

A new powder production route for transparent spinel windows: powder synthesis and window properties

Ronald Cook*^a, Michael Kochis^a, Ivar Reimanis^b and Hans-Joachim Kleebe^b

^aTDA Research, Inc., 12345 West 52nd Ave, Wheat Ridge, CO 80033

^bDepartment of Metallurgical & Materials Engineering, Colorado School of Mines, 1500 Illinois Street, Golden, Colorado 80401

ABSTRACT

Spinel powders for the production of transparent polycrystalline ceramic windows have been produced using a number of traditional ceramic and sol-gel methods. We have demonstrated that magnesium aluminate spinel powders produced from the reaction of organo-magnesium compounds with surface modified boehmite precursors can be used to produce high quality transparent spinel parts. The new powder production method allows fine control over the starting particle size, size distribution, purity and stoichiometry. The new process involves formation of a boehmite sol-gel from the hydrolysis of aluminum alkoxides followed by surface modification of the boehmite nanoparticles using carboxylic acids. The resulting surface modified boehmite nanoparticles can then be metal exchanged at room temperature with magnesium acetylacetonate to make a precursor powder that is readily transformed into pure phase spinel.

Keywords: boehmite, metal exchange, alumoxane, organomagnesium, spinel, transparent, nanoparticles

1. INTRODUCTION

Transparent optical ceramics are integral components (e.g. radomes, IR domes, sensor protection, and multi-spectral windows) of many advanced weapon systems. Sapphire is the most mature transparent ceramic window material and is available from several manufacturers. Unfortunately, the cost of sapphire windows is high due in part to the processing temperatures involved, and because the most expensive step by far in producing sapphire domes is the large amount of grinding needed to turn discs cut from a single crystal boule into domes (1). The transition to lower cost electromagnetic windows has taken the path of developing powders and processing techniques to convert ceramic powders to high quality, transparent polycrystalline windows. The optical properties of the polycrystalline materials used for these applications are very important, since the transmission range and related cut-offs (UV, IR) determine the useful operational electromagnetic wavelengths over which the window can be used. In addition to their optical properties, the ceramic windows must also possess good abrasion resistance and high strength because of the extreme conditions experienced during missile flight.

Ceramic materials that have been used to make transparent windows include magnesium aluminate ($MgAl_2O_4$, spinel), magnesium fluoride, aluminum oxynitride, aluminum niobate and alumina (i.e. sapphire) itself. Spinel and aluminum oxynitride (AION, $Al_{23}O_{27}N_5$) are the front-runners for production of transparent polycrystalline ceramic windows. Aluminum oxynitride is produced by Raytheon Corporation. The incorporation of nitrogen into the aluminum oxide lattice stabilizes the spinel crystal phase producing an isotropic cubic crystal structure. High temperature processing using a transient liquid phase sintering approach produces samples with a transmission of 85% and haze of 14% (2). Magnesium aluminate spinel ($MgAl_2O_4$) also possesses a cubic crystal structure and is transparent in its polycrystalline form. Spinel offers some advantages over AION including lower processing temperatures and superior optical properties within the IR region (3)

Early commercial production of transparent spinel domes for missile dome applications for the Stinger-Post missile were carried out in the early 1990's by Alpha Optical and its parent company Coors Ceramics. Unfortunately, Coors Ceramics stopped commercial production of hot-pressed spinel in 1993 because poor yields and low throughput made the process unprofitable. Poor yields of spinel parts were in part due to the inconsistent quality of the starting materials.

Copyright 2005 Society of Photo-Optical Instrumentation Engineers

This paper was published in the proceedings of the Defense and Security Symposium 2005 and is made available as an electronic reprint with permission of SPIE. One print or electronic copy may be made for personal use only. Systematic or multiple reproduction, distribution to multiple locations via electronic or other means, duplication of any material in this paper for a fee or for commercial purposes, or modification of the paper are prohibited.

