New insights towards strikingly improved room temperature ethanol sensing properties of p-type Ce-doped SnO$_2$ sensors

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In this article, room temperature ethanol sensing behavior of p-type Ce doped SnO$_2$ nanostructures are investigated successfully. Interestingly, it is examined that the abnormal n to p-type transition behavior is caused by Ce doping in SnO$_2$ lattice. In p-type Ce doped SnO$_2$, Ce ion substituting the Sn is in favor of generating excess holes as oxygen vacancies, which is associated with the improved sensing performance. Although, p-type SnO$_2$ is one of the important materials for practical applications, it is less studied as compared to n-type SnO$_2$. Pure and Ce doped SnO$_2$ nanostructures were successfully synthesized by chemical co-precipitation method. The structure, surface morphology, unpaired electrons (such as free radicals), and chemical composition of obtained nanoparticles were studied by various kinds of characterization techniques. The 9% Ce doped SnO$_2$ sensors exhibit maximum sensor response of $\sim$382 for 400 ppm of ethanol exposure with fast response time of $\sim$5 to 25 sec respectively. Moreover, it is quite interesting that such enhancement of ethanol sensing is unveiled at room temperature, which plays a key role in the quest for better ethanol sensors. These remarkably improved sensing results are attributed to uniformly distributed nanoparticles, lattice strain, complex defect chemistry and presence of large number of unpaired electrons on the surface.

In past six decades, metal oxide semiconductors (MOS) have been one of the most prevailing gas sensing materials among large miscellany of materials on the grounds of its low production cost, tranquility during use and prominent selectivity for various gases in addition to high detection$^{1-5}$. Over the past few decades, an intense requirement of gas sensors has become progressively greater by virtue of elevated atmospheric pollution leading towards the emission of hazardous gases$^{6-10}$. One of the vital requirements of such gas sensors can be ethanol sensors. Those working on ethanol synthesis, experience hardship from the huge probability of being victims of digestive track cancer and increased risk of respiratory symptoms of a threshold limit (1000 ppm). Thus, an increasing demands and emerging challenges for detection of ethanol gas at ppm/ppb level have enforced the researchers to fabricate low cost, high performance and relatively stable ethanol sensors. With the growing interest in progression of sensing devices, more and more exhilarating results of MOS have been reported in literature$^{10-14}$. The gas sensors developed by various types of MOS exhibited good sensitivity to ethanol at different operating temperatures (OT)$^{15-19}$ suggesting that most of the ethanol sensors work at higher temperature. Various MOS such as TiO$_2$, GeO$_2$, Cr$_2$O$_3$, Mn$_2$O$_3$, NiO, CuO, CdO, CeO$_2$, MgO, BaO, In$_2$O$_3$, WO$_3$, V$_2$O$_5$, Fe$_2$O$_3$, Nb$_2$O$_5$, MoO$_3$, Co$_3$O$_4$, Ta$_2$O$_5$, La$_2$O$_3$, Nd$_2$O$_3$ etc. are well-known and widely used for metal oxide based sensors for the detection of different chemical inputs$^{20,21}$.

Among them, pure SnO$_2$ is one of the most prominent n-type, wide band gap (3.6 eV) MOS with a carrier concentration of $5.7 \times 10^{20}$ cm$^{-3}$ making it an outstanding material for chemical gas sensors$^{22-24}$. Although pure SnO$_2$ has an excellent sensitivity but the major drawbacks are its poor selectivity which hinders a lot to meet

