Laser-Induced Nanostructuring and Surface Phonon Behavior in ZnO/MnO Nanocomposites

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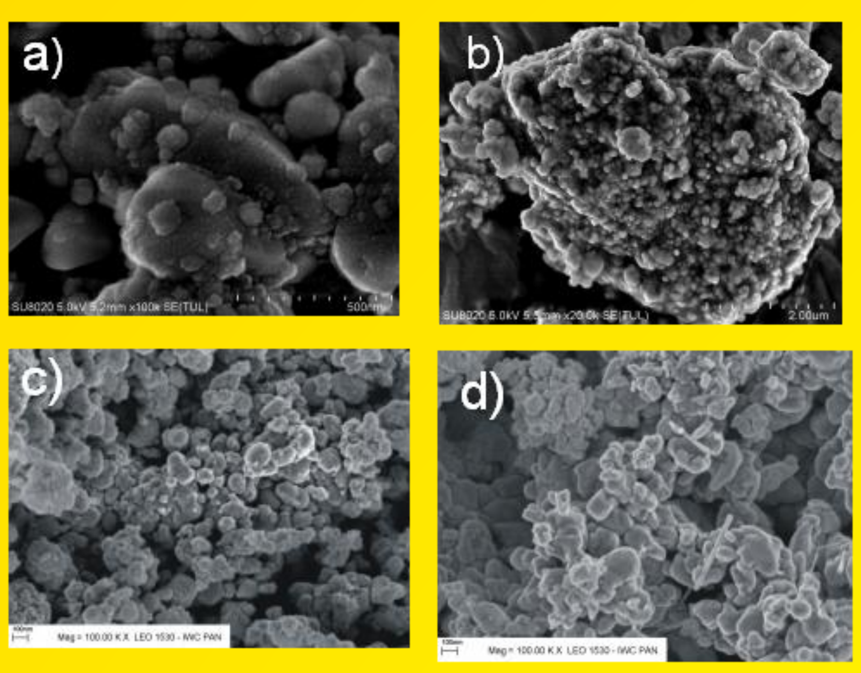
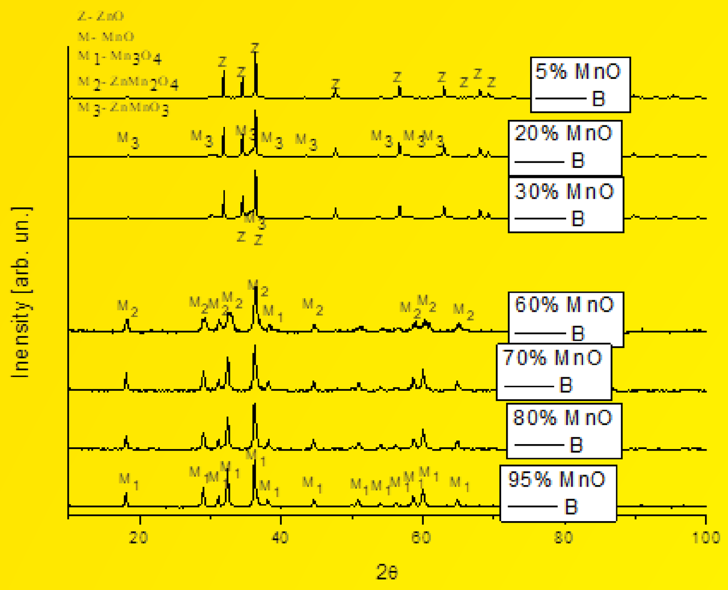
Methods and materials

The ZnO(Mn) nanoparticles were synthesized via a wet chemical co-precipitation method followed by calcination at 300 °C. The initial mixtures were prepared with varying concentrations of MnO dopant, ranging from 5% to 95%. X-ray diffraction (XRD) analysis confirmed the presence of ZnO and Mn_3O_4, $ZnMn_2O_4$, and $ZnMnO_3$ phases, with the mean crystalline size between 9 and 13 nm for $ZnMnO_3$ phases, from 24 to 47 nm for Mn_3O_4 phases, and above 100 nm for ZnO and $ZnMn_2O_4$ phases.

