Exploring Optical Nonlinearities of Glass Nanocomposites Made of Bimetallic Nanoparticles and Mesogenic Metal Alkanoates

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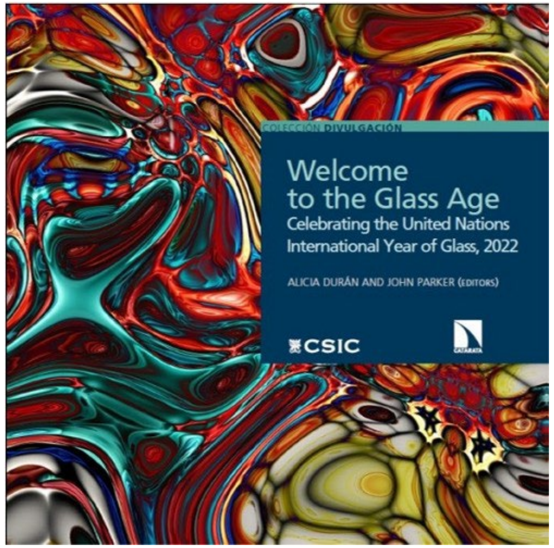
Motivation:
New optical and nonlinear-optical materials for new applications
Merging liquid crystals, glass science and nanotechnology



https://www.iyog2022.org/

INTERNATIONAL YEAR OF GLASS 2022

https://www.optica.org/en-us/history/milestones/international_year_of_glass/

The American Ceramic Society
www.ceramics.org
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INTERNATIONAL YEAR OF GLASS 2022

Outline

Introduction: metal alkanoates as glass forming ionic liquid crystal materials

Nanoparticles embedded in smectic glass

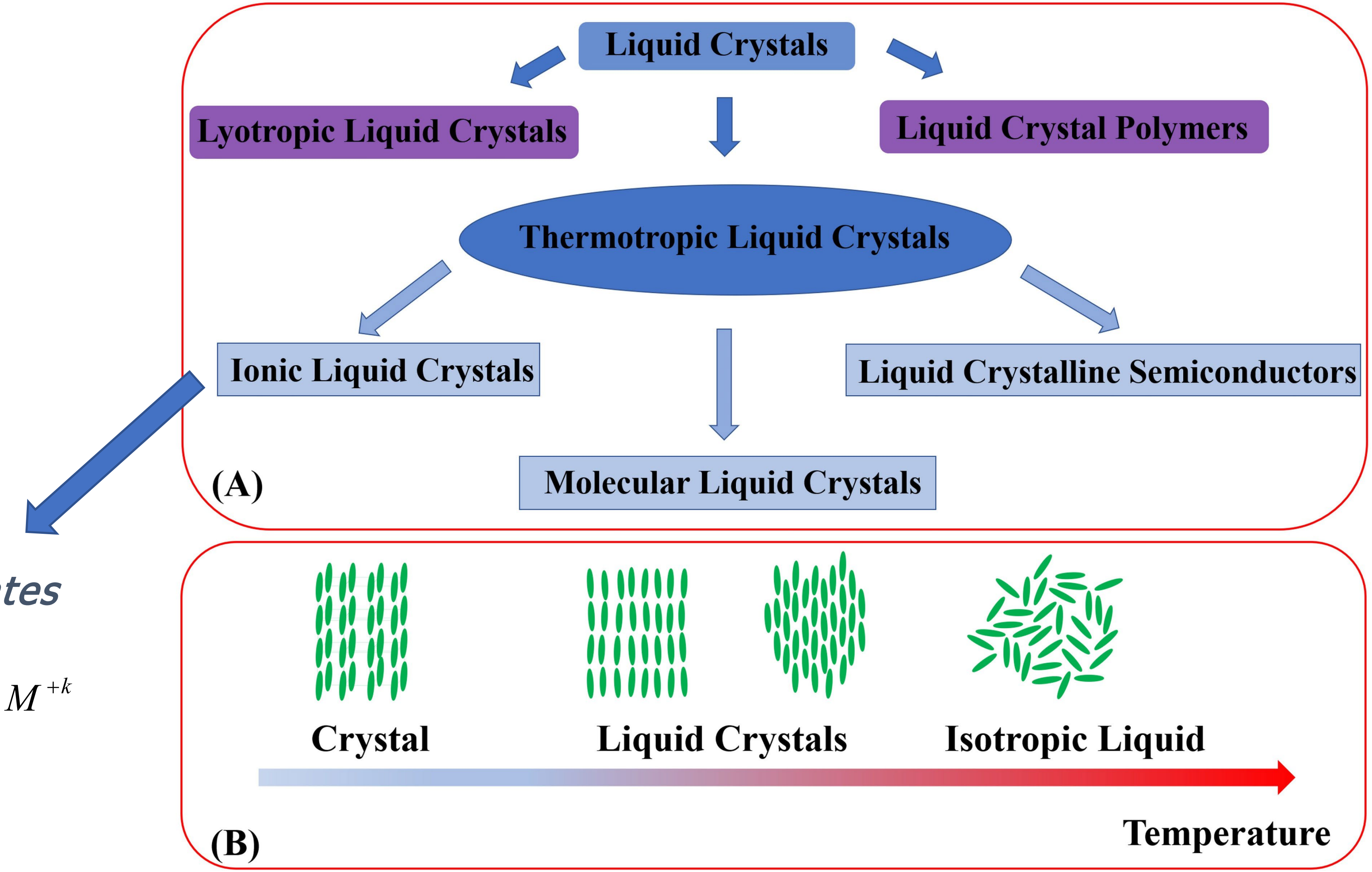
- **Materials:**
- **Spherical metal (Ag, Au) nanoparticles in CdC8**
- **Core-shell bimetallic (Ag, Au) nanoparticles in CdC8**
- **Experimental setup**
- **Nonlinear-optical response**

Conclusion

Introduction: metal alkanoates as glass forming ionic liquid crystal materials

metal alkanoates

$$\left(C_nH_{2n+1}COO^-\right)_2^{-\frac{k}{2}} M^{+k}$$



Y. Garbovskiy 2021 *Nano Ex.* **2** 012004

Polymorphism of metal alkanoates

$$\left(C_nH_{2n+1}COO^-\right)_2^{-\frac{k}{2}}M^{+k}$$

Some examples of metal cation

Me – K, Na, Cs, Li, Ag, Tl (k=1);

Co, Pb, Ba, Ca, Mg, Cu (k=2);

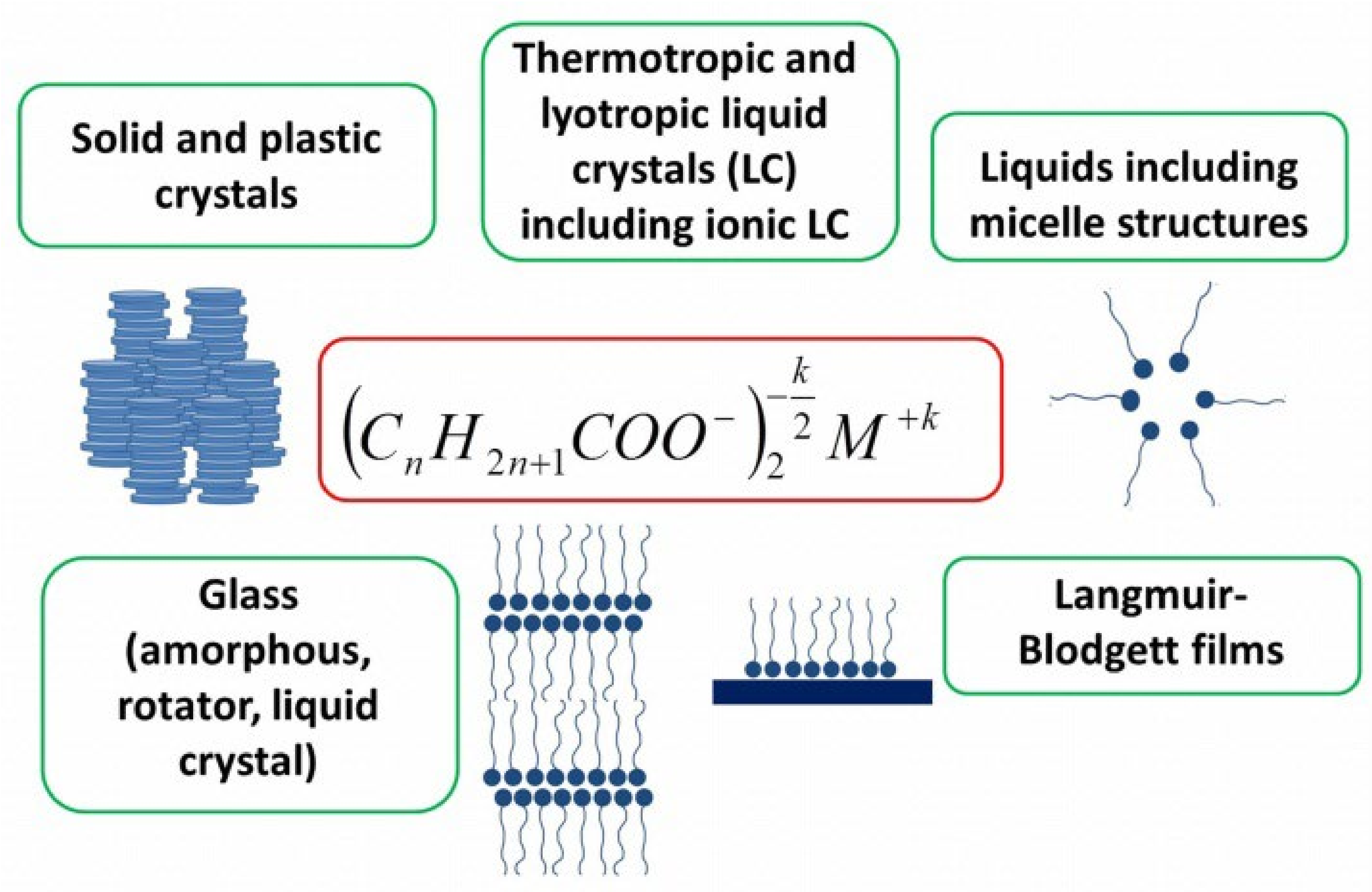
La, Nd, Eu (k=3)