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up all practical key parameters such as high sensitivity, faster response-recovery time, stability and low power consumption for realistic sensor applications. Thus, despite of substantial research work carried out on sensing materials, still there is a scope of exploration for hazardous gases at room temperature (RT). For that, metal ion doping in SnO$_2$ lattice may be one of the influencing factors for the furtherance in sensing properties of SnO$_2$. In case of doped SnO$_2$, substitutional and interstitial point defects may exist depending on the rearrangement of the internal defects in SnO$_2$ lattice. In addition, the semiconducting behavior can be predicted depending on the type of doping (donor or acceptor) introduced to the host material in order to tailor the band bending and band alignments on which the amount of gas sensing enhancement relies. It is noteworthy that gas sensing has been explored using SnO$_2$ exhibiting n-type behavior but their equivalent p-type counterpart was unexpectedly absent for a long time. In past a decade, the exploration of novel p-type SnO$_2$ for gas sensors has been started and the researchers and technologists around the globe are making an effort to discover an effective method to attain the p-type conduction in the n-type SnO$_2$. In literature, p-type conductivity in SnO$_2$ has been achieved by doping M$_{50}$ metal ions (where, M = Li, Al, Ga, In and Cd) acting as a substitutional dopant in SnO$_2$ playing an important role to enhance the gas sensing characteristics. Hence, the understanding of synthesis and fabrication of p-type SnO$_2$ gas sensors would be a worthy research area to open up several new possibilities in device applications.

In this study, authors have used the state of art to explore p-type conduction mechanism in Ce-doped SnO$_2$ to characterize RT ethanol sensing. Although Ce-doped n-type SnO$_2$ based sensors have already been used for the detection of ethanol but reported operating temperatures of these sensors are as high as 300 to 500 °C and no reports have been shown on p-type conduction in Ce-doped SnO$_2$ ethanol sensors at RT. Therefore, the fabrication of stable and highly selective gas sensing materials working at RT is still highly desirable. Present work demonstrated the RT ethanol sensors based on p-type Ce-doped SnO$_2$ nanostructured devices to understand their mechanism under consideration of several aspects that influence the sensor performance including defect chemistry, surface morphology, several diffusion processes, and associated unpaired electrons in the form of free radicals. However, from the literature and present study, authors realized that the level of understanding of these mechanisms is still lacking and in-depth research in this area is required. To the best of our knowledge, it is the first systematic report on p-type Ce doped SnO$_2$ nanostructure based RT ethanol sensor. The results described in this article indicates that 9 wt % Ce doped SnO$_2$ sensor is highly sensitive and selective towards ethanol detection at RT.

**Results**

**XRD analysis.** The XRD patterns of pure and Ce doped SnO$_2$ nanostructured samples are elucidated in Fig. 1. As it can be seen that, pure SnO$_2$ have tetragonal rutile structure which is indexed with JCPDS file 00-041-1445.

![XRD patterns](Image)
It has been observed from Fig. 1(b–d) that Ce doped SnO₂ nanomaterials have all the peaks of SnO₂ with a few peaks of CeO₂. These peaks were indexed with the JCPDS files of SnO₂ and CeO₂ (JCPDS file no.: 01-075-0120). The XRD pattern of pure and Ce doped SnO₂ nanomaterials have been refined by Rietveld refinement using FULLPROF Suite programme. The background for all samples was refined by 6th degree Polynomial function. The pseudo-voigt profile function (linear combination of Gaussian and Lorentzian) was used to describe the peak shape of all the samples. The Rietveld refinement data of pure and Ce doped SnO₂ nanomaterial samples are summarized in Table 1. It can be seen from Fig. 1 that the diffraction peaks of all the samples were well fitted. The lattice parameters, atomic position and phase fraction are listed in Table 1. The increase in magnitude of the peak shape of all the samples. The Rietveld refinement data of pure and Ce doped SnO₂ nanomaterial samples are presented in Table 1. It can be seen from Fig. 1 that the diffraction peaks of all the samples were well fitted. The increase in magnitude of lattice parameter and cell volume of Ce doped SnO₂ are shown in Table 1. The lattice parameter a’ and c’ of the Ce doped SnO₂ unit cell is found to increase linearly with the Ce concentration following Vegards law. It is shown in figure (see Supporting Information, Fig. S1). It is also observed that the full width at half maxima (FWHM) increases with an increase in Ce content in the SnO₂. Hence, this indicates that Ce doping in the SnO₂ lattice leads to decrease in crystallite size. From the increased lattice constant with the addition of Ce content, it is confirmed that Ce ions have been effectively doped in SnO₂ lattice and some part is present in the form of CeO₂. The substitution of Sn by Ce creates vacancies and disturb local arrangements of the crystal structure which is further confirmed from ESR analysis. Similar observations have been reported in the literature by Yang et al.

