and MgSO$_4$, preferably on a molecular level, must be retained throughout the whole process. Experimental results indicate that the individual crystallites of anhydrous Al$_2$(SO$_4$)$_3$ and MgSO$_4$ grow in size upon slow heating. The calcination temperature should thus be reached
Figure 18. Free energy change for the reaction

\[ \text{MgSO}_4(s) + \text{Al}_2(\text{SO}_4)_3(s) = \text{MgAl}_2\text{O}_4(s) + 4\text{SO}_2(g) + \text{O}_2(g) \]

at different temperatures.
by the powders immediately or as quickly as possible.

(4) **Effect of Freeze Drying Temperature**

An aqueous solution containing 19% by weight of equal molar amounts of magnesium sulfate and aluminum sulfate was freeze dried at six different temperatures: 25, 50, 80, 100, 120 and 140°C. One-half gram of each powder was calcined in air at 920°C for one and a half hours. X-ray diffraction analyses indicated that the powder dried at 25°C was the only one that showed all of the spinel diffraction peaks without any indication of residue sulfates.

In X-ray diffraction, the total energy of the diffracted beam from a crystal as it rotates through a Bragg angle is called the integrated intensity. The integrated intensity for a diffraction pattern can be measured as that area under the diffraction profile which is above the background. This procedure assumes that the powders are packed so that the particles are oriented completely at random and that the packing density is the same for different powders. The integrated intensity of the diffraction pattern of different spinel powders will be proportional to the amount of a given phase present and thus can be used as a measure to evaluate the percentage of conversion of spinel from the decomposition of the sulfates. The integrated intensity of a diffracted X-ray beam depends on the particular Bragg reflection involved while the other variables are kept constant. To make a correct comparison of the completion of the decomposition reaction for different spinel powders, the integrated intensity of the same Bragg angle has to be compared for each pattern. Bragg angles of 31.3 and 59.4 degree, which correspond to the d spacings of 2.85 Å and 1.55 Å, were chosen to make this comparison.
The percentage completion of the decomposition reaction for each of the powders was calculated based on 100% conversion to spinel of the powder freeze dried at 25°C. The results are plotted against the drying temperatures in Fig. 19. The percent weight loss on calcining of each powder is also shown in the figure.

The percentages of conversion to spinel on calcining freeze dried powders dried at different temperatures can be correlated with the X-ray diffraction patterns of the six freeze dried powders. The powder dried at 25°C shows two broad peaks at Bragg angles of about 15 and 25 degrees. As the drying temperature increased, the intensity of the two diffuse peaks increased indicating that the fine sulfate crystallites grew in size which hindered the reaction to form spinel. The higher integrated intensities at 120 and 140°C in comparison with the values for 80 and 100°C are not understood. The same trend of integrated intensities was also observed for a similar series.

(5) Effect of Calcination Temperature

One gram samples of freeze dried powder, formed from an aqueous solution of 19% by weight of the total anhydrous salts and dried at 120°C, were calcined in air for one hour at 800, 900, 915, 925, 950, 1000, 1100, 1225 and 1300°C. The average crystallite size is plotted versus the calcining temperature in Fig. 20. A rapid increase of the crystallite size occurs above about 1200°C. The integrated intensity for each powder, representing the completion of the reaction, was determined and plotted versus temperature in the same figure. Completion of reaction is indicated at temperatures of about 1000°C and above.
Figure 19. Variation of calcination reactivities for powders freeze dried at different temperatures and calcined at 920°C for 1-1/2 hours.
Temperature dependent spinel crystallite growth on calcining the freeze dried powders for 1 hour.
The average spinel crystallite size as a function of drying temperature was measured by the X-ray line broadening technique assuming that the calcined powders were strain free and that the X-ray line broadening was due only to the small crystallite size. This method only allows the determination of the average thickness of crystallites at certain crystallographic orientations, whereas a distinct particle may consist of many crystallites of different orientations. The crystallite size was measured at Bragg angles equal to 31.3 and 59.4 degree which correspond to \{220\} and \{511\} orientations. The crystallite size measured at the two different orientations for all six powders matched each other closely.