Transparent spinel parts can be made using both hot pressing and hot isostatic pressing (either alone or in combination). The hot pressing of spinel parts is carried out using combined high temperatures (up to ~1500°C) and high pressures (between 2500 to 3500 psi (uniaxial pressure)) to produce a compacted powder in shaped graphite dies. In hot isostatic pressing (HIP) of ceramic parts, application of up to 20,000 psi (gas pressure) in an autoclave at temperatures of up to 2000 °C are used to produce complex shapes. With the proper starting materials, these processes can have high yields, produce near net shapes (greatly reducing grinding time), and make possible the production of spinel windows at prices significantly below that of sapphire.

The quality of spinel windows is very sensitive to the quality of the raw material (both purity and morphology). Previously (for example at Coors Ceramics), the commercial production of spinel domes started with alumina and magnesia oxides produced from sulfate or a chloride based processes. Unfortunately, residual anions impurities (>500ppm) remain after the precursors are calcined. These anions can later become trapped in the grain boundaries of the hot pressed spinel, which leads to light scattering and gives the domes a foggy appearance. The poor optical quality is particularly prevalent when multiple parts are simultaneously hot-pressed (as one does to reduce manufacturing costs). Powder production methods that allow high purity with tight control of composition, purity, particle size, particle size distribution and surface area are needed to produce better spinel starting materials. Prior research has shown that high quality spinels with excellent optical properties could (sometimes) be prepared from powders that were made using a mixed sol-gel route (4).

We have developed and patented a materials synthesis approach that can be used to produce a high quality spinel powders. The approach combines the sol-gel synthesis of boehmite with a patented low temperature metal exchange process to produce a magnesium aluminate precursor using a single pot aqueous synthesis (the magnesium reagents are not mixed into with the aluminum sol-gel thereby simplifying the sol-gel process and thus improving process control and batch to batch consistency). The magnesium aluminate (spinel) precursor powder can then be transformed to spinel at temperatures are low as 900°C. Lower surface area powders used for the actual production of transparent parts are produced by heating the spinel to 1200°C.

2. METHODOLOGY

2.1 Synthesis of the Mg-Doped Boehmite Precursor Powders

The MgAl₂O₄ powders used to prepare the transparent spinel parts were produced in a three step, single pot process. The first step was the hydrolysis of aluminum sec-butoxide (Al(CH₃CH(O)CH₂CH₃)₃ (ASB, Chattem Chemicals) to produce a boehmite sol. The hydrolysis was carried out using a ratio of water to ASB of 100:1 by adding the ASB to 80°C water. At 80°C, the stable hydrolysis product is boehmite (i.e. Al(O)OH) instead of Al(OH)₃. Shortly after hydrolysis was started (~15 minutes) the mixture was peptized using propionic acid. The temperature was then increased to 95°C and the condenser removed to allow the butanol released during hydrolysis of the ASB to be evaporated. The condenser was then replaced and the temperature reduced to 80°C, and additional propionic acid was added and the mixture stirred overnight.

Mg(acetylacetonate)₂ was added to the reaction mixture and the reaction mixture stirred for an additional two hours at 80°C, during which time the magnesium from the Mg(acetylacetonate)₂ exchanges with aluminum at the boehmite surface (5). The resulting mixture was then cooled to room temperature and spray-dried. The spray-dried powder is in the form of one-micron agglomerates of the 40 nm to 70 nm primary crystallites. This synthesis produces a fine white powder with a high surface area (~250 m²/g) that is indistinguishable from boehmite by XRD patterns (Figure 1)

2.2 Conversion Of The Mg-Doped Boehmite Precursor Powders To MgAl₂O₄

The Mg-doped boehmite precursor powders prepared as described above were then heated to produce the MgAl₂O₄ powders that were subsequently densified to produce the spinel parts. Heating the boehmite powders to temperatures exceeding ~300°C causes the loss of propionic acid from the boehmite surface and further heating to above 500°C transforms the Mg doped boehmite into Mg-doped γ-alumina by loss of water (e.g. Mg/2Al(O)OH → Mg/Al₂O₃ +

