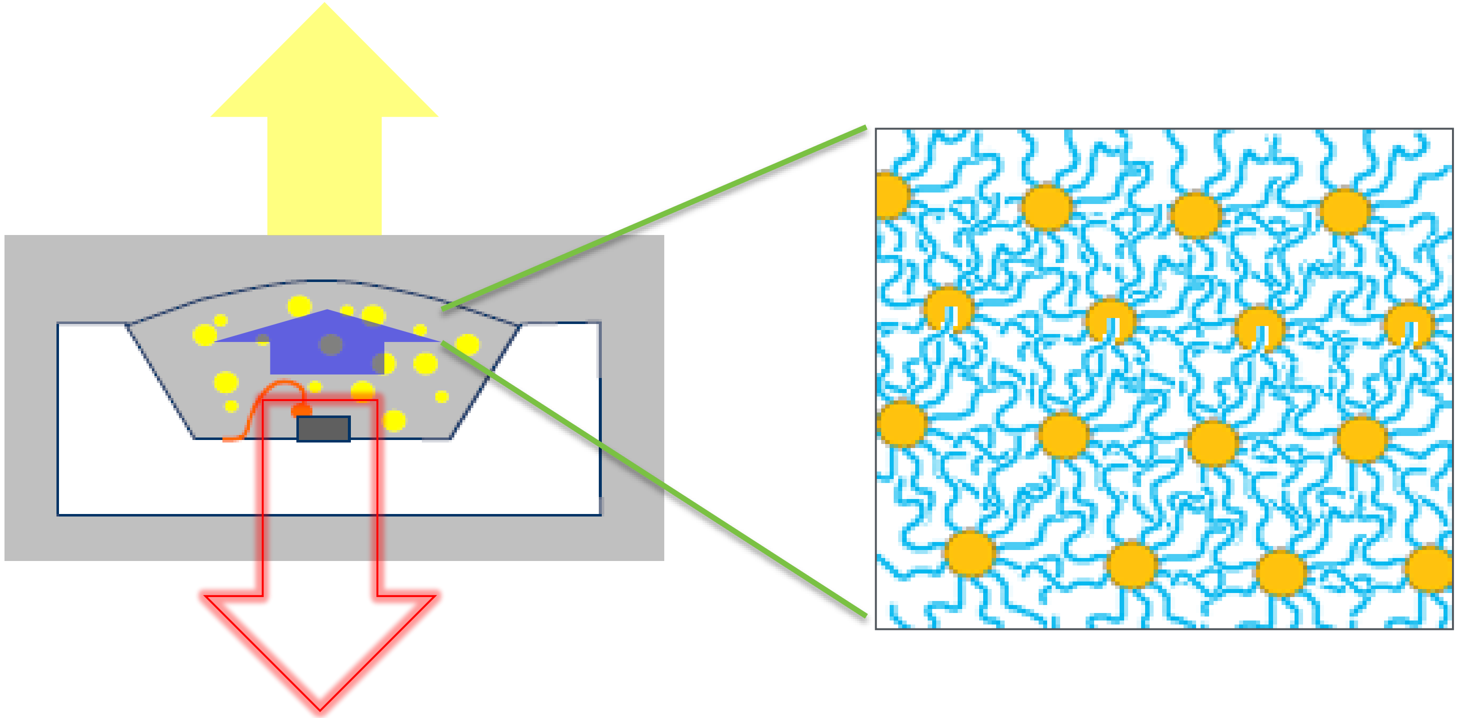
Novel Transparent Phosphor Conversion Matrix with High Thermal Conductivity for Next Generation Phosphor Converted LED-based Solid State Lighting

2016 Building Technologies Office Peer Review



U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

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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

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

Budget:

Total Project $ to Date:

- DOE: $XX
- Cost Share: $XX

Total Project $:

