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Name, title, email address, and phone number for the Prime Recipient:	Anand Murugaiah BN Powders New Products Leader, Momentive Performance Materials Quartz, Inc. anand.murugaiah@momentive.com (440) 878 5808
Prime Recipient type	Private Company
Project title	**Next-Generation LED Package Architectures Enabled by Thermally Conductive Transparent Encapsulants**
Principal Investigator(s)	Anand Murugaiah
Prime Recipient's DUNS number	828567342
Consortium/teaming members	Lumileds Lighting Company Momentive Performance Materials, Silicones, Inc.
Date of the report	30-December-2016
Period covered by the report:	**October 1, 2014 to September 30, 2016**

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Section II: Executive Summary

The overarching goal of this program is to develop innovative LED package architectures enabled by thermally conductive encapsulants. This proposal focuses on increasing lm/$ by driving LED chips at increasing power with innovative package architectures and materials. We had proposed higher drive currents without increasing operating temperature is possible by improved thermal management achieved in the new architectures. Additional benefits of improved thermal management will be realized in chromaticity (du'v') and phosphor efficiency (lm/W). The key goal is increasing thermal conductivity of silicone encapsulants from 0.2 W/mK (native silicone) to a goal of 1 W/mK that will enable package architectures that will increase lm/$.

The objective of this program is to generate novel LED package designs that would provide 30% improvement in lumen/$ output. This was to be achieved by improving thermal management in encapsulants/ phosphors to reduce their temperatures. Currently, the heat that is generated during down conversion of blue light to longer wavelengths by the phosphors dispersed in the encapsulant does not have optimum thermal pathways for dissipation due to poor thermal conductivity of the encapsulant material. Additionally, high temperature in the encapsulant during operation is one of the primary failure modes in LED luminaires resulting in much shorter than expected life. The thermal issues manifest in color instability (yellowing, browning), cracking and hot spots in the encapsulant leading to failures.

This work explored boron nitride (hBN) as thermal fillers in encapsulants to improve thermal conductivity while minimally impacting optical properties. Various approaches to Boron Nitride (BN) were evaluated and over 380 samples were generated to down select appropriate BN morphologies. We developed a range or BN materials for enabling thermal properties while attempting to minimally impact to optical properties. We were able to demonstrate improved thermal conductivities for the encapsulants and demonstrated them in devices, albeit with some impact to optical properties. However, recent work has shown that impact can be minimized with appropriate design of the LED architectures.

This work has enhanced understanding of filler morphologies, surface properties, functionalization, and the effect on light scattering from the particles. The work also uncovered relationships between filler properties to encapsulant thermal and optical performances. Relationships between encapsulant properties (thermal conductivity and transmissivity) to device performance (phosphor junction temperatures and device light output) were established for the device design in this work.

The down selected BN process developed form this work is feasible to be scaled up. Additionally, these new BN materials would be manufactured in the United States. By appropriately utilizing these materials in well-designed novel LED package architectures, we believe these materials can positively impact LED devices such as lumen/$, life of the luminaire, and also avoid failures and hazards due to thermal issues.

Control devices were used as a technical baseline for comparison, both with single dies and COB packages. The targeted metrics for the program were quite aggressive: a 30% lumen/$ improvement by achieving thermal conductivities of 1W/mK in the encapsulant without adversely affecting optical properties (for comparison, neat silicone thermal conductivity is only 0.17W/mK). While > 1W/mK thermal conductivities are not uncommon with BN loaded resins (with high filler loadings), they result in optically opaque systems. The challenge here was to ensure optical properties were not adversely impacted.

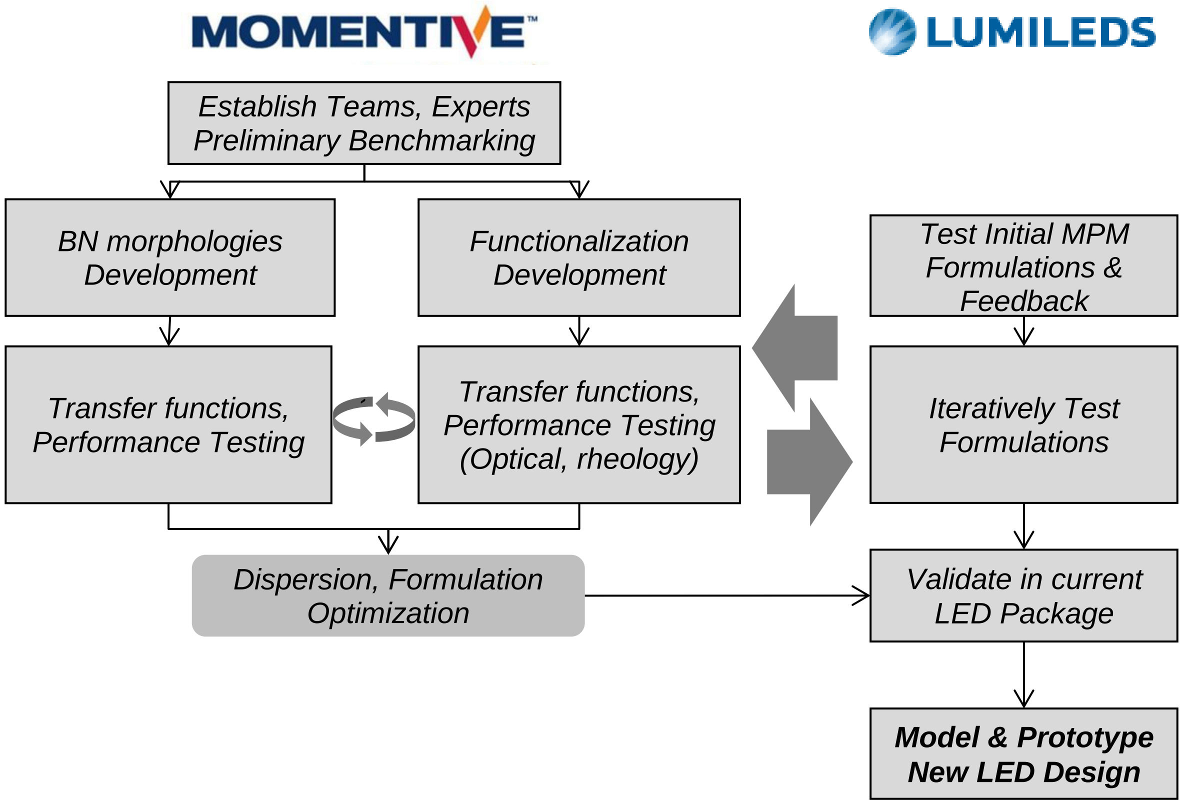

Figure 1. Overall approach for the thermally conductive encapsulant program

Section III: Goals, Objectives, and Accomplishments of the Project

The objectives were broken down into task specific goals and are listed in Table 1, with actual achievements listed alongside. There were numerous challenges, both technical and non-technical while executing this program; these were identified and mitigation plans were developed that included soliciting advice and collaboration from top experts in the field.

Table 1. Comprehensive Milestone Summary

Task #	Task Title	Metric	Milestone #	Milestone Description	Target Month	Actual Time	Status
1.1	Demo BNNF Exfoliation	Thermal conductivity	M1.1	Demonstrate BN exfoliation and disperse in siloxanes and **0.4 W/mK**	6	6	Completed
1.2	Characterization/ Optimization	-	M1.2	Further optimized BN morphologies enabled by predictive models and feedback from Tasks 2 and 3.	15	15	Morphologies identified and demonstrated
2.1	BNNF Dispersion	-	M2.1	Demonstrate stable dispersions & maximize thermal conductivity per unit scattering for prototyping.	15	15	Demonstrated pathways and dispersions. New morphologies with lower scattering developed.
2.2	BNNF-Resin Formulation - 1	Thermal conductivity	M2.2	Demonstrate thermal conductivity improvement to **0.6 W/mK** in siloxane	**12**	**24**	Demonstrated better than benchmark. Demonstrated in new package systems with BN+phosphor loaded silicone.
2.2	BNNF-Resin Formulation - 2	Thermal conductivity	M2.2	Demonstrate requisite thermal conductivity (**1W/mK**), optical properties, and processability.	**18**	**24**	Demonstrated ~0.7W/mK with BN+phosphor systems, enabled by new package architecture. Minimal penalty in light output. High TC made possible by new package architecture from Lumileds
3.1	Existing Package Prototypes	-	M3.1	Verify reduced phosphor temperature for electrical power input.	12	12	Completed
-	Selected Package Prototypes	Lumen/$ improvement	-	**Lumen/$ > selected benchmark**	12	12	Completed

Task #	Task Title	Metric	Milestone #	Milestone Description	Target Month	Actual Time	Status
4.2, 4.3	Next Gen Packages (Design, Prototype)	-	M4.2, M4.3	Confirm 30% gain in input power for same color shift and LOP drop in HTOL tests.	**18**	**24**	New device architecture shows very good improvement in thermal conductivity/ heat transfer: this is due to different design and phosphor silicone mixtures than contribution from BN alone: the phosphor temperatures with and without BN were not very different for the formulations tested. They however offer opportunities for further improvement with optimization with BN. This will be taken up with Lumileds for further discussion (post DoE program)
-	Selected Package Prototypes	Lumen/$ improvement	-	30% improvement in Lumen/$	**18**	**24**	
4.4	Manufacturing Assessment	-	M4.4	Verify the new silicone material to be compatible with production process and production equipment.	**18**	**24**	Silicone material is compatible with the production process. Adding BN may require some modifications to the process to ensure proper application.

Section IV: Summary of Project Activities

This report summarizes the work done to date and focuses primarily on the BN development; work done on functionalization and device testing are included as well. This report covers approaches that worked and also the ones that did not. During this program, we have been able to achieve close to 0.7W/mK composite thermal conductivity against a target of 1W/mK enabled primarily by new package architecture. While the final target was 1W/mK, this is a very substantial increase: more than 300% improvement over neat resin thermal conductivity (0.17 WmK). The technical progresses made during this program were very significant. The initial thermal conductivity improvements had penalties in optical performance due to scattering effects; they were minimized with new BN development and when incorporated into new package architecture design developed by Lumileds. The testing of this package design happened during the later stages of the program and has not been fully optimized for this design. This work will be discussed with Lumileds post DoE program.