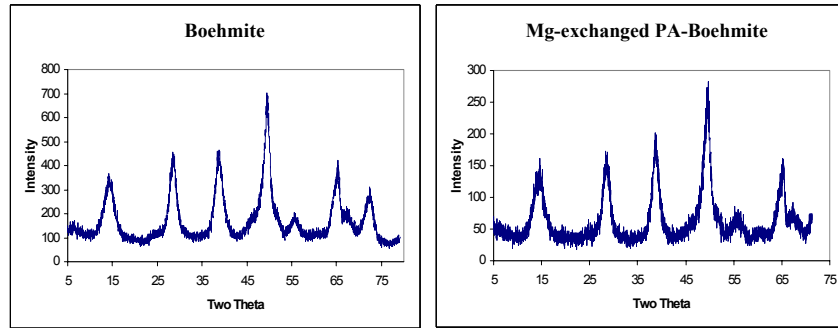


Figure 2. XRD patterns for boehmite (left) and Mg exchanged PA-boehmite (right)

H₂O). No further significant transformation is observed by XRD pattern analysis for the Mg-doped γ -alumina powders until $\sim 900^\circ\text{C}$ at which point the spinel forms. Further heating to 1000°C and 1200°C improves crystallinity (Figure 2) and reduces the surface area to $77\text{ m}^2/\text{g}$ and $24\text{ m}^2/\text{g}$ respectively.

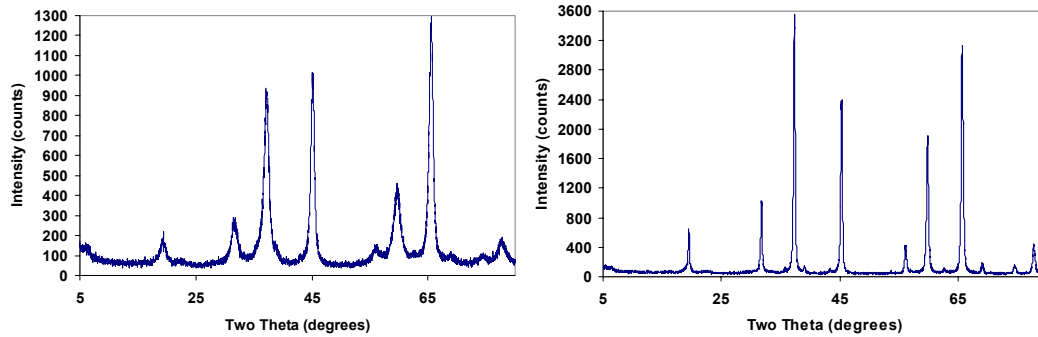


Figure 1 XRD patterns for MgAl_2O_4 calcined at 1000°C (left) and 1200°C (right).

2.3 Hot Pressing of the Spinel Powders

The spinel powders were transformed into the polycrystalline spinel parts by hot pressing. The samples were hot pressed using Graphoil® spacers and a 1.25-inch diameter graphite die. The spinel powders were loaded into the die and then cold pressed at 500 psi. The die was then inserted into the hot press and the unit closed and a dynamic vacuum was applied to the hot press chamber. The chamber pressure was allowed to drop to a level of 50 microns and then the sample heated with mechanical pressure (500 psi) applied to the sample. The heating schedule was briefly paused at $\sim 200^\circ\text{C}$ to let adsorbed water desorb. The temperature was then ramped to 1200°C . At 1200°C , we applied a pressure ramp while continuing to heat the sample. The heat and pressure are increased until the maximum temperature (1550°C) and pressure (5000 psi) were reached. Then samples were then soaked at maximum temperature and pressure for 2 hours. The chamber was then allowed to cool naturally while releasing pressure at a rate of 100 psi per minute. For all of the discs prepared (transparent or not), the density of the hot pressed discs was $3.58\text{g}/\text{cc}$ (full theoretical density).

