SANDIA REPORT

SAND2005-0763
Unlimited Release
Printed March 2005

Restart of the Chemical Preparation Process for the Fabrication of ZnO Varistors for Ferroelectric Neutron Generator Power Supplies

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Restart of the Chemical Preparation Process for the Fabrication of ZnO Varistors for Ferroelectric Neutron Generator Power Supplies

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Abstract

To date, all varistors used in ferroelectric neutron generators have been supplied from a single, proprietary source, General Electric Corporate Research and Development (GE CR&D). To protect against the vulnerability of a single source, Sandia initiated a program in the early 1980's to develop a second source for this material. A chemical preparation process for making homogenous, high purity ZnO-based varistor powder was generated, scaled to production quantities, and transferred to external suppliers. In 1992, the chem-prep varistor program was suspended when it appeared there was sufficient inventory of GE CR&D material to supply ferroelectric neutron generator production for many years. In 1999, neutron generator production schedules increased substantially, resulting in a predicted exhaustion of the existing supply of varistor material within five years.

The chem-prep program was restarted in January, 2000. The goals of the program were to 1) duplicate the chem-prep powder synthesis process that had been qualified for WR production, 2) demonstrate sintered billets from the chem-prep powder met requirements, 3) develop a process for rod fabrication and demonstrate that all component specifications could be met, and 4) optimize the process from powder synthesis through component fabrication for full-scale production. The first three of these goals have been met and are discussed in this report.

A facility for the fabrication of production quantities of chem-prep powder has been established. All batches since the restart have met compositional requirements, but differences in sintering behavior between the original process and the restarted process were noted. Investigation into the equipment, precipitant stoichiometry, and powder processing procedures were not able to resolve the discrepancies. It was determined that the restarted process, which incorporated Na doping for electrical stability (a process that was not introduced until the end of the initial program and had not been investigated for processing effects), was responsible for the differences. Rod components fabricated since the restart have met requirements and have performed at a level comparable to chem-prep rods from the original program and GE CR&D rods currently in production.

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

Acknowledgments

The author would like to acknowledge the tremendous contribution of Stephen Zenker, who was responsible for the set up of the facility for restarting the chem-prep varistor program, for preparing the batches, and for challenging the established assumptions from the past. Other key contributors to this work include the Active Ceramics production team (rod grinding, fabrication, and testing), Diana Moore who performed the particle size analyses, and Jeanne Barrera who performed the compositional analyses.

Contents

Figures

Tables

Introduction

High field varistors are used as voltage regulators (rods) in the power supplies for ferroelectric neutron generators. Varistors function as electrical insulators (resistors) at low electric fields, but become electrically conducting at or above a value known as the switching field. At fields above the switching value, varistors exhibit nonlinear current-voltage behavior, described by the following equation:

$$J = KE^{\alpha}$$

where J is the current density, K is a constant, E is the electric field, and α is the non-linearity coefficient. The non-linearity coefficient is the reciprocal of the slope of the J-E curve in the nonlinear region and is therefore a measure of the sharpness of the transition from resistor to conductor.

To date, all varistors have been supplied from a single, proprietary source, GE CR&D. Although those varistors (hereafter referred to as Mixed Oxide) satisfactorily met production requirements, there was concern regarding the vulnerability of depending on a single source that had only a limited number of personnel fully knowledgeable in the processing technology. As a result, Sandia initiated a program in the early 1980's to develop a second source of this material. A chemical preparation process for making homogenous, high purity ZnO-based varistor powder was generated, scaled to production quantities, transferred to external suppliers Alliant Techsystems, Inc. (ATI) and Martin Marietta Specialty Components (MMSC), and qualified for WR production at ATI in 1990.[1] However, neutron generator production schedules decreased significantly just after ATI was WR qualified and during MMSC's WR qualification. In 1992, the chem-prep varistor program was suspended at Sandia, at the chem-prep varistor suppliers, and at GE CR&D when it was determined that the existing supply of Mixed Oxide varistors would meet production needs for many years.

In 1999, the planned production schedules were increased dramatically with the result that the existing supply of Mixed Oxide varistor material was predicted to be exhausted within five years. It was decided to incorporate chem-prep rods into the W80 program which was just beginning development at that time. The chem-prep program was restarted in January, 2000. The goals of the program were to (1) duplicate the chem-prep powder synthesis process that had been qualified for WR production, (2) demonstrate sintered billets from the chem-prep powder met requirements, (3) develop a process for rod fabrication and demonstrate that all component specifications could be met, and (4) optimize the process from powder synthesis through component fabrication for full-scale production.

A decade of research and development had gone into developing a process that was qualified for WR production and as such, process documentation was still retrievable, much of the same processing equipment was available, and key personnel from the earlier program were still present. However, it was not a foregone conclusion that qualified rods would be immediately generated. The three stage powder synthesis process (zincite synthesis, Bi doping, Na doping), which includes a four component co-precipitation step in the first stage is quite complex. Subtleties of the process were exposed throughout its original development. The initial scale-up of the powder synthesis process from a laboratory-scale[2] of 190 g to the production quantity of one kg revealed several critical factors in generating acceptable material.[3] These included the pH-time relationship during the initial precipitation[3], the requirement for low level doping of Al[4], and the relationship among washing, filtration, and the effect of Cl^- contamination.[5] Optimization of billet fabrication for production had not been completed at the time of program suspension. The ATI-qualified process utilized thin, 60 g wafers for rod fabrication, a very inefficient

geometry for even low volume production. Earlier research had characterized the sintering characteristics as a function of billet geometry and electrical properties.[6,7] Although these studies did identify sintering conditions that could generate billets with more efficient geometries while meeting electrical requirements, the powder used in those studies were not doped with Na, an additive for electrical stability that was not incorporated into the process until near the end of the program.[8] As a result, there was not an opportunity to repeat much of the previous research with the new composition before the program was suspended. As will be seen in the discussion below, the effect of Na on sintering is very significant, and has driven the direction of work for much of the restarted program.

This report covers the period of time from the restart of the chem-prep varistor program in 2000 through validation of the process and demonstration of rod manufacturing capability.