SEM: a) 5%, b) 30%, c) 70%, and d) 95% of MnO





Compound	Raman wavenumber [cm^{-1}]								
	ν_1	ν_2	ν_2	ν_4	ν_5	ν_5	ν_6	ν_7	ν_8
β-MnO_2	-	319	377	486	538	-	665	-	750
γ-MnO_2[a]	264	337	379	491	520	572	631	670	738
R-MnO_2	275	-	387	490	522	575	630	648	742
α-Mn_2O_3	192	314	404	481	-	592	645	698	-
γ- Mn_2O_3	263	308	-	-	512	-	631	670	-
Mn_3O_4	-	310	357	485	-	579	-	653	-
MnO	250	-	-	531	591	-	654	-	-
MnOOH	213	253	352	384	528	552	615	648	-
$ZnMnO_3$	237	-	-	448	-	-	610	-	-
$ZnMn_2O_4$	-	300	320	382	476	-	-	678	-

ZnO

Frequency [cm^{-1}] Ref [6,7,20]	Symmetry/assignation
99	E_2^{low}
203	2TA; E_2^{low}
284	B_1^{high}-B_1^{low}
333	E_2^{high}-E_2^{low}
378	A_1(TO)
410	E_1(TO)
438	E_2^{high}
483	2LA
536	$2B_1^{low}$; 2LA
574	A_1(LO)
590	E_1(LO)
618	TA+TO
657	TA+LO
666	TA+LO
700	LA+TO
723	LA+TO
745	LA+TO
773	LA+TO
812	LA+LO
980	2TO
1044	TO+LO
1072	TO+LO
1105	2 LO
1158	$2A_1$(LO);$2E_1$(LO);2LO

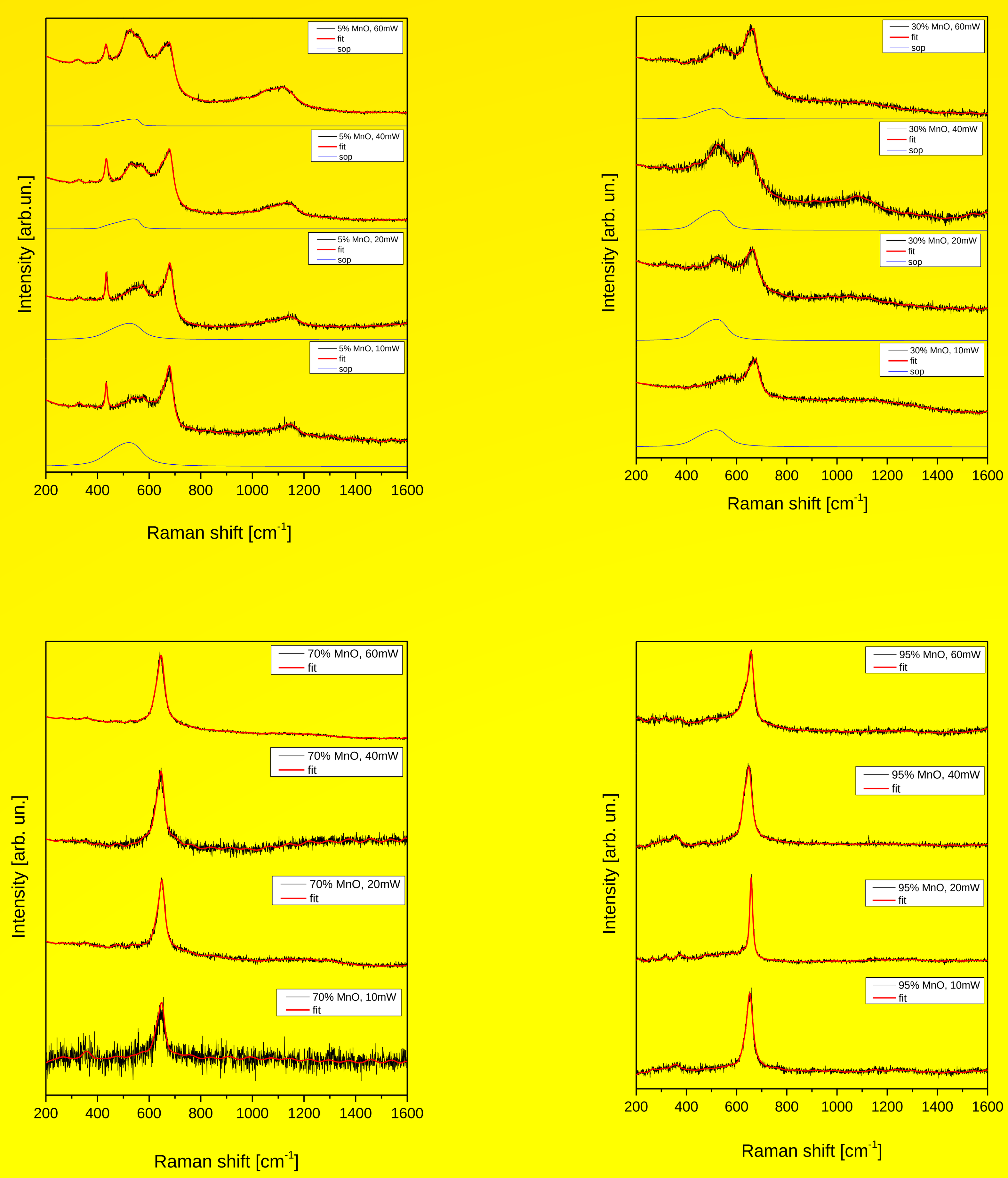
The bulk ZnO semiconductor sublimes at 1800°C and melts at 2200°C, while ZnO nanocrystal powder evaporates at 1380°C.
The melting point of Mn_3O_4 is relatively high, around 1567°C.

