Novel Transparent Phosphor Conversion Matrix with High Thermal Conductivity for Next Generation Phosphor Converted LED-based Solid State Lighting

2016 Building Technologies Office Peer Review

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Project Summary

Timeline:
Start date: 10/01/2014
Planned end date: 09/30/2016

Key Milestones
1. theoretical prediction of hybrid encapsulant composition with high transparency; 04/25/14
2. synthesis of index-matched hybrid siloxane with >50 wt% inorganic content; 03/16/16

Budget:

Total Project $ to Date:
- DOE: $XX
- Cost Share: $XX

Total Project $:
- DOE: $1,499,999.00
- Cost Share: $434,775.00

Key Partners:

K. Matyjaszewski (CMU) | B. Ozdoganlar (CMU)
R. Davis (CMU) | M. Tchoul (OSI)
S. Shen (CMU) | M. Hannah (OSI)
J. Malen (CMU)
A. McGaughey (CMU)

CMU – Carnegie Mellon University, OSI – OSRAM Sylvania

Project Outcome:
In this project, novel high thermal transmittance siloxane encapsulant materials based on polysiloxane-grafted Al₂O₃ and ZnO particle fillers with thermal conductivities approaching 1 W/mK will be developed. To date the synthesis of ZnO-siloxane hybrid particles and their processing into encapsulants with >50 wt% inorganic content has been demonstrated. Current focus is on photothermal stability and conductivity evaluation.
**Problem Statement:** 20-30% of the absorbed energy of phosphors is lost due to Stokes loss and <1 QE. Low thermal conductivity of current siloxane encapsulants gives rise to heat accumulation in phosphors during operation of pc-LEDs. Heating of phosphors is predominant cause for efficiency loss and lifetime limitation.

**pc-LED scheme**

![Diagram of pc-LED scheme](image)

**phosphor efficiency profile (OSI)**

<table>
<thead>
<tr>
<th>T (phosphor cast layer), °C</th>
<th>0</th>
<th>100</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ (phosphor cast layer), W/m*K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yellow phosphor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Red phosphor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T (cast layer)</td>
<td></td>
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</table>

**State of the art**

- Yellow phosphor
- Red phosphor

*courtesy of OSRAM Sylvania*
Purpose and Objectives

Problem Statement: Low thermal conductivity of current siloxane encapsulants gives rise to heat accumulation in phosphors during operation of pc-LEDs. Heating of phosphors is predominant cause for efficiency loss and lifetime limitation.

Target Market and Audience: The new material technology targets improvements primarily in the design of volume cast mid-power pc-LEDs. Because of low cost volume-cast mid-power LEDs find application in back- and display lighting as well as general lighting applications.

Impact of Project: The availability of encapsulants with a thermal conductivity of $k \sim 1$ W/(m K) is projected to increase the efficiency of phosphors in LEDs operating consistently at 35 A/cm$^2$ up to 95% of the 25 °C values. This will translate in improved efficiency, reliability, & marketability of pc-LED technologies. The specific performance goals of this project are:

1. Near term: demonstrate hybrid encapsulant with $k \sim 1$ W/(m K) with adequate photothermal stability
2. Mid term: develop methodology for scale-up & integration
3. Long term: demonstrate commercial viability/commercialization
Approach

**Scope of Research:** Apply novel theoretical models to predict ‘particle-surfactant compositions’ that enable increased thermal transport and reduced optical scattering. Apply novel surface polymerization techniques to synthesize particle fillers matched to predicted optimum compositions, integrate particles into hybrid siloxanes, demonstrate improved thermal transport and photothermal stability and evaluate materials in pc-LED device architectures.

scheme of hybrid encapsulant

![Scheme of Hybrid Encapsulant](image-url)
Concept:

use surface polymerization processes to engineer surface properties of particle fillers to enable:

- increase of thermal conductance of particle/matrix interface
  - enable higher $k_{\text{eff}}$ at reduced inorganic loading

- uniform dispersion of particle within matrix
  - reduce scattering losses, improve auxiliary physical properties

- reduction of the scattering cross section of particle fillers
  - enable higher optical transparency at given inorganic loading
## Approach