Procedure

Except as noted in the Results and Discussion section, powders were synthesized per the process description used for WR qualification.[9] The same sized equipment was used with the restarted process, including reaction vessels, stirrers, filter funnels, and calcining dishes/crucibles. The same sintering furnace was used and the calcining furnace, although new, had the same specifications as the original furnace. A high level flow chart of the powder synthesis process, the nominal composition, and the electrical specifications for the sintered billets is presented in Figure 1.

Synthesis of the powder is a three stage process, with the first stage generating Co-Mn-Al doped zincite powder. Aqueous chloride salts of Zn, Co, Mn, and Al are combined and diluted to a specified volume. A hydrous oxide co-precipitate is formed by the rapid addition of a concentrated aqueous NaOH solution. After two minutes, a saturated, aqueous solution of oxalic acid (heated to ~50°C) is added to convert the co-precipitate to its corresponding metal oxalates. The slurry is continuously stirred until the pH reaches 8.0, at which time it is pumped into filter funnels, washed with deionized water, and then acetone. The dried cake is calcined at 600°C to convert the oxalates to oxides. For stage two, a bismuth nitrate solution is added to an aqueous slurry of the zincite powder, mixed for a short period of time, filtered, washed, and then calcined to convert the bismuth nitrate to bismuth oxide. The final stage involves the addition of a sodium oxalate solution to an aqueous slurry of the Bi-doped zincite powder. The resulting slurry is freeze dried to prevent segregation of the Na, and then calcined to generate the final powder.

Billet fabrication, except as noted in the Results and Discussion section, followed the WR process description.[10] The same presses and furnace as used in the 1980s and 1990s were used for the current program. Billet fabrication followed this general procedure (1) load the requisite amount of powder in the appropriate size dual-action steel die, (2) press to one half the final uniaxial pressure, flip die, press to final uniaxial pressure, (3) isostatically press billet to 15 kpsi, (4) place billet in alumina boat on a bed of MgO sand, bury billet in MgO sand, and sinter in furnace with supplemental flowing O_2.

Sintered billets were ground to remove Bi that diffused to the surfaces and to generate flat surfaces for electrode application. Silver electrodes were sprayed on to both faces of the billet to generate one or more, depending on the diameter of the billet, 0.2cm^2 electrodes. Testing was generally performed on the PT3688 slug and rod tester. In a few cases, when the PT3688 was unavailable, the SE3257 slug and rod tester was used.

Rod fabrication was performed to meet the MC4578 rod specification for the W80 neutron generator.[11-13] Rods were generally fabricated to the MC4148/MC4148A Work Instructions.[14] Minor modifications to the procedures were made due to billet size differences and the different grindability of the chem-prep material as compared to the Mixed Oxide material.