3. RESULTS

Nanosized boehmite is readily produced using the Yoldas method (6). The Yoldas method produces boehmite via the hydrolysis of aluminum *sec*-butoxide in an excess of distilled water ($\text{H}_2\text{O}/\text{Al} = 100$) under vigorous stirring at 85°C . The Yoldas method produces nanocrystalline boehmite powders with crystallites that are rectangular platelets typically averaging 8 by 9 nm and 2–3 nm in thickness. There are a number of parameters that can be tuned to adjust the particle size and surface area of the boehmite sol-gel, including the amount of the peptizing acid, the temperature at which the hydrolysis takes place and the length of time before the peptizing acid is added to the hydrolyzing aluminum *sec*-

butoxide. To allow us to optimize the properties of the spinel powders for use in producing strong transparent spinel windows, we evaluated the effect of synthesis properties on the surface areas of the spinel powders. Although the initial synthesis parameters were selectively modified, each powder was heated under the same conditions and to the same final temperature (1200°C). We found that we could model the spinel surface area using a combination of the initial hydrolysis temperature, the time elapsed from the start of the hydrolysis to the addition of the peptizing acid (propionic acid) and a ripening time (e.g. the time elapsed before spray drying the surface modified boehmite particles). We found that these three variables allowed us to produce spinel powders with surface areas between 1 and 42 m²/g. Furthermore, the model possesses good predictive capabilities (Figure 3) allowing us to dial in the surface areas (and particle sizes since the boehmite nanoparticles do not have internal porosity). Thus, TDA's powder synthesis process provides control over the particle size/surface area of the spinel powders that is independent from the introduction of magnesium atoms into the crystal lattice. By carrying out the same synthesis protocol but reducing the calcination temperature to 1000°C we could produce spinel powders with surface areas in the range of 50 m²/g to 150 m²/g

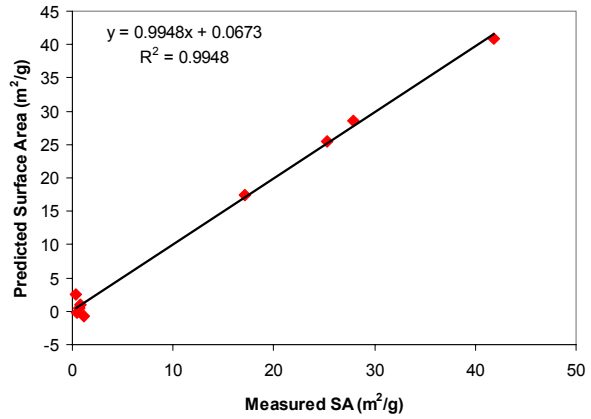


Figure 3 Plot of measured and predicted surface areas for spinel powders.

Initial hot press runs were carried out using spinel powders calcined at 1000°C and at 1200°C. The spinel powders calcined at 1000°C has surface areas of the 77 m²/g powders and spinel powders calcined at 1200°C had surface areas of 24 m²/g. The MgAl₂O₄ powders were milled with 1.0-wt% LiF as a sintering aid. Graphite dies were used to hot press the powders and Grafoil® spacers were placed on each side of the powder. The powder was cold pressed at 500 psi. The die containing the powder was then placed into the hot press furnace. The powders were hot pressed using a procedure that included a soak period at 950°C for 15 minutes to allow gases to desorb from the high surface area powders and then starting at 1200°C, the pressure was ramped to 5000psi and the temperature ramped to 1550°C such that the maximum temperature and pressure were reached at the same time. The temperature and pressure were then held at these values for two hours. After the disc was removed from the die and polished, the disc showed very limited translucency around the edges and was opaque in the center of the disc (Disc 1, Figure 4).

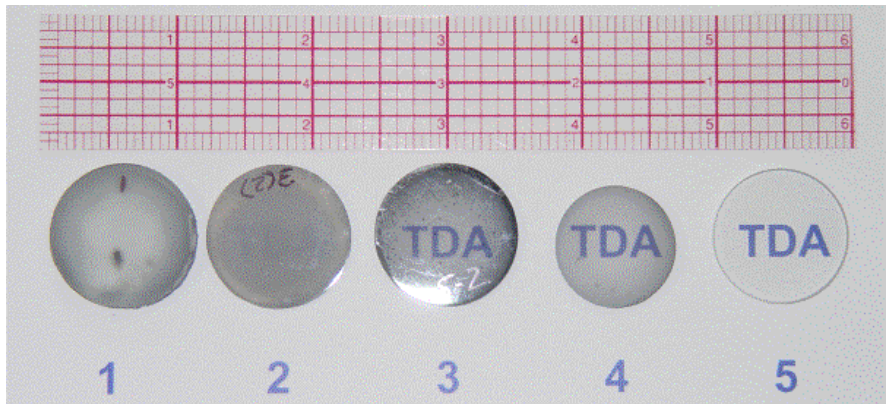


Figure 4. Progression of the transparency of the hot-pressed MgAl₂O₄ discs the process improved