The key challenge in keeping operating temperatures low in LEDs is to efficiently transport heat from the LED and phosphor layers out of the package. Heat is generated in both the LED and phosphor layers and must be conducted through encapsulant/phosphor, die, die bond line, and board dielectric layers to the heat sink. The key barriers to heat transfer are the two silicone-containing layers (phosphor and die bond line). Increasing encapsulant and die bond line thermal conductivity will have a significant impact on operating temperature. As thermal conductivity of encapsulants increases, this differential drops. Higher TC enables higher drive currents.

The original hypothesis for this program envisioned improving lumens/$ by increasing LED encapsulant thermal conductivity using BN materials as fillers in the silicone encapsulant to effectively dissipate the heat generated by the phosphors during down conversion. Existing encapsulant formulations have poor thermal conductivities (~0.3W/mK or less for phosphors + silicone systems) and limit drive currents that can be used in LEDs, particularly when using high RI encapsulants that are very sensitive to temperature. Additionally, higher operating temperatures result in reliability, lifetime, and also affect the efficiency of the phosphors.

The objective of this program is to generate novel LED package designs that provide 30% improvement in lumen/$ output by developing thermally conductive LED encapsulants with desirable optical properties. The overall program can be broadly classified into 3 technical thrust areas:

1. BN development for the thermally conductive filler, which should also provide desired optical properties in the composite. This work focused on developing new BN morphologies to provide high thermal conductivities to the silicone resin while minimally impacting the optical properties

(%Transmission). Various approaches were evaluated and more than 200 samples were generated and tested, out of which select samples were tested in LED devices.

2. Compatibilizing / functionalizing BN with the silicone resin and dispersion to meet desired optical and thermal properties. Various approaches for treating the BN surfaces with functional groups were also evaluated.
3. Testing and developing novel package architectures based on these new materials

These approaches are briefly summarized below.

4.A BN development

4.A.1 Exfoliation Processes:

The original BN approach was generating BN nanosheets such that the particle sizes are below scattering wavelength to enable maintaining desired optical properties. Hexagonal BN (h-BN) is a layered material analogous to graphite with very strong in-plane covalent bonds and weak through-plane bonds. Due to rapid phonon transport along the covalently bonded layers, h-BN is a very good thermal conductor. However, unlike graphite, the through-plane bonds in h-BN are also partially ionic due the lattice stacking of boron atoms and nitrogen atoms. The electrons are localized leading to a very high band gap; pristine h-BN is transparent in the optical spectrum (300 nm to 800 nm). It also possesses high refractive index (RI 1.8 – 2.1; BN is a birefringent material).

Our initial approach was aimed at minimizing optical scattering due to RI mismatch between the BN and the silicone; we set out to make BN nano-flakes much below the wavelength of light (450nm). Once the BN powders have been reduced in dimension into the nanoscale regime with an optimized exfoliation process, we were confident to get low attenuation, especially at much lower anticipated particle loadings than typically expected with BN as fillers. Various synthesis routes were considered for BN nanoflakes, however, producing BN nanoflakes is challenging.

We evaluated different mechanical and chemical routes exhaustively for BN exfoliation. These are summarized in Table 2. Almost all of these approaches were able to generate BN nano flakes to varying degrees. A wide range of particle sizes were generated (Figure 1).

SEM micrographs of a couple of approaches are shown in Figures 2 and 3.

Table 2. Mechanical and Chemical Exfoliation Summary

Process Type	Thermal Cond. W/mK	% T	Description	Results	Reporting Period
A	N/A	N/A	High shear process similar to Graphene: Very high surface areas, high oxygen impurities (despite purification), low crystallinity.	Was not tested for optical properties as the samples were opaque	1Q 2015
B	0.4 - 0.6	58%	High shear liquid process: Wide, controllable particle sizes. Increase in thermal conductivity, but poor optical properties.	Enabled initial narrowing of BN properties	1Q - 2Q 2015
C	N/A	N/A	High shear mechanical process: Very low crystallinity, severe agglomeration, high oxygen impurities, and poor yields.	Not tested for thermal/ optical properties due to poor BN properties	2Q 2015
D	0.26	20%	Sonication assisted process. Higher purity than other mechanical exfoliation methods. However, poor optical properties.	Excessive scattering. Smaller crystals are needed to avoid scattering	2Q 2015
E	N/A	N/A	High shear mechanical process. BN materials similar to other high shear processes: high oxygen impurities, low crystallinity.	Scalable process. Decided to continue only if the other high shear processes showed promise.	2Q 2015
F	0.26	<5%	Mechanical shear process: High oxygen, low crystallinity, severe agglomeration. Low thermal conductivity and optical properties.	Agglomeration may have further contributed to poor optical properties.	3Q 2015
G	N/A	N/A	High shear mechanical process: High oxygen, low crystallinity, severe agglomeration.	Samples not tested due to poor BN properties	3Q 2015
H	N/A	N/A	Chemical exfoliation: High oxygen, low crystallinity, severe agglomeration, and low yields.	Was not found suitable for further evaluation	2Q 2015
I	N/A	N/A	Chemical exfoliation modified from graphene: High surface area, small particle size BN. However with high oxygen and defects.	Poor thermal conductivities and opaque samples	1Q - 2Q 2015
J	N/A	N/A	Chemical exfoliation: High oxygen, low crystallinity, low yields.	Was not evaluated further	4Q 2014 - 1Q 2015

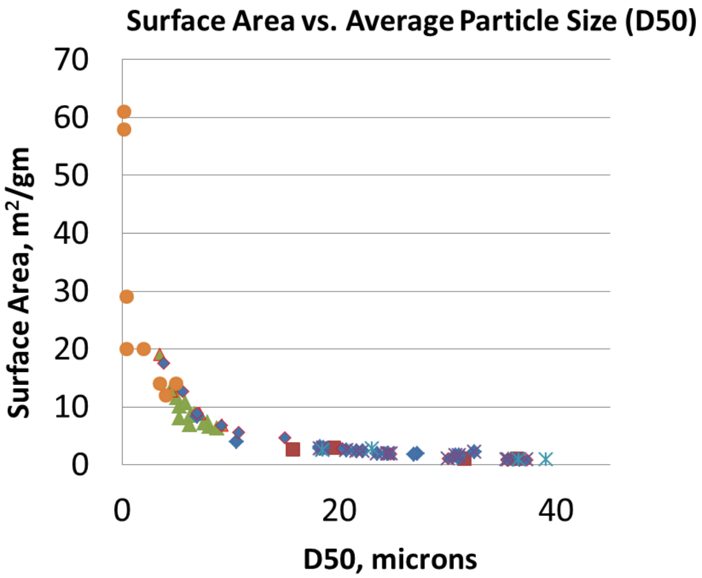

Figure 1: Comparison of particle size to surface area after the BN platelets were subjected to a mechanical shear exfoliation process.

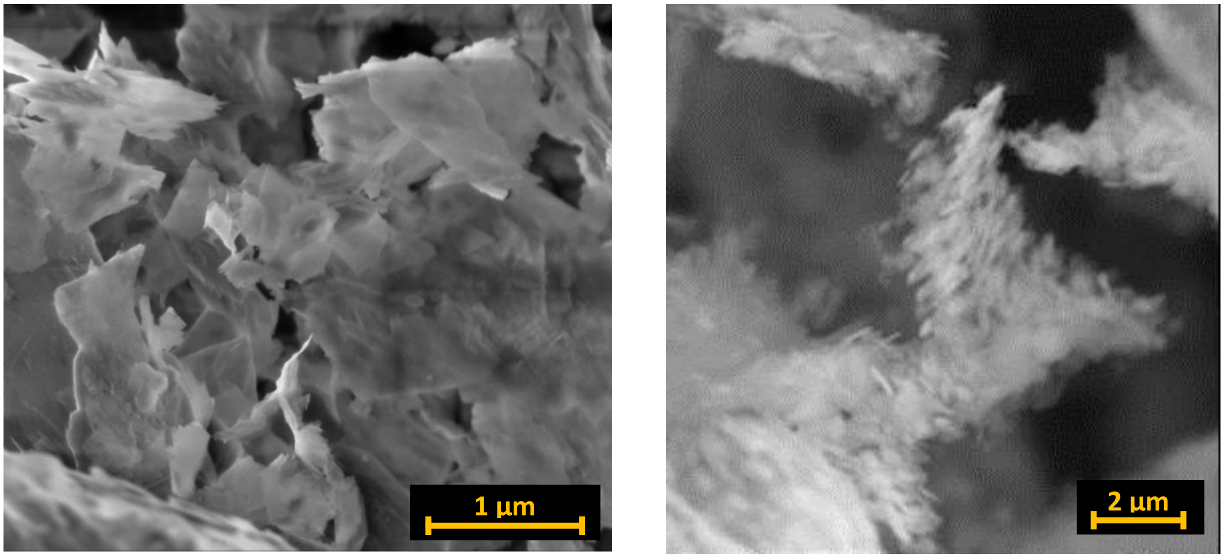

Figure 2 (2Q 2015 Report): Processing via functionalized planetary ball milling: the particle sizes were significantly reduced from the starting materials.