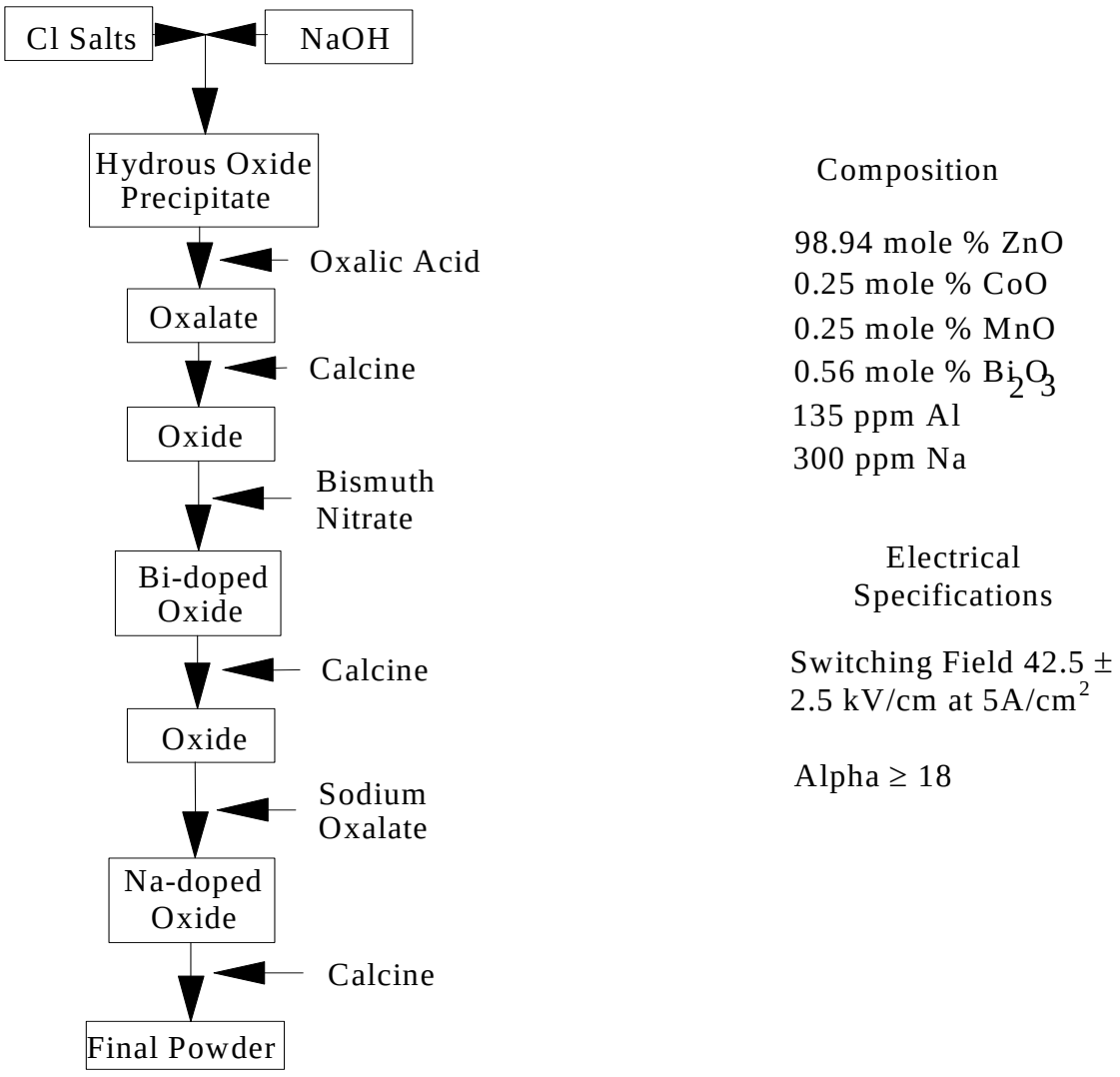

Figure 1. Synthesis Process for Chemically Prepared ZnO-based Varistor Powder

Results and Discussion

Process Reestablishment

The first three batches were prepared to the composition listed in Figure 1. The calculated Na addition assumed no residual Na, but as can be seen in Figure 2, the Na level was 70-130 ppm higher than targeted. For batches CPV-4 through CPV-12 the amount of Na added was reduced to 250 ppm. The ranges shown in Figure 2 are the drawing specified limits for each constituent. With the exception of Na in CPV-1, all constituents were within specification for the first twelve batches.

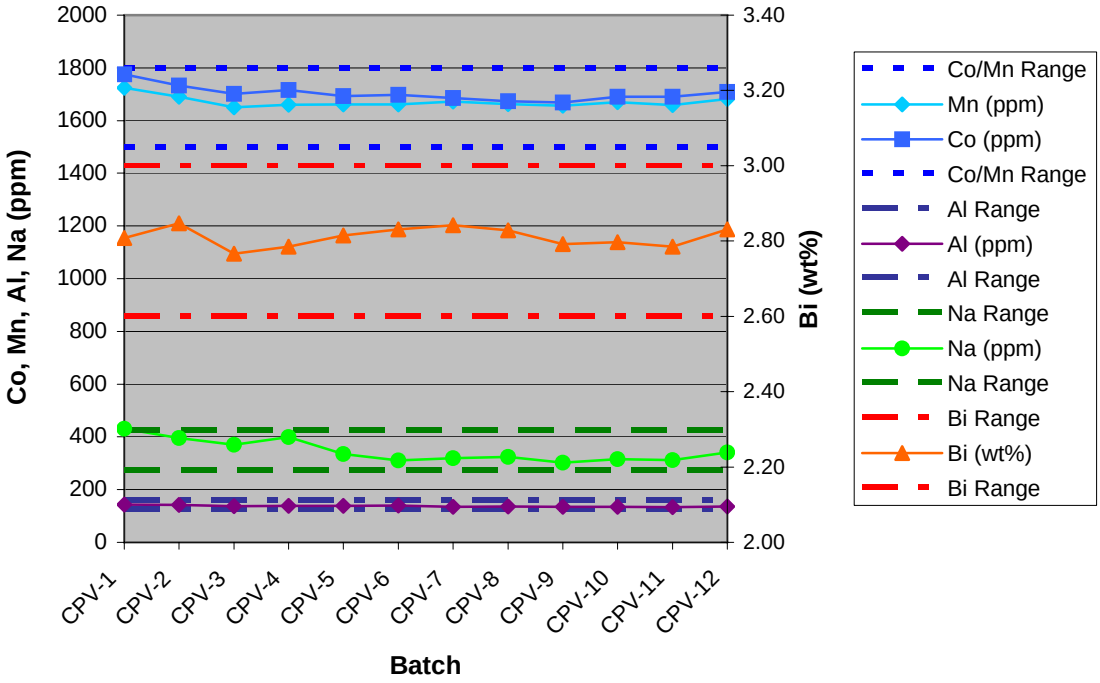

Figure 2. Compositional Analysis of CPV-1 – CPV-12 by ICP-AES

The first test wafers (50 g, 2.125 in. diameter die) prepared from CPV-1 were to verify that the WR specified billet physical characteristics and electrical properties could be generated from the restarted process. The CPV-1 wafers were fired using the "A" schedule to 730°C (the standard sintering schedule and temperature for WR wafers in 1992). Previous design specifications required material with no open porosity. However, this presented difficulties in scaling up the billets to a manufacturable size. Oxygen is required to develop fully functional varistor grain boundaries.[15] As billet volume increases, varistor properties (field and alpha) degrade in the interior of a fully dense sample due to the inability of sufficient oxygen to reach the interior. Current design specifications allow for open porosity in the sintered varistors. Therefore, CPV-2 wafers were fired using the "B" schedule to 730°C. This schedule had been shown to generate sintered billets with lower density (~90% of theoretical) and open porosity (2-10%). Table 1 lists the temperature profiles for schedules A and B.

Table 1. Sintering Schedules A and B

Schedule A
RT → Soak temp. @ 3°C/min, soak for 16 h
Soak temp. → 400°C@ 1.5°C/min
400°C → 100°C @ 3.0°C/min

Schedule B
RT → 500°C @ 3°C/min, soak for 2 h
500°C → 675°C @ 1°C/min, soak for 2 h
675°C → 700°C @ 0.5°C/min, soak for 2h
700°C → Soak temp. @ 0.5°C/min, soak for 16 h
Soak temp. → 400°C@ 1.5°C/min
400°C→100°C @ 3.0°C/min

Initial testing was encouraging, but it also generated some unexpected results. The standard firing conditions generated 50 g wafers that just met the minimum field specification level. The wafers were fully dense with no open porosity. It was expected that a slight decrease in sintering temperature would bring the field values into the center of the specification. Unexpectedly, the B-schedule fired 50 g wafers resulted in only slight decreases in densities (97-98% of theoretical) and no open porosity. Field values for these samples were below specification. Billets from both firing runs showed similar behavior with increasing thickness, both field and alpha decreased. This behavior was expected for the A-schedule material, but previous work with B-schedule material had shown that the field and alpha remained stable with increasing part thickness. These results are presented in Figure 3.