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

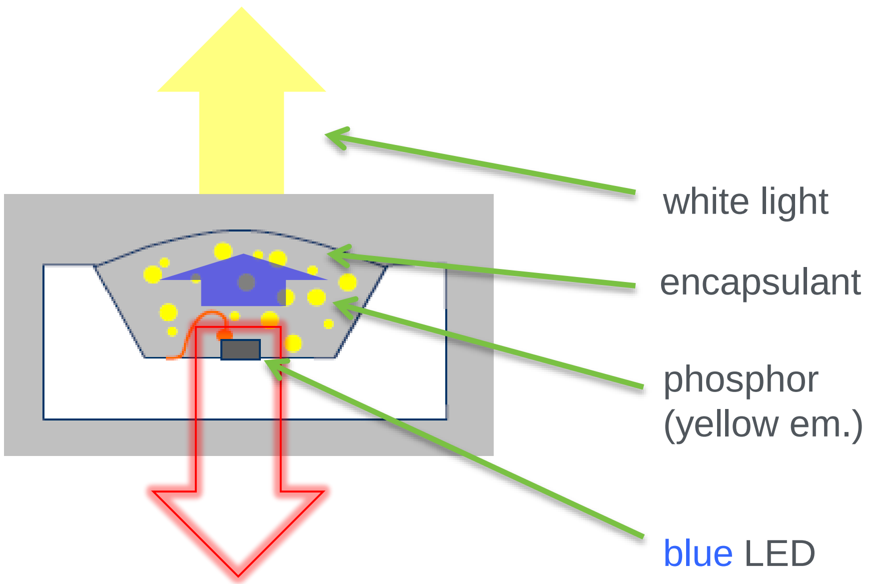
Project Outcome:

In this project, novel high thermal transmittance siloxane encapsulant materials based on polysiloxane-grafted Al_2O_3 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 photo-thermal stability and conductivity evaluation.

Purpose and Objectives

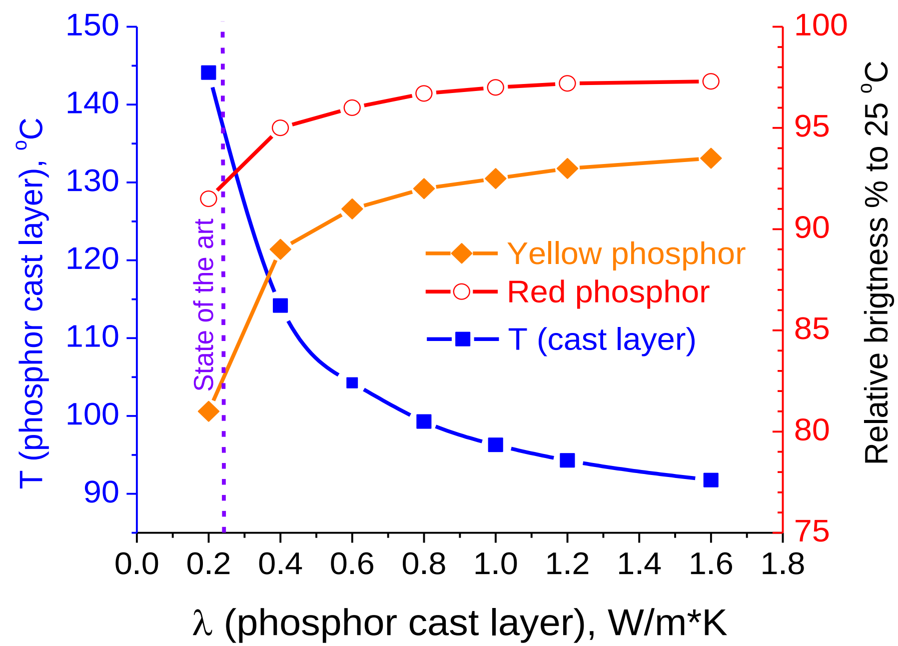
Problem Statement: 20-30 % of the absorbed energy of phsophors is lost due to Stokes loss and <1 QE. Low thermal conductivity of current siloxane encapsulants gives rise to heat accumulation in phosphors during operation of pc-LEDs. Heating of phosphors is predominant cause for efficiency loss and lifetime limitation.

pc-LED scheme



courtesy of OSRAM Sylvania

phosphor efficiency profile (OSI)



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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* ~ 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 ^oC 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* ~ 1 W/(m K) with adequate photothermal stability