### Work Breakdown: 2 performance periods – 10 research tasks

<table>
<thead>
<tr>
<th>Task 1</th>
<th>synthesis of polymer-tethered particle fillers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Task 2</td>
<td>modeling of thermal transport properties</td>
</tr>
<tr>
<td>Task 3</td>
<td>modeling of optical properties Transparency</td>
</tr>
<tr>
<td>Task 4</td>
<td>forming schemes for hybrid siloxane model systems</td>
</tr>
<tr>
<td>Task 5</td>
<td>evaluation of photothermal stability of polymer/particle constituents</td>
</tr>
<tr>
<td>Task 6</td>
<td>synthesis of siloxane/particle hybrid materials</td>
</tr>
<tr>
<td>Task 7</td>
<td>characterization of thermal transport properties</td>
</tr>
<tr>
<td>Task 8</td>
<td>characterization of optical properties (scattering, absorption)</td>
</tr>
<tr>
<td>Task 9</td>
<td>processing of hybrid encapsulants &amp; test sample preparation</td>
</tr>
<tr>
<td>Task 10</td>
<td>evaluation of photothermal stability, integration, &amp; performance</td>
</tr>
</tbody>
</table>
Approach

Key Issues:

(1) optimize mechanical properties of hybrid siloxanes to facilitate evaluation of photo-thermal stability and device integration

Distinctive Characteristics:

(1) Project addresses foundational challenge. Low thermal conductivity (photothermal stability) of existing encapsulants is relevant to host of degradation and failure pathways.

(2) Broad technology significance. High thermal conductivity encapsulants would be relevant to a range of distinct LED architectures & outside of SSL arena
Accomplishments - 1: Predicting the role of ligands on thermal boundary resistance

**Lesson learned:** thermal boundary conductance ($G$) increases with coupling strength in Alkane-ZnO system. Use covalent bonds!!!
Accomplishments - 2: Predicting the role of ligands on optical properties of particle filled siloxanes

**Figure**
Calculated scattering cross section of $d = 30$ nm alumina particles grafted with PMMA embedded in siloxane encapsulant ($n = 1.55$, refractive index value provided by Dow Corning).

**lesson learned:** reduction of scattering cross section by three orders of magnitude possible. Prescription of ‘optimum compositions’.
Progress and Accomplishments

Accomplishments - 3: Synthesis of organic (polymer) modified Al$_2$O$_3$/ZnO

SI-Atom-Transfer Radical Polymerization

material systems (partial list)

<table>
<thead>
<tr>
<th>Particle</th>
<th>Polymer</th>
<th>$N$</th>
<th>$\sigma$ (nm$^2$)</th>
<th>$\Phi_{\text{inorg}}$ (%)</th>
<th>approx. amount (mg)</th>
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<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>PMMA</td>
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<td>0.35</td>
<td>90</td>
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<td>PSAN</td>
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<td>PSAN</td>
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<td>NA</td>
<td>29</td>
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</tbody>
</table>

particle sources:
Al$_2$O$_3$ commercial - d ~ 30 nm; ZnO: commercial – d = 30 nm; synthesis - d = 5 nm

lesson learned: developed method for surface activation, excellent control of particle/polymer composition, dense grafting possible
Progress and Accomplishments

**Accomplishments** - 4: Synthesis of hybrid siloxanes

**FROM:** PPMS/ZnO-siloxane  
\[ f_{\text{ZnO}} = 30 \text{ wt}\% \]

**TO:** PPMS/ZnO novel surfacant system  
\[ f_{\text{ZnO}} = 40 \text{ wt}\% \]

\[ k = 0.5 \text{ W/m K} \quad \text{TO:} \quad k = 0.62 \text{ W/m K} \]

**lesson learned:** ligand chemistry facilitates control of particle dispersion, reduction of scattering cross section & enhanced thermal conductivity of hybrid siloxanes
Progress and Accomplishments

Accomplishments - 5: Photothermal Stability Study

**lesson learned:** siloxanes exhibit superior photothermal stability (PDMS > PPMS) acrylate-based polymers potentially compatible with pc-LED design reduction of density of heteroatoms increases stability
Project Integration and Collaboration

**Project Integration**: Work Breakdown

- **material synthesis**
- **thermal model. & characterization**
- **processing & characterization**
- **material integration & testing**
- **optical model. & characterization**
Project Integration and Collaboration