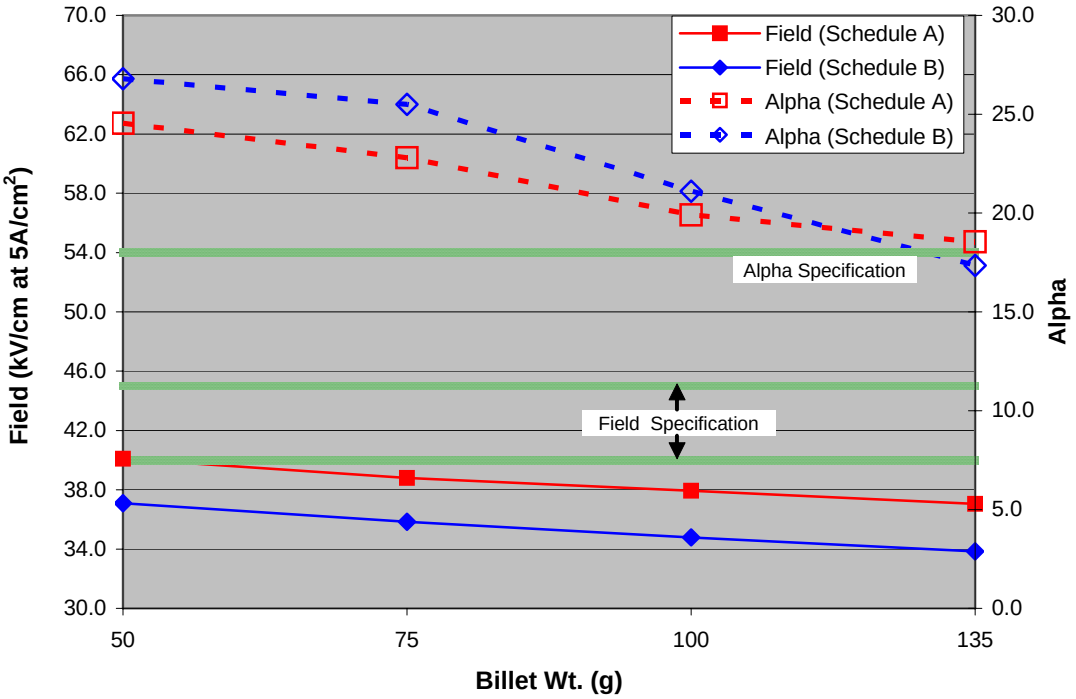

Figure 3. Field and Alpha for Schedule A and Schedule B Fired Billets

Previous work had shown that the field was very sensitive to sintering temperature, with the electric field increasing 0.5 kV/cm (at 5A/cm^2) per °C reduction in sintering temperature for A schedule material. However, when the sintering temperature for either sintering schedule was lowered by 5°C, that level of sensitivity was not observed, and thus, further firings at lower temperatures were conducted (Figure 4). Several unanticipated results were observed from the sintering temperature study. For both schedules the sintering-field relationship was non-linear, especially for material sintered using the B schedule. Both schedules, but particularly the B schedule, showed a surprisingly sharp transition from a mature microstructure with fully developed varistor grain boundaries to a microstructure which exhibited highly unstable varistor properties, presumably due to insufficient grain boundary development. The region of the curves where stable varistor properties were exhibited (> 715-720°C) showed the two schedules with similar slopes, but a field offset of approximately 3 kV/cm.

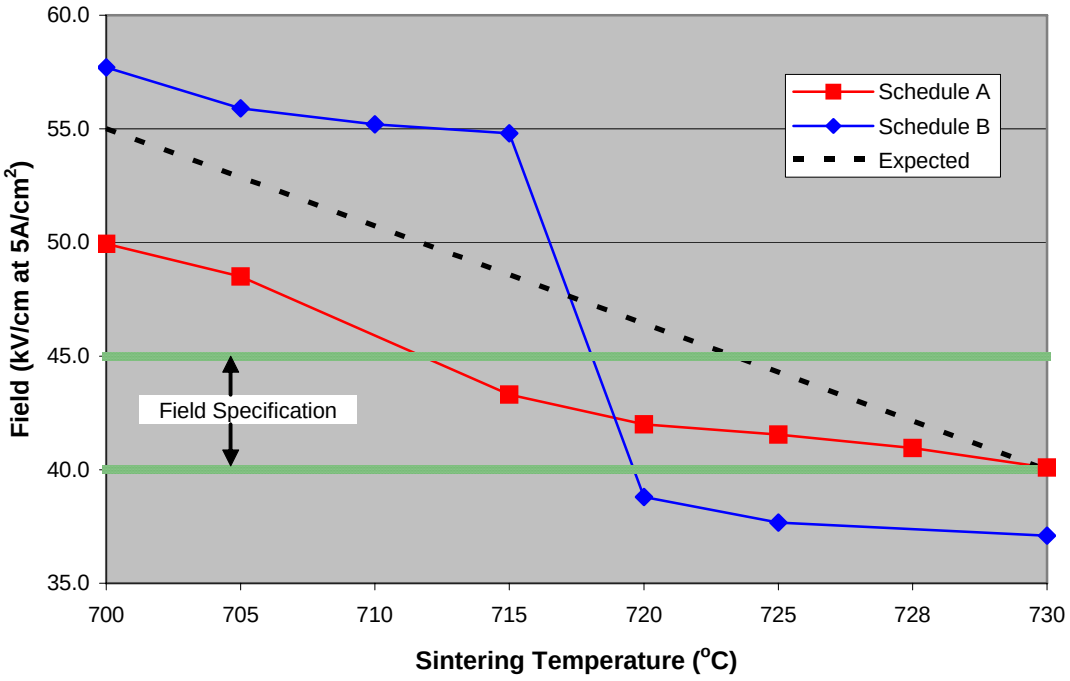

Figure 4. Effects of Sintering Temperature on Electric Field

In parallel with the sintering temperature study, billets with increased thicknesses, pressed in the same diameter die, and fired at 730°C, were also prepared from the first two powder lots to determine the relationship of billet volume to electrical properties. Again, contrary to expectations, the two schedules behaved almost identically (Figure 5). It was expected that only the fully dense Schedule A material would exhibit degrading field and alpha with increasing thickness due to the lack of oxygenation in the interior of the billet. However, regardless of thickness, the Schedule B billets densified to almost full density with no open porosity, so the similar electrical behavior was consistent considering the matched physical characteristics. But again, the intermediate soaks in the Schedule B profile did not provide the open porosity generated in billets fired using the B Schedule during the original program.

