# Cost-effective screen printing approach for Ce/Nd-doped ZnAl$_2$O$_4$ films: tuning the crystallinity induced by the substrate

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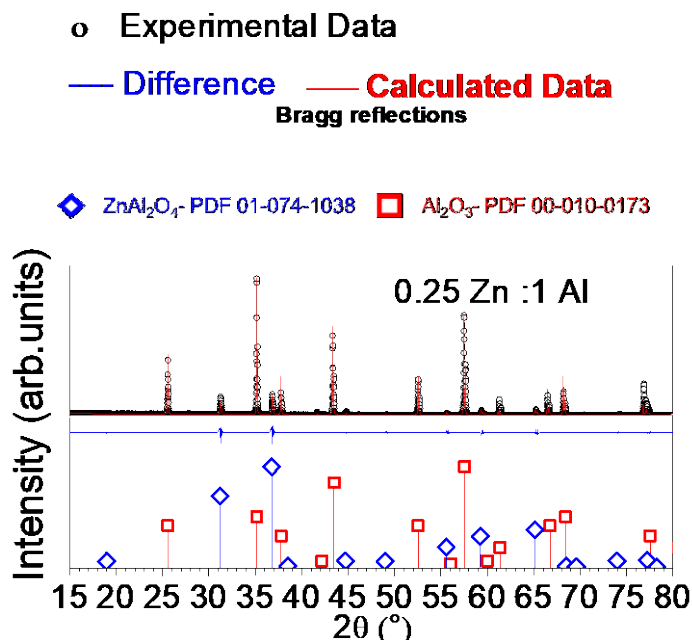
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**Supplementary Information 1.**



**Figure S1.** XRD patterns of films synthesized at 1200 ºC with varying zinc oxide contents, denoted as 0.25Zn:1Al. The lower section of the figure showcases red and blue peaks, corresponding to the reflection positions of $Al_2O_3$ and zinc aluminate phases, respectively. The red line represents the fitting achieved via Rietveld refinement, while the blue line represents the difference between the fitting and the scatter-line, which corresponds to the experimental data. Notably, the symbols marked on the figure highlight the Bragg positions of $Al_2O_3$ (red-open squares) and $ZnAl_2O_4$ (blue-open diamond).

In order to gain deeper insights into the extent of spinel inversion, we conducted Rietveld refinement, as depicted in **Figure S1**. Through meticulous refinement of site occupation fractions, we determined a remarkably low spinel inversion degree of 0.082 for the ZnAl2O4 film synthesized with a Zn:Al ratio of 0.25 (**Table 1**). This finding attests to the exceptional crystalline structure of the film, exhibiting minimal perturbations in the occupation of crystallographic sites.

**Table 1. Rietveld refinement results. x,y,z O -** oxygen refined position. **Occ Zn tetra** - occupation factor of Zn in the tetrahedral site. **Occ Al tetra** - occupation factor of Al in the tetrahedral site. **Occ Zn octa** - occupation factor of Zn in the octahedral site. **Occ Al octa** - occupation factor of Al in the octahedral site.

| | **025 Zn:1Al** |
|---|---|
| **ZnAl₂O₄** | |
| **Cell param. a (Å)** | 8.0905 (25) |
| **x,y,z O** | 0.2644 (1) |
| **Occ Zn tetra** | 0.9173 (5) |
| **Occ Al tetra** | 0.0826 (8) |
| **Occ Zn octa** | 0.1186 (4) |
| **Occ Al octa** | 0.8813 (3) |
| **R_wp (%)** | 9.89 |

Regarding the lattice cell of alumina, both before and after sintering, the experimental values of unit-cell parameters were determined as follows: a = 4.7508 (21) Å, b = 4.7508 (21) Å, c = 12.9858 (21) Å, and a volume of 253.817 Å³ for alumina before sintering. After sintering, the unit-cell parameters were found to be a = 4.7592 (18) Å, c = 12.9952 (12) Å, with a volume of 254.899 Å³. These measurements provide valuable insights into the structural changes that occur in alumina during the sintering process, demonstrating the slight modifications in the unit-cell parameters and volume of the material.

The unit-cell parameters were calculated to be a= 4.7373 (21) Å , b= 4.7373 (21) Å, c= 13.0186 (21) Å and Vol = 253.02 Å³ and a= 4.7592 (18) Å, c= 12.9952 (12) Å and Vol = 254.92 Å³ for the alumina before and after sintering respectively.

