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Role of interface states associated with transitional nanophase precipitates in the photoluminescence enhancement of $SrTiO_3$:Pr^{3+},Al^{3+}.

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Thermoanalytical studies:

Fig. S1 shows the simultaneous TG/DTA curves of the gel-carbonate precipitate. TG of the precipitate after heating at 110°C for 24 hours shows that the mass loss occurs in two steps: (i) initial mass loss of about 5% below 200°C due to the resorbed water. This is followed by a near constant mass through the broad range of temperature upto 700°C and (ii) the mass loss of about 15% occurs again through the broad range of temperature from 850 to 1000°C due to the reaction of nanoparticles of $SrCO_3$ with the TiO_2 xerogel accompanied by the release of CO_2. Mass loss experiments were also carried out under isothermal conditions by heating the samples for several hours at selected temperatures. After drying at 110°C for extended periods, the residue shows the mass loss of 6% upto 750°C and 15% upto 950°C. Above 950°C, the weight remains almost unchanged, indicating the complete evolution of CO_2 from $SrCO_3 + TiO_2$ reaction.

The endothermic maximum around 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 leads to the broad exotherm and is due to partial recrystallization of the xerogel to crystalline TiO_2. The endotherm around 930°C corresponds to the reaction of $SrCO_3$ with TiO_2.

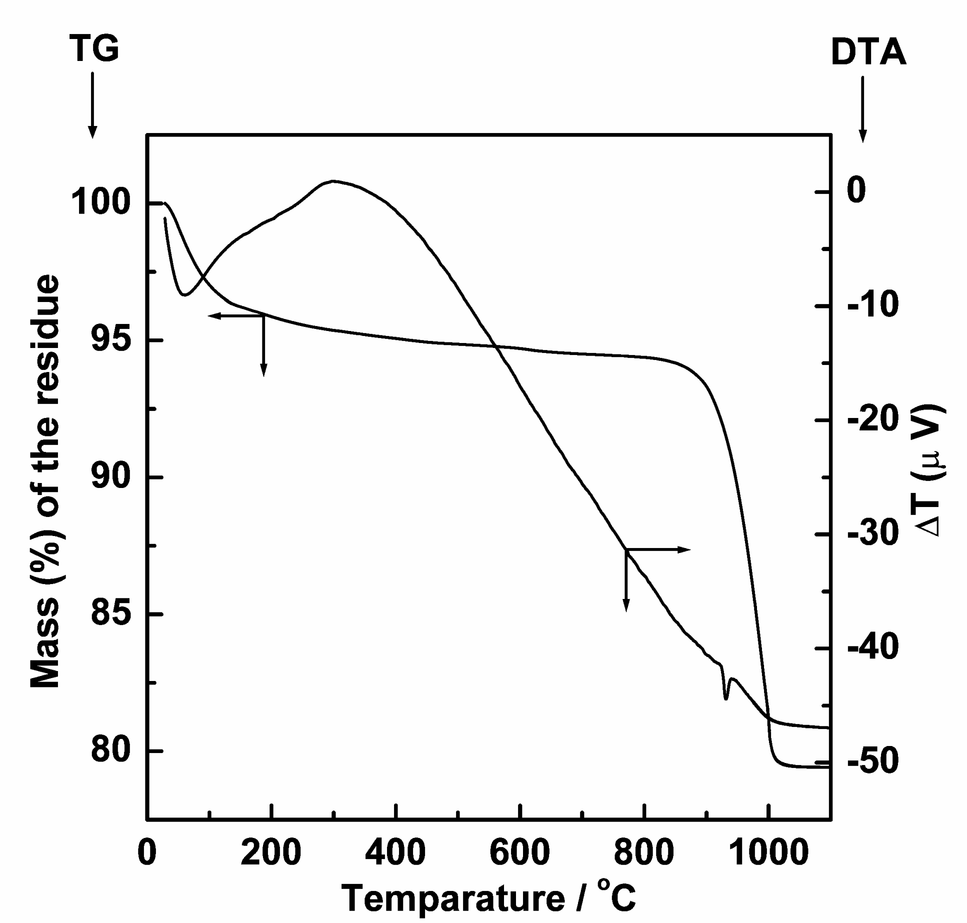

Fig. S1. TG-DTA curve of a composite precipitate of $SrCO_3$ and hydrated titania in air at a heating rate of 10°C min^{-1}

