

Photoluminescence of $\text{Sr}_{2-x}\text{Ln}_x\text{CeO}_{4+x/2}$ (Ln = Eu, Sm or Yb) prepared by a wet chemical method.

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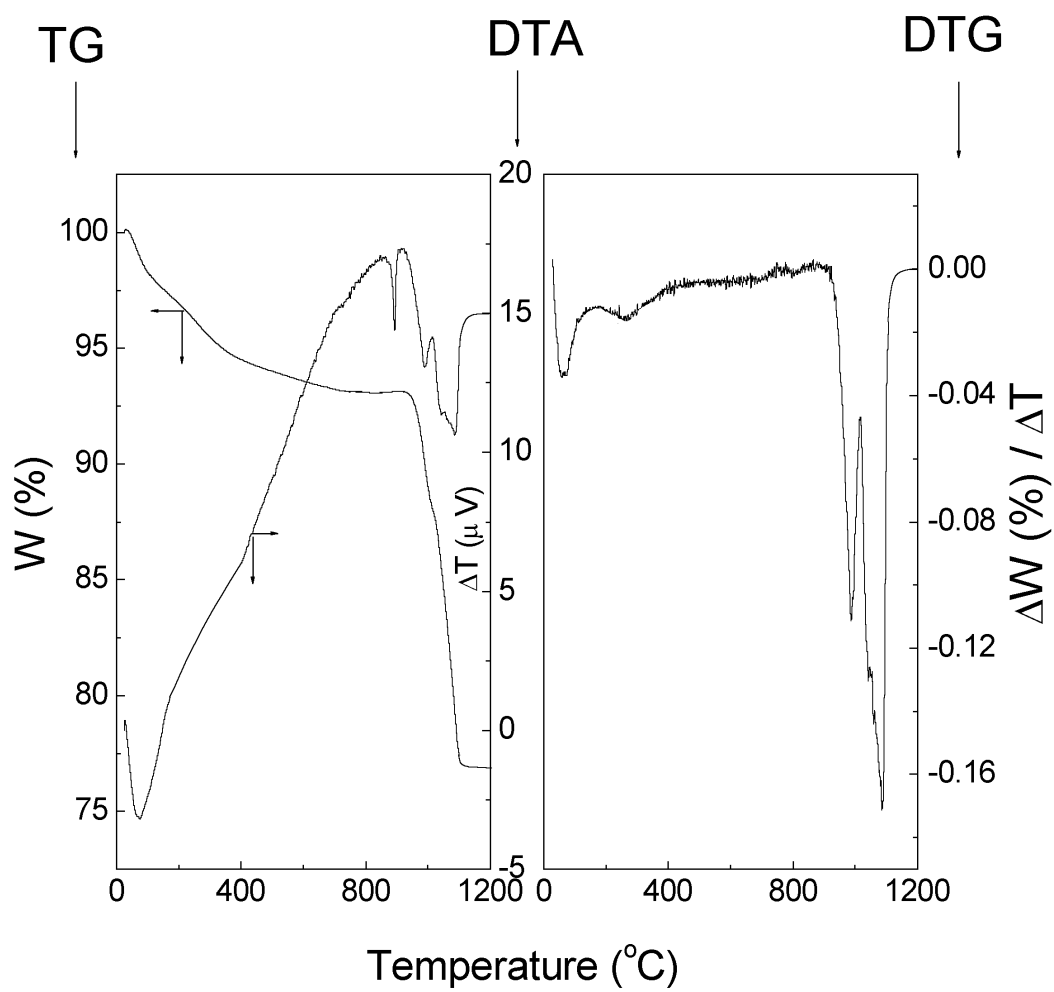
Thermoanalytical studies

Fig. S1 shows the simultaneous TG / DTA curves of the gel-carbonate precipitate. TG of the as-prepared solids after oven drying shows that the mass loss occurs in two steps: (i) initial mass loss of about 5% through the broad range of temperature up to 700°C is arising due to the removal of water from ceria gel and (ii) the mass loss of about 16% occurs again through the broad range of temperature from 950 to 1100°C, due to the reaction between CeO_2 and SrCO_3 accompanied by the release of CO_2 . The differential thermogravimetry (DTG) [Fig. S1] also shows that the mass loss is complete by 1100°C. Mass loss measurements were also carried out under isothermal conditions by heating the samples for several hours at selected temperatures. The total mass loss of the as-prepared sample obtained in the present experiments is about 23%. After drying at 120°C for extended periods, the residue shows the mass loss of 9.5% up to 700°C, 11% at 950°C and 2.5% at 1100°C. This indicates that there is a difference in mass loss between the dynamic (TG / DTA) and isothermal heating conditions. However both the cases clearly indicate that the phosphor formation reactions are over by 1100°C.