Project Integration: Team

- Matyjazewski
  MB, Dow Corning

- Malen McGaughey
  MB, OSI

- Ozdoganlar Bockstaller

- Davis Shen
  MB, OSI

- Tchoul
  OSRAM Sylvania
Progress and Accomplishments

Accomplishments - 5: Publications to date


Other accomplishments

8 invited presentations at National Meetings of American Chemical Society & American Physical Society

4 students graduated
Next Steps and Future Plans

**Task Breakdown:** Performance Period II

**6.1:** Functionalization of PMMA@Al2O3/PMMA@ZnO

**6.2:** Synthesis of siloxane/PMMA@Al2O3, siloxane/PMMA@ZnO encapsulants

**6.3:** Functionalization of PSAN@Al2O3/PSAN@ZnO

**6.4:** Synthesis of siloxane/PSAN@Al2O3, siloxane/PSAN@ZnO encapsulants

**7.1:** FDTR and heat flow measurements on siloxane

**7.2:** FDTR and heat flow measurements on siloxane/PMMA@Al2O3

**7.3:** FDTR and heat flow measurements on siloxane/PMMA@ZnO

**7.4:** FDTR and heat flow measurements on PSAN hybrids

**8.1:** Optical (UV/vis) characterization of siloxane

**8.2:** Optical (UV/vis) characterization of siloxane/PMMA@Al2O3

**8.3:** Optical (UV/vis) characterization of siloxane/PMMA@ZnO

**8.4:** Optical (UV/vis) characterization of PSAN hybrids

**9.1:** Micro-molding of siloxane in lens shape

**9.2:** Rheology and DMA of hybrid encapsulants

**9.3:** Micro-molding of siloxane/PMMA@ZnO (Al2O3)

**9.4:** Micro-molding of PSAN hybrids

**10.1:** Photo-thermal stability study of PSAN@ZnO

**10.2:** Evaluation of siloxane/PMMA@Al2O3 and DCMS system

**10.3:** QE measurements on siloxane/PMMA@ZnO (Al2O3)/phosphor system

**10.4:** QE measurements on siloxane/PSAN@ZnO(Al2O3)/phosphor systems

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*green* – completed

*orange* – ongoing

*black* – not yet started
REFERENCE SLIDES
Project Budget

Project Budget: $1,499,999.99 (DOE), $1,934,774.00 (total)
Variances: n/a
Cost to Date: information could not be retrieved in time for review
Additional Funding: n/a

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<tr>
<td>DOE</td>
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<tr>
<td>749,998.00</td>
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**Project Plan and Schedule**

**Performance Period I: Milestones**

**M 1.1:** 1g PMMA@Al2O3 with N ~10-100 and \( \bar{\rho} \) ~ 0.1-0.7 nm\(^{-2}\)

**M 1.2:** 1g PSAN@Al2O3 with N ~ 10-100 and \( \bar{\rho} \) ~ 0.1-0.7 nm\(^{-2}\)

**M 1.3:** 1g PMMA@ZnO with N ~ 10-100 and \( \bar{\rho} \) ~ 0.1-0.7 nm\(^{-2}\)

**M 1.4:** 1g PSAN@ZnO with N ~ 10-100 and \( \bar{\rho} \) ~ 0.1-0.7 nm\(^{-2}\)

**M 2.1:** Establish framework for modeling of atomic interaction

**M 2.2:** Calculate thermal boundary resistance for different bond strength approximations

**M 2.3:** Establish equil. conformation of polymer tether

**M 2.4:** Calculate thermal transport properties of polymer graft layers for N ~ 10 – 100

**M 3.1:** eff. med. prediction of opt. properties of tethered particles

**M 3.2:** Mie calculation for core-shell particle systems corresponding

**M 3.3:** Predict PMMA@ZnO config. with 50% reduced C\(_{\text{scatt}}\) of PMMA@ZnO/siloxane/phosphor for d(ZnO) = 20 nm, f(ZnO) = 0.05-0.4, d(ph) = 5 \( \mu \)m, f(ph) = 0.4 by eff. med.