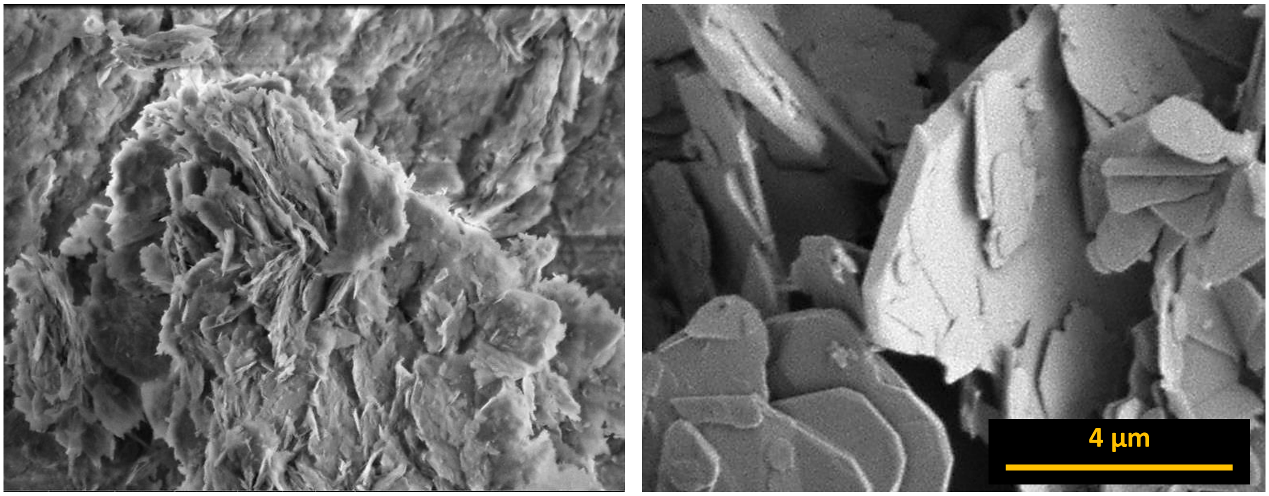

Figure 3 (3Q 2015 Report): SEM image of exfoliated BN via mechanical shear. Image on the left is after exfoliation; image in the right is before exfoliation

The exfoliation approaches however invariably resulted in significant damage to the crystals. BN's inherent high thermal conductivity is due to phonon transport along the layer planes and can be severely impacted if defects are present in the crystal structure. The exfoliation processes are very aggressive and introduced a large number of defects in the crystals. Attempts to reverse these defects by thermal annealing post exfoliation did not appear to improve thermal conductivities by much. More over such attempts during recrystallization could cause grain growth, impacting crystal sizes.

The exfoliated nano sized particles also caused significant agglomeration of the particles. Dispersion methods were developed for distributing these particles as uniform as possible in the resin. However, there was still considerable scattering that resulted in a severe penalty in optical properties (% Transmission).

Overall, it was determined that either defect free particles with sizes even smaller than what was achieved would be needed (with adequate dispersion), or a different particle size distribution will have to be evaluated. Smaller particles however will create a large number of particle-resin interfaces which are a major source of thermal resistance; we were attempting to mitigate this interface resistance via functionalization approaches in parallel. However, with the interface issues and creation of significant number of defects during exfoliation, it was decided to deselect mechanical and chemical exfoliation processes as the primary approach and evaluate a different particle size distribution to steer clear of the scattering wavelengths as shown in Figure 4.

The size range of these particles and particles developed via exfoliation to date fall in the scattering range for visible light: smaller particles than this would be ideal for optical properties, as shown in Figure 4, though not ideal for thermal conductivity due to increased thermal interfaces. Currently, we have achieved exfoliated particles > 100 nm, which still provides significant scattering.

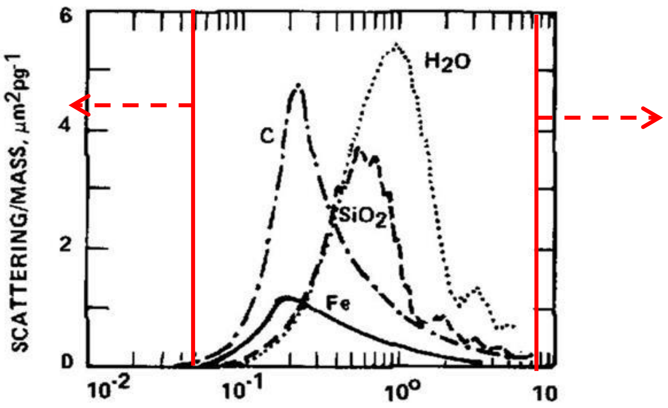

Figure 4 (3Q 2015 Report): Single particle light scattering for several substances. Via Faxvog, 1975. (http://capita.wustl.edu/CAPITA/CapitaReports/ProtectingVisibility/Chapter2/Chapter2.htm)

4.A.2. Particle Size Control

Compared to the exfoliated particles, we also evaluated larger BN particles, such that they were above the scattering particle size ranges. The scattering phenomenon is a function of the wavelength of light, particle size and shape, and also the relative RI mismatch between the two mediums (silicone and BN). We evaluated a variety of BN particle sizes and narrowed the morphologies to an optimum starting BN type. This had much improved optical properties over the exfoliated BN, as shown in Figure 5. One of these samples was used as a control for further optimization and comparison.

A few different particle size control approaches were evaluated for these trails. Further, effect of particle size distribution (spread in the particle size distribution, or 'Span') was also evaluated on their impact on % Transmission and thermal conductivity.

Initial trials employing a particular process method (Process K) are shown in Figure 6. These trials showed that controlled particle sizes did result in improved optical properties though it did not impact thermal conductivities. The results, along with the other approaches, are shown in Table3. Further trials were carried out with a different process (Process L) that enabled better control over the size distribution. The thermal conductivities were higher than what was achieved with the control sample. This process had lower yields but provided valuable data for further optimization for both thermal and optical properties.

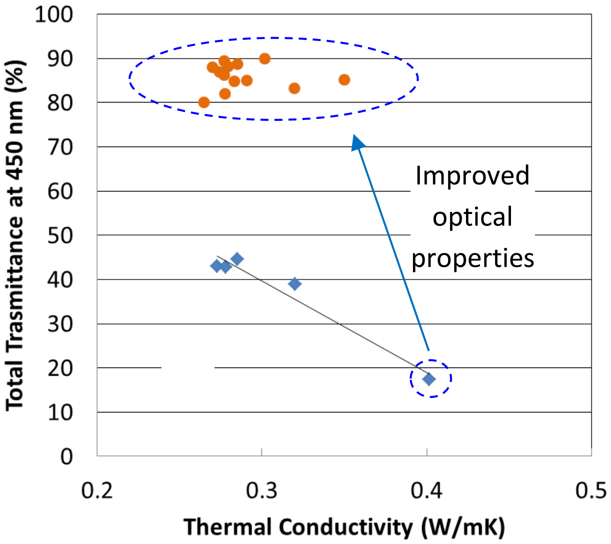

Figure 5 (3Q 2015 Report): New BN morphologies evaluated were selected to have significantly higher transmission values.

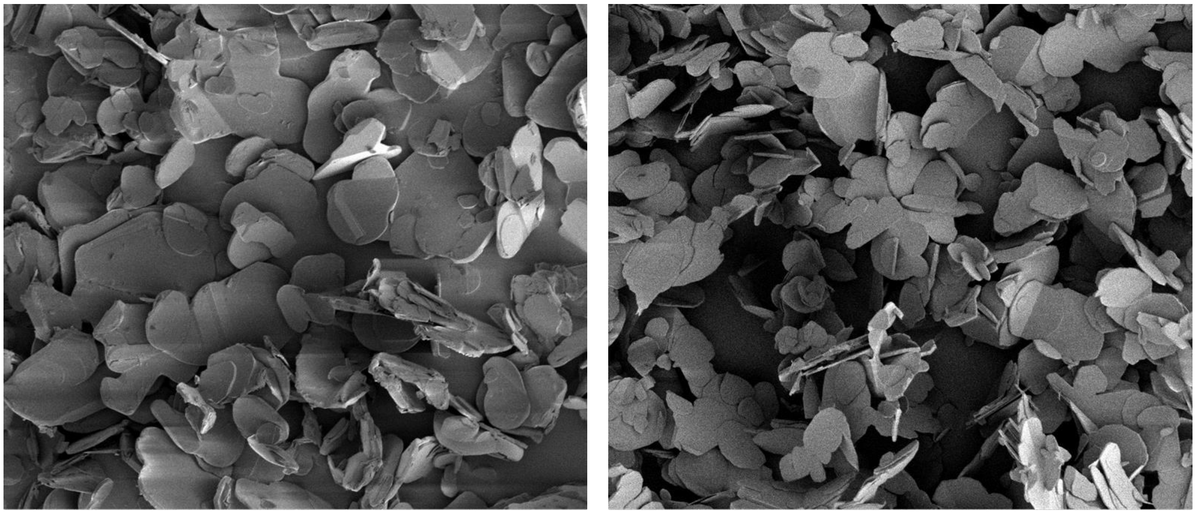

Figure 6 (4Q 2015 Report): Comparison of samples (a) from one of Process K settings, (b) with control sample. In this trial setting, Process K sample showed more uniform particles.

Table 3. Particle Size Control Trials Summary

Process Type	Thermal Cond. W/mK	% T	Description	Results	Reporting Period
K	0.26 - 0.28	80 - 95%	Improved properties over "as synthesized" material (as control).	Initial particle size control trials. Scalable process. However, have low process yields.	4Q 2015
L	0.26 - 0.35	80 - 90%	Enabled optimization of "as synthesized" material. Achieved higher thermal conductivities with decent optical properties	Low yields, however, laid ground work for further processing	1Q 2016
M	0.25 - 0.3	80 - 91%	Fine-tuned process for particle size control with tighter particle size distribution.	Was crucial in enabling narrowing down BN properties for optimization of optical properties.	2Q - 3Q 2016

Based on the results from processes K and L, a new approach, Process M, was specifically developed to provide tight particle size distributions as shown in Figure 7. Process M (listed here as Approach 3) was able to generate tight particle sizes that was useful to determine optimum particle sizes for optical and thermal properties for a given resin system.