We suspected that the high surface area of the spinel powders might be responsible for the opaque area in the center of the spinel disc. With high surface area powders there are more grain boundary edges to grow together to form the transparent part and therefore more chances for scattering and impurity segregation. Therefore, next evaluated the 1200°C calcined powder (24 m²/g). The firing schedule was the same as Disc 1 (Figure 4). The new disc showed better translucency throughout the pellet and showed transparency around the edges of the disc. After the hot press runs described above, we believed that the translucency in the center of the discs was caused by scattering by voids that were caused by gases trapped in the discs when the pores closed during heating. Therefore, we next instituted a longer (two-

hour) hold at 1000°C to allow time for the gases adsorbed on the grain boundaries to be desorbed. The spinel discs produced by this firing schedule were transparent throughout (Disc 3, 4; Figure 4).

Unfortunately, the discs were a dark grey in color and possessed many dark spots throughout the disc. Evaluation of the samples using a SEM/EDX system (Colorado School of Mines) identified the black spots as zinc-based impurities decorating the grain boundaries of the $MgAl_2O_4$ crystals. X-ray fluorescence analyses for alumina made from the aluminum sec-butoxide showed that no impurities greater than 10 ppm were found for the alumina produced from the aluminum sec-butoxide. However, both the $Mg(\text{acetylacetonate})_2$ and the calcined $MgAl_2O_4$ powder, were found to have zinc present (e.g. ~200 ppm in the final product). To test the hypothesis that the zinc impurities were causing the defects in the spinel parts we prepared a very high purity $Mg(\text{acetylacetonate})_2$ reagent

To produce the high purity $Mg(\text{acetylacetonate})_2$ we started from 99.999% magnesium acetate. This material was dissolved in water. Acetylacetonone 99%+ (Aldrich) was repeatedly distilled from glassware that had been washed with concentrated nitric acid and 18 Mohm water to remove metal impurities. The acetylacetonone was then added to the aqueous magnesium acetate solution and refluxed overnight and the water removed under vacuum. The resulting powder was washed with ice-cold water and dried at 50°C under vacuum. The resulting white powder was then used to prepare a new batch of $MgAl_2O_4$ powder. X-ray fluorescence of the new $Mg(\text{acetylacetonate})_2$ samples showed no impurities above 20 ppm. The new high purity spinel powders (24 m^2/g) were then used to produce new discs using the same firing schedule procedure used for Discs 3 and 4. The resulting disc showed excellent transparency and no black spots (Figure 4, Disc 5).

As produced, the spinel discs have rough surfaces and are contaminated with graphite from the die and the Grafoil spacers. Prior to optical characterization the discs were polished. The spinel discs were polished with a 3-micron diamond paste using a Buehler Ecomet polisher and finished with a 0.05-micron alumina paste. Optical measurements of the discs were then obtained using three spectrometers. The data from 0.190-0.820 microns was obtained using a UV-Vis spectrometer (HP 8452A UV-VIS spectrophotometer). The 0.820nm-2.50 micron spectra were taken using a near IR spectrometer (Perkin Elmer Lambda 19 UV/VIS/NIR). And the 2.50-7.00 micron data was taken with a Nicolet FTIR spectrometer. The scans were normalized and added together (the noise spikes are artifacts of adding the spectra from three different instruments together). Figure 5 shows the compiled spectra for three samples (TDA-548-35, TDA-548-21B and TDA-548-21A.).