The influences of increased lattice parameter and micro strain on sensing characteristics have been discussed at the end of this section. The surface morphology and elemental composition of the sensor materials have been studied using FESEM and EDS measurement (see Supporting Information, Figs S3 and S4).

### TEM and HRTEM analysis

Figure 2(a–c) shows the TEM images of pure and Ce doped SnO₂ nanomaterials. From TEM images, it is clear that the particle size is decreasing with the addition of Ce content. The nanoparticles are random/polygon in shape with the average particle size of ~16 nm, ~12 nm and ~6 nm for Pure SnO₂, and Ce doped SnO₂ (0, 6 and 9%) respectively. 9% Ce doped SnO₂ nanomaterial results in formation of uniformly rings of pure SnO₂ are indexed as (110), (101), (200), (211) and (301) confirming the tetragonal rutile structure.

| Samples (wt. % of Ce) | Atomic position | a (Å) | y (Å) | z (Å) | Phase Fraction (%) | χ² | Lattice Parameter | Volume (Å³) | Strain |
|-----------------------|----------------|------|------|------|-------------------|-----|------------------|------------|--------|
| 0                     | Sn 0.00 0.00 0.00 | SnO₂ 100 1.96 | 4.741 | 3.188 | 71.656 | 1.28×10⁻³ |
| 3                     | Sn 0.00 0.00 0.00 | SnO₂ 93.23 1.70 | 4.742 | 3.189 | 71.709 | 2.3×10⁻³ |
| 6                     | Sn 0.00 0.00 0.00 | SnO₂ 90.68 2.08 | 4.745 | 3.190 | 71.762 | 3.2×10⁻³ |
| 9                     | Sn 0.00 0.00 0.00 | CeO₂ 85.85 2.3 | 4.744 | 3.191 | 71.815 | 3.4×10⁻³ |

Table 1. Atomic position, Phase fraction, Lattice parameter, Volume, χ² values obtained by Rietveld refinement and strain value using W-H analysis.

### ESR analysis

The presence of unpaired electrons in the form of free radicals and charge carriers has been studied using ESR spectroscopy. The Fig. 4 shows the ESR dispersion derivative (dp/dH) as a function of magnetic field. The ESR measurements were performed at microwave frequency of ~9.45 GHz (X-band). When the external magnetic field is applied, the spin interactions of the unpaired electrons can be studied from ESR spectra recorded for pure and Ce doped SnO₂ at RT. As it is known that the spin quantum number (s) of ½ with the magnetic moments consisting of two magnetic components ms = +½ and −½ in parallel and antiparallel respectively. These magnetic components are aligned to the applied field with the strength of B₀, having a specific energy. There is a possibility of either absorption or emission of electromagnetic radiation by unpaired electrons and they also consist of two energy levels between which the unpaired electrons can move. The change in the two energy levels of an electron can be obtained by ΔE = gμₐB₀, where, g and μₐ are electron’s g factor and Bohr magnetron
\( \mu_B = 9.274 \times 10^{-24}\) JT\(^{-1}\) respectively. ESR spectra show a resonance at 336.07, 336.1, 336.2 and 336.4 mT for pure and Ce doped SnO\(_2\) (0, 3, 6 and 9%) samples respectively. Although resonance field is not affected much, Fig. 4 shows that peak to peak line width and power absorption during resonance increases remarkably upon Ce addition. Small \( \Delta H_{pp} \) and high intensity observed in 9% Ce doped SnO\(_2\) may be attributed to the existence of large number of intrinsic oxygen vacancies. The g-value for all samples were calculated from resonance magnetic field

Figure 2. TEM micrograph of pure and Ce doped SnO\(_2\) with addition of different concentrations of Ce: (a) 0%, (b) 6% and (c) 9%.