**Supplementary Information 2.**
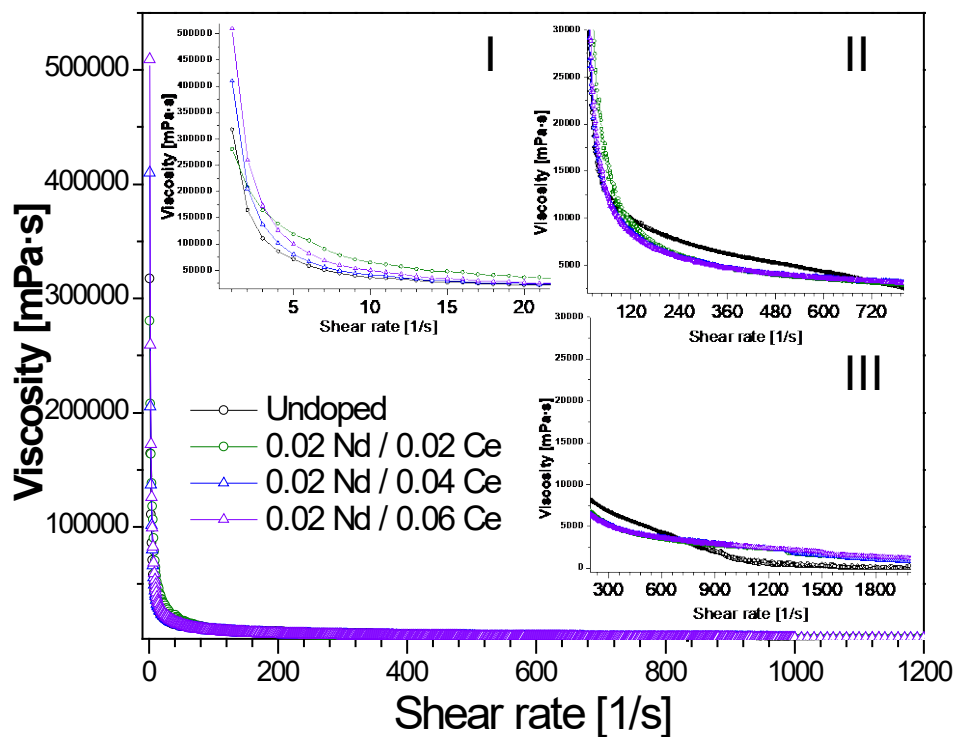


**Figure S2.** Rheology of the ZnAl₂O₄ inks undoped and co-doped with Ce and Nd including a fix content of Nd and three different Ce concentrations, ZnAl₂O₄: xNd, yCe (x=0.02, and y= 0.02, 0.04 and 0.06 mol%). The insets show the zoom of the plot for different shear rate ranges.

Rheological analysis of the ink undoped and with the incorporation of Nd and Ce dopants were performed using an Anton Paar MCR-72 Rheometer with a cone and plate (CP50) geometry (radius of the cone: 25 mm and angle of the cone: 1 degree). The ink is placed on the plate and the cone is lowered up, the excess of the ink is trimmed from the gap. The experiments were done at room temperature, with a shear rate ranging from 1 to 2000 s⁻¹. The incorporation of the dopants in the ink increase the viscosity at shear rates

lower than 50 s$^{-1}$ (**Fig. S1-Inset I**); later the viscosity decrease for the co-doped inks and when the shear rate exceeds the value about 800 s$^{-1}$, the viscosity of the undoped ink decreases again (**Fig. S1-Inset II-III**). The measured viscosity ($\eta$) of the inks as a function of the shear rate is almost similar for all the inks prepared; showing that the paste formulation and fabrication process including homogenization and dispersion step provides reproducibility in the ink rheology.

**Supplementary Information 3.**
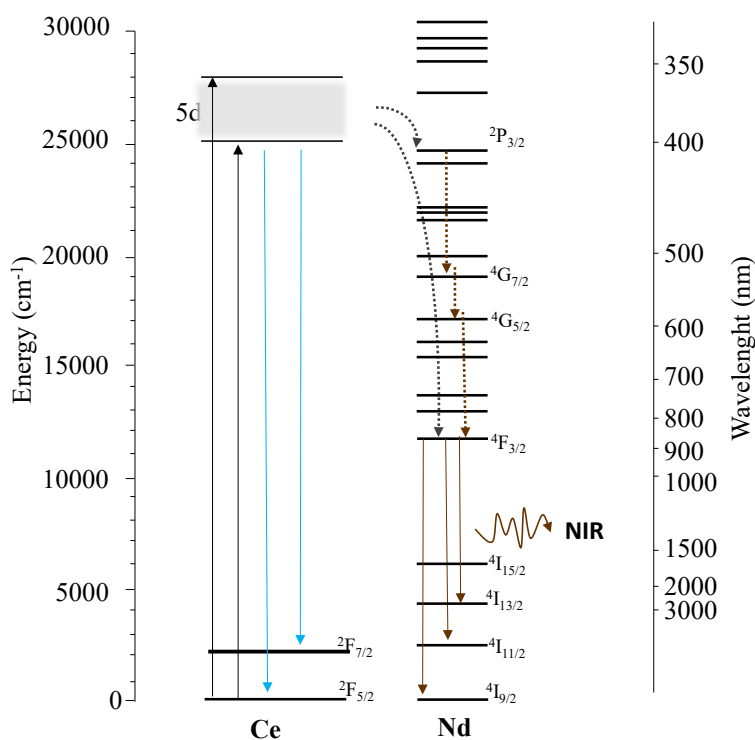


**Figure S3.** Schematic of the proposed energy transfer mechanism from Ce ions to Nd.

In Figure **S3** the energy transfer mechanisms between Ce and Nd cations are depicted in an energy level diagram. Nd$^{3+}$ has several energy levels. Some of them are located in the UV region having good overlap with Ce absorption. When photons at wavelengths around 359 are absorbed, the Ce cations are excited from the $^2F_{5/2}$ ground state to the broad pump 5D band. Thus, there are several channels for energy transfer from Ce to Nd. $^2P_j$ levels of Nd are populated by energy transfer from Ce. Nd can then relax to $^4F_{3/2}$ state by emitting phonons in several steps. And consencuently, the NIR emission is obtained by transitions from $^4F_{3/2}$ to lower lying $^4I_j$ levels. Another possibility is that from 5D states Nd can de-excite to $^4F_{3/2}$ level by cross relaxation, taking a nearby Nd cation to excited state.