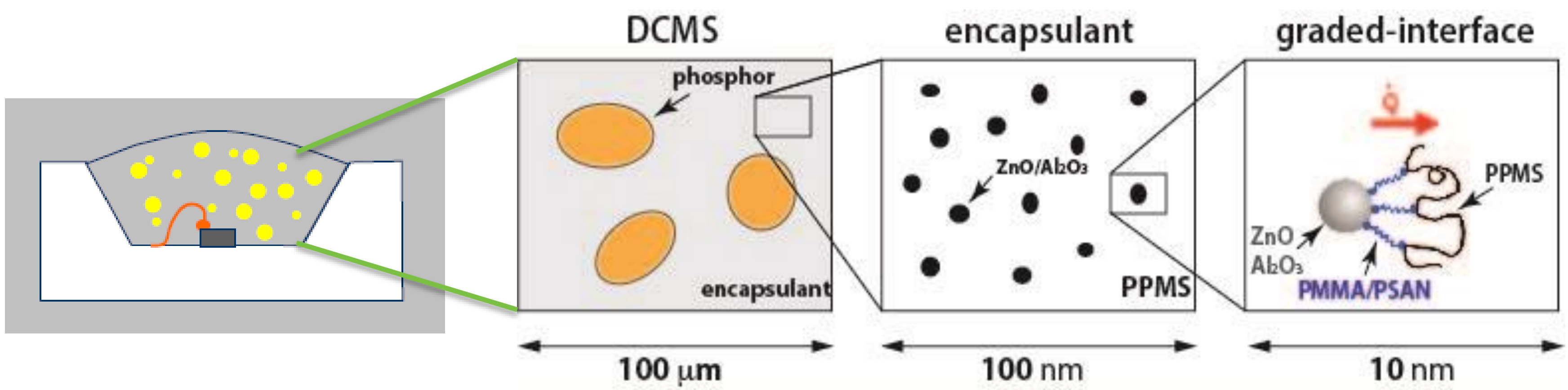
(2) Mid term: develop methodology for scale-up & integration

(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



Approach

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_{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

performance period I		**performance period II**	
Task 1	synthesis of polymer-tethered particle fillers	**Task 6**	synthesis of siloxane/particle hybrid materials
Task 2	modeling of thermal transport properties	**Task 7**	characterization of thermal transport properties
Task 3	modeling of optical properties Transparency	**Task 8**	characterization of optical properties (scattering, absorption)
Task 4	forming schemes for hybrid siloxane model systems	**Task 9**	processing of hybrid encapsulants & test sample preparation
Task 5	evaluation of photothermal stability of polymer/particle constituents	**Task 10**	evaluation of photothermal stability, integration, & performance

Approach

Key Issues:

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

Distinctive Characteristics:

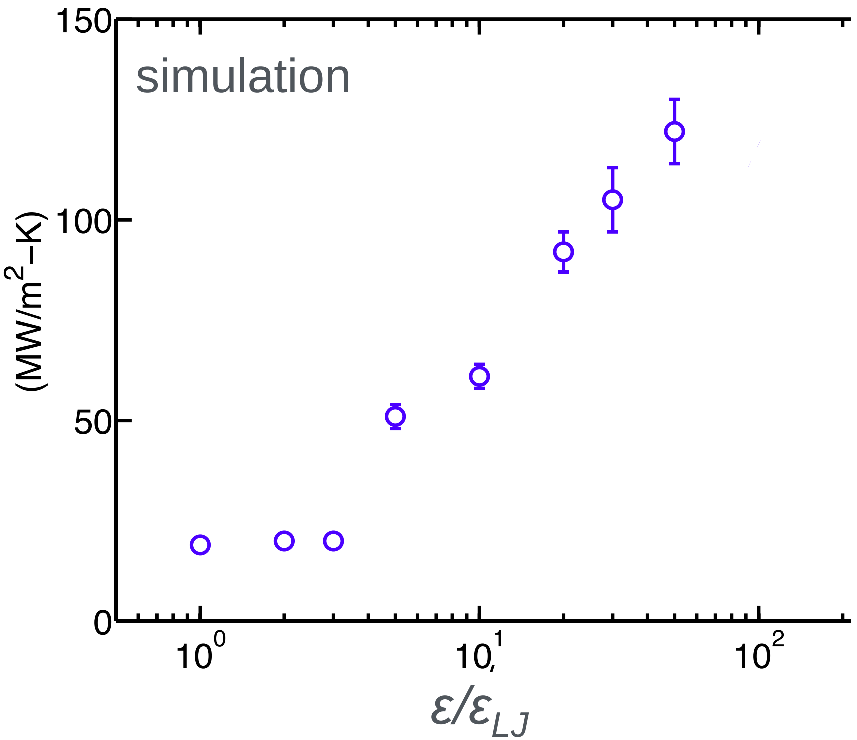
(1) Project addresses foundational challenge. Low thermal conductivity (photothermal stability) of existing encapsulants is relevant to host of degradation and failure pathways.