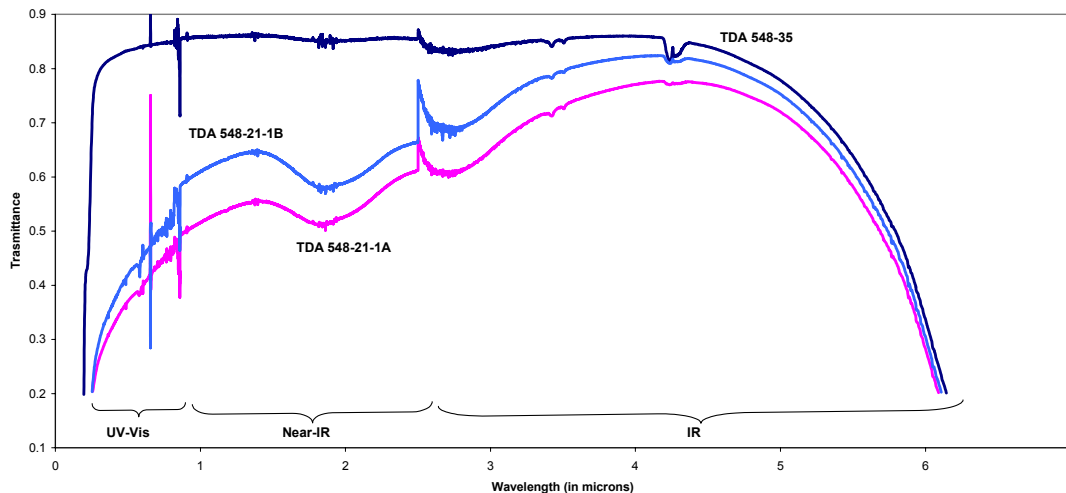


Figure 5. Optical Spectra of the $MgAl_2O_4$ samples.

The difference between TDA-548-21A and TDA-548-21B is that TDA-548-21B was calcined for six hours at 1000°C in flowing air to remove residual carbon. TDA-548-35 was the sample described above that used the highly purified $Mg(\text{acetylacetonate})_2$ in the powder synthesis and was also calcined for six hours at 1000°C in flowing air to remove residual carbon. Excepting the noise in the optical spectra that occurred at the beginning and ends of the spectral ranges

of the individual instruments, Figure 5 shows that the boehmite sol-gel plus metal exchange process can produce a high quality spinel part with good transparency across the visible and infrared spectral regions.

The high quality spinel disc (Figure 4, Disc 5) was also optically compared to discs produced using other process. Dr. Daniel Harris at the Naval Air Warfare Center, China Lake performed these comparisons against “legacy” spinel samples produced by Coors Ceramics, the Army Research Lab and Reaction Controlled Sintering, Inc.. The spinel produced using the boehmite sol-gel plus metal exchange process compared favorably with the legacy samples (Figure 6). The high transmission and sharp rolloff in the ultraviolet suggests that the optical scatter in our sample is exceptionally low.