Multiple choices to design materials

- **Vary the length of the alkanoate anion**
- **Vary the type of metal cation**
- **Mixing several components (binary, ternary etc.)**

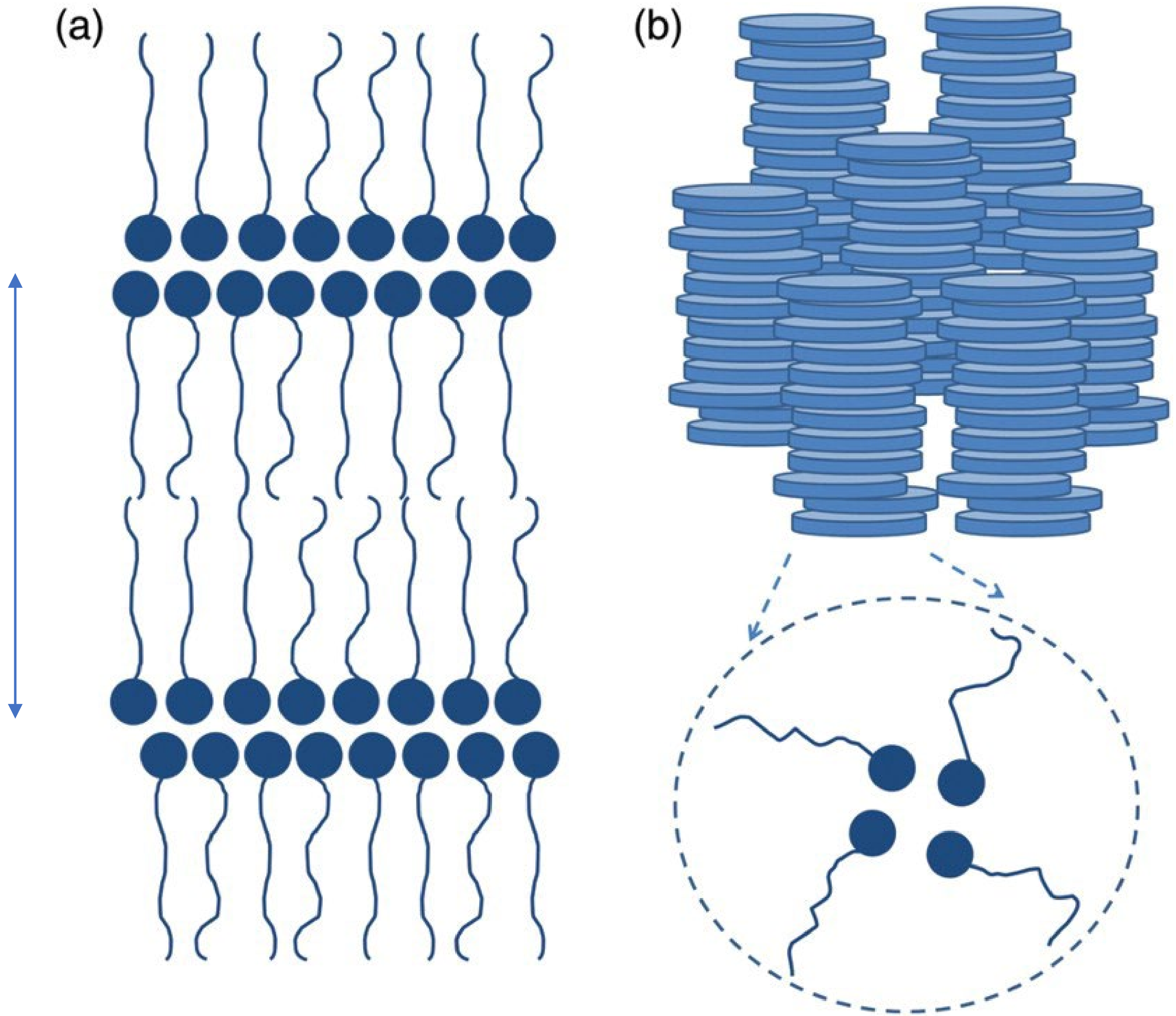
G. Klimusheva, T. Mirnaya & Y. Garbovskiy, Liquid Crystals Reviews, **2(1)**; 28-57 (2015).

Polymorphism of metal alkanoates



J Therm Anal Calorim. 2012;108:399–413.
Liquid Crystals Reviews, **2(1)**; 28-57 (2015).

Polymorphism of metal alkanoates: bi-layered (a) and columnar (b) structures

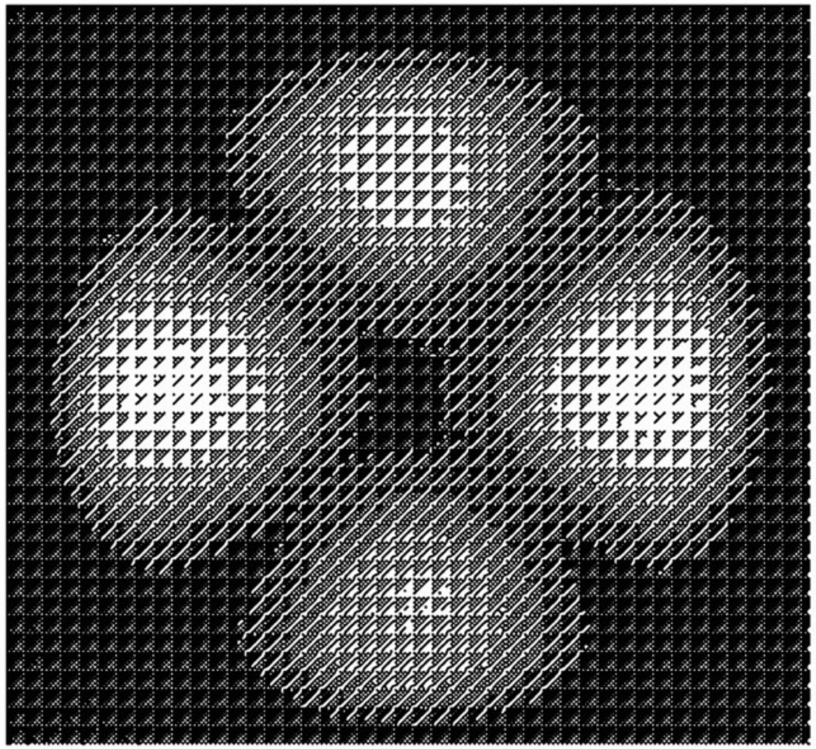


Liquid Crystals Reviews, **2(1)**; 28-57 (2015).