Figure 3. HRTEM micrograph of (a) pure SnO\(_2\) (b) 9% Ce doped SnO\(_2\) samples. SAD pattern of the (c) pure SnO\(_2\) (d) 9% Ce doped SnO\(_2\) samples.
as shown in Table 2, which is nearly equal to the g−value of (2.008) of free electron44. The g-factor was calculated as $g = \frac{\mu}{\vartheta g h B}$ similar to the reported in literature45. The width of the ESR signal was found to be the lowest (~0.92) in 9% Ce doped SnO$_2$ sample. The narrowing of ESR line is attributed to strong exchange of unpaired electrons and delocalization of unpaired electrons over a large system of conjugated chemical bonds46. Thus, the defect chemistry of Ce-doped samples were characterized by studying the presence of free electrons using ESR spectroscopy and the analysis suggested that Ce doping in SnO$_2$ create a huge amount of free electrons which is certainly responsible for improved sensitivity.

### XPS analysis.

The core level x-ray photoelectron spectra’s of 9 wt.% Ce doped SnO$_2$ sample has been investigated in vacuum of the order of $2.4 \times 10^{-9}$ torr. All obtained peaks were fitted by the coalition of Lorentzian and Gaussian function to reduce the least square error of the fit. A linear and tougaard background function was used to account the inelastic background in the XPS spectrum. All the XPS spectra shown in Fig. 5, are referenced to C 1s peak (284.6 eV). The deconvoluted XPS core level Sn 3d spectra’s of 9 wt.% Ce doped SnO$_2$ sample indicates the presence of Sn with two oxidation state i.e Sn$^{2+}$ and Sn$^{4+}$ respectively shown in Fig. 5(a)47–50. Figure 5(b) shows the deconvoluted XPS core level Ce 3d spectra of 9 wt.% Ce doped SnO$_2$ sample. The valence state of Ce 3d was determined by deconvolation of Ce 3d spectra. The Ce 3d spectra is fitted with the five subpeaks. These subpeaks corresponding to Ce$^{3+}$ and Ce$^{4+}$ valance state respectively. In Fig. 5(b), binding energy at 882.2 eV, 900.8 eV and 916.7 eV sub peaks were assigned to Ce$^{4+}$ valance state51–53, whereas 885.8 eV and 903.9 eV sub peaks were ascribed to Ce$^{3+}$ valence state54,55. Above results confirmed that 9 wt.% Ce doped SnO$_2$ sample displayed the presence of mixed valence state of Ce$^{3+}$ and Ce$^{4+}$ with the relative percentage of 70% and 30% respectively. This suggest that the content of Ce$^{3+}$ is higher than Ce$^{4+}$ valence state, which indicates that Ce$^{3+}$ ion were substituted into SnO$_2$ lattice. Hence Ce$^{3+}$ substitution at Sn$^{4+}$ site is a firm reason for n to p-type transition by Ce doping in SnO$_2$ lattice which is further confirmed from Hall measurement results (see Supporting Information, Table S1). The substitution at Sn$^{4+}$ by Ce$^{3+}$ triggered the creation of oxygen vacancy defects in SnO$_2$ lattice, which is well matched with ESR results. The O 1s spectrum for 9 wt.% Ce doped SnO$_2$ presented in the Fig. 5(c). It has been observed from the Fig. 5(c), that two components are present at 530.5 eV and 531.7 eV. This first peak (530.5 eV) is associated to lattice oxygen bound to Sn$^{66,67}$ and second peak at 531.7 eV corresponds to oxygen deficient region in SnO$_2$ matrix$^{68,69}$.

### Sensing measurements.

The gas sensing measurements of pure and Ce doped SnO$_2$ sensors were performed at RT for ethanol detection. Before starting the measurements, each sensor was initially purged with synthetic air for 10 minutes to stabilise the base line resistance. The exposure time to the chemical inputs was maintained to be 5 sec and for recovery, the exposure to reference synthetic air was maintained to 10 sec.

| Samples                  | g-factor | $\Delta H_{pp}$ (mT) |
|--------------------------|----------|---------------------|
| Pure SnO$_2$             | 2.009    | 1.32                |
| 3 wt.% Ce doped SnO$_2$  | 2.009    | 1.26                |
| 6 wt.% Ce doped SnO$_2$  | 2.007    | 1.46                |
| 9 wt.% Ce doped SnO$_2$  | 2.008    | 0.92                |