The endothermic maximum below 100°C in DTA curve is due to the loss of water resorbed by the oven-dried samples when handled in air. The shift in the baseline of the DTA curve corresponds to the broad mass loss due to recrystallization

of the xerogel to crystalline CeO_2 . The endotherm at $\sim 900^\circ\text{C}$ in DTA curve is due to the phase transformation of SrCO_3 from orthorhombic to rhombohedral as it is not associated with any mass loss. The two endothermic maxima at $\sim 950^\circ\text{C}$ and $\sim 1100^\circ\text{C}$ in DTA curve correspond to the mass loss due to the release of CO_2 in the TG curves. The appearance of two endotherm may indicate the successive reactions; initially CeO_2 reacts with SrCO_3 and forms Sr_2CeO_4 as the major phase and SrCeO_3 as an impurity phase. SrCeO_3 further reacts with excess SrCO_3 giving rise to phase pure Sr_2CeO_4 .

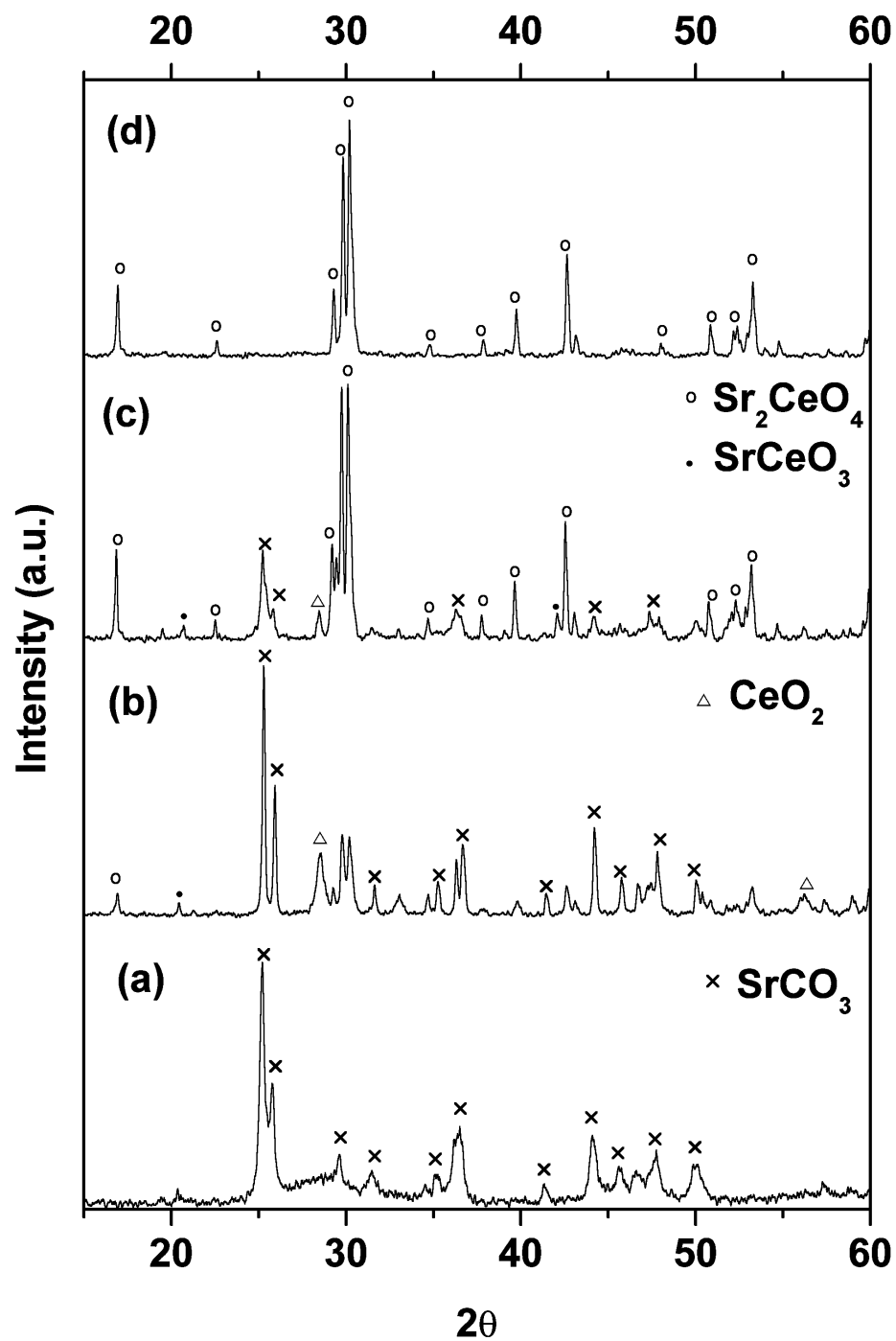
Figure S1. TG-DTA and DTG curves of a composite precipitate of SrCO_3 and hydrated ceria in air at a heating rate of $10^\circ\text{C min}^{-1}$.