The Raman spectra of ZnO nanoparticles doped with 5% to 95% of MnO were recorded at four different laser powers, on the lasers 10, 20, 40, and 60 mW.

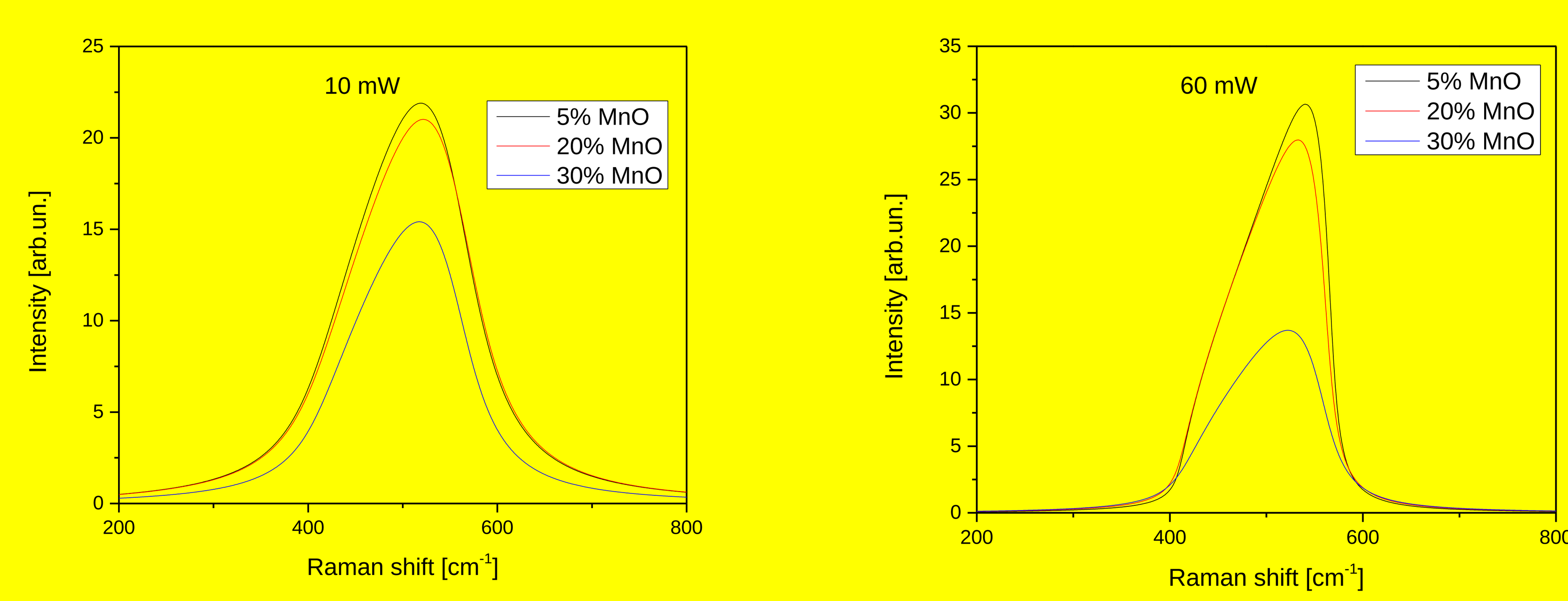
Conclusion

This comprehensive investigation highlights the complex relationship between laser power, dopant concentration, phase evolution, and optical phonon dynamics in ZnO/MnO nanocomposites. It underscores the utility of laser processing as a tool for fine-tuning the structural and vibrational properties of multifunctional oxide materials.

Raman spectroscopy



Change in size and shape of SOP modes



Change in position, shape, and intensity at approximately 650 cm^{-1}