Table 2. ESR data of pure and Ce doped SnO$_2$ samples.
respectively. The resistance of sensing materials increased or decreased to the exposure and removal of chemical inputs. The gas sensitivity is defined as follows:

\[
S_R = \frac{R_g - R_a}{R_a} \times 100 \quad \text{(For reducing gas)}
\]

\[
S_O = \frac{R_a - R_g}{R_g} \times 100 \quad \text{(For oxidizing gas)}
\]

where, \( R_g \) is the electrical resistance in presence of gas and \( R_a \) is the electrical resistance in clean synthetic air atmosphere only. Figure 6(a,b) shows the repeatable operation cycles of 9 and 6\% Ce doped SnO\(_2\) sensors in the ethanol exposure at RT. The response signal of 9, 6 and 3\% Ce doped SnO\(_2\) sensors for various amount of concentration at RT is shown in Fig. 6(a–c). Figure 6(d) shows the response signal of 9\% Ce doped SnO\(_2\) sensors for NO\(_2\) and ethanol exposure. It has also been observed that sensor response (recovery) times are of the order of ~5–30 secs (30–60 secs) as seen from Fig. 6(a–d). The sensor response of pure and Ce doped SnO\(_2\) as a function of ethanol concentration is shown in Fig. 7(a). It is evident from the Fig. that 9\% Ce doped SnO\(_2\) sensor exhibits higher sensitivity for various amount of ethanol concentration at RT. The 9\% Ce doped SnO\(_2\) sensor shows a striking improvement of RT ethanol sensing behaviour as compared to pure SnO\(_2\). Selectivity behaviour of the pure and Ce doped SnO\(_2\) sensor was tested with 400 ppm of C\(_2\)H\(_5\)OH (ethanol), NH\(_3\) (ammonia) and NO\(_2\) gas. The sensitivity values for all the above-mentioned chemical inputs are shown in Fig. 7(b). We can clearly observe from the Fig. 7(b) that 9\% Ce doped SnO\(_2\) sensor is highly selective to ethanol gas at RT. The use of the sensing device for longer duration with accuracy depends upon reproducibility, reliability and repeatability. The sensor performance should not vary with time and operation cycles. The stability of 9\% Ce doped SnO\(_2\) sensor towards ethanol at RT has been studied for 180 days. It has been confirmed that 9\% Ce doped SnO\(_2\) sensor displays better stability and repeatability even at the end of 6\(^{th}\) month which is ~97–98\% as compared to initial measurements (see Supporting Information, Fig. S5). Such stability and repeatability analysis suggest that the 9\% Ce doped SnO\(_2\) sensor can be used for long duration, which is one of the major advantages for practical applications.
Discussion