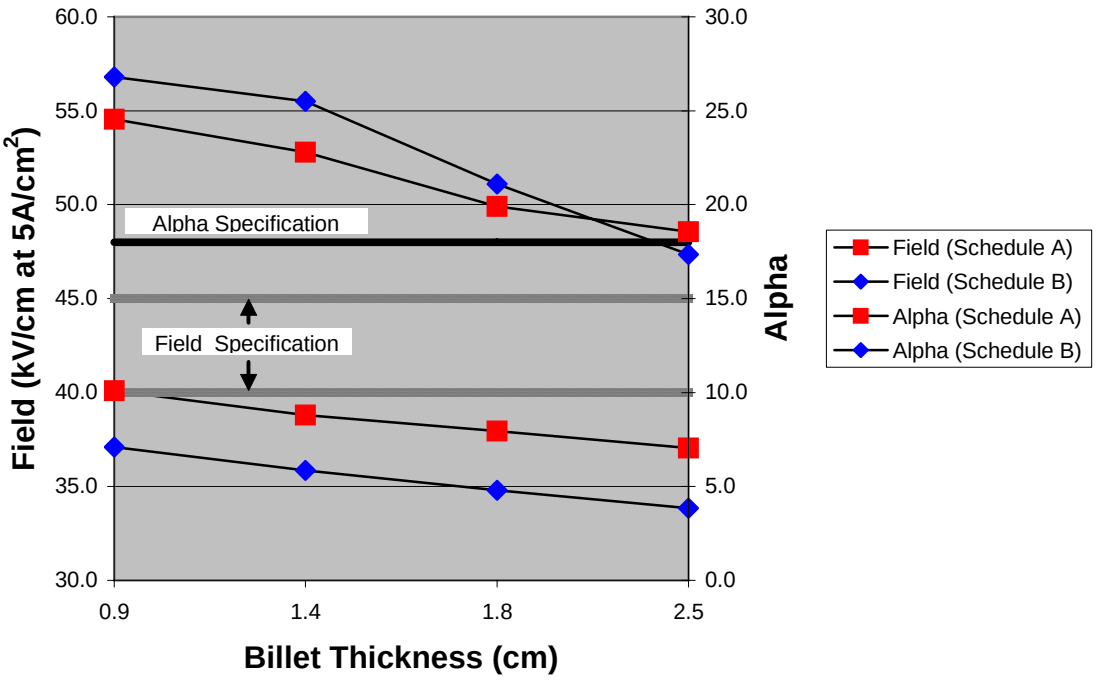

Figure 5. Electric Field and Alpha as a Function of Billet Thickness

At this point in the program two major avenues were pursued. Although there were a number of differences in behavior of the recent material as compared to the original material, wafers could be generated meeting property specifications that were of sufficient size to fabricate rods. In parallel to rod fabrication efforts, studies were continued to understand the differences in the recent material and to move toward establishing processing conditions that would generate billets of efficient manufacturing size.

Old vs New Material

Following the results of sintering schedule and billet geometry experiments, a detailed review of the process was conducted to determine what differences, if any, existed between the original (Old) process and the re-started (New) process. With respect to the powders, there was no difference compositionally in additives/dopants or cation contaminants (e.g., Ca, Mg, Si). With respect to anionic contaminants, residual chloride from the starting salts is present in the process and can affect both electrical and physical properties.[5] However, chloride was not routinely analyzed in the past and therefore, it was not known if the chloride level in the new material was different. The new material did appear to have a slightly larger particle size (Table 2). Two caveats must be noted before drawing any conclusions regarding the particle size differences: only two samples were available from the old material, and both were from experimental batches, that although the processing would not have been expected to alter the particle size, cannot be completely ruled out as a factor.

Table 2. Particle Sizes of Old and New Material

Batch ID	Material	Particle Size (μm)
GB-158	Old	1.53
GB-166	Old	1.71
CPV-7	New	1.93
CPV-8	New	1.80
CVP-9	New	1.76
CPV-13	New	1.77
CPV-14	New	1.71

Three differences in processing between the Old and New processes were identified as potentially significant: (1) freeze drying efficiency, (2) O_2 flow rates during sintering, and (3) the precipitant stoichiometry.

Although the major processing equipment was either the same as used for the Old process or if replaced, was specified identically as the Old process, there was one difference of note. The freeze dryer, although matching previous specifications, was able to fully dry the Na-doped powder in less than half the time as the original freeze dryer. Freeze drying potentially could affect agglomerate characteristics, which in turn could affect sintering and densification. This issue was addressed by preparing a batch that was split in half and then freeze dried slowly (labeled “Old” in Figure 6) or rapidly (labeled “New” in Figure 6). Billets fired using the 715A schedule were prepared to evaluate the two processing conditions. Old material fired at 715°C would not sinter sufficiently to generate stable varistors and the resulting fields would be expected to be well above specifications. Therefore, if the freeze drying process was responsible for the differences between Old and New material, large differences in switching field values would be expected. As can be seen in Figure 6, there was no significant difference in field values, as both materials met switching field specifications.

The O_2 supplemental flow rate during sintering was considered due to discrepancies among the drawing specification, processing notes, and flow meter markings on the sintering furnace creating some uncertainty of the exact flow rate to duplicate. To evaluate the effect of O_2 flow, a batch was prepared and billets from the batch were sintered under either low or high O_2 flow conditions using the 715A schedule (Figure 6). By the same reasoning given above, significant differences in switching field values would be expected if the O_2 flow rate was a key factor in the electrical performance of the Old material. As was the case for the freeze drying, both O_2 flow rates generated material meeting specifications at 715°C.