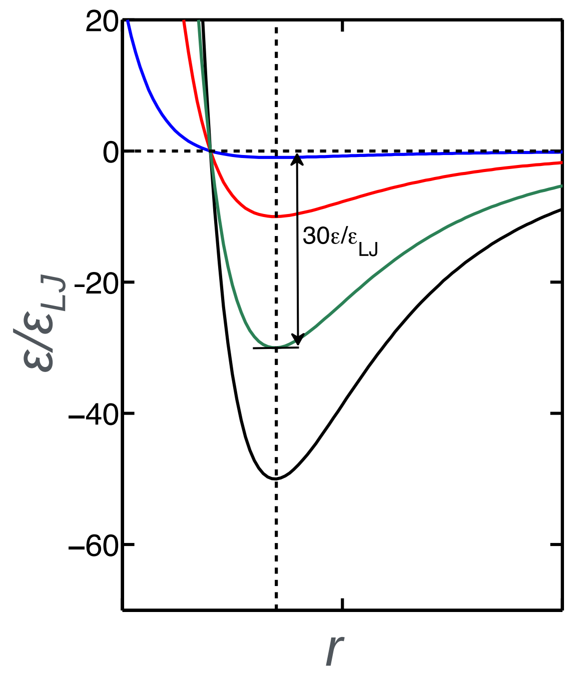
(2) Broad technology significance. High thermal conductivity encapsulants would be relevant to a range of distinct LED architectures & outside of SSL arena

Progress and Accomplishments

Accomplishments - 1: Predicting the role of ligands on thermal boundary resistance

MD simulation





lesson learned: thermal boundary conductance (*G*) increases with coupling strength in Alkane-ZnO system. Use covalent bonds!!!

courtesy: McGauhey, J. Malen

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Accomplishments - 2: Predicting the role of ligands on optical properties of particle filled siloxanes

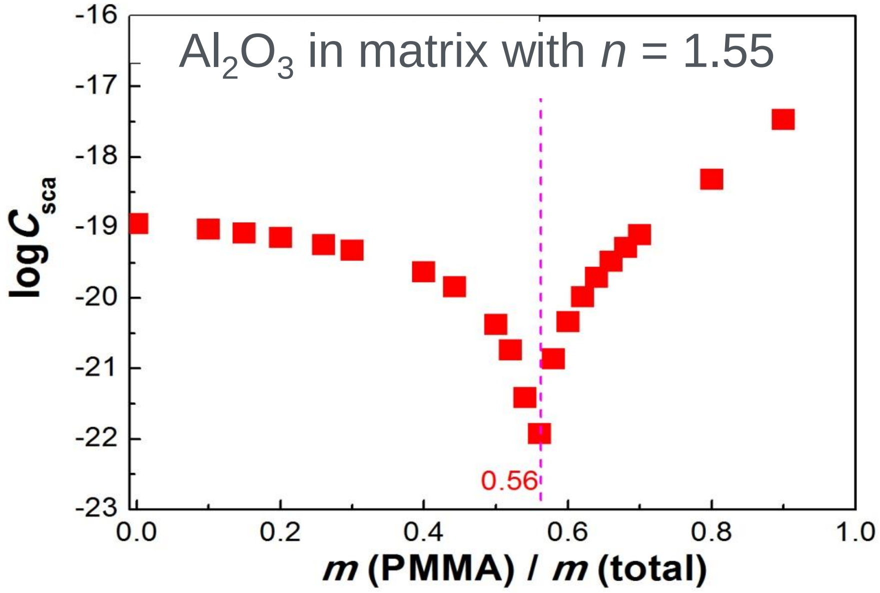


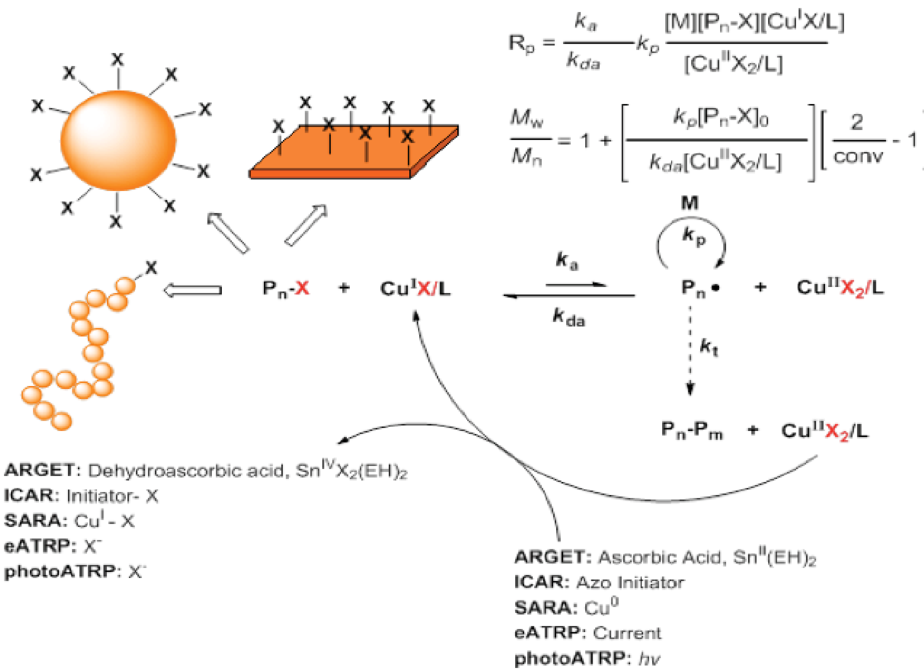
Figure
Calculated scattering cross section of d = 30 nm alumina particles grafted with PMMA embedded in siloxane encapsulant (n = 1.55, refractive index value provided by Dow Corning).