The Scherrer equation is used to calculate the crystallite size:\textsuperscript{26}

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

where

- $D =$ the average crystallite thickness normal to the diffraction plane
- $K =$ the shape constant, a value of 0.9 is the best when little is known of the crystallite shape and size distribution
- $\lambda =$ the wavelength of the incident X-ray, 1.54 Å for the Cu K$\alpha$ radiation
- $\beta =$ the broadening of the diffraction peak which is due to the small size crystallite
- $2\theta =$ the Bragg diffraction angle at which the half peak width is measured.
APPENDIX

The chemical determinations of the concentrations of the MgSO₄ and Al₂(SO₄)₃ solutions were made by Ursula Abed, Analytical Laboratory, Nuclear Chemistry Dept., Lawrence Berkeley Laboratory, and the following description of the chemical procedures was prepared by her on Oct. 27, 1971.

Mg was determined titrimetrically with ethylene diamine tetraacetic acid (EDTA) which, in turn, was standardized with standard Mg of known purity. The precision of the standardization was ± 5 parts in 2350 parts; that of three MgSO₄ sample aliquots was ± 1 part in 2650 parts. The molarity of the MgSO₄ solution was found to be 1.14.

(1) Method
(a) Reagents. Analytically pure reagent grades were used throughout. The Mg standard was prepared from highest purity available Mg slab, i.e., 99.95% as ascertained by spectrographic analysis. An amount weighed to five significant figures was dissolved in HCL and made to volume in such a manner as to give 0.10029 in moles Mg/ml. The EDTA titrant employed was approximately 0.01 M. A pH 10 buffer required was made by combining 5.4g NH₄Cl with 8.75 ml NH₄OH and diluting to 100.0 ml with dist. H₂O. Solid Eriochrome Black T indicator (supplier unknown) was mixed with solid NaCl in a 1:100 ratio and was used in this form.
(b) Procedure. Three 2.00 ml Std. Mg and three 2.00 ml aliquots of the MgSO₄ sample, previously diluted 10 fold, were delivered each into 125 ml Erlenweier flasks. Seventy-five ml H₂O and 10 ml buffer were added, followed by a few grains of the indicator which changes the colorless solutions to a deep magenta. While the titrant was added, the solutions
were magnetically stirred until the color passed through a transient violet to a pure blue endpoint. Based upon the average ml of titrant consumed for the three Mg standard solutions, the concentration of the EDTA was calculated. The resulting value was then applied to the calculation of the unknown MgSO₄ sample solution.

Al was determined gravimetrically by precipitation with 8-hydroxyquinoline. The average of three results was:

21.62 mgs Al/ml ± 1% or 0.40 M Al₂(SO₄)₃.

(2) Method

(a) Reagents. Analytically pure reagent grades were used throughout. 5g of 8-hydroxyquinoline were combined with 12 ml glacial acetic acid, 75 ml dist. H₂O and were warmed to dissolve the reagent which was subsequently filtered through whatman paper into a brown bottle and diluted to 100 ml with dist. H₂O. A 2 N ammonium acetate solution was prepared by dissolving 30.8g of the salt in dist. H₂O and by diluting to a final volume of 200 ml. H₂SO₄ was used for a slight acidification of the sample solution. Sintered glass crucibles, having an F (fine) porosity bottom, were washed, oven-dried, cooled in a dessicator and weighed to six significant figures prior to their receiving the Al-8 hydroxyquinoline precipitate.

(b) Procedure. 1.00 ml Al₂(SO₄)₃ sample aliquots were delivered, in triplicate, into 250 ml beakers containing 100 ml H₂O and 3 drops of H₂SO₄. After warming to 60-80°C, 7.0-8.0 ml of 8-hydroxyquinoline reagent were added, followed by a dropwise addition of ammonium acetate until a permanent precipitate formed while stirring. To insure complete
The value of $\beta$ is obtained by making a correction of the measured half peak width $B$ with the inherent half peak width $b$. Depending upon the shape of the diffraction curve, two methods are used to calculate the value of $\beta$, Scherrer's method and Warren's method. For Scherrer's method, $\beta = B - b$, and $\beta = (B^2 - b^2)^{1/2}$ for Warren's method. For a given diffraction peak, if a straight line is obtained by plotting the inverse of the intensities along the diffracted curve against $(2\theta - 2\theta_{\text{max}})^2$, Scherrer's method will be applicable. On the other hand, Warren's method applied if a straight line is obtained by plotting the logarithm of the intensities versus $(2\theta - 2\theta_{\text{max}})^2$. If neither one of the plots gives a straight line, the geometric mean of Scherrer's width and Warren's width can be used. Figures 21 and 22 are the plots for the diffraction peak with the Bragg angle of 31.3 degree. A straight line is obtained in Fig. 21 which indicates that Scherrer's method is the correct one to use in these calculations.