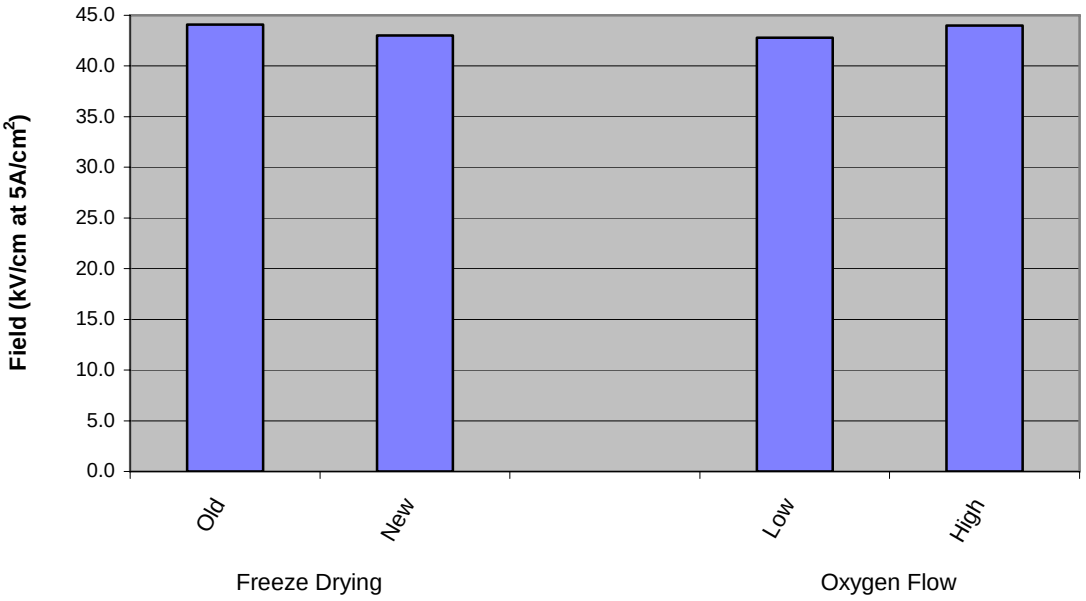

Figure 6. Effects of Freeze Drying and Oxygen Flow on Electric Field

In terms of the synthesis process one major difference was noted: process reliability was significantly lower at ATI and MMSC than at Sandia. Toward the end of the original program, a study was conducted to look at the robustness of the synthesis process through an analytical laboratory round robin and a mixture Design of Experiments investigating the two precipitants (NaOH and oxalic acid) and the major constituent ($ZnCl_2$). [16] The study found that there was a large processing plateau that would generate material meeting all physical and electrical requirements, but that the current process was near a very sharp edge of that processing plateau. As a result, it was recommended that the precursor concentrations be repositioned toward the center of the plateau. When the program was re-started, the precursor concentrations were set at the center of the plateau as recommended. However, extensive testing of material under different firing conditions (i.e., multiple sintering schedules and soak temperatures) had not been conducted prior to termination of the original program, leaving as a question whether material prepared from the modified precursor concentrations would behave similarly under all billet fabrication conditions.

For the precursor concentration issue, three sets of samples were prepared from the following: (1) powder from the original program (labeled Original Material in Figure 7), (2) powder prepared since the restart, but with original precursor concentrations (label Old Composition in Figure 7), and (3) powder prepared since the restart with precursor concentrations adjusted to the center of the plateau (labeled New Composition in Figure 7). From Figure 7 it can be seen that although there are small differences in field values among the three materials, there is no correlation between field value and material age or composition. These results indicate that the current material is comparable to the material synthesized in the original program and that the change in precipitant stoichiometry has no significant effect on wafers fired under a variety of sintering conditions. Another interesting result of this experiment was that the original material exhibited the same decrease in sensitivity to sintering temperature as the current material and that the B-schedule firing resulted in fully dense material, matching the behavior of the current material, not the original material. Furthermore, these results ruled out other compositional explanations, such as the Cl^- contamination levels in the restarted process or subtle changes in the precursors from the vendors after a 10+ year hiatus of purchasing.

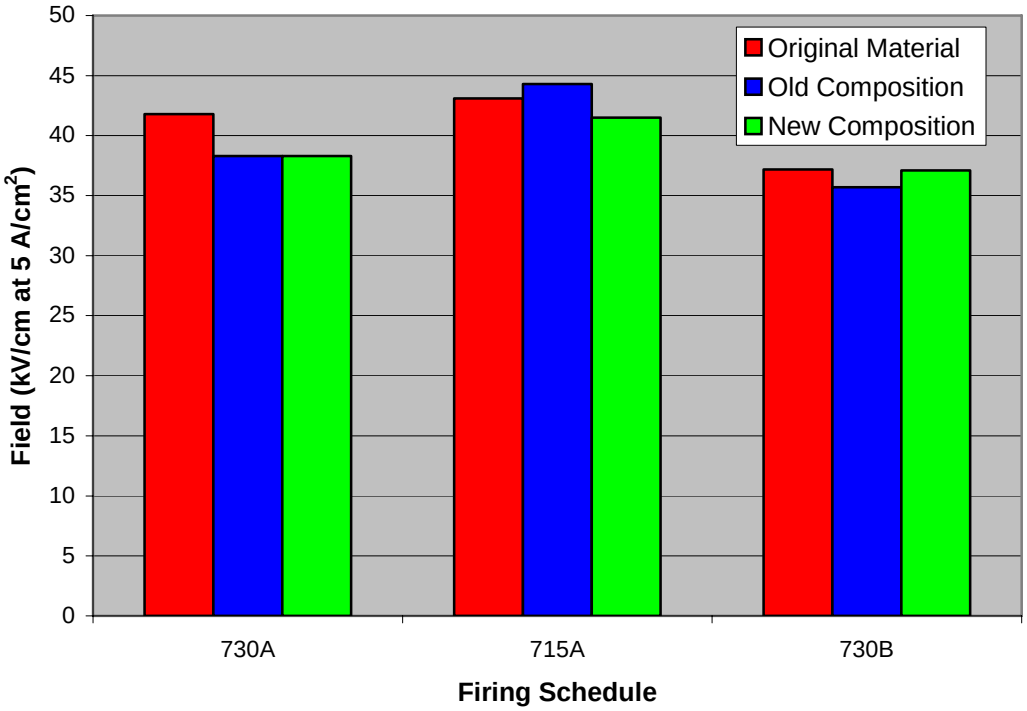

Figure 7. Comparison of Old and New Material and Old and New Composition

With the synthesis of the powder apparently ruled out, the focus moved to the processing of the powder for possible explanations for the differences between Old and New material. The same dies and uniaxial press were used as with the current material. Historical data on green densities for the Old material showed no significant differences as compared with the New material. To further eliminate pressing as a factor, New material was also processed into billets at various pressing pressures with no significant effects on the sintered physical characteristics or the electrical properties.