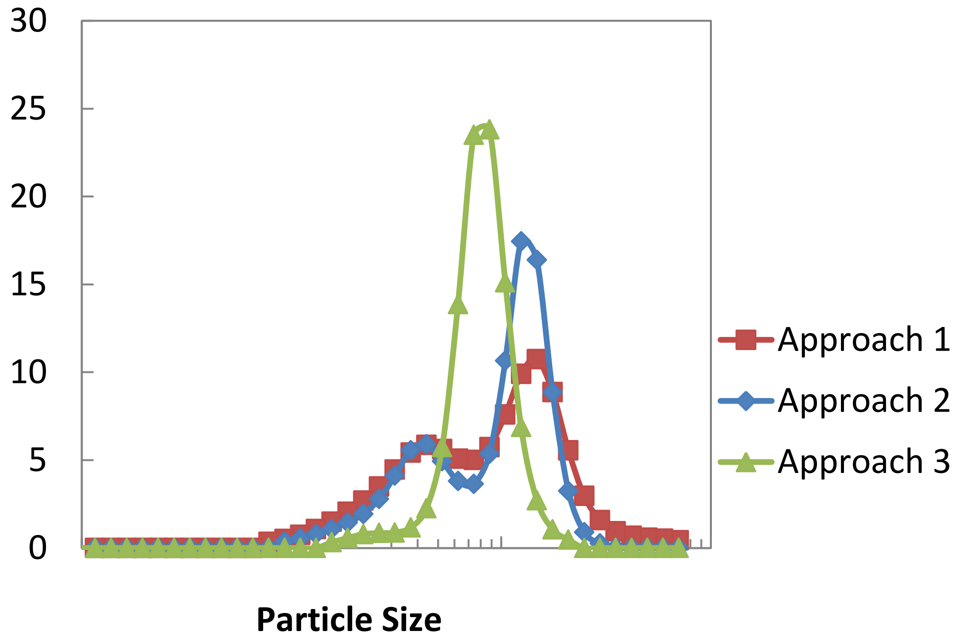

Figure 7 (1Q 2016 Report): Particle size distribution with the 3 different approaches.

During this time, optical microscopy was also used as a visual tool to evaluate optical properties for BN in silicone to understand the impact of morphologies on scattering and transmission. Comparison between with and without PSD control is shown in Figure 8. One key observation was that PSD control provided more consistent results compared to samples with no PSD control.

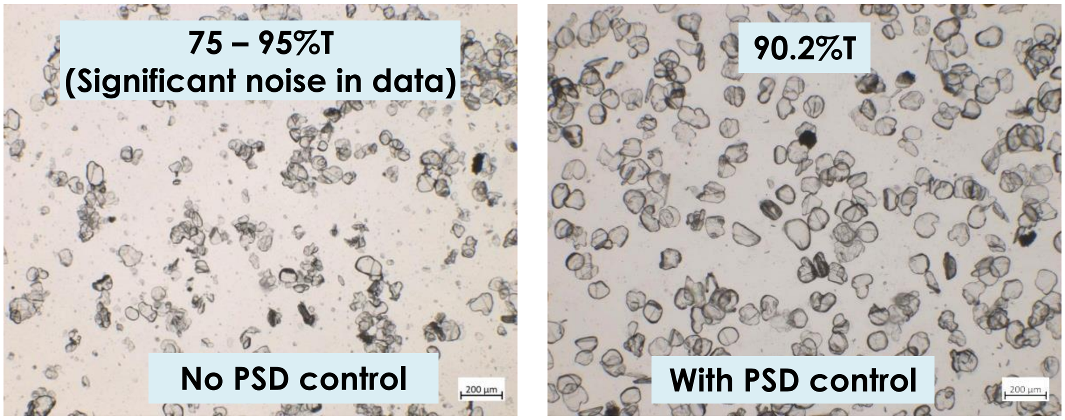

Figure 8 : Optical micrograph of BN particles in silicone. PSD control sample was cleaner and had consistent optical properties, whereas sample with no PSD control showed considerable scatter in optical properties.

Materials generated from this process were used for evaluating in LED devices. This process can be used for further BN optimization in conjunction with the other approaches developed, namely via direct synthesis. Due to the timeline of the program, these have not been evaluated. However, this will be taken up for further discussion with Lumileds as potential future optimization if this program is taken up for commercial discussion.

4.A.3. Direct Synthesis

There were two primary motivating factors that drove our approach for direct synthesis: Firstly, exfoliation processes or any other modification process caused damage to the crystals causing poor thermal conductivities. To minimize such defects, direct synthesis was evaluated. Secondly, the crystal surface (such as excessive damage) and the morphologies of the crystals impact light scattering. In particular, for the PSD control approach, the thicknesses of the crystals appeared to play a role as shown in Figure 9. Crystalline BN does not absorb light, the dark regions seen at the crystal edges are light scattered in a different direction. We attempted to make thinner crystals to evaluate minimizing scattering from the edges. Additionally, with all else being equal, higher aspect ratios provide better thermal conductivities as shown in Figure 10 and we explored direct synthesis routes as a means to obtain such higher aspect ratio crystals.

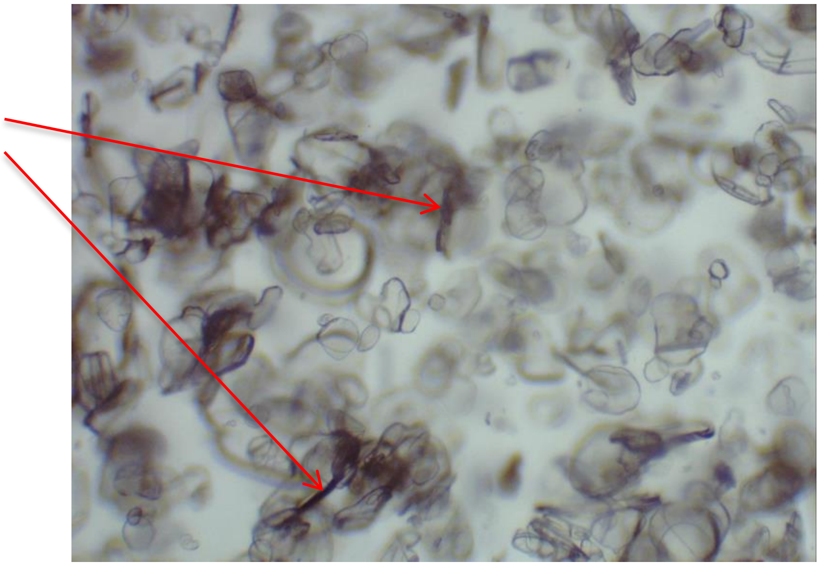
Scattering on crystal edges

Figure 9 (4Q 2015 Report): BN particles with higher thickness showing considerably more scattering on the edges. Particles that have thinner profiles do not show as heavy scattering.

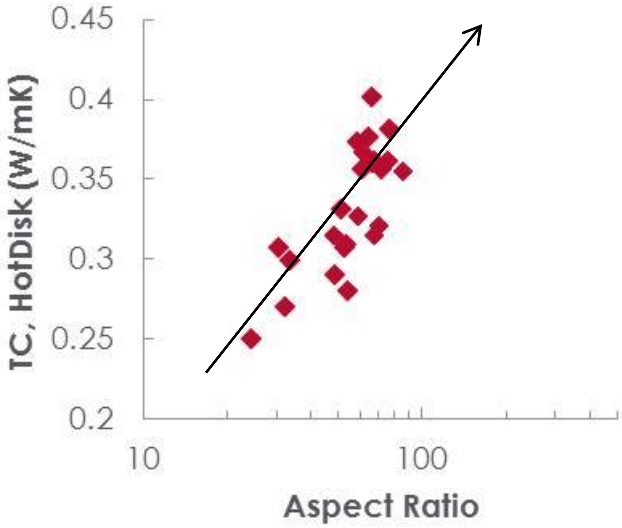

Figure 10 (1Q 2015 Report): Aspect ratio vs. thermal conductivity for crystalline powders with clean & smooth crystals.

For this approach, various factors were explored such as starting raw materials/ precursors, their preparation/ conditioning, processing conditions, various additives, and post treatment purification were explored. Trials were done in lab scale furnaces and also utilized production scale furnaces. After various trials, the processing conditions were narrowed to a select few systems and were further explored. Select samples are shown in Figure 11 below. The summary of the trials are listed in Table 4.

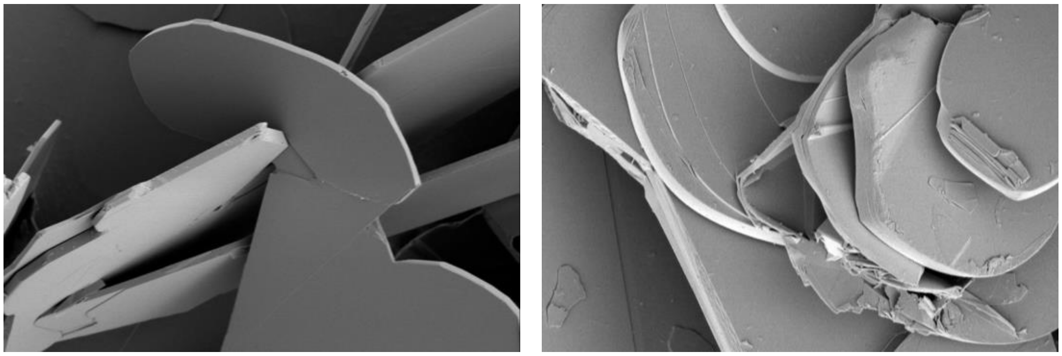

Figure 11 (4Q 2015 Report): Thickness profile comparisons between (a) one of Process O samples and (b) a control sample.

Table 4. Direct Synthesis Trials Summary

Process Type	Thermal Cond. W/mK	% T	Description	Results	Reporting Period
N	0.26 - 0.3	86 - 89%	Improved optical properties, but lower thermal conductivities compared to some of the high shear processes	Formed the baseline for next set of BN morphologies developed	3Q 2015
O	0.34 - 0.5	60 - 75%	~50% improvement in thermal conductivity over control, but with some optical penalty	Shows good potential, but timing required to optimize exceeds program timeline	4Q 2015 - 1Q 2016
P	0.3 - 0.35	88 - 91%	Improved optical properties with good thermal conductivities	This is one of processes chosen for moving forward.	3Q 2016

Process N did not use any additives and was used as a control sample. Process O was exhaustively explored for generating high aspect ratio particles. These materials showed significant improvement in thermal conductivities and required only ~half the BN loading. However, due to increased span (wider particle size distribution), there was increased scattering that affected optical properties. Graphical comparison of sample from process O is shown in Figure 12, showing thermal conductivity vs % Transmission with a control sample (no PSD control) and the control sample subjected to PSD control (Process K).