The formation of spinel crystallites and their growth can be considered as a nucleation and growth mechanism. The low bulk density of the freeze dried material is due to its structure of large channels and very fine pores. The large channels are due to the sublimation of the primary crystallized water, and the fine pores are due to the sublimation of the water which solidified with concentrated sulfate solution as an intimate solid mixture. The endothermic decomposition starts from the surface of the freeze dried particles. Heterogeneous nucleation of spinel occurs and the nuclei grow in size. The spinel crystallites will grow until they impinge on each other when the reaction to form spinel is completed. A grain growth mechanism must then follow.
Figure 21. Scherrer's treatment to determine half width of the X-ray diffraction peak.
Figure 22. Warren's treatment to determine half width of the X-ray diffraction peak.
The lower growth rates of the crystallite sizes for freeze dried powders calcined at the lower temperatures are probably associated primarily with growth of nuclei. The rapid increase in growth rate at the higher temperatures, on the other hand, could be associated with grain growth, as would be expected with completion of the reaction. The size of the crystallites at the time the grain growth mechanism became dominant should be determined by the number of nuclei.

(6) Effect of Solution Concentration

Droplets formed from aqueous solutions containing 7, 12, 19 and 39 percent by weight of equal molar magnesium sulfate and aluminum sulfate were freeze dried at 25°C. One gram of each powder was calcined at 920°C for one hour in air. X-ray diffraction analysis showed that the powder formed from the solution with 12 weight percent of salts was the only one completely reacted to spinel. Quantitative measurements of the integrated intensity was not possible because of the variation in the fluffiness of the four calcined powders, making it impossible to obtain the same packing density. The fluffiest powder was the one made from the solution with the lowest salt content.

C. Microstructure Analysis

Powder formed by freeze drying an aqueous solution containing 12% by weight of total anhydrous salts at 25°C was used for the sintering study. Equal amounts of powder were calcined in vacuum at 950°C and 1150°C for one hour and two hours. The spinel crystallite sizes measured by X-ray line broadening are indicated in Table II. The table also lists the chemically analyzed residue sulfate content.*

*This chemical analysis was done by Anamet Labs., Inc., Berkeley, Calif.
Table II. Data for spinel powders and their sintered bodies

<table>
<thead>
<tr>
<th>Specimen Number</th>
<th>Powder Calcination</th>
<th>Crystallite Size Å</th>
<th>Green Density % Theoretical</th>
<th>Residue Sulfur % Weight</th>
<th>Fired Density % Theoretical</th>
<th>Approximate Average Grain Size (Microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1 hr at 950°C</td>
<td>65</td>
<td>43.5</td>
<td>0.32</td>
<td>95.3</td>
<td>~3</td>
</tr>
<tr>
<td>B</td>
<td>2 hr at 950°C</td>
<td>67</td>
<td>43.4</td>
<td>0.26</td>
<td>97.8</td>
<td>~4</td>
</tr>
<tr>
<td>C</td>
<td>1 hr at 1150°C</td>
<td>150</td>
<td>43.4</td>
<td>0.07</td>
<td>93.1</td>
<td>~7</td>
</tr>
<tr>
<td>D</td>
<td>1 hr at 1150°C</td>
<td>242</td>
<td>43.0</td>
<td>0.07</td>
<td>96.6</td>
<td>~9</td>
</tr>
</tbody>
</table>
The four calcined powders were cold pressed to approximately the same green density as shown in Table II. Similar green density should allow a comparison of the sintering reactivity of the calcined powders. The specimens were then sintered for three hours at 1550°C. The sintered specimens were polished, etched and examined with a scanning electron microscope. An examination of the polished sections at a relatively low magnification, Figs. 23, 24, 25 and 26 indicates a nonhomogeneous microstructure of a continuous dense matrix with pockets of less dense material which apparently were gouged during polishing. These pockets were undoubtedly due to the presence of large aggregates similar to those observed in the scanning electron microscope examination of the calcined powders shown in Fig. 15, 16 and 17, which did not sinter as readily as the fine loose powder which was densely packed in pressing. It would be expected that the amount and strength of these aggregates would increase with temperature and time of calcining as suggested by the microstructures shown in Figs. 23, 24, 25 and 26. The micrographs also suggest that some crushing of the aggregates occurred in cold pressing, resulting in elongation and alignment of the gouged areas perpendicular to the vertical pressing direction.