Glassy state of metal alkanoates

Elevated temperatures (~100-150 ^{0}C) are required to reach liquid crystal phases

- **Thermotropic liquid crystals can be easily vitrified**
- **The liquid crystal ordering is preserved in the glassy state**
- **Glass materials are at room temperature**



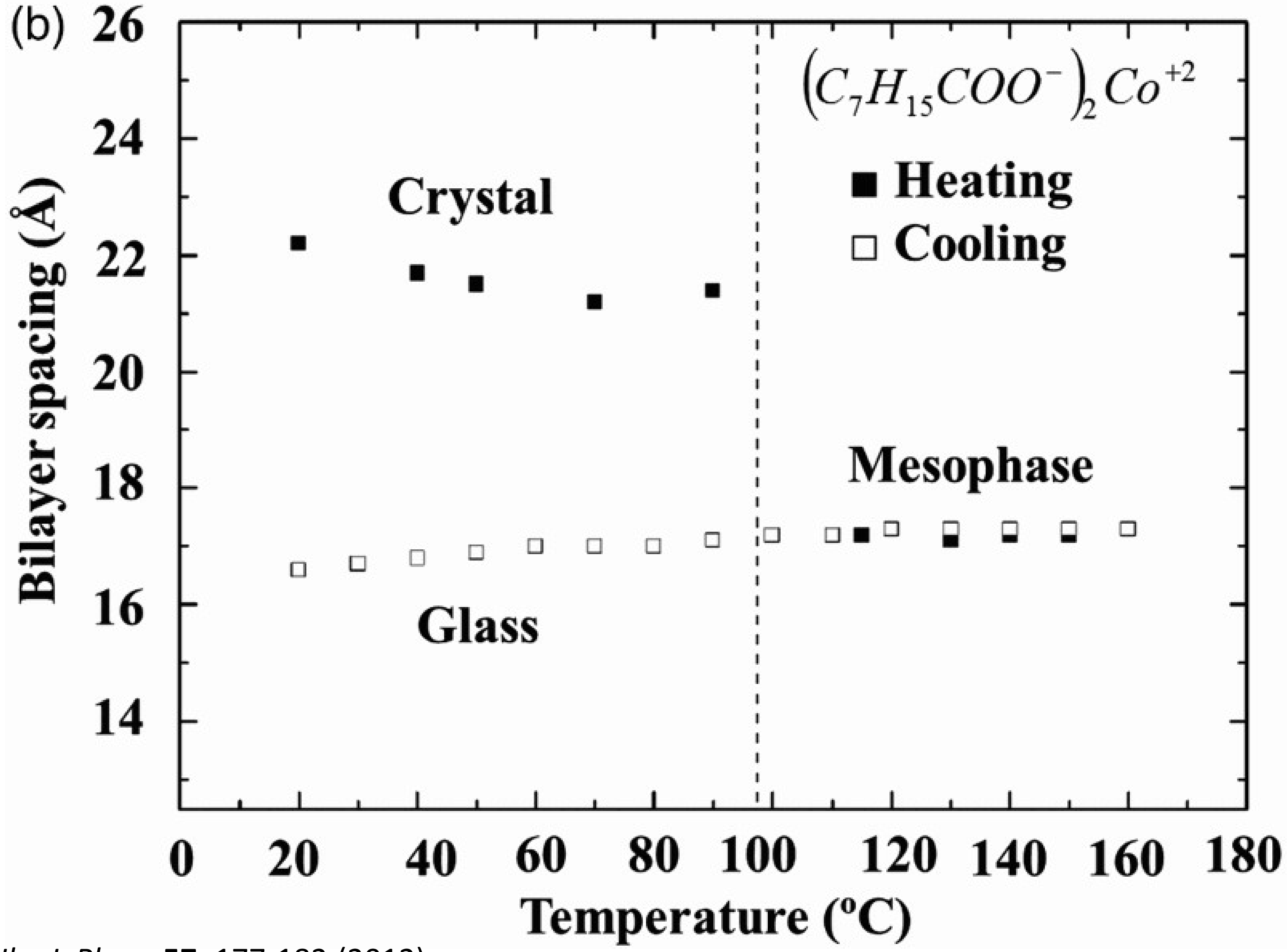
$$\left(C_7H_{15}COO^-\right)_2 Co^{+2} = CoC_8$$

Conoscopic studies of the cobalt octanoate

Ukr. J. Phys., **57**; 177-182 (2012).

Glassy state of metal alkanoates $\left(C_7H_{15}COO^-\right)_2 Co^{+2} = CoC_8$

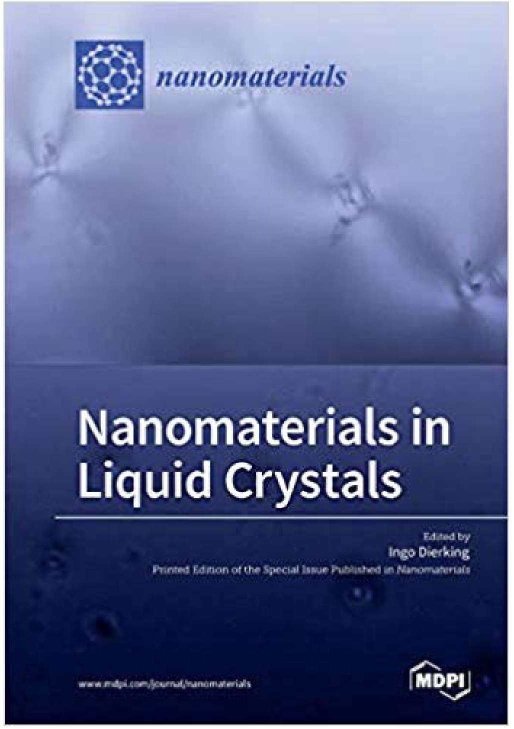
Small-angle X-ray scattering

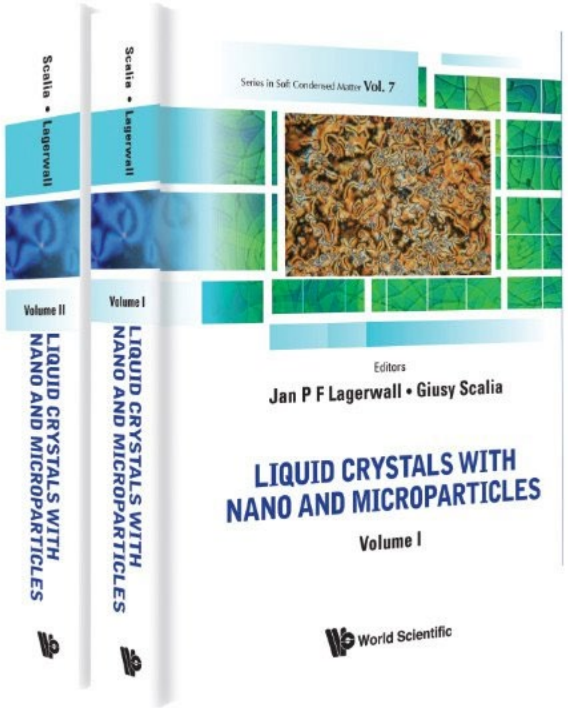


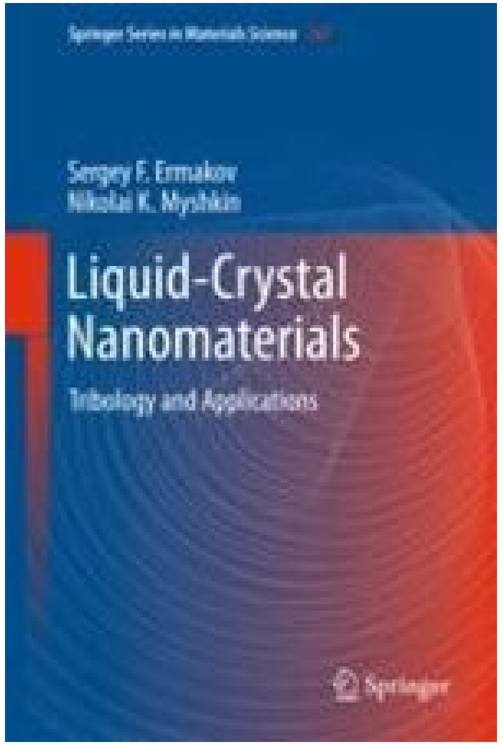
Ukr. J. Phys., **57**; 177-182 (2012).