As it is clear that the undoped SnO$_2$ will never exhibit p-type semiconducting behaviour. In order to overcome the barriers regarding the enhancement of the gas sensing, different amount of Ce has been doped into pure n-type SnO$_2$ and sensing measurements of p-type Ce doped SnO$_2$ has been studied systematically. As shown in Fig. 7(a), a linear sensor response has been observed for C$_2$H$_5$OH concentration (ppm) varying from 100 to 400 ppm indicating enhanced sensing for 9 wt% Ce doped SnO$_2$ material at RT. As discussed from XRD measurements, it is evident that Ce has been incorporated in SnO$_2$ lattice which causes increase in lattice parameter and micro strain. From the above analysis, it is confirmed that defect chemistry has been modified with the incorporation of Ce into SnO$_2$. The assumptions regarding defect states can be made in order to identify the type of defects induced in the structure with doping: (i) substitution of Ce in place of Sn (Ce$_{Sn}$) (ii) interstitial oxygen (O$_i$) formation because of the occupation of Sn position by Ce atom and (iii) a complex defect (Ce$_{Sn}$ + 2O$_i$) may be
present at the Sn site. Figure 8 shows the schematic illustration of defect chemistry caused by Ce doping in SnO₂ lattice. In order to justify the drastically enhanced sensing mechanism in Ce doped SnO₂, one needs to identify the dominance of the defects as mentioned above and an in-depth analysis is required. As discussed earlier from the ESR measurements, it is clear that there is a strong exchange of unpaired electrons and delocalized unpaired electrons in the form of free radicals. Small ΔHpp and high intensity is observed in 9% Ce-doped SnO₂ may be attributed to the existence of large number of intrinsic oxygen vacancies. This suggested that the increase in the Ce doping concentrations leads to the increase in the interstitial oxygen atoms present in the structure/system. This is because there is a reduction in the Sn content via substitution of Ce (CeSn) which is also evident from EDS analysis (see Supporting Information, Fig. S4). Hence, it is revealed that the doping conditions have been resulted in Sn-poor/O-rich condition which should be the reason for p-type semiconductor. From the literature, it is confirmed that the CeSn acts as a donor because of the lower formation energy. In addition, the complex defect (CeSn + 2O) present at the Sn site consists of relatively high formation energy and behaves as an acceptor. It is here to be understood that there is a chance of existence of self-compensation between lower formation energized donors and acceptors respectively. Such self-compensation will suppress CeSn by (CeSn + 2O) complex defect and can be predicted to behave like an acceptor concluding that the Ce doped SnO₂ behaves as a p-type semiconductor. It has been confirmed that, when C₂H₅OH gas exposed to all the sensors, the 9% Ce-doped SnO₂ sensor shows the highest response (SR = 382) for 100 to 400 ppm concentrations of C₂H₅OH at RT. The improved sensors response of the p-type Ce-doped SnO₂ nanostructures to ethanol at RT can be studied in more detail in order to clarify sensing mechanism. The defect of the p-type Ce-doped SnO₂ and their sensing mechanism can be explained using the following reactions (in Kröger-Vink notation)

SnO₂ → 2CeSn + 3O⁰ₓ + V° (3)

\[ \frac{1}{2}O_{2(g)} \leftrightarrow O_{(ads)} + h \] (4)

However, CeSn is the Ce substitution in Sn sites and O⁰ₓ is the lattice oxygen and V° denotes the two positively charged vacancies on an oxygen sites. Thus, in p-type Ce-doped SnO₂, the adsorption of negatively charged oxygen ion can produce the holes for conduction which is shown in the reaction-4. The interactions between ethanol and surface adsorbed oxygen in p-type Ce-doped SnO₂ can be described by reaction 5. The resulting gas-sensing equation may be considered according to the charges of the adsorbed oxygen ions under the hypothesis of complete oxidation of C₂H₅OH.

C₂H₅OH(g) + 6O⁻(ads) + 6h → 2CO₂(ads) + 3H₂O(g) (5)

Thus, complete oxidation of C₂H₅OH in the above reactions increased the resistance and concurrently decreases the conductance of the surface region of p-type Ce-doped SnO₂ upon exposure to ethanol. Such changes in resistance while exposure to ethanol in Ce-doped sensors shown in Fig. 6.