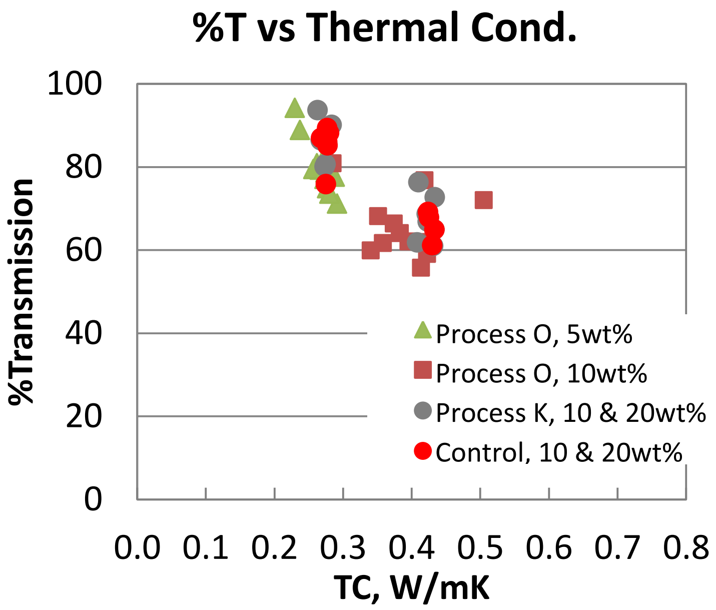

Figure 12 (4Q 2015 Report): % Transmission vs. thermal conductivity of BN materials produced via Process O (5 and 10wt%). For comparison, samples from process K and control samples are also shown at 10 and 20wt% (10 and 20wt%, though having the same color, are bunched in two distinct groups)

To improve optical properties, PSD control methods were employed to Process O sample and results are shown in Figure 13 from one such trial. Due to its higher aspect ratios (thinner crystals and tend to be more fragile), the particle size control process does not seem to be very effective: there is still considerable spread in the particle sizes.

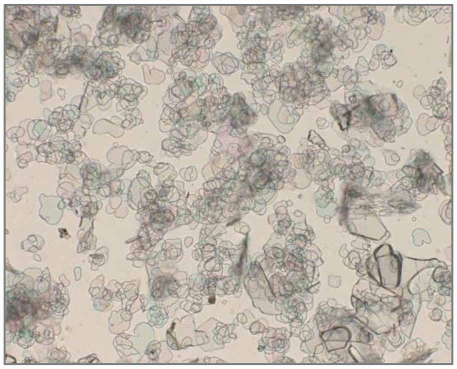

Figure 13 (1Q 2016 Report): Optical micrograph with higher aspect ratio BN. Despite controls to get tighter particle sizes, there is considerable spread in particle sizes than desired.

More aggressive methods of particle separation were employed (Process M) and was partially successful in getting a tighter particle size distribution as shown in Figure 14. However, this was highly dependent on the particular batch used. Since these thin crystals are more fragile than the control samples, they caused excessive damage and particle size reduction in other batches. The image however does show that with tighter particle sizes, the thinner crystals tend to fade away in the back ground, which is an indication of lower scattering.

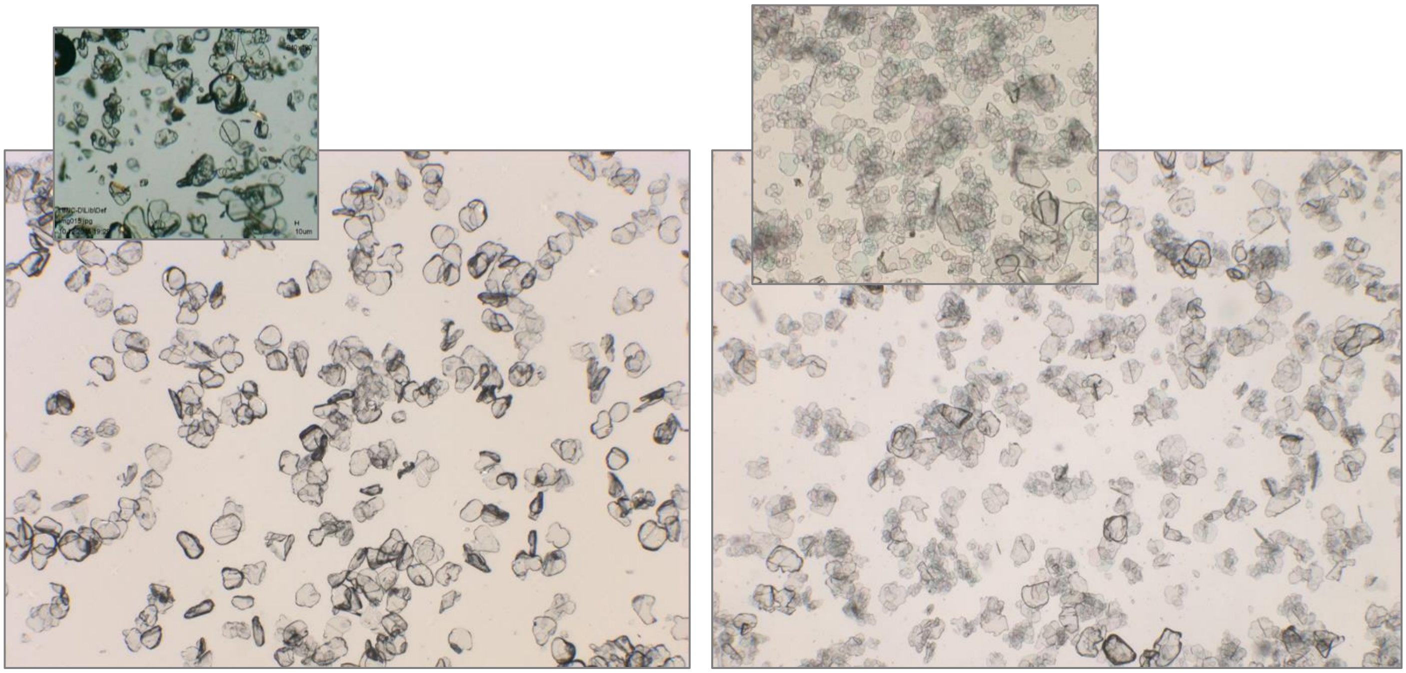

Figure 14 (1Q 2016 Report): Optical image of BN dispersed in silicone: control sample compared to Process O (insets). Image on the left is from Process M, and image on the right is Process O with some PSD control. Images are approximately to scale with each other.

Despite these minor shortcomings, process O showed a lot of promise, however, to develop this further and complete optimization, and also evaluate larger scale trials would require full process development and would exceed the program timeline. It was thus deselected from contention.

A modified process, process P, that used different raw materials and processing conditions than O was used instead to evaluate a different set of morphologies, not necessarily with higher aspect ratios, but one that can provide improved optical properties and one that is scalable.

Trials were done in lab scale quantities initially and then were scaled up to full production scale trials. The results are shown in Figure 15, in comparison with Process M (subjected to particle size control resulting in tight particle size distributions). Process P showed here was not subjected to any additional particle size control. Process P showed even better performance in optical and thermal properties over those obtained via particle size control. These improvements could be due to larger particle sizes, lower surface areas, and also improved crystallinity.

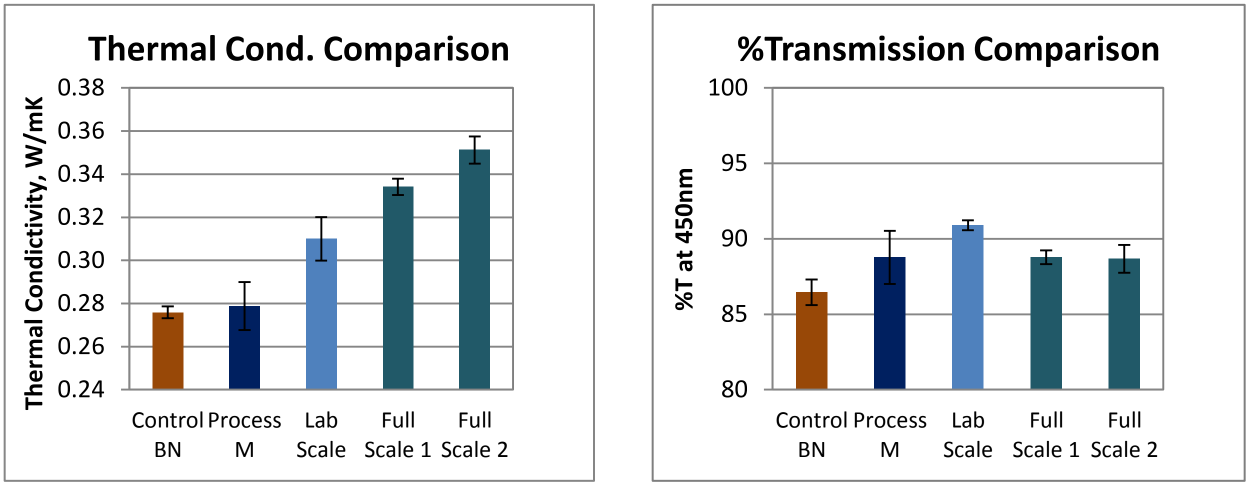

Figure 15 (3Q 2016 Report). a) Thermal conductivity comparison at 10wt% BN in RTV 615 silicone (via Liquid sample in HotDisk®). b) Optical transmission comparison. Films with 10wt% BN loading in RTV 615

Process O and P samples have not been extensively tested in LED devices as they were developed towards the end of this program. We will discuss these materials with Lumileds on prospects post DoE program. We expect that if particle size control is employed over and above to Process P, it may be possible to improve optical properties further.

4.B. Other Trials:

There were a few other trials that were done during this program that did not show promise, but are included here for the sake of completion.

Non-BN synergic fillers were evaluated that may further enable BN in both optical and thermal properties. Select fillers were determined after literature survey, material properties and also after consultation with external experts. Two primary classes of fillers were evaluated: nano sized optically clear materials that can also provide some thermal conductivity benefits and high aspect ratio particles that are optically clear and that have shown thermal conductivity improvement in experimental studies. These were evaluated in silicone resins at different loadings. The results are summarized in Table 5. These materials had to be aggressively dispersed in silicone and different approaches including using solvents were evaluated.