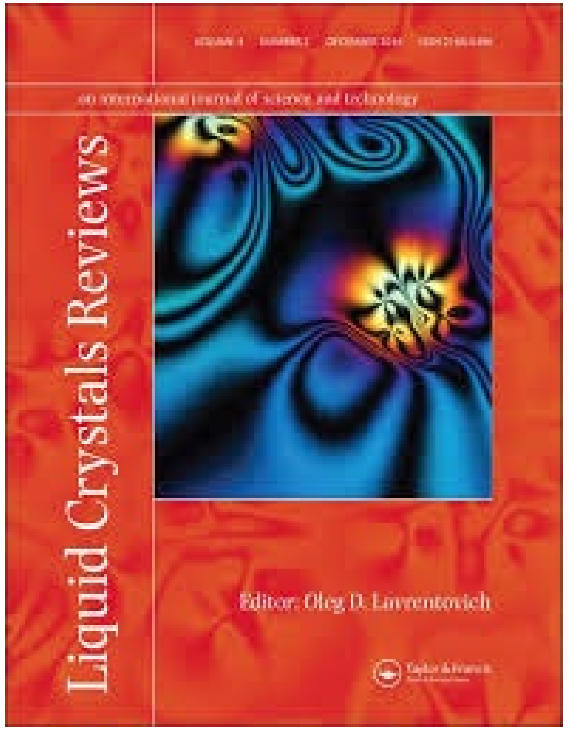
Nanoparticles embedded in smectic glass

Nanomaterials in Liquid Crystals: Fascinating Research Topic









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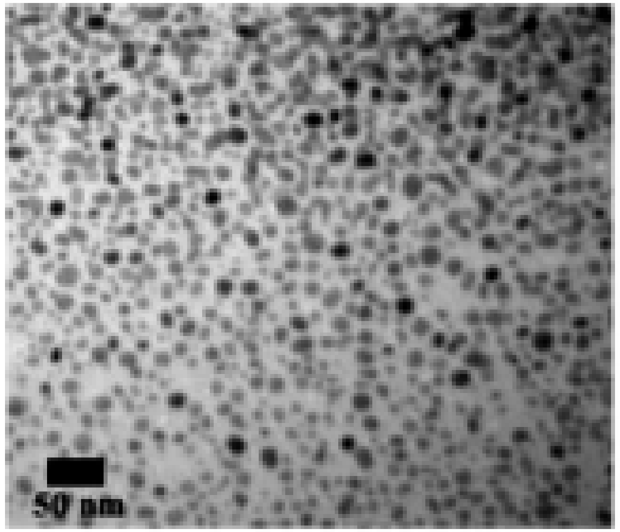
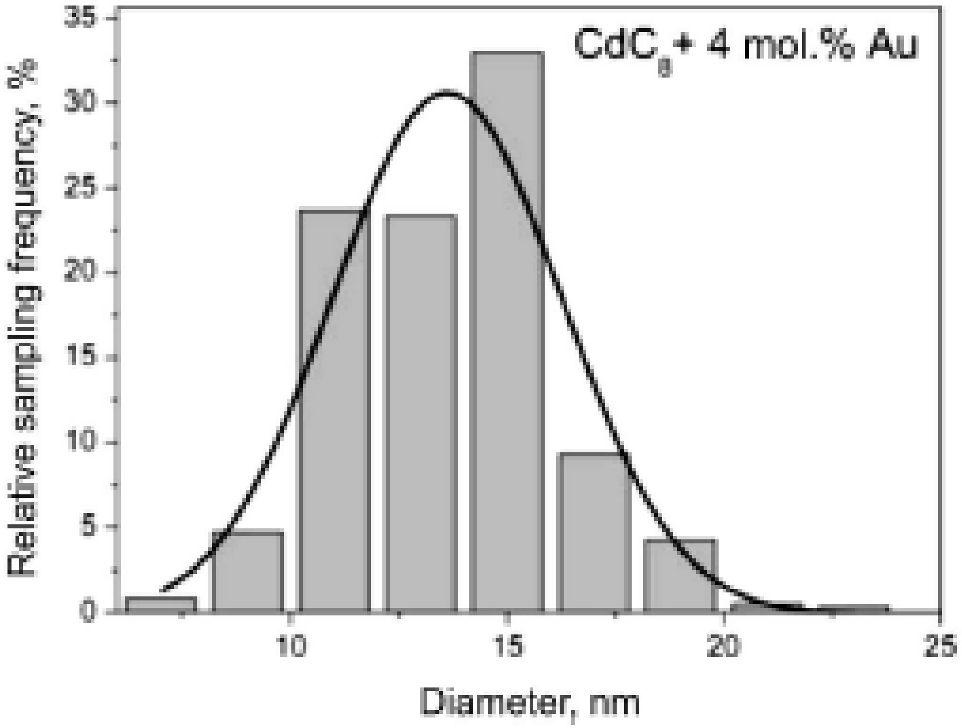
Metal alkanoates as nanoreactors

Nanoparticles made of various materials can be synthesized using metal alkanoates as nanoreactors

Mesomorphic glass - metal nanoparticles

Spherical metal (Ag, Au) nanoparticles in CdC8





Ukr. J. Phys., **60 (4)**; 356-361 (2015).

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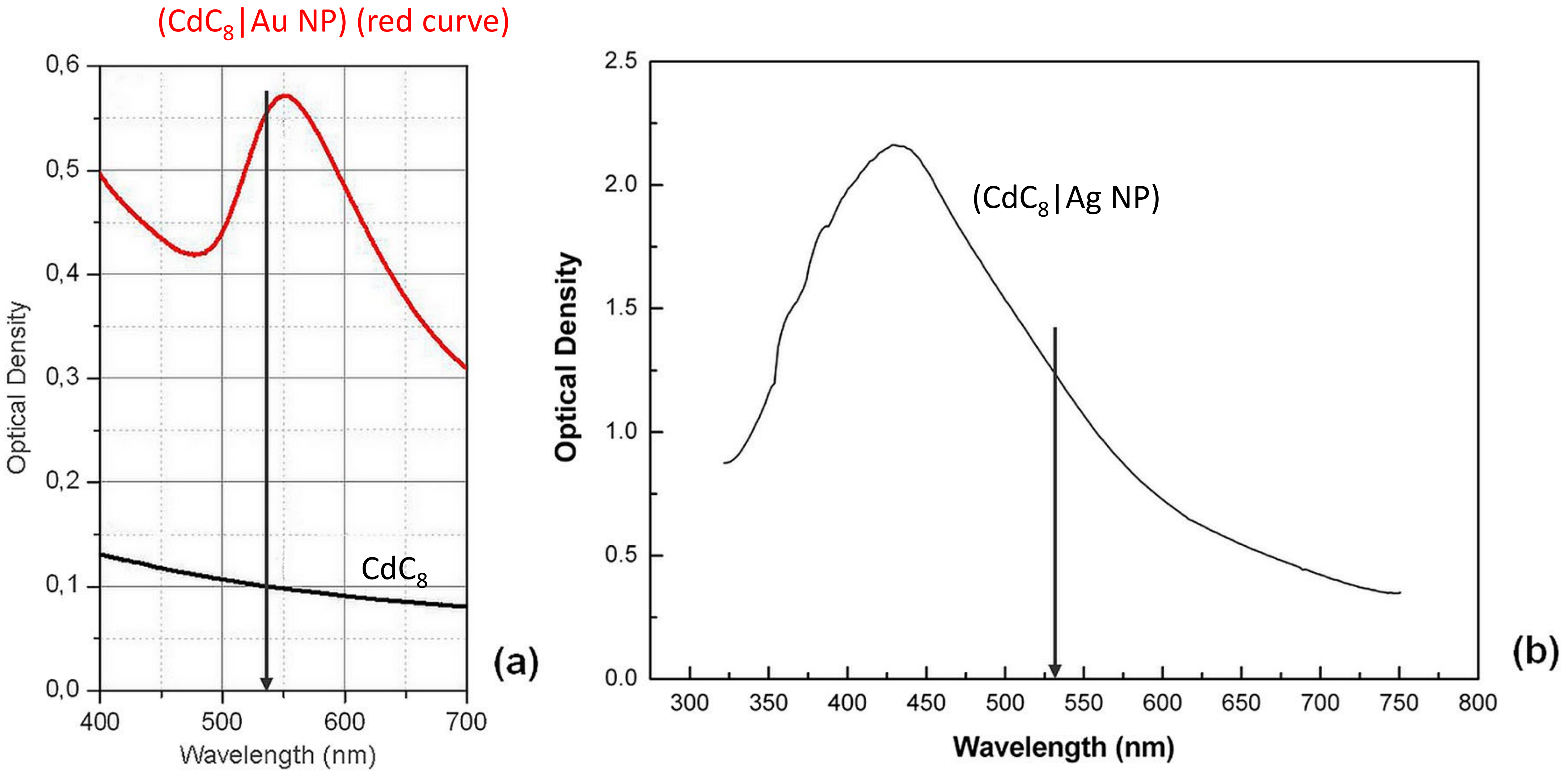
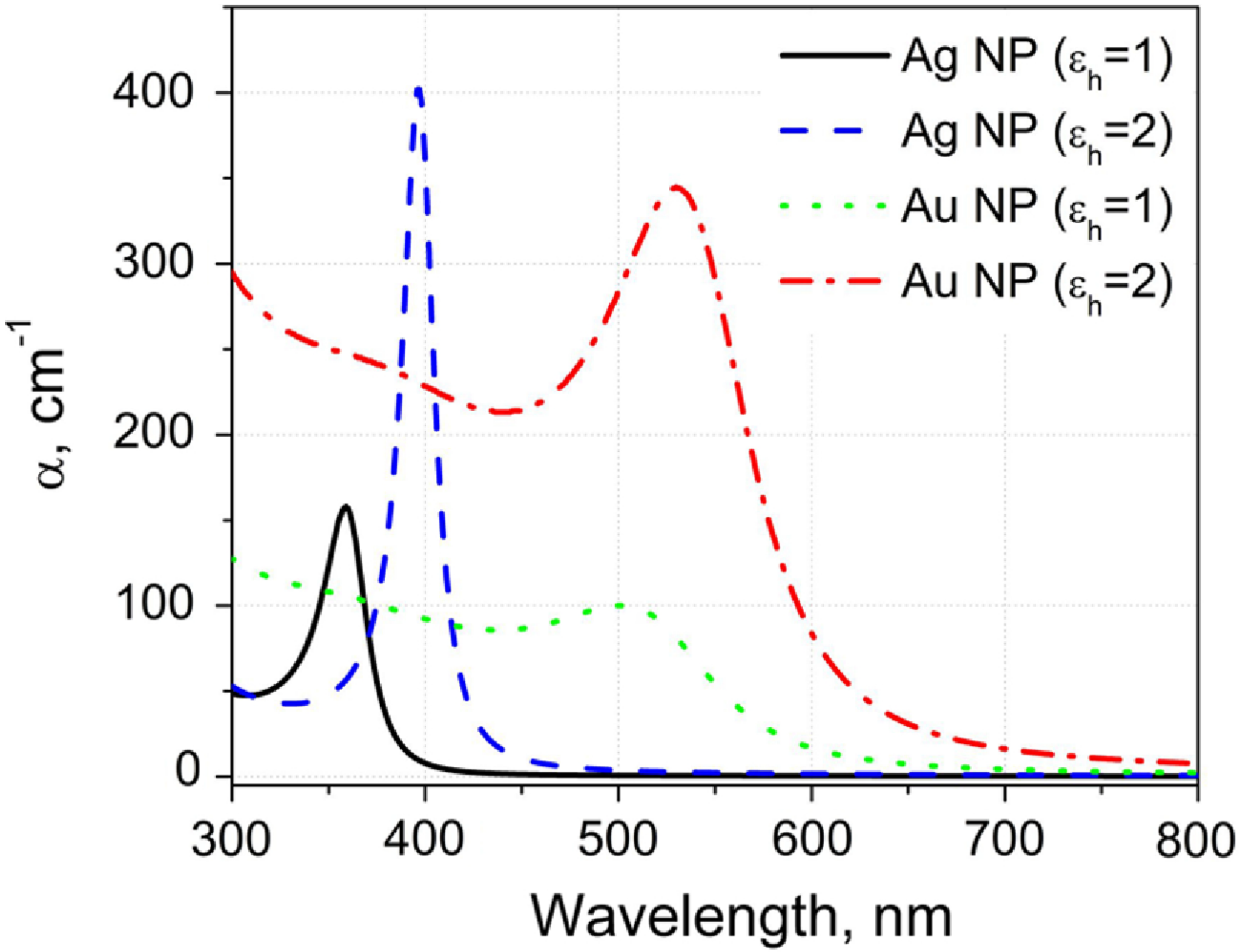