In order to summarize the improved gas sensing behaviour of 9 wt % Ce doped SnO₂ sensor towards ethanol at RT, four major factors are responsible (i) more structural defects present in the sample, (ii) particle size becomes twice of the Debye length and (iii) high surface to volume ratio and (iv) presence of a large number of unpaired electrons on the sensor surface. It can therefore, be inferred from XRD analysis that Ce doping in SnO₂ leads to an increase in lattice strain as well as deviation from atomic position of the host material observed. This deviation from atomic position of the host material and increased lattice strain will result in the formation of more structural defects within the system. When Sn is substituted by isovalent Ce atoms, Ce⁴⁺ could be easily reduced to Ce³⁺ which leads to the formation of an acceptor-like defects resulting the Ce doped SnO₂ behaviour as a p-type semiconductor. On the other hand, it was essential to mention that above 3% Ce, the semiconducting behaviour transforms into p-type which has been one of the reason for the drastic increase in ethanol sensing. Analogous behaviour has been reported by Chattopahhyay and co-workers in case of Al doped SnO₂. It has been reported that below 12.05% Al substitution in SnO₂, the sample exhibited n-type semiconducting
evaluate the gas response is related to the Debye length ($L_D$). There may be three cases to be assumed: (i) present study that the 9 wt% Ce doped SnO$_2$ sensor remarkably enhanced the ethanol sensor response at RT with temperatures, sensor response, and recovery times of some ethanol sensors. However, sensor response of SnO$_2$ based in case of 9% Ce-SnO$_2$, the particle size becomes twice of the Debye length i.e. $d \gg 2L_s$ because of the conduction mechanism taking place across the grain boundary is limited by Schottky barriers. But as discussed earlier from the TEM analysis, the variation in the particle size from 16 nm to 6 nm has been observed during resonance increases remarkably with Ce doping. Small $\Delta H_{pp}$ and highest intensity is noticed in 9% Ce doped SnO$_2$ and resulted into the existence of large number of free electrons in the form of oxygen vacancies. Increase in sensitivity due to higher oxygen vacancies is previously reported in literature. FESEM studies also confirmed that 9 wt % Ce doped SnO$_2$ sensor exhibited the lowest grain size ~8 (2) nm and the number of grain boundaries increases by decreasing the gain size (see Supporting Information, Fig. S3). Therefore, surface areas increase steadily with the increased Ce concentration. Hence 9 wt % Ce doped SnO$_2$ sensor shows a higher sensor response to ethanol at RT due to their larger surface areas. More surface areas provide more active sites for the adsorption of the chemical inputs which are responsible for the improvement of the gas sensor response. As discussed earlier from the TEM analysis, the variation in the particle size from 16 nm to 6 nm has been observed for the doping wt% ranging from 0 to 9% respectively. To understand the effect of particle size on the sensing mechanism, one needs to establish the relationship of particle size with Debye length depending on the type of metal oxide, the analyzed gas, and detection mechanism to be taken place. The main fundamental parameter to evaluate the gas response is related to the Debye length (LD). There may be three cases to be assumed: (i) $d \gg 2L_s$ (ii) $d \sim 2L_s$ (iii) $d < 2L_s$. From the literature, it is considered that LD of SnO$_2$ is about ~3 nm. In case of 0%, 3% and 6% Ce-SnO$_2$, assumption 1 has been satisfied stating that the gas sensing behavior may be practically independent of d because of the conduction mechanism taking place across the grain boundary is limited by Schottky barriers. But in case of 9% Ce-SnO$_2$, the particle size becomes twice of the Debye length i.e. $d \sim 2L_s$. This shows that the conductive channels between grains are overlapped attributed to the complete depletion of space charge region while interacting with the oxygen molecules. Hence, whole particle takes part in the gas sensing and as a result higher sensitivity is observed. So, the major factor for the higher sensing are attributed to the increased concentration of adsorbed oxygen species on the fully depleted junctions across the grains resulting into the higher sensing for ethanol at RT. In Table 3, the ethanol sensing response of the 9 wt% Ce doped SnO$_2$ sensors are compared with those of the earlier published reports. Table 3 displays materials used, deposition technique, operating temperatures, sensor response, and recovery times of some ethanol sensors. However, sensor response of SnO$_2$ based sensors are good, but operating temperatures are very high. On the other hand, it must also be observed from the present study that the 9 wt% Ce doped SnO$_2$ sensor remarkably enhanced the ethanol sensor response at RT with faster response (recovery) time ~5–20 sec (~30–60 sec). Hence, the strikingly improved sensor response of 9% Ce-doped SnO$_2$ sensor upon exposure of C$_2$H$_5$OH is associated to the uniformly distributed nanoparticles with size approximately twice of the Debye length; high surface area, defect chemistry and presence of a large number of unpaired electrons of the sensor surface.

