Studies on Gas Sensing Performance of Surface modified Lanthanum dope Barium Titnate

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Abstract

Nanocrystalline Lanthanum dope Barium titanate ($BaLaTiO_3$) are synthesized by hydrothermal route and surface modified Lanthanum dope Barium titanate ($BaLaTiO_3$) by dipping method. The formations of nano crystalline were characterized by X-ray diffraction studies (XRD), SEM and XRD analysis confirms material, crystallite size calculated from Scherer's equation ranging from 31 to 50 nm. The thick films of Nanocrystalline $BaLaTiO_3$ were prepared by screen -printing technique in desired pattern and surface modification was done by 2% stannous chloride. The gas sensing performance of the materials have been investigated for various interfering gases such as CO, NH_3, H_2S, LPG, CO_2, H_2, SO_2 etc. At operating temperature varying from 50 ^oC to 450 ^oC. The result indicate that the 2% Sn dipped surface modified Nanocrystalline $BaLaTiO_3$ material thick film showed much better response to H_2S gas at 100^oC. The surface modified Nanocrystalline $BaLaTiO_3$ nanomaterial is excellent potential candidate for gas sensors at lower temperature and lower concentration as compare to the Nanocrystalline Lanthanum dope Barium titanate ($BaLaTiO_3$) .

Key words: Hydrothermal , Surface modification, Nanocrystalline $BaLaTiO_3$ (BLT) , H_2S gas

INTRODUCTION:

Barium titanate($BaTiO_3$: BT) is key member of the family of technologically potential material mainly because of its ferromagnetic response and high dielectric constant which are regarded to be quite useful for the further development of electronic industry. BT is suitable material for multilayer ceramic capacitor (MLCC) because of its high electrical permittivity and low losses. Typical perovskite ferroelectric oxide Barium titanates (BaTiO3) have been extensively studied. In recent days trend of miniaturisation of these electronic devices (thermister, MLCC) with improved properties the nanosized $BaTiO_3$ materials are desirable. Ceramic produced from agglomerated free nanosized powder with narrow size distribution have shown unique consolidation and compaction properties [1]. To achieve this goal particle with improved quality and uniform size of the order of 100nm (nanosized) are highly required. However conventional $BaTiO_3$ particles obtained by solid state chemical reaction between $BaCO_3$ and TiO_2 at high temperature 900 ^oC are generally rather coarse with uncontrolled and irregular morphologies which are not suitable for thin dielectric layers. To improve the drawback of solid state reaction various kinds of solution processes have been investigated