**M 3.4** Predict PMMA@ZnO config. with 50% reduced C\(_{\text{scatt}}\) of PMMA@ZnO/siloxane/phosphor for d(ZnO) = 20 nm, f(ZnO) = 0.05-0.4, d(ph) = 5 \( \mu \)m, f(ph) = 0.4 by Mie theory

**M 4.1:** Demonstrate measurement of mechanical properties of siloxane Intermediates

**M 4.2:** Demonstrate siloxane lens shape with diameter in the range 3-10 mm

**M 4.3:** Complete DoE analysis

**M 4.4:** Complete ANOVA. Fab. of siloxane lens shapes with surf. rough. < 200 nm and variability of <20%

**M 5.1:** trans. loss as f (int, T ) for I~ 0.1 – 1 W/cm\(^2\) and T ~ 25 – 150 °C of pristine polymers PSAN, PMMA

**M 5.2:** trans. loss as f (int, T ) for I~ 0.1 – 1 W/cm\(^2\) and T ~ 25 – 150 °C of PMMA@Al2O3

**M 5.3:** trans. loss as f (int, T ) for I~ 0.1 – 1 W/cm\(^2\) and T ~ 25 – 150 °C of PSAN@Al2O3

**M 5.4:** trans. loss as f (int, T ) for I~ 0.1 – 1 W/cm\(^2\) and T ~ 25 – 150 °C of PMMA@ZnO

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**green** – completed

**orange** – ongoing

**black** – not yet started
Project Plan and Schedule

Go/No-Go Decision Point  (June, 2015)

Demonstrate PSAN/PMMA-tethered ZnO/Al$_2$O$_3$ systems with composition consistent with minimal boundary resistance and scattering cross-section

Demonstrate photothermal stability of polymer/particle systems comparable to PPMS under pc-LED operating conditions
**Performance Period II: Milestones**

**M 6.1:** Demonstrate functionalization of PMMA@Al2O3/PMMA@ZnO using chemical analysis

**M 6.2:** Synthesis of 1g siloxane/PMMA@Al2O3, siloxane/PMMA@ZnO with f(ZnO) = 0.05-0.4

**M 6.3:** Demonstrate functionalization of PSAN@Al2O3/PSAN@ZnO using chemical analysis

**M 6.4:** Synthesis of 1g siloxane/PSAN@Al2O3, siloxane/PSAN@ZnO with f = 0.05-0.4

**M 7.1:** FDTR and/or heat flow measurements on siloxane with < 20% variability

**M 7.2:** FDTR and/or heat flow measurements on siloxane/PMMA@Al2O3 composites. Establish k for f = 0.05 – 0.4

**M 7.3:** FDTR and/or heat flow measurements on siloxane/PMMA@ZnO. Establish k for f = 0.05 – 0.4

**M 7.4:** FDTR and/or heat flow measurements on PSAN hybrids with f = 0.05 – 0.4. Establish compositions with k >= 1 W/mK

**M 8.1:** Determine optical abs and transmission of siloxane

**M 8.2:** Determine extinction cross section of siloxane PMMA@Al2O3 f = 0.05 – 0.4

**M 8.3:** Determine extinction cross section of siloxane PMMA@ZnO f = 0.05 – 0.4

**M 8.4:** Determine extinction cross section of PSAN hybrids with f = 0.05 – 0.4. Identify materials with trans >= 0.7/mm

**M 9.1:** Fabrication of siloxane lens-shaped specimen with d ~ 3-5 mm

**M 9.2:** Establish rheological and mechanical properties of hybrids

**M 9.3:** Siloxane/PMMA@ZnO and siloxane/PMMA@Al2O3 lens shape with d ~ 3 – 5 mm

**M 9.4:** Microforming of PSAN hybrids into lens shape with d ~ 3 – 5 mm

**M 10.1:** Trans loss as function of light intensity (0.1 – 1 W/cm2) and T = 25 – 150 °C of PSAN@ZnO

**M 10.2:** Rate of trans loss as function of light intensity (0.1 – 1 W/cm2) and T (25 – 150 °C) of siloxane/PMMA@Al2O3 and DCMS system.

Determine QE at 35 A/cm2

**M 10.3:** QE of siloxane/PMMA@ZnO and siloxane/PMMA@Al2O3 at 35 A/cm2

**M 10.4:** Determine QE of PSAN hybrid encapsulant DCMS at 35 A/cm2. Demonstrate QE >= 95% at 35 A/cm2

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**orange** – ongoing

**black** – not yet started