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_2O_3/ZnO

SI-Atom-Transfer Radical Polymerization



material systems (partial list)

Particle	Polymer	*N*	σ (nm^{-2})	ϕ_{inorg} (%)	approx. amount (mg)
Al_2O_3	PMMA	20-50	0.35	90	200
Al_2O_3	PMMA	350	NA	95	1000
Al_2O_3	PMMA	380	NA	93	1000
Al_2O_3	PMMA	NA	NA	34	500
Al_2O_3	PMMA	290	0.15	60	700
Al_2O_3	PSAN	230	0.01	92	700
Al_2O_3	PSAN	20-50	0.10	97	500
Al_2O_3	PSAN	16-24	0.50	92	500
Al_2O_3	PSAN	200	0.07	84	800
Al_2O_3	PSAN	8-32	0.25	91	500
ZnO	PMMA	2200	NA	15	500
ZnO	PMMA	137	0.06	92	200
ZnO	PMMA	1700	NA	36	1200
ZnO	PMMA	2000	NA	25	1400
ZnO	PSAN	25	NA	96	200
ZnO	PSAN	980	NA	44	600
ZnO	PSAN	400	0.10	96	200
ZnO	PSAN	1100	NA	29	350

particle sources:
Al_2O_3 commercial - *d* ~ 30 nm; ZnO: commercial – d = 30 nm; synthesis - *d* = 5 nm

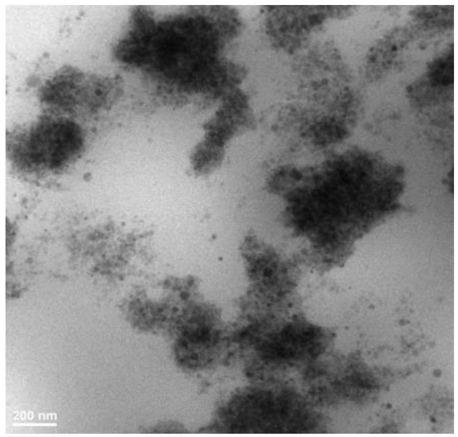
lesson learned: developed method for surface activation, excellent control of particle/polymer composition, dense grafting possible