The nano sized fillers (that were transparent in solvents) could not be effectively dispersed in the silicone resin (despite using functionalization agents) and resulted in poor % transmission. They did not show any improvements in thermal conductivities as well.

The higher aspect ratio fillers were dispersed using similar methods, however their measured % Transmission showed promise. These were then mixed with BN in the silicone resin as a hybrid system. However, they did not show any appreciable improvements in optical or thermal properties. These were discontinued in order to focus on the other BN development approaches.

Table 5. Hybrid Filler Trials Summary

Process Type	Thermal Cond. W/mK	% T	Description	Results	Reporting Period
Q	0.2	43 - 85%	Hybrid non BN fillers evaluation. Included functionalized particles. Poor thermal conductivities and excessive scattering leading to poor transmission.	Discontinued	3Q 2015
R	0.2	~100%	Hybrid non BN fillers (very high aspect ratios). Included functionalization. Poor thermal conductivity but showed good % transmission.	Used with BN trials (Process S)	3Q 2015
S	0.24 - 0.26	87 - 91%	Contained BN + a non BN filler. Developed a process for dispersing these hybrid fillers. However, no improvement in thermal conductivity or optical properties.	Discontinued	4Q 2015

During the course of this program, additional activities included establishing methods and procedures for thermal conductivity measurements in liquids (BN in uncured silicone to minimize orientation effects) and also establishing methods for optical measurements (% Transmission); sample preparation and optical property measurements were developed both at our Ceramics facility in Strongsville, OH and also at our silicones division at Waterford, NY. Correlations were developed between the two systems for consistency.

With device results from Lumileds on selected device architecture, initial transfer functions for %Transmission and thermal conductivity with device Light output and Phosphor temperature reduction were established. While this was device specific, this enabled initial optimization on our BN morphologies.

We also evaluated effect of particle orientation of BN platelets in the silicone resin and its effect on thermal conductivity. There is significant orientation of the BN particles in the encapsulant in the device as shown in Figure 16. The most effective thermal conductive direction is along the crystals. In this case the preferential alignment of the BN platelets along the horizontal direction. This will act as an excellent heat spreader rather than dissipate the heat.

In current LEDs, the most effective thermal pathway for the heat generated in the phosphors is in the vertical direction though the sandwich construction: through the encapsulant down to the chip, which would in turn transfer it to the heat sink through the die-attach layer and below. The preferential orientation of the platelets in the horizontal direction in the encapsulant will not provide the most effective thermal transfer.

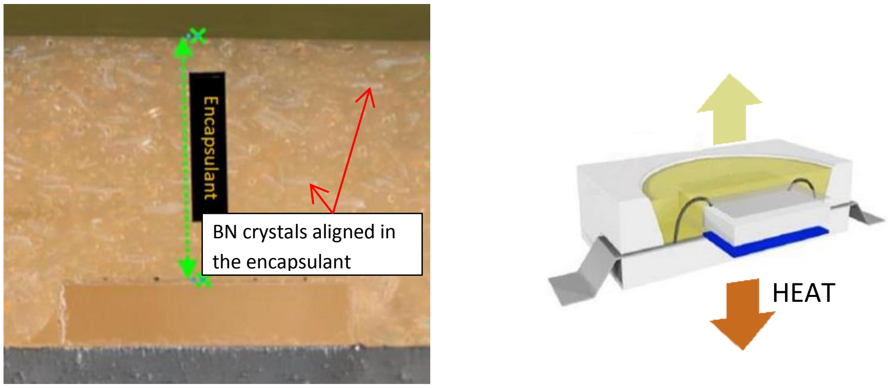

Figure 16 (1Q 2016 Report). Dispersion of BN crystals in the encapsulant in LED showing preferential orientation in the horizontal direction. Effective heat transfer is required along the vertical direction.

A new sample preparation method was developed such that the BN platelets are oriented in 2 different directions as shown in Figure 17.

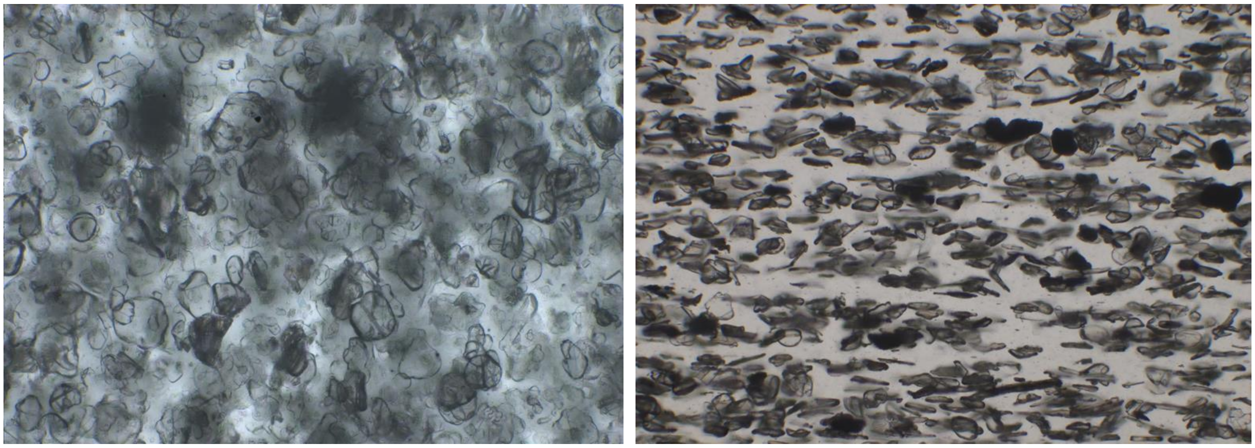

Figure 17 (2Q 2016 Report). BN orientation in films. a) As cast film showing BN platelets lying flat. b) Laminated stack of films transversely cut with BN platelets oriented in the vertical direction

Thermal conductivities of these samples were measured using Laser flash method and are listed in Table 6. There is a considerable difference between the in-plane and through plane measurements. For the in-plane measurements, the difference between measured and theoretical values (for perfectly oriented particles calculated using Lewis Nielson model for filled systems) can be explained in terms of less than perfect orientation, and more importantly possible limitations in the sample preparation and measurement.

Sample	**Table 6. Orientation Effects Thermal Conductivities, W/mK**			
	In-Plane	Through-Plane	Improvement over through plane, %	Theoretical In-Plane
A	0.324	0.154	210%	0.82
B	0.367	0.186	197%	0.64

If the platelets can be oriented vertically in the device, it can result considerable improvement. However, vertically orienting the platelets conflicts with the natural flow of the particles in the resin and hence would have to be modified to achieve such orientation. This is quite challenging and the orientations normally cannot be pre-dispersed/preset in the resin. Some methods for orienting the platelets have been looked into, however since effective means of orienting the platelets are during dispersion or processing in the device, the approaches are not pursued at this stage.

4.C. Functionalization Approaches:

Our technical plan consisted of pursuing dispersing aids and chemical treatments for functionalizing BN particles to enable compatibilizing BN with the silicone resin. The motivation for this work is twofold: One is to reduce the interface mismatch between the resin and BN by providing a functionalization bridge to minimize thermal resistance in the interface. Second is to enable regulating viscosity and uniform dispersion of the particles.

BN is notoriously difficult to functionalize due to its inert nature. There have been a few successful attempts to treat BN surfaces, and Momentive carries a few products in its portfolio that have surface treatments on the BN. Our expectation for the effect of particle functionalization was to observe a 10-20% increase in thermal conductivity, which is much higher than what has been achieved earlier. Also, the functionalization should not impact the performance in the LED device such as interacting with the phosphors or impact color and long term reliability.

To this end, various approaches were evaluated with physical adsorption and covalent functionalization. Pretreatment approaches with acids, bases, and oxidants, and various dispersion methods (internal approaches and via external experts) were evaluated as well. For functionalization approaches, various formulations were explored including surfactants (silicone based and other chemistries including anionic, cationic, and non-ionic systems), dispersants with polymeric or oligomeric species, and organo-functional silanes, and silylating agents/ mono functional silanes. External expertise where needed was solicited, such as mixing and dispersing methods, particle wetting, and non-silicone/ silane based functionalization chemistries.

We established treatment methods and analytical techniques such as attenuated total reflectance infrared spectroscopy (ATR-IR), X-ray fluorescence spectroscopy (XRF), and thermogravimetric analysis (TGA) for determining the nature (covalent or adsorbed) and overall loading level of treatment on the BN particles. We have compared the physical properties of silicone systems using treated and untreated BN particles.

For the physical adsorption, we evaluated compatibilization of BN via two different approaches: chemisorption and physisorption. For the chemisorption approach, we establish the deposition of “durable silicon” on the BN particles using different reagents and treatment methods as well as specific analytical methods. For physisorption work, we leveraged expertise and equipment both internal and external to Momentive for this approach.

Amongst the various approaches evaluated, only a couple of them showed effective treatment on the BN particles. Figure 18 shows presence of silicon on BN measured with XRF. The BN particles were treated with an organo-functional silane and washed thoroughly after treatment. The presence of silicon after washing indicates it is possible to functionalize BN surface with appropriate treatment. A 10-15% reduction in viscosity was achieved. Though we clearly demonstrated the ability to durably apply silicon to a particle surface, we did not observe significant optical or thermal benefits in our representative formulation.