V. Rudenko, Y. Garbovskiy, G. Klimusheva, T. Mirnaya, "Intensity dependent nonlinear absorption coefficients and nonlinear refractive indices of glass-forming ionic liquid crystals doped with gold and silver nanoparticles", *Journal of Molecular Liquids*, 267, 56-60 (2018).

Reminder: optical properties of noble metal nanoparticles



JOSA B, **33 (4)**; 648-655 (2016).

Method of critical points and Maxwell-Garnett approximation

$$\varepsilon_{bulk}(\omega) = \varepsilon_{\infty} - \frac{w_p^2}{\omega^2 + i\Gamma\omega} + G_1(\omega) + G_2(\omega)$$

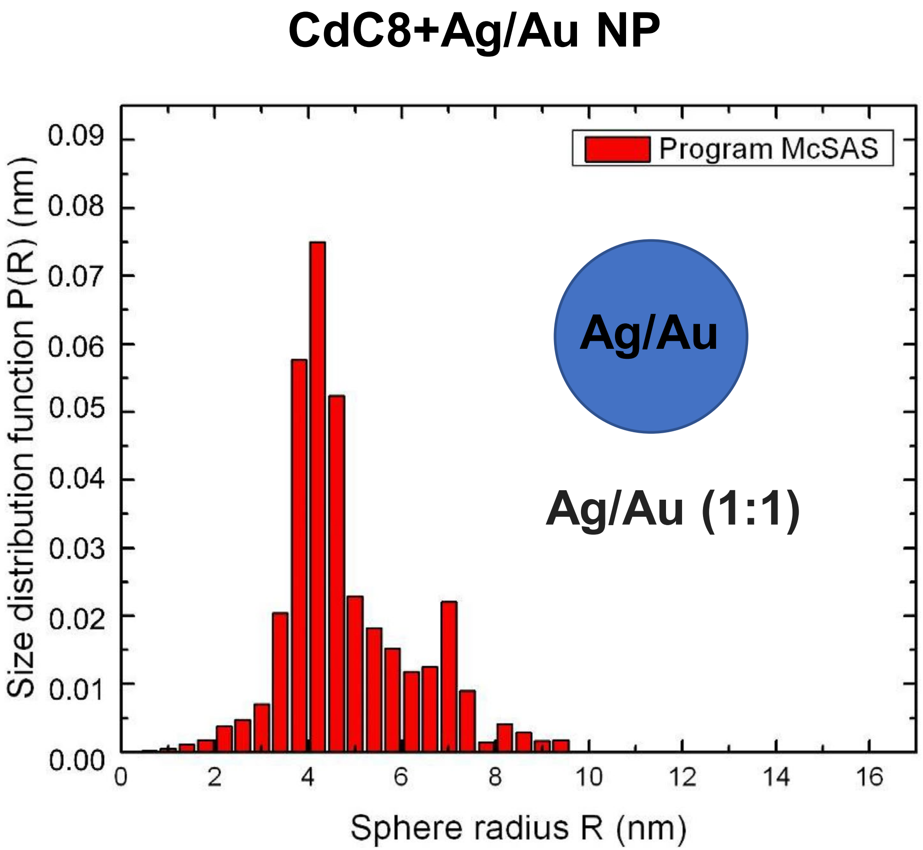
$$G_i(\omega) = C_i\left(\frac{e^{i\phi_i}}{\omega_i - \omega - i\Gamma_i} + \frac{e^{-i\phi_i}}{\omega_i + \omega + i\Gamma_i}\right), i = 1, 2$$

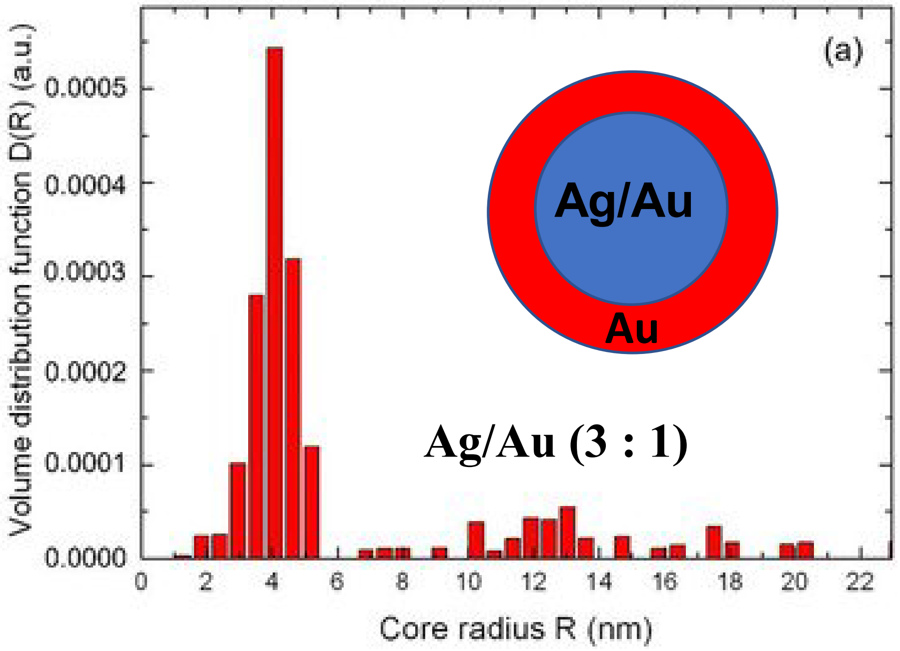
$$\varepsilon_{NP}(\omega, R_{NP}) = \varepsilon_{bulk}(\omega) + i\frac{A\omega_p^2 v_F}{\omega^3 R_{NP}}$$