Progress and Accomplishments

Accomplishments - 4: Synthesis of hybrid siloxanes

FROM: PPMS/ZnO-siloxane

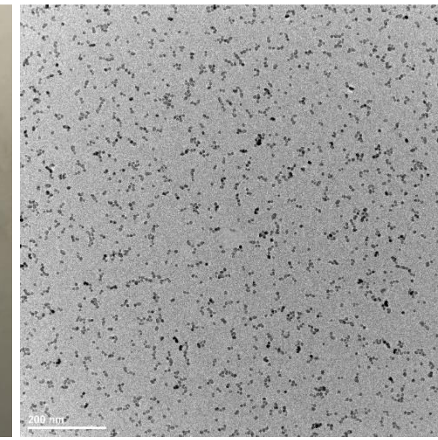
f_{ZnO} = 30 wt%



k = 0.5 W/m K

TO: PPMS/ZnO novel surfacant system

f_{ZnO} = 40 wt%



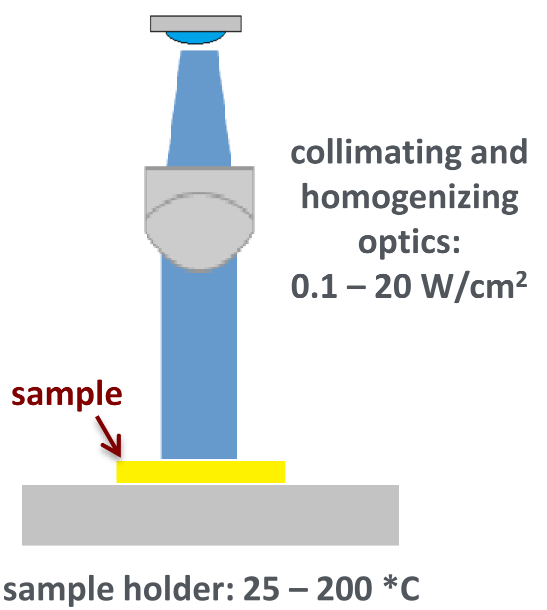
k = 0.62 W/m K

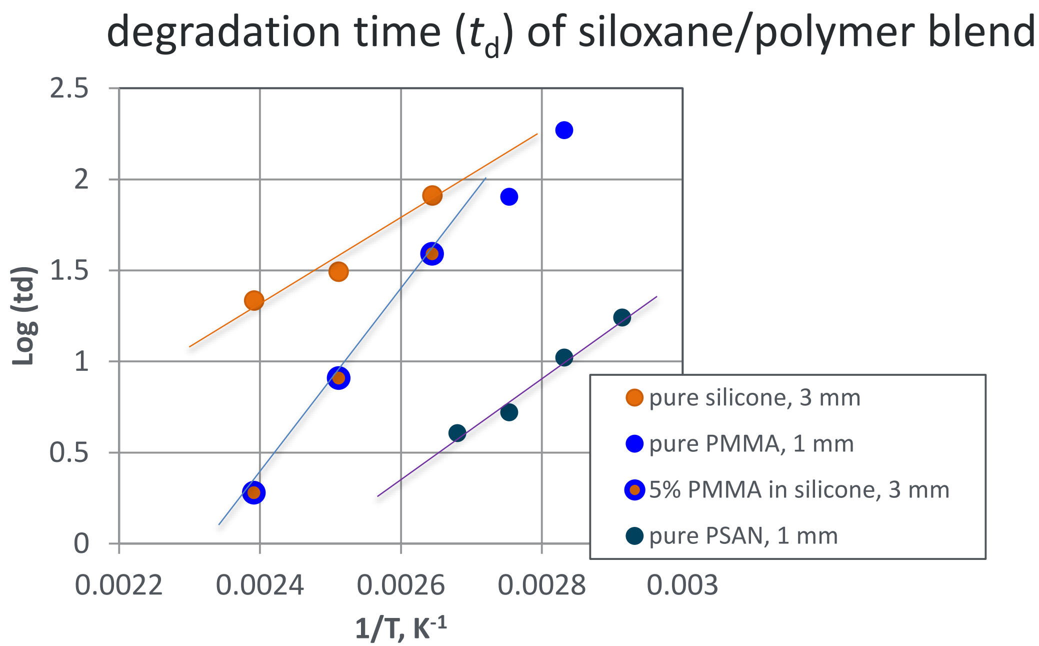
lesson learned: ligand chemistry facilitates control of particle dispersion, reduction of scattering cross section & enhanced thermal conductivity of hybrid siloxanes