X-ray Diffraction analyses

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 powder dried at 110°C shows the presence of $SrCO_3$ as the only crystalline phase [Fig. S2(a)]. No TiO_2 is detected since it is in the amorphous form, as xerogel of hydrated titania. Heat treatment of the powder at 650°C gives only reflections corresponding to $SrCO_3$. On heat treatment at 750°C, $SrTiO_3$ formation is discernible, whereas no reflection of TiO_2 is observed [Fig. S2(b)]. As the calcination temperature is increased to 850°C, reflections corresponding to $SrTiO_3$, Sr_2TiO_4, TiO_2 (rutile) and $SrCO_3$ are observed [Fig. S2(c)]. Heat treatment at 950°C results in powders containing $SrTiO_3$, Sr_2TiO_4 and TiO_2 with increased intensities of $SrTiO_3$ reflections [Fig. S2(d)]. Further calcination at 1050°C results in the evolution of the perovskite, $SrTiO_3$, with complete phase purity [Fig. S2(e)].

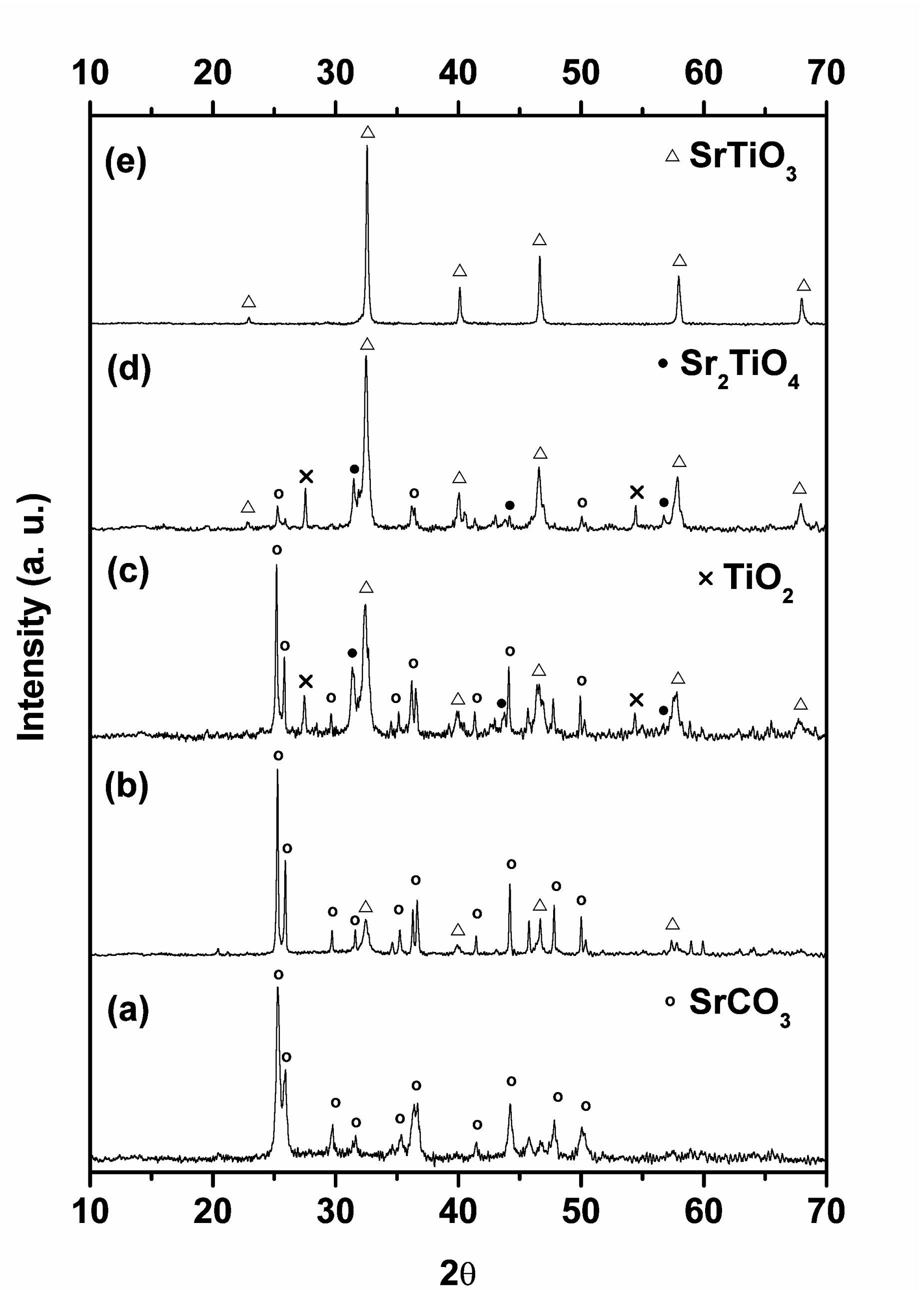

Fig. S2. X-ray diffraction patterns of the sample at (a) 110°C, (b) 750°C, (c) 850°C, (d) 950°C and (e) 1050°C show the evolution of crystalline $SrTiO_3$ from the composite powder.

Reactions involved during the course of gel-carbonate preparation

The precipitation method described in this paper gives rise to composite powders wherein nanometer sized particles of strontium carbonate crystallites are embedded within the amorphous gels of hydrated titanium oxide. The carbonates of titanium are not formed, as they are unstable. Since aluminium hydroxide gel has the same chemical behavior as of titania gel (i.e. the corresponding carbonates are unstable) both could be precipitated as hydrated mixed gels. Further, titanium has the tendency to form polymeric chains such as $(Ti{-}O{-}Ti)_n$ in preference to isolated Ti^{4+} ions. These polymeric chains of metal hydroxide form entangled network within the gel and thereby the solvent is entrapped. The effective