### Conclusions

In conclusion, systematic studies have been performed on the synthesis, characterization and RT gas sensing behaviour of p-type Ce doped SnO$_2$ sensor. Pure and Ce doped SnO$_2$ sensor have been successfully synthesized by chemical co-precipitation method and used to detect ethanol at RT. To the best of our knowledge, this is the first time a p-type Ce-doped SnO$_2$ has been studied and demonstrated to meet the requirements for highly sensitive,
selective and long-time stable low cost sensing device. The maximum sensitivity is ~382 for 400 ppm with fast response time of ~5 to 25 sec have been obtained in 9% Ce doped SnO₂ towards ethanol at RT. The high sensitivity of Ce doped SnO₂ sensor towards C₂H₅OH is attributed to the uniformly distributed nanoparticles with size approximately twice of the Debye length, defect chemistry, presence of a large number of unpaired electrons, and creating the excess of holes, as oxygen vacancies. This study suggests a practical approach to the fabrication and design of high performance ethanol sensors working at RT.

Experimental Materials and Reagents. Tin(IV) chloride pentahydrate (SnCl₄·5H₂O), cerium(III) Chloride heptahydrate (CeCl₃·7H₂O), and stearic acid were purchased from Sigma-Aldrich. Ethanol (C₂H₅OH) and ammonia were purchased from Merck limited. All reagents were used without further purification.

Synthesis. In present work, pure and Ce doped SnO₂ samples are synthesized with three different Ce concentrations (the mole ratio of Ce/Sn = 3, 6 and 9 wt%) through a chemical co-precipitation method. Ethanol is used as a solvent for the synthesis of metal oxide nanoparticles. In a typical synthesis of Ce doped SnO₂ sensor, SnCl₄·5H₂O and CeCl₃·7H₂O in stoichiometric proportions were dissolved in ethanol (C₂H₅OH). For the precipitation of the solution, ammonia and stearic acid was added drop wise to the precursor solution with continuous stirring and the final pH was maintained at 10. Obtained precipitates were filtered and washed several times with absolute alcohol and distilled water, then dried in a vacuum oven at 95°C for 4 hours. These obtained powder samples (undoped and Ce doped SnO₂) were annealed at 800°C for six hours using a muffle furnace and were cool down at the rate of 100°C per hour. The obtained powder samples have been used to fabricate the sensor device. The gold interdigital six finger electrodes patterns were deposited on the alumina substrates by thermal evaporation. The width of each finger is 500μm and the interspacing between the fingers is 700μm respectively. Then, the gas sensor was fabricated by drop casting technique. The pure and Ce-doped SnO₂ dispersed in appropriate amount of ethanol followed by ultrasonication for 30 minutes. Thereafter, the solution was drop casted on the Au interdigital electrodes patterned substrate. The deposited sensor films were sintered at 95°C for 30 minutes in a vacuum oven.

Characterizations. The samples were characterized using X-ray diffraction (XRD, Bruker D8 advanced diffractometer) in the scanning range of 20–80° (2θ) with the step size of 0.0195° using Cu-Kα radiations. The Rietveld refinement of XRD data has been done by FULLPROF program. Surface morphology and chemical composition of sensor materials were determined using field emission scanning electron microscope (FESEM, Model Sigma, Carl Zeiss). The morphological and structural information were carried out using high-resolution transmission electron microscope (TEM, FEI Tecnai G230, Hillsboro, U.S.A.). To study the presence of unpaired electrons, electron spin resonance (ESR) spectra was recorded at RT by using ESR X-band spectrometer operating at 9.45 GHz frequency, 2.99 mW power with the sweeping time of 2 mins. X-ray photo-electron spectroscopy XPS (Perkin Elmer-1257 with hemispherical section analyzer with 25 mEV resolution) has been used. XPS set up consist of dual anode X-ray source, which is capable of generating Al Kα (1486.6 eV) or Mg Kα (1253.6 eV) X-ray radiations. The sensing measurements were performed in custom designed gas sensing set up attached with mass flow controllers for precise measurement of gas flow at ppm level.

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Author Contributions
M.K. performed the experiments and wrote the manuscript. V.B. interpreted the data. J.H.Y. and A.C.A. designed the experiments and supervised the project. S.H.P. helped in XPS measurements of the samples. A.K. and J.K. polished the paper.

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