Progress and Accomplishments

Accomplishments - 5: Photothermal Stability Study

courtesy: OSRAM Sylvania

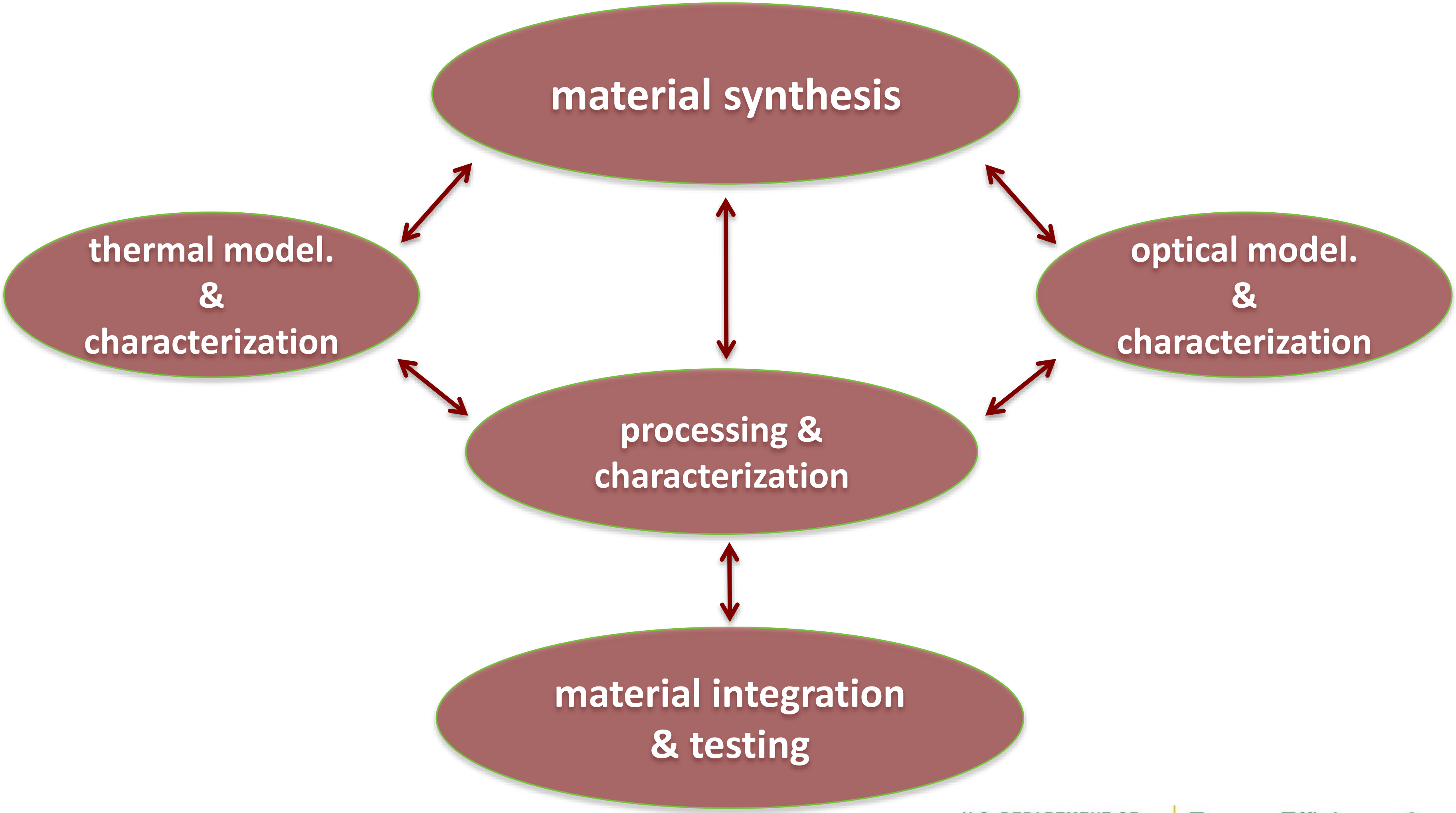




lesson learned: siloxanes exhibit superior photothermal stability (PDMS > PPMS)
acrylate-based polymers potentially compatible with pc-LED design
reduction of density of heteroatoms increases stability