With the processing, equipment, and stoichiometry ruled out as explanations for the unexpected sintering behavior, a more thorough review of the historical data was made. The doping of Na was incorporated into the process late in the development program. Records show that fully dense material became the baseline requirement in December, 1986, and the last "B" schedule slug was fabricated in March, 1988. Na doping was not introduced until June, 1989. As a result there is no record of any billet fabrication of Na-doped material utilizing a "B" schedule. It was noted at the time that the Na-doped material sintered slightly higher, but since the "A" schedule generated parts close to theoretical density with non Na-doped material, the magnitude of the effect was not apparent. It was now clear that the "failure" of the B-schedule to introduce porosity into the sintered billets was not due to an inability to replicate the previous work, but was an entirely new issue. Porous, fully functional, Na-doped material had never been demonstrated. For final confirmation, a non-Na doped batch of material was prepared and fired on the B schedule at 715°C and 730°C. The open porosity for the 730B schedule wafers was 9%, which is comparable with the values observed with similarly fired wafers during the original program. Sensitivity of field to sintering temperature was also observed, with a slope of 0.25 kV/cm per °C fitted to the data (Figure 8). With the realization that the differences between the original process

and the restarted process were due to comparing non-Na doped material with Na-doped material, it was concluded that the restarted process had been successfully demonstrated.

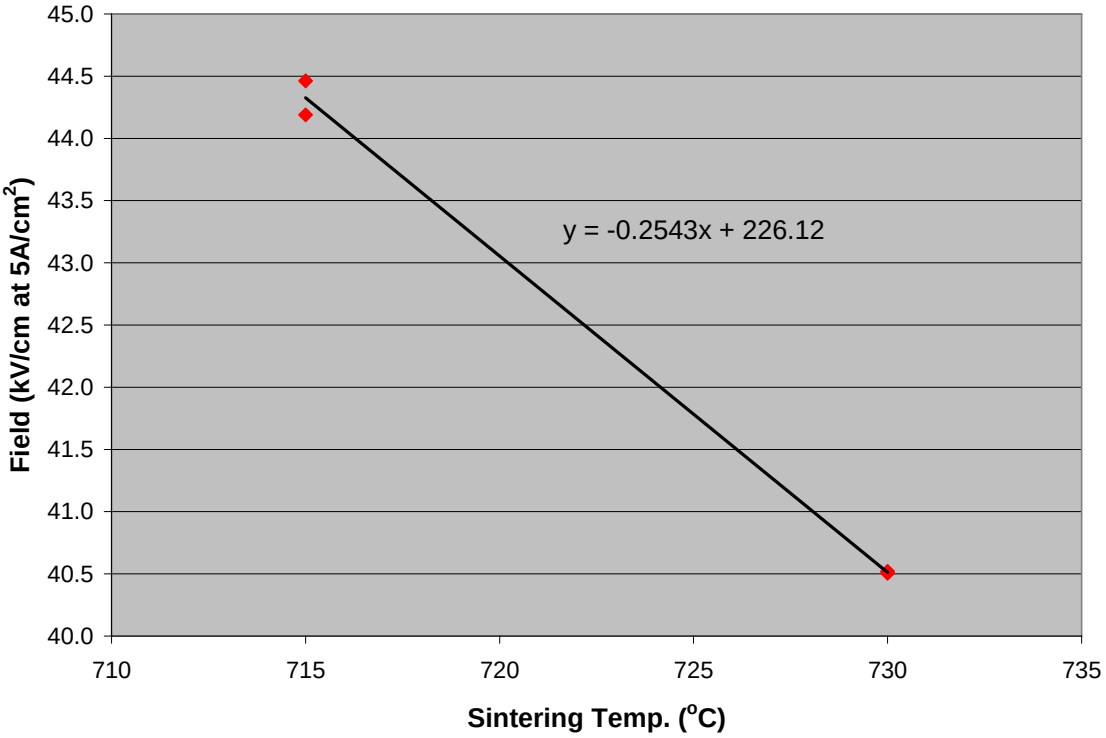

Figure 8. Affect of Sintering Temperature on Field for non-Na Doped Material

Rod Fabrication

Although, as described above, the initial results of wafer testing indicated that the restarted process differed somewhat from the original process, the resolution of those differences did not delay an evaluation of rods made from the New material. It was not clear how long it would take to identify the source(s) of the differences between the Old and New materials, and ultimately, the goal was to make rods meeting neutron generator requirements, regardless of whether or not the restarted process was identical to the original one.

Initial results from material from the restarted process indicated that wafers of the size used to qualify the production process at ATI could be generated. Rods were fabricated from ten 60 g wafers from CPV-3 – CPV-6. For this geometry fewer than five rods, cored radially (i.e., through the diameter of the wafer parallel to the pressed surfaces), could be generated from each wafer. Additionally, a larger die was used to fabricate three wafers from CPV-6 and CPV-7. This larger wafer could yield 10-15 cores. A total of 63 rods from five powder batches were fabricated. Rod fabrication followed standard procedures as used for the Mixed Oxide WR production material as was applicable. It was noted that the chem-prep material being fully dense ground much differently than the very porous (~35% open porosity) Mixed Oxide material. Using the Mixed Oxide grinding parameters resulted in significantly more damage to the chem-prep cores, particularly chipping on the edges during core drilling. Although grinding parameters were modified, CPV-7 still exhibited significant chipping.