XRD studies

The sequence of reactions during thermal analyses is studied by identifying the intermediate phases under isothermal heating conditions at selected temperatures for several hours using x-ray diffraction (Fig. S2). XRD pattern of the gel dried at 120°C [Fig. S2(a)] shows the presence of SrCO₃ as the only crystalline phase. No CeO₂ is detected since it is in the form of amorphous CeO₂.xH₂O. Heat treatment of the powder at 700°C [Fig. S2(b)] shows that CeO₂.xH₂O gel ($x \leq 2$) is totally converted to CeO₂ with cubic symmetry and appears as a crystalline phase along with SrCO₃. This is also indicated in TG-DTA analyses. The appearance of the XRD reflections of orthorhombic Sr₂CeO₄ and SrCeO₃ (JCPDS card no. 47-1689) phases indicate that SrCO₃ starts reacting with CeO₂ even at 700°C under isothermal condition. The (hkl) values and the relative intensities of Sr₂CeO₄ phase are calculated using a computer program (LAZY PULVERIX). The crystallographic data and the atomic positions were taken from Danielson *et al.*⁶ As the calcination temperature is increased to 950°C the XRD pattern [Fig. S2(c)] shows the presence of Sr₂CeO₄ with orthorhombic symmetry as the major phase although SrCO₃, CeO₂ and SrCeO₃ still remain as minor phases. Further annealing at >1000°C for extended periods in air, O₂ or N₂ atmosphere leads to the formation of crystalline Sr₂CeO₄ [Fig. S2(d)] with complete phase purity. However annealing in H₂ atmosphere or heating to temperatures >1300°C causes the formation of SrCeO₃ phase, indicating that Sr₂CeO₄ phase is unstable in strongly reducing atmosphere as well as at higher temperatures.

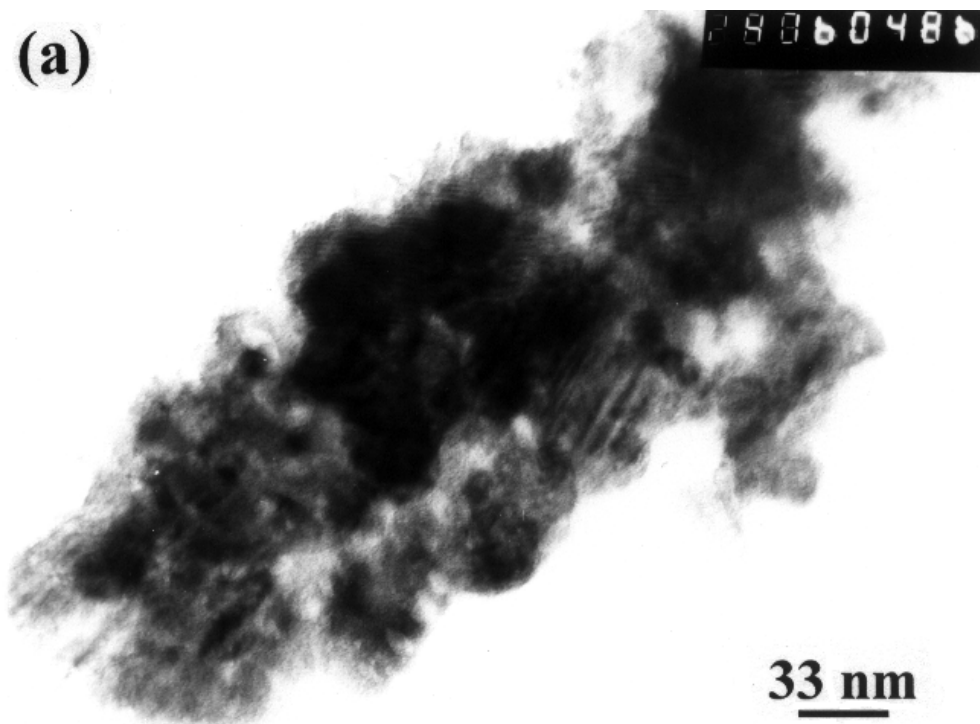
Figure S2. X-ray diffraction patterns of the sample at (a) 120°C, (b) 700°C, (c) 950°C, (d) 1100°C shows the evolution of crystalline Sr_2CeO_4 from the composite powder.