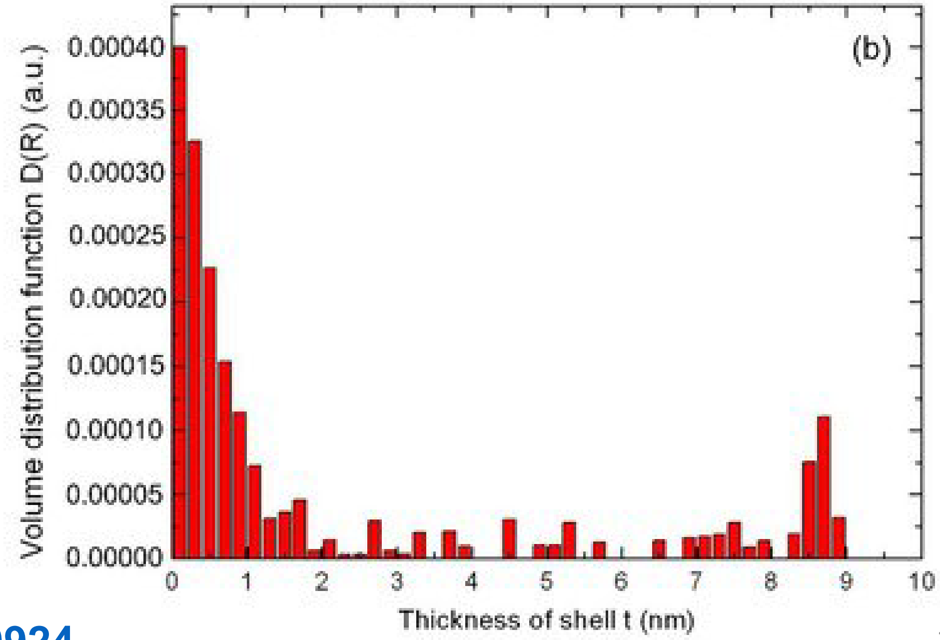
$$\alpha_{0,NP} = \frac{18\pi p}{\lambda}\varepsilon_h^{3/2}\frac{\mathrm{Im}(\varepsilon_{NP})}{\left(\mathrm{Re}(\varepsilon_{NP}) + 2\varepsilon_h\right)^2 + \left(\mathrm{Im}(\varepsilon_{NP})\right)^2}$$

J. Chem. Phys. **125**, 164705 (2006). *J. Opt. Soc. Am. B* **29**, 1793–1798 (2012).

Core-shell bimetallic (Ag, Au) nanoparticles in CdC8







Nanomaterials **2022**, *12*(6), 924; https://doi.org/10.3390/nano12060924

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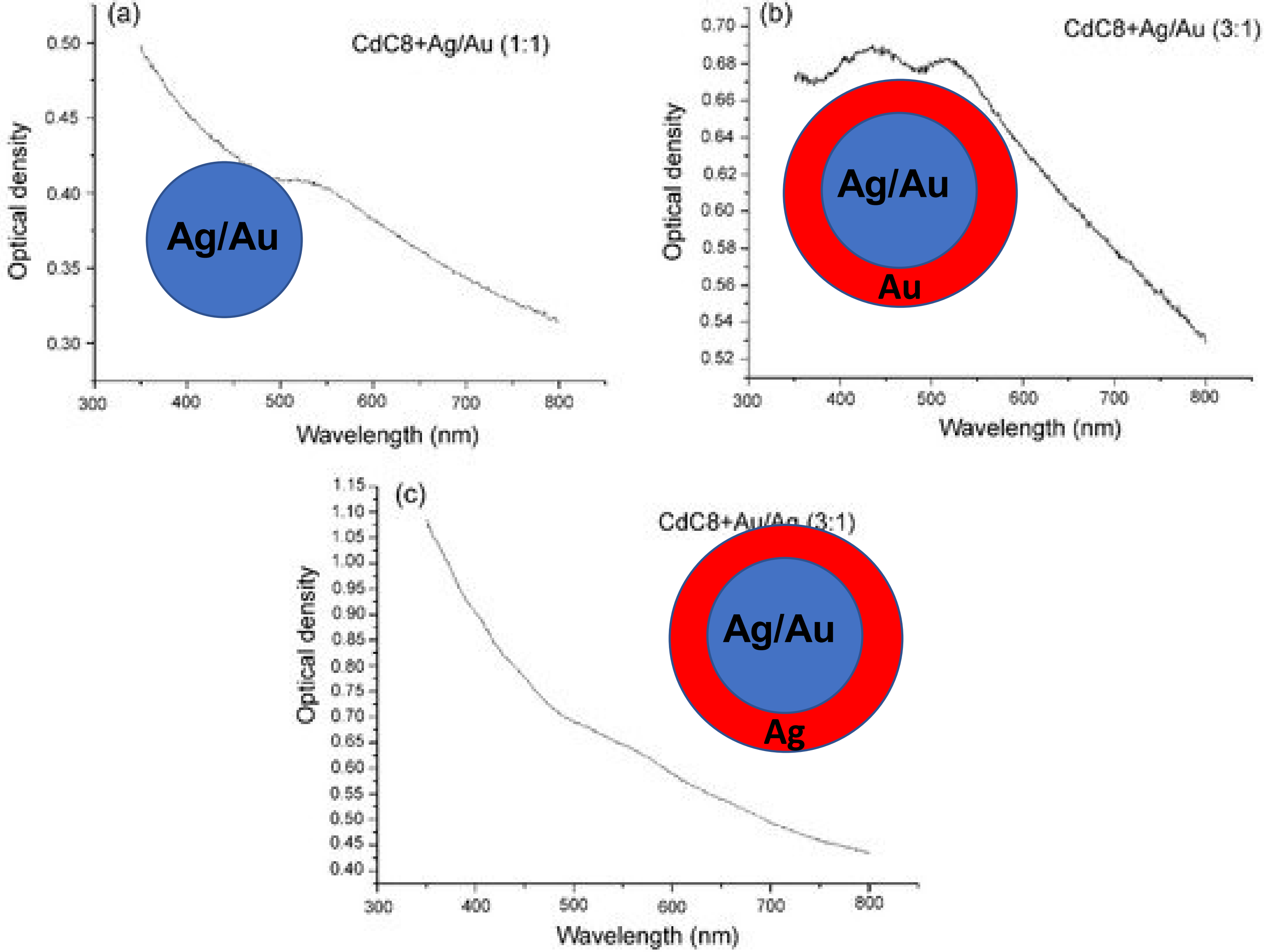
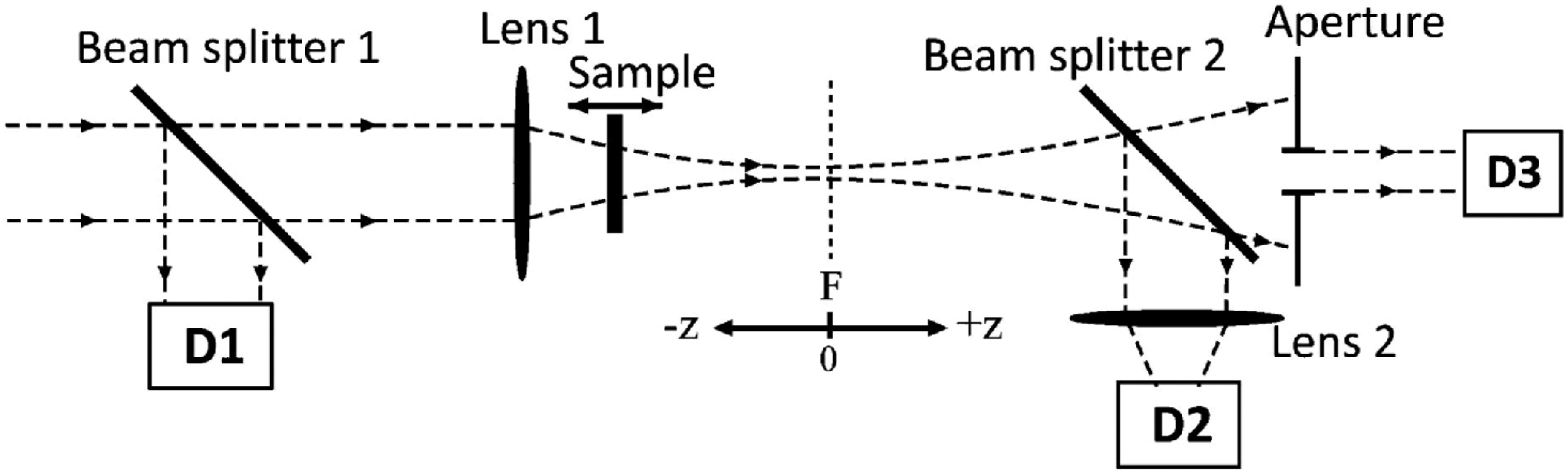


Nanomaterials **2022**, *12*(6), 924; https://doi.org/10.3390/nano12060924

Experimental setup: Z-scan



Q-switched Nd^{3+}YAG laser

Laser beam parameters:

1064/532 nm
0.5 Hz
9 ns

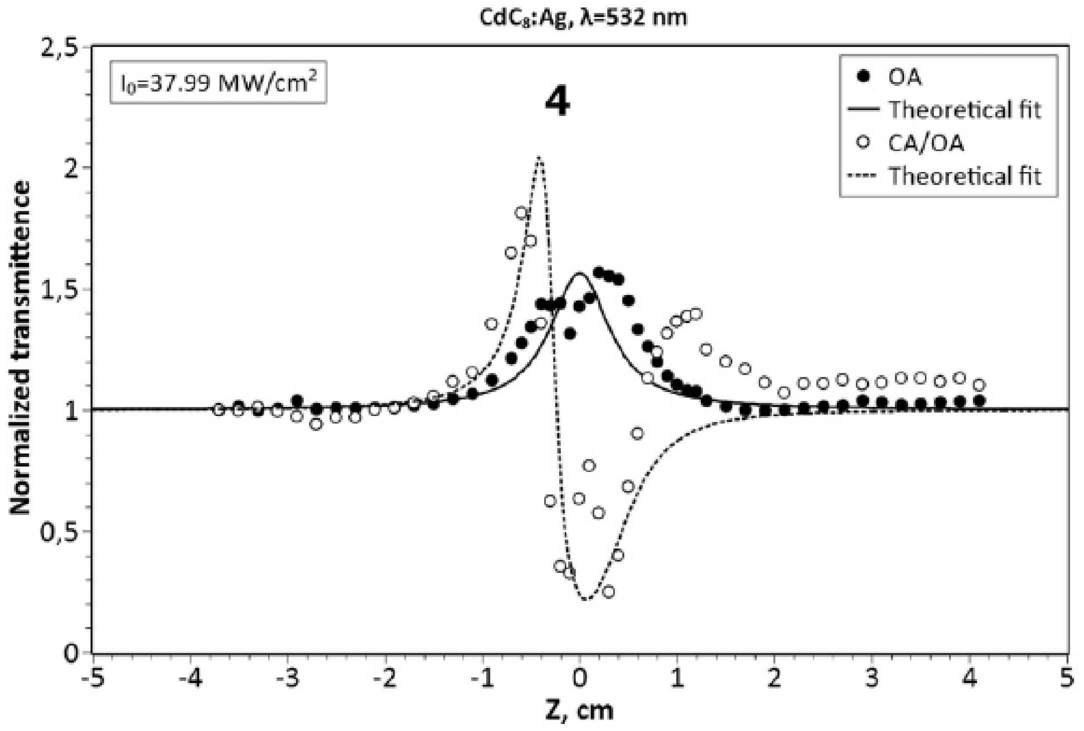
$8 - 40\ MW/cm^2$

JOSA B, **33 (4)**; 648-655 (2016).

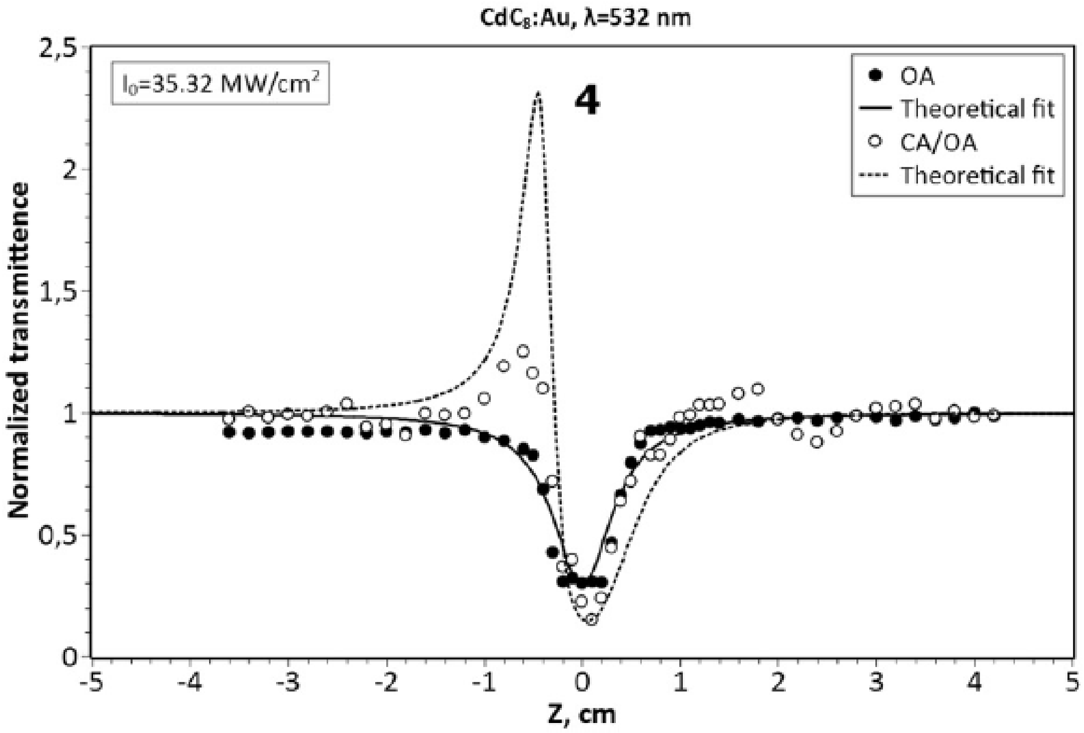
Nanomaterials **2022**, *12*(6), 924; https://doi.org/10.3390/nano12060924

Nonlinear-optical response

Ag



Au



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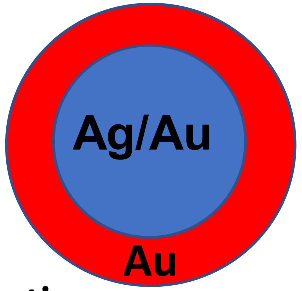
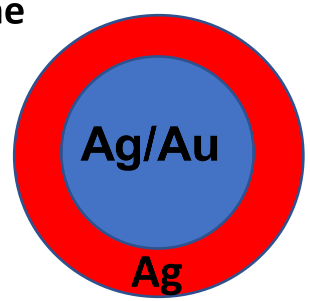
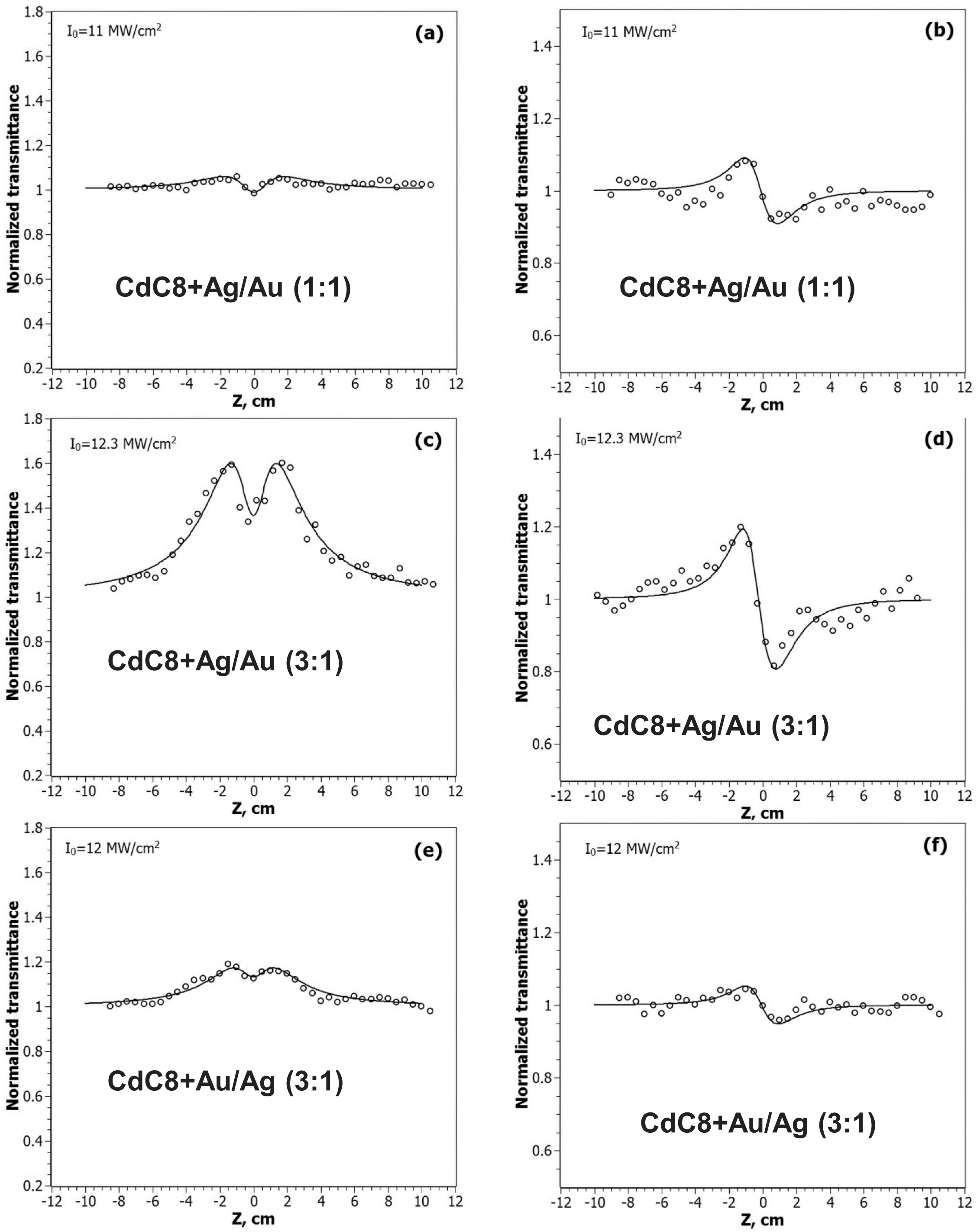