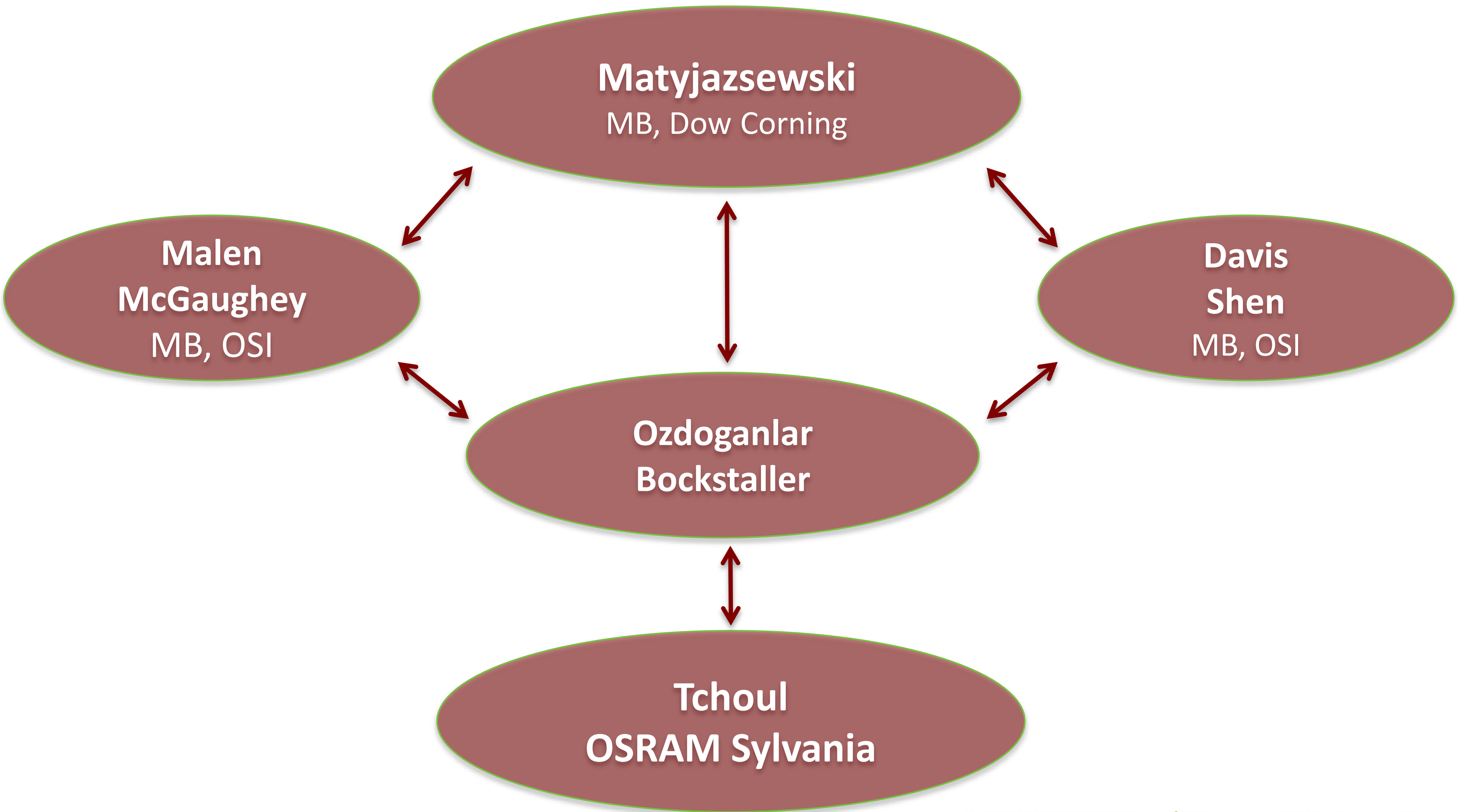
Project Integration and Collaboration

Project Integration: Work Breakdown



Project Integration and Collaboration

Project Integration: Team



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Progress and Accomplishments

Accomplishments - 5: Publications to date

Langmuir **2014** – *Chem. Mater.* **2014** – *Appl. Mater. & Int.* **2014** – *Macromolecules* **2014** – *ECS J. Sol. Sci. & Tech.* **2014** – *Polymer* **2015** – *Polymer* **2015** – *Nature Comm.* **2015** – *Macromolecules* **2016** – *Appl. Mater. & Int.* **2016** – *Soft Matter* **2016** – *Farad. Dis.* **2016** •••

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

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

Budget History					
10/01/2014 – FY 2015 (past)		FY 2016 (current)		FY 2017 – Insert End Date (planned)	
DOE	Cost-share	DOE	Cost-share	DOE	Cost-share
749,998.00	204,174.00				

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Project Plan and Schedule

Performance Period I : Milestones

M 1.1: 1g PMMA@Al2O3 with N ~10-100 and ~ 0.1-0.7 nm-2
M 1.2: 1 g PSAN@Al2O3 with N ~ 10-100 and ~ 0.1-0.7 nm-2
M 1.3: 1g PMMA@ZnO with N ~ 10-100 and ~ 0.1-0.7 nm-2
M 1.4: 1g PSAN@ZnO with N ~ 10-100 and ~ 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 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 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_scatt of PMMA@ZnO/siloxane/ phosphor for d(ZnO) = 20 nm, f(ZnO) = 0.05-0.4, d(ph) = 5 m, f(ph) = 0.4 by eff. med.
M 3.4 Predict PMMA@ZnO config. with 50% reduced C_scatt of PMMA@ZnO/siloxane/ phosphor for d(ZnO) = 20 nm, f(ZnO) = 0.05-0.4, d(ph) = 5 m, f(ph) = 0.4 by Mie theory

M 5.1: trans. loss as f (int, *T*) for I~ 0.1 – 1 W/cm2 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/cm2 and T ~ 25 – 150 °C of PMMA@Al2O3
M 5.3: trans. loss as f (int, *T*) for I~ 0.1 – 1 W/cm2 and T ~ 25 – 150 °C of PSAN@Al2O3
M 5.4: trans. loss as f (int, *T*) for I~ 0.1 – 1 W/cm2 and T ~ 25 – 150 °C of PMMA@ZnO

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_2O_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

Project Plan and Schedule

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 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 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 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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