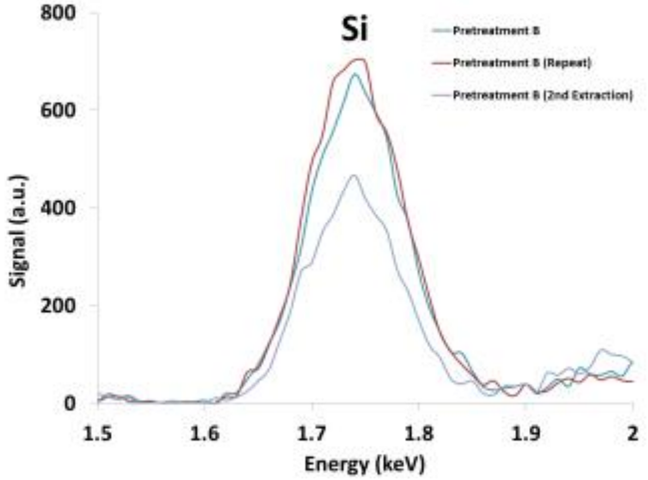

Figure 18 (2Q 2015 Report): Evidence of Silicon attached to BN particles after washing (post treatment)

Dispersants and thixotropic agents were also evaluated to improve dispersion and stability of the BN filled formulations. We investigated several different dispersants from various suppliers to gauge the importance of molecular structure on dispersion and formulation performance. We evaluated the effect of these agents on optical properties in detail such as % Transmission and haze index. We also developed a method for quantitatively determining dispersion of BN particles via optical microscopy. Analysis of the grayscale information of each captured image results in a histogram specific to that image. A well dispersed image had a tighter gray scale values compared to one with poor dispersion (more white spaces between particles/ agglomerates), Figure 19. A good correlation between the gray scale mean and the haze index was seen as well.

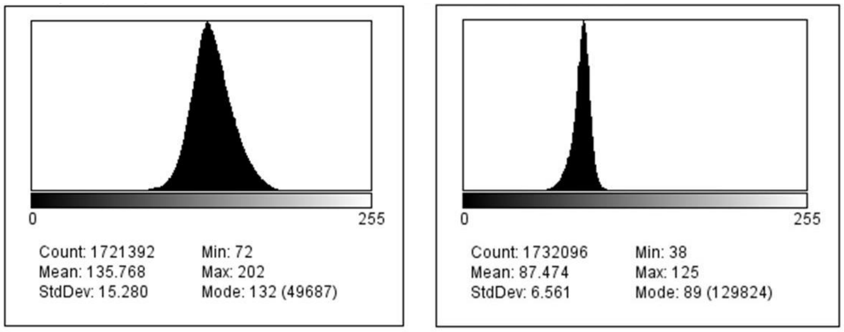

Figure 19 (3Q 2015 Report): Comparative gray scale histogram of two samples with differences in particles dispersed in the resin. The one with lower Standard deviation indicates better dispersion.

After exhaustive evaluation of a multitude of treatment agents, only a couple of formulations exhibited some improvement. The results are shown in in Figure 20. The results are plotted for 20wt% BN in this case. The results for 10wt% were not as significant.

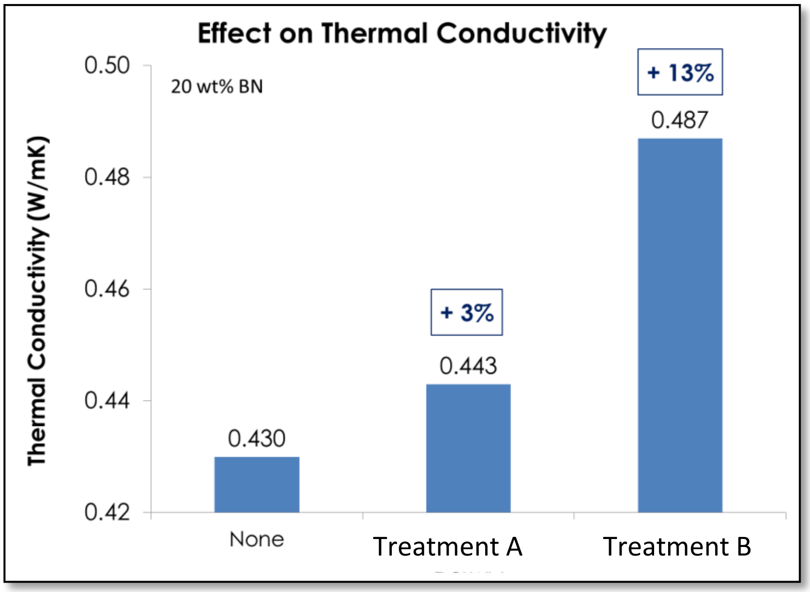

Figure 20 (4Q 2015). Effect of select surface treatments on thermal conductivity for formulations containing 20wt% BN in silicone

We have explored the chemical functionalization of BN particles of various sizes and morphologies and the compatibilization of those particles with different silicone formulations. We have demonstrated via spectroscopic and gravimetric methods the presence of durable silicon in BN particle samples. We have screened a vast number of compounds as dispersants and discovered formulations with thermal conductivities as much as 13% higher than the simple BN-filled formulations. We have developed masterbatch formulations that improve dispersion of BN particles, determined by optical properties and image analysis methods. We have identified several formulations with the potential to serve as viable candidates for use as LED encapsulant materials.

Our approaches with LED device testing has been with samples that did not include any functionalization, primarily to establish most suited BN morphologies for improving thermal conductivities without impacting optical properties. Furthermore, impact of functionalization on operating conditions (high temperatures, UV light exposure) needs to be evaluated as well as this may impact device performance and life. While there is some promise shown with BN, some additional confirmation and optimization is needed. Functionalization chemistries may be applied after establishing such performance and reliability testing.

4.D. Device Testing

Select samples from the BN developed were sent to Lumileds for device testing. Initial LEDs tested were single LEDs and COB architectures. The BN used for these tests were smooth crystals (akin to the control BN samples used for Processes K, L , and M). These results were crucial for further BN development.

These first LEDs were used to verify the reduced phosphor temperature for chip-on-board (CoB) LED architectures. The CoB LED architecture is based on an LED array design where by a 36 die LEDs are attached onto a ceramic substrate. The mixture of a thixotropic agent, red and green phosphors, BN particles, and silicone are premixed to ensure uniform distribution and the liquid slurry is dispensed into the cavity. An image of a 9mm diameter COB is shown in Figure 21. The thickness of the phosphor/silicone/BN film is fairly thick, at approximately 400µm and the LEDs are driven at 100 to 200 mA per die.

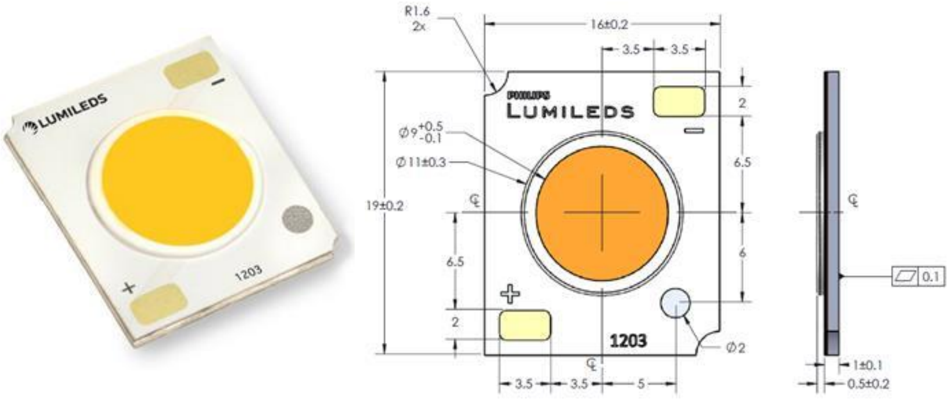

Figure 21. Luxeon COB

The phosphor temperature is typically measured by an IR camera imaging the top surface of the LED. Since the phosphor-silicone material has poor thermal conductivity, the top surface is representative of the maximum temperature of the LED device. This temperature of the phosphor and silicone mixture limits the operating conditions for drive current and heat sink temperature due to faster degradation.

Figure 22 shows the LED temperature comparison between the control silicone and silicone with 10% BN particles loaded. In the CoB structure, the phosphor temperature is reduced by almost 12 C at 600mA. As an example, the LED with BN particles can be driven at 600 mA and maintain the same silicone temperature as an LED without BN particles at 500mA. The impact is especially important in LED applications that require a high lumen density and long reliability.

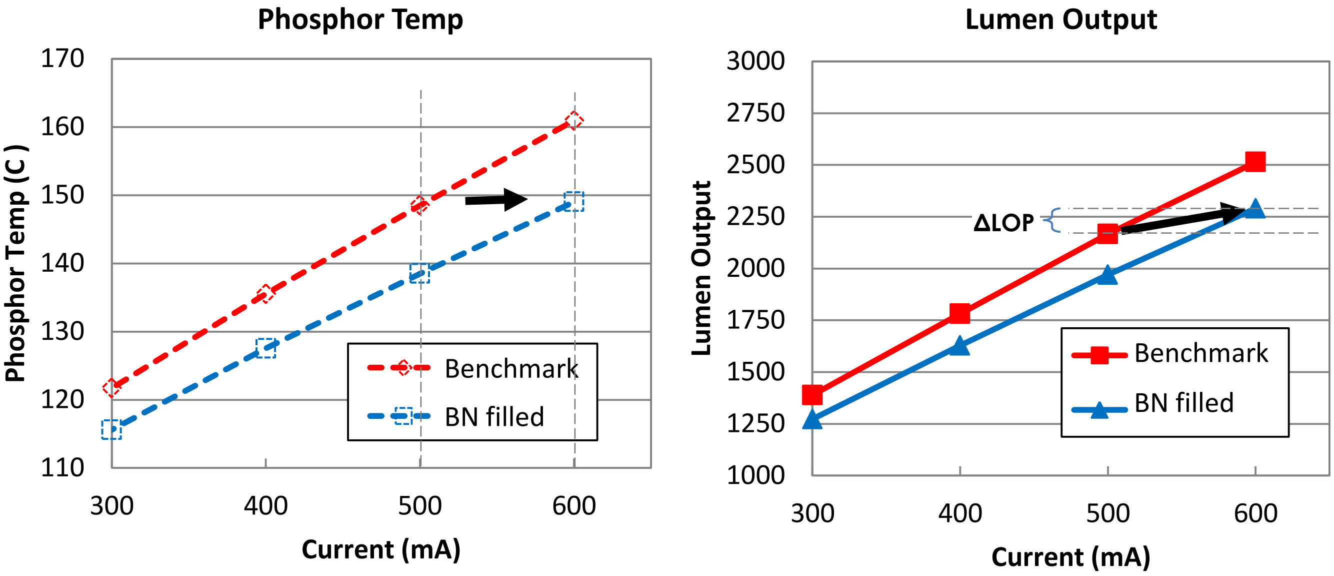

Figure 22: a) CoB Temperature measurement of LED silicone surface vs drive current at heat sink temperature of 85 °C, b) CoB Optical measurement of LED vs drive current at heat sink temperature of 85 °C.