The 63 rods were given a standard MC4148A pulse pair qualification test.[17] It should be noted that the chem-prep material was scheduled for use in the MC4578 (W80) and that mixed oxide material was intended for use in the MC4148A (W76). However, the MC4578 specifications had not been defined at the time of the testing. It was expected that the W80 specifications would not be substantially different than the W76 specifications, so testing to the W76 would provide a reasonable evaluation. One rod exhibited a high voltage breakdown, the remaining 62 met specifications. The surviving 62 rods were then subjected to the standard MC4148A 50 pulse endurance test.[17] A summary of the lots and the percentage of rods passing the endurance test are presented in Table 3.

Table 3. Summary of Rod Endurance Testing

Batch ID	# of Wafers	# of Rods Tested	% Passing 50 Pulses
CPV-3	4	11	55
CPV-4	2	5	100
CPV-5	3	8	63
CPV-6	3	16	63
CPV-7	2	22	68
Overall	14	62	66

The overall passing rate of 66% was comparable to what was observed previously with chem-prep rods as well as currently manufactured Mixed Oxide rods. However, the distribution of breakdowns (Figure 9) was of concern. Five of the 21 failures occurred before pulse 5 (light colored bars in Figure 9). Product specifications for both the MC4148A and the MC4578 state that a lot is rejected if any of the endurance tested rods fail before pulse 5. Treating all of the wafers from a given batch of powder as one lot, three of the five lots would have been rejected for a failure before pulse 5. In comparison, only four of 64 mixed oxide WR rod lots of Mixed Oxide rods have had a rod that failed before pulse 5. Very early failures are most likely attributable to significant physical defects (e.g., cracks) that serve to focus the current and cause an almost immediate catastrophic high voltage breakdown. It is hypothesized that due to the high density of the material, subsurface cracks radiated from the chips. Cracks that are aligned with the direction of current flow are known to initiate rapid high voltage breakdowns. Consistent with this hypothesis are recent results from rods for neutron generator final development builds (details of which will be covered in a subsequent SAND Report). Grinding parameters have been improved and chipping damage has been significantly reduced. Over 90% of endurance tested rods with no evidence of chipping have survived 50 pulses, with the few failures generally occurring after pulse 10.

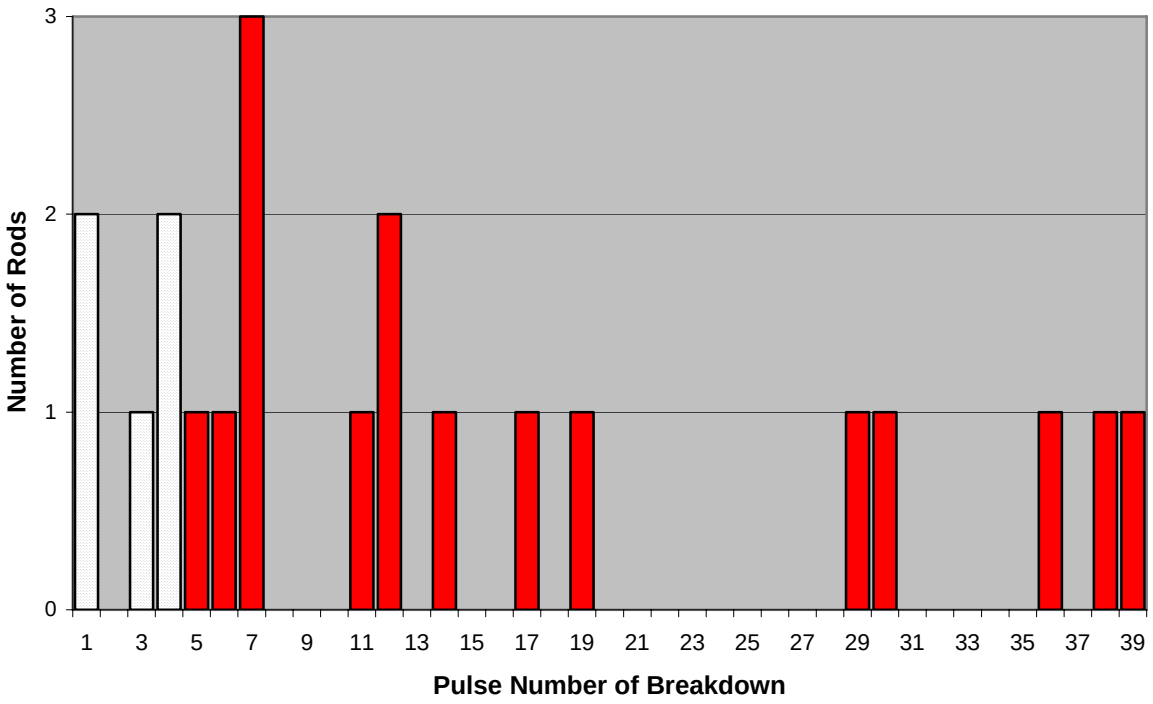

Figure 9. Failure Pulse Number Distribution of Endurance Tested Rods

Summary

A chemical preparation process for the fabrication of ZnO varistors for ferroelectric neutron generator power supplies, initially developed in the 1980s, was restarted in 2000 to provide a source of varistor material for weapons programs once the existing supply of vendor-supplied Mixed Oxide material was exhausted. Despite following the original procedures and utilizing much of the same equipment, the restarted process material, although meeting requirements, appeared to exhibit a different sintering behavior than the original material. A series of experiments determined that O_2 flow during sintering, freeze drying variations, precipitant stoichiometry, and billet fabrication processes did not explain the differences. It was finally determined that the apparent discrepancies were due the significant effect of Na on sintering behavior, a characteristic that had not been fully recognized in the original program. Na had been introduced at the end of the original program as a low level dopant to improve electrical stability. Its effect on sintering was minimal for the narrow baseline conditions for which it was evaluated, but its full role on sintering was not investigated before the program was suspended. As a result, the material performance since the restart was concluded to be consistent with the original process. Rods fabricated from material since the restart have performed comparably to chem-prep rods from the original program and Mixed Oxide rods currently in production.

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