molar volume of this network is very large in comparison to that of strontium carbonate which is formed simultaneously as crystalline fine particles. As a result, $SrCO_3$ gets embedded within the polymeric network of the gel. This accounts for the generation of the composite precipitate. During calcination, dehydroxylation of $TiO_2.xH_2O$ takes place which, in turn, reacts with $SrCO_3$ to yield phase-pure $SrTiO_3$ through the formation of the intermediate Sr_2TiO_4. The sequence of reactions occurring during the formation of $SrTiO_3$ can be formulated as follows:

$$TiO_2.xH_2O \xrightarrow{<400\ ^oC} TiO_2\ (xerogel) + xH_2O\ (80<x<110) \qquad ....(1)$$

$$SrCO_3 + TiO_2\ (xerogel) \xrightarrow{750^oC} SrTiO_3 + CO_2 \uparrow \qquad ....(2)$$

$$\left.\begin{array}{l} 2SrCO_3 + TiO_2\ (xerogel) \xrightarrow{>750\ ^oC} Sr_2TiO_4 + 2CO_2 \uparrow \\ TiO_2\ (xerogel) \xrightarrow{>750\ ^oC} TiO_2\ (rutile) \end{array}\right] ..(3)$$

$$Sr_2TiO_4 + TiO_2\ (rutile) \xrightarrow{950\ -\ 1050^oC} 2SrTiO_3 \qquad ....(4)$$

Formation of $SrTiO_3$ around 750°C from the reaction of the titania xerogel with the carbonate is only partial. This is because of the onset of the parallel reaction of Sr_2TiO_4 formation. This is accompanied by the conversion of TiO_2 xerogel to the rutile phase. In turn, Sr_2TiO_4 reacts with rutile to yield phase-pure $SrTiO_3$. Therefore, the reaction pathway followed by the composite powders is completely different from those of the products from other wet chemical processes as also of the solid-solid reaction between the binary oxides. The gel-carbonate route yields homogenous, highly reactive powders which produce phase-pure crystalline $SrTiO_3$ at relatively low temperatures in comparison to the ceramic process. This method also yields Al-containing as well as Ti-excess $SrTiO_3$ which may prevail metastability because of the specific reaction path mentioned above.