The corresponding light output measurement shows that the addition of BN particles reduced the total light output by 6~7%. Current batches of the BN silicone mixture show optical scattering of 40% of the incoming light at 400-µm thickness. This light output loss of 7% is directly correlated to the optical scattering behavior. While the scattering caused a drop in light output, the net effect of reduced phosphor temp and increased scattering resulted in an improved total lumen output of ~5% at the same silicone temperature of 150 °C.

While these results were encouraging, there was significant variability in results during further trials. Subsequent samples (with BN from ongoing optimization trials) were tested by Lumileds to determine any improvement in phosphor temperatures and/ or light output. These trials were very challenging on the BN development due to scattering effects that seemed to impact light output, hence net-net did not show any appreciable performance benefit.

We evaluated various approaches to minimize scattering including developing higher aspect ratio particles, larger crystal sizes with smoother surfaces. We also looked at orientating the BN platelets in the resin to enable lowering BN wt% loading (thereby lessening the number of scattering surfaces). Except the most recent samples (Process P), % Transmission to thermal conductivity ratio did not improve significantly. Since scattering was the biggest issue confronting BN, from device stand point, focus was shifted to a different package architecture, one that had a much thinner dispersed phosphor layer.

In the new design, the phosphors and the BN are dispersed close to the chip and have a much thinner layer thickness (compared to COB), which is then encapsulated with a dome (Figure 23). All else being equal, for a given BN weight loading in the silicone, a thinner layer offered less number of scattering surfaces while providing similar thermal conductivity.

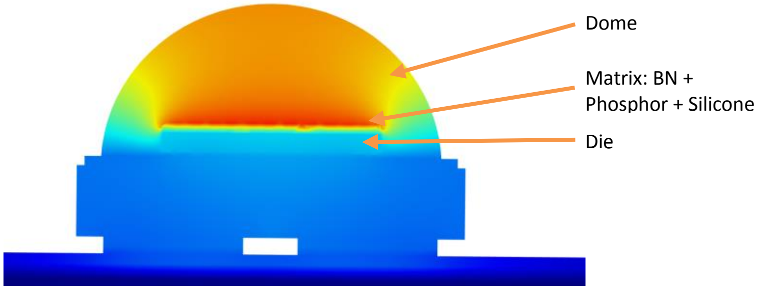

Figure 23. Schematic of thermal pathway in LED device and a different device design for current trials.

While this device design is more applicable to high power systems, it can be used to validate this concept. If pertinent, this could be studied for adaptability to mid power systems.

Thermal simulation was run for this device with different scenarios such as the thermal conductivities of the phosphor layer and the dome. The results are shown in Table 7. Improvement in phosphor layer thermal conductivity shows good improvement in phosphor temperature. This type of design allows for high drive applications, and may run at ~70A/cm2, providing further impactful reduction in Tp.

Table 7. Thermal simulation results with a phosphor matrix layer and dome.				
Scenario	$K_{\text{Phosphor Layer}}$ (W/mK)	K_{Dome} (W/mK)	Tp, max ('C)	Tp, avg ('C)
1	**0.2**	0.2	108.9	103.4
2	**0.2**	1	105.7	100.9
3	**1**	0.2	99.4	97.1
4	**1**	1	98.8	96.7

LED device was fabricated with the BN dispersed along with the phosphor in the matrix layer. While a higher BN loading could have been tested, only 4 wt%) was used initially. The BN grade used in this trial was a variation from the 'control BN' that had controlled particle size to minimize the number of finer particles to provide improved optical properties. It had a thermal conductivity of ~0.267W.mK and %T of 91.4% (as measured at 10wt% loading in RTV615 resin).

There was no discernable difference between the BN and non-BN control sample in terms of light output which was very encouraging (Figure 24). This can be attributed to the low BN+phosphor layer thickness.

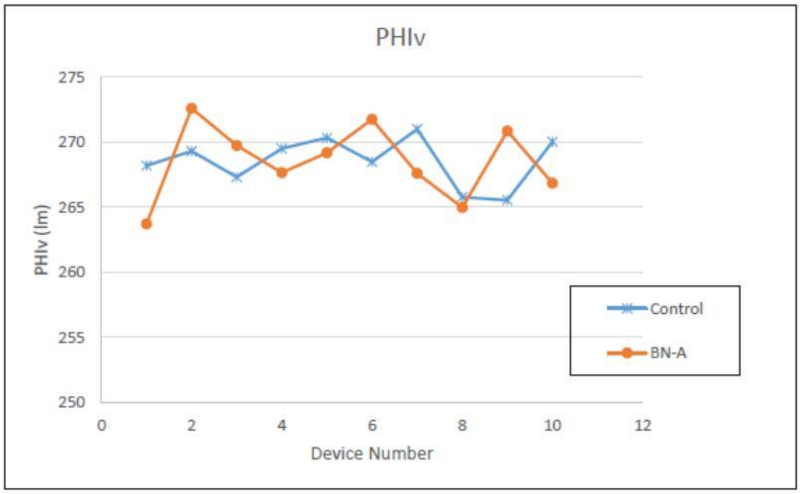

Figure 24.Light output from multiple measurements. There was negligible difference between the control and BN + Phosphor samples.

However, in terms of Phosphor junction temperature, there was not a significant improvement despite considerable scatter in these results. The low BN loading probably was not sufficient to impact the phosphor temperatures.

Based on the above results, it was decided to increase the BN content to 8wt% (2x) to improve thermal properties while maintaining the optical properties. Also, a “cool white” device with lower phosphor content compared to the earlier device was envisioned since thermal challenges are more critical for lower loading films. Separately, BN+phosphor films were fabricated for thermal conductivity testing and were tested using Laser flash (measured by folding the films 2x and 4x to enable consistent measurements). The results are shown in Figure 25. Due to high phosphor loading, the phosphor only system had inherently higher thermal conductivities. Despite this, there is ~0% improvement in thermal conductivities.

This formulation was tested in the device: there was not a significant impact to optical properties, which was very encouraging. However, phosphor temperature has not been measured yet and is undergoing testing for thermal performance at Lumileds.

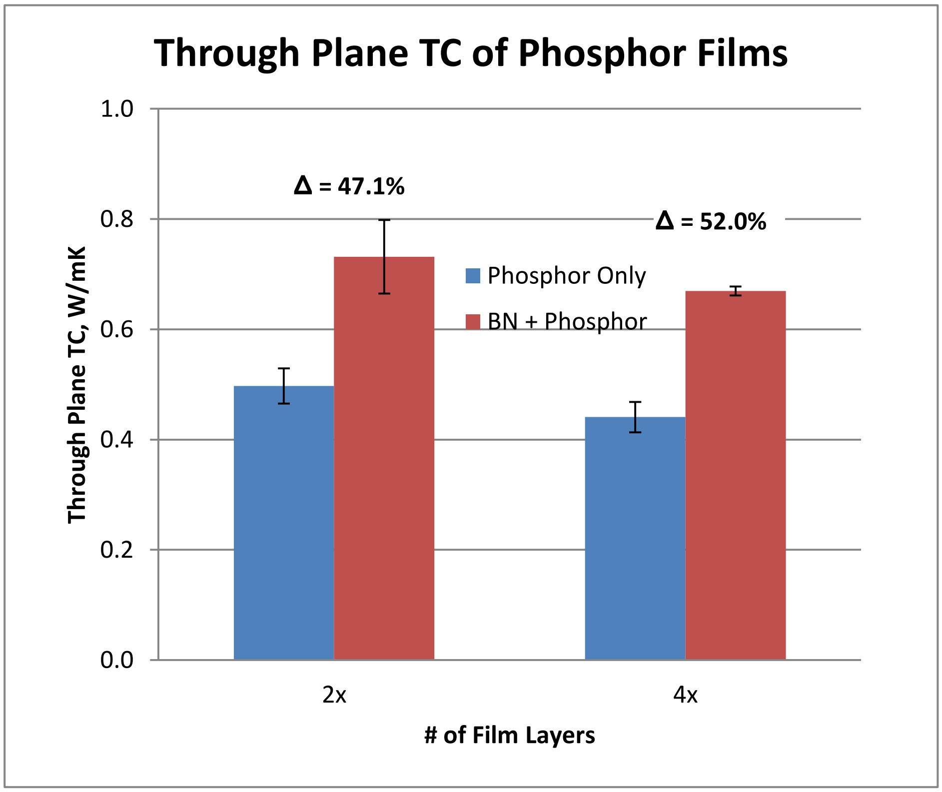

Figure 25. Through plane thermal conductivities measured via Laser flash for the Phosphor only and BN + Phosphor films for the next formulation.

4.E. Next Steps

The device testing from the above formulation will determine if BN + phosphor formulations can provide improved thermal performances while maintaining optical properties/ light outputs. If the results are promising, we would like to evaluate the optimized BN morphologies from Process P above in these devices to validate their performance. This should give us sufficient data to determine our next stage of activities. If the results show promise, we would like to evaluate these materials for reliability testing to evaluate their response to color stability and other properties for life cycle. Based on these results, we will determine to move forward with commercialization discussions and activities.

5	**Identify products developed under the Award and technology transfer activities, such as:**	
a	Publications (list journal name, volume, issue), conference papers, or other public releases of results. If not provided previously, attach or send copies of any public releases to the DOE Program Manager identified in Block 15 of the Assistance Agreement Cover Page; -	None
b	Web site or other Internet sites that reflect the results of this project;	None
c	Networks or collaborations fostered;	Collaborations with Case Western Reserve University (Prof. Liming Dai) and network with Univ. of Maryland (Prof. Liangbing Hu) were developed.
d	Technologies/Techniques;	Internal BN processing technologies were evaluated for this program. External approaches that were proprietary to the respective owners were evaluated for BN
e	Inventions/Patent Applications, licensing agreements; and	None
f	Other products, such as data or databases, physical collections, audio or video, software or netware, models, educational aid or curricula, instruments or equipment.	None