Nonlinear absorption:
(i) Saturation absorption regime
(ii) Reverse saturation absorption regime

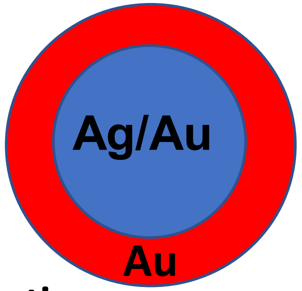




Visible
λ = 532 nm

Nonlinear refraction:
Self-defocusing due to thermal effects

Nanomaterials **2022**, *12*(6), 924; **https://doi.org/10.3390/nano12060924**



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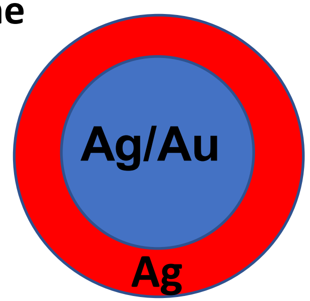

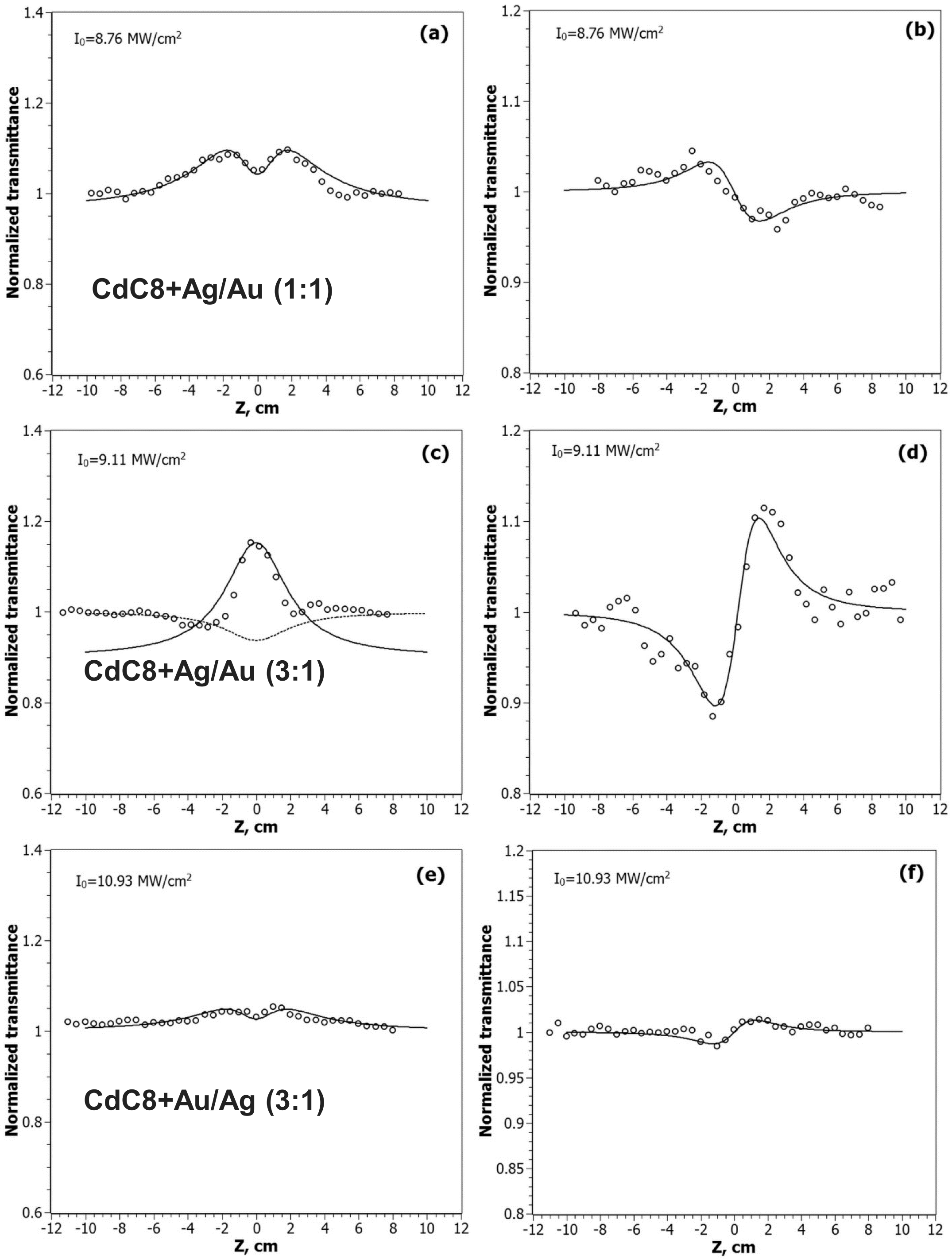

IR
λ = 1064 nm

Nonlinear refraction:
Self-defocusing

Nonlinear refraction:
Self-focusing

interplay between intrinsic optical nonlinearities of bimetallic nanoparticles (two-photon transitions and the smearing of the Fermi–Dirac distribution), the local field factor effect, and thermal nonlinearity

Nonlinear-optical parameters of the studied nanocomposites.

$$FoM = \left|\frac{4n_2}{\beta\lambda}\right|$$

Sample	I_0, MW/cm²	λ, nm	n_2, cm²/W	β, cm/W	FoM*	Ref.
CdC8 +Ag	10.45	532	-	-9.17×10^{-5}	-	[8]
	17.69		-3.91×10^{-10}	-7.50×10^{-5}	0.392	
	26.45		-5.03×10^{-10}	-4.74×10^{-5}	0.798	
	37.99		-6.96×10^{-10}	-3.11×10^{-5}	1.683	
CdC8 +Au	10.85		-	-1.29×10^{-5}	-	[8]
	18.23		-3.53×10^{-10}	2.03×10^{-5}	1.308	
	26.01		-2.87×10^{-10}	3.44×10^{-5}	0.627	
	35.32		-4.96×10^{-10}	3.96×10^{-5}	0.942	
CdC8 +Ag/Au (homogeneous alloy)	2.21	1064	-1.13×10^{-9}	1.63×10^{-4}	0.261	[9,10]
	3.79		-6.68×10^{-10}	0.95×10^{-4}	0.264	
	8.76		-2.31×10^{-10}	1.03×10^{-4}	0.084	
	9.44		-1.49×10^{-10}	-	-	
	13.7		-6.77×10^{-11}	-	-	
CdC8 +Ag/Au homogeneous alloy	11	532	-2.39×10^{-10}	3.7×10^{-5}	0.486	[9]
CdC8 +Ag/Au core and Au shell	12.5	532	-3.55×10^{-10}	2.5×10^{-5}	1.068	[9]
CdC8 +Ag/Au core and Au shell	2.29	1064	5.1×10^{-9}	0.35×10^{-4}	5.478	[10]
	3.52		1.88×10^{-9}	0.37×10^{-4}	1.910	
	9.11		6.56×10^{-10}	0.05×10^{-4}	4.93	
	10.58		3.04×10^{-10}	-	-	

J Mol Liq. **2018**, 267, 56-60. *Nanomaterials* **2022**, 12, 924. *Liquid Crystals*. **2022**, published online https://doi.org/10.1080/02678292.2022.2127952

Conclusion

Mesogenic metal alkanoates are excellent glass forming materials. In addition, they can be used as nanoreactors for template synthesis of nanoparticles. By vitrifying liquid crystals containing nanoparticles nonlinear-optical glass nanocomposites can be obtained.

Liquid crystal glass made of cadmium octanoate and containing metal (Ag/Au and bimetallic Ag/Au nanoparticles of two types (homogeneous Ag/Au alloy and core – shell) exhibit strong (~ 10^{-8} esu) and intensity-dependent nonlinear-optical response suitable for photonics applications relying on third-order optical nonlinearities.

Thank You!

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CSU - AAUP Faculty Research Grant