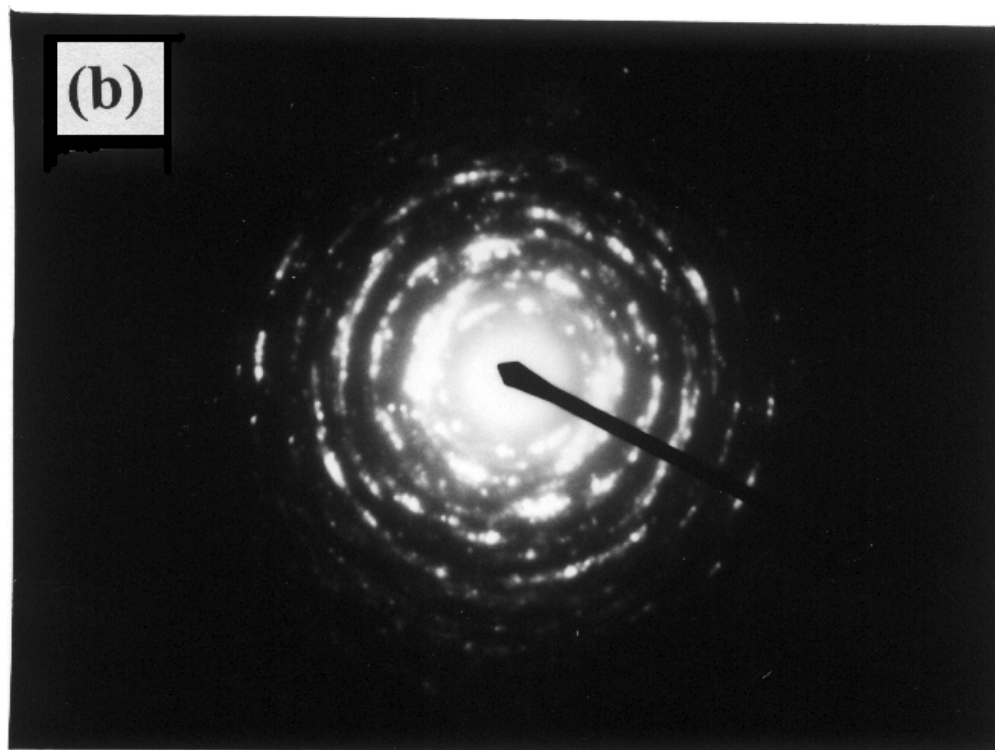


TEM studies

The TEM studies clearly illustrate the composite nature of the precipitates. Fig. S3(a) shows micrograph of the as-prepared powders. The aggregates of the small particles are identified as amorphous hydrated ceria. The appearance of lattice images oriented in the same direction indicates the presence of crystalline SrCO_3 particles, which are embedded within the ceria gel. The corresponding electron diffraction [Fig. S3(b)] shows spotty patterns superimposed with diffused rings, further confirming the presence of two phases in the system, i.e. $\text{CeO}_2 \cdot x\text{H}_2\text{O}$ as the amorphous and SrCO_3 as the crystalline phases.

Figure S3. (a) TEM image of composite precipitate of SrCO_3 and hydrated ceria, (b) the corresponding electron diffraction pattern.





Photoluminescence of undoped Sr_2CeO_4

The excitation spectra recorded for the compound Sr_2CeO_4 at room temperature are presented in Fig. S4. Excitation spectrum monitored at $\lambda_{\text{em}} = 472$ nm shows a broad band with two maxima at 282 and 336 nm. The latter appears as a broad and sharp shoulder. The feature of the excitation spectrum remains unchanged when monitored at $\lambda_{\text{em}} = 456$ nm except for the difference in intensity. The emission spectra recorded on exciting at 282 as well as 336 nm show broad band with the maximum in the blue-green region ($\text{FWHM} = 3821 \text{ cm}^{-1}$) with the extended emission into longer wavelengths. In fact, there are two maxima, one at 456 nm (low intensity) and another high intense band peaking around 472 nm. These bands have been assigned as intraconfigurational $\text{Ce}^{4+}\text{--O}^{2-}$ charge-transfer (CT) transition by Danielson *et al*³. There is no overlap between excitation and emission spectra, with a large Stokes shift (8875 cm^{-1}). Annealing for longer periods at 1100°C does not change the general features of excitation nor emission spectra; annealing only increases the intensity, irrespective of the atmosphere. The increase in intensity may be related to the removal of oxygen vacancy related defect centers as reported by Pieterse *et al*⁴.

Figure S4. Excitation (solid line: λ_{em} is 472 nm; dashed line: λ_{em} is 456 nm) and emission (solid line: λ_{ex} is 282 nm; dashed line: λ_{ex} is 336 nm) spectra of Sr_2CeO_4 recorded at room temperature.