Figures 29, 30, 31 and 32 show scanning electron microscope observations at a higher magnification of the continuous denser matrix observed in Figs. 25, 26, 27 and 28, respectively. Table II lists the approximate average grain size, and the apparent fired density as percent theoretical density. Although there are an insufficient number of specimens for a detailed analysis, a correlation of the bulk fired density values and the numbers of the porous pockets suggests that the
Fig. 23. Sintered spinel body prepared from the freeze dried powder calcined at 950°C for 1 hour in vacuum.

Fig. 24. Sintered spinel body prepared from the freeze dried powder calcined at 950°C for 2 hours in vacuum.

Fig. 25. Sintered spinel body prepared from the freeze dried powder calcined at 1150°C for 2 hours in vacuum.

Fig. 26. Sintered spinel body prepared from the freeze dried powder calcined at 1150°C for 2 hours in vacuum.
matrix of the specimen made from powder calcined at 1150°C for two hours is the most dense, as appears to be the case in Fig. 32 in comparison with Figs. 29, 30 and 31. This apparently higher reactivity for the spinel powder with the largest crystallite size may be due to a lower residue sulfur content (Table II) and a higher green density in the matrix of the cold pressed compact because of the larger amount of large aggregates in the starting powder. On this basis the small grain size in the compacts made from powder calcined at 950°C may be due to the residue sulfur content which inhibits grain growth and densification in some unknown manner.

Additional work is necessary on densification factors since normally accepted theories are based on the concept that reactivity of a powder increases with decrease in crystallite size.
Fig. 27. Dense area of the sintered specimen shown in Fig. 23.

Fig. 28. Dense area of the sintered specimen shown in Fig. 24.

Fig. 29. Dense area of the sintered specimen shown in Fig. 25.

Fig. 30. Dense area of the sintered specimen shown in Fig. 26.
V. CONCLUSIONS

The goal of this study was to provide a better understanding of the synthesis of ultrafine spinel powders by use of the freeze drying technique as a mixing method for the starting materials. An understanding of the reaction mechanisms and sintering behavior of the ultrafine powders was also an objective.

Freeze drying is a promising method to synthesize homogeneous complex inorganic materials of desired composition, such as MgAl$_2$O$_4$ spinel. The success of this method is dependent on the existence of mutual solubility of the desired salts in an aqueous solvent and on the completeness of thermal reactions of the starting materials. The understanding of solution chemistry including phase transformation is of the greatest importance for establishing procedures for a new system.

Differential thermal analysis, thermogravimetric analysis, and X-ray diffraction analysis provided the means for understanding the thermal behavior of the freeze dried powder. The postulated aluminum sulfate decomposition-activated formation of spinel is supported by thermodynamic calculations. The spinel crystallites grew at an increasing rate proportional to temperature up to about 1200°C and then at a much higher growth rate.

On the basis of the understanding gained of the mechanisms of the thermal reactions, it is realized that the intimate mixing of the two starting salts obtained in aqueous solution must be maintained throughout the freeze drying and calcining processes in order to obtain a homogeneous spinel powder of fine crystallite size.
The 25°C freeze drying temperature produces a freeze dried powder that has the most complete thermal reaction as compared with the powders dried at higher temperatures. The higher temperature dried powders seem to have lost their intimate mixing condition and thus were not as reactive upon calcination.

Starting solution containing 12% by weight of anhydrous sulfate salts resulted in powders that showed the most complete reaction in comparison with solutions lower and higher in sulfate salts content. This difference was not evaluated.

Calcination in vacuum cause the reaction to occur at lower temperatures because of the lower partial pressure of the reaction gas products. The lower temperature reaction results in finer crystallite sizes.

X-ray diffraction analysis shows that the different sizes of freeze dried powders when calcined under the same conditions have the same average crystallite size. No correlation has been made in this study of the size distribution of the freeze dried powder to the distribution of the aggregate sizes of the calcined powders.

The large aggregates in the submicron spinel powders appear to be responsible for the nonhomogeneous sintered microstructure. The large aggregates probably correspond to the porous pockets in the microstructure.

The residue sulfate in the calcined powder appears to play a role in sintering. Their actual role, however, has not been determined. Additional study on microstructure development is needed.
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precipitation, an excess of 20 ml of ammonium acetate was allowed. When
the precipitate had settled (preferably over night), it was quantita-
tively transferred to weighed crucibles, water washed, dried for two
hours at 120-140°C, cooled, and weighed as Al(C₅H₇ON)₃.

Conversion factor to Al:

\[ \text{mgs } \text{Al (C₅H₇ON)₃} \times 0.0587 = \text{mgs Al} \]
REFERENCES


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