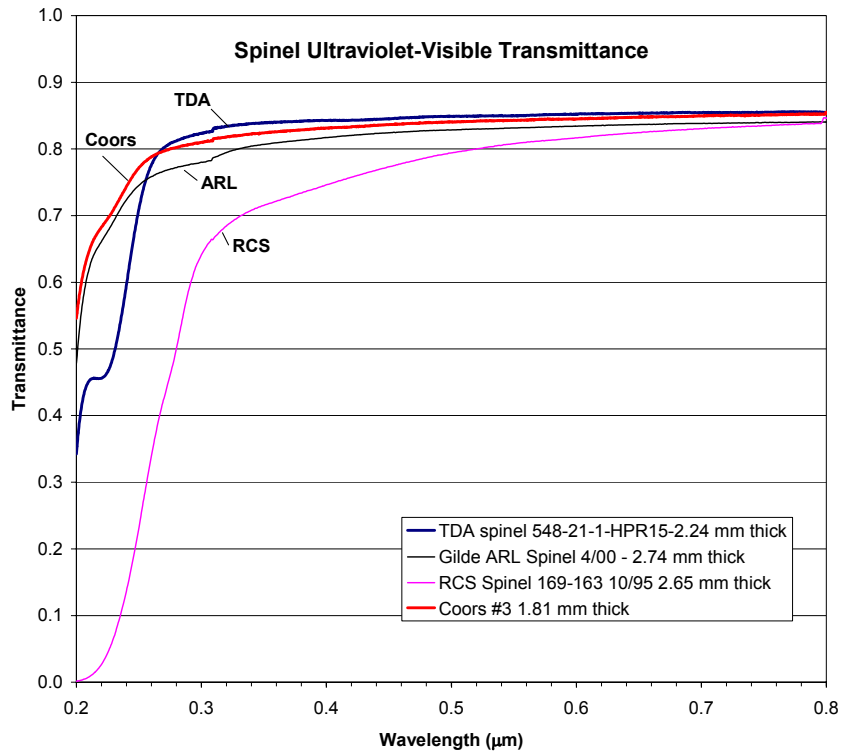


Figure 6 Comparison of TDA produced spinel sample with legacy samples.

4. Conclusions

The objective of this work was to demonstrate the utility of a new powder production method for the preparation of spinel powders for transparent spinel parts. The process uses a patented metal-exchange process that begins by first hydrolyzing aluminum sec-butoxide in water at 80°C to form boehmite and then modifying the boehmite by bonding propionic acid to its surface. The carboxylate-modified boehmite is then treated with $Mg(\text{acetylacetonate})_2$ that induces a metal-exchange reaction that uniformly inserts Mg^{2+} cations into the surface of the boehmite nanoparticles at the atomic level. The Mg-doped boehmite nanoparticles are then spray-dried to form a stable white powder. Heating the Mg-doped boehmite powders in air converts them first to Mg-doped g-alumina, then to pure phase $MgAl_2O_4$ powders around 900°C to 1000°C.

Initial hot pressing runs with $MgAl_2O_4$ powders having surface areas of 77 m²/g were unsuccessful. The powders were then heated to 1200°C to reduce the surface area to 24 m²/g. By varying the hot press time/temperature work cycle variables we were able to prepare transparent spinel discs. However, the transparent discs contained black spots (impurities). By modifying the calcination schedule and by preparing high-purity $Mg(\text{acetylacetonate})_2$ precursors to

use in the metal exchange process, we were able to produce a completely transparent spinel disc with excellent transparency across the infrared and visible bands.

Acknowledgements

This work was funded under an Army Phase I SBIR project (Contract Number DAAH01-03-C-R142) and an Army Phase II project (W31P4Q-05-C-R137). We would like to acknowledge Dr. Daniel Harris for providing us with the comparison of our samples with his legacy samples. We would also like to acknowledge useful conversions with our program manager Dr. James Kirsch and also with Dr. Mark Patterson. IER also acknowledges the U.S. Army Research Office for support under grant DAAD19-01-1-0590.

REFERENCES

1. Daniel C. Harris, *Overview Of Progress In Strengthening Sapphire At Elevated Temperatures*, Proc. SPIE Vol. 3705, 2-11, 1999.
2. Parimal J. Patel, Gary A. Gilde, Peter G. Dehmer, and James W. McCauley, *Transparent Armor*, The AMTIAC Newsletter, Fall 2000.
3. D.C. Harris, *Infrared window and dome materials*, SPIE, Washington, pg. 32, 1992
4. D.W. Roy, *History of Spinel Development*, presented to DARPA/ARL, Transparent Armor Workshop, Annapolis, MD. Nov 16, 1998.
5. A.C. Kareiva, J. Harlan, D. B. MacQueen, R. Cook, and A. R. Barron *Carboxylate Substituted Alumoxanes As Processable Precursors To Transition Metal-Aluminum And Lanthanide-Aluminum Mixed Metal Oxides: Atomic Scale Mixing Via A New Transmetalation Reaction*, Chem. Mater., 8, 2331, 1996.
6. B.E. Yoldas. *Transparent Activated Nonparticulate Alumina and Method for Preparing Same*, US Patent, 3,941,719 (1976).

*cookrl@tda.com; phone 303-940-2302, fax 303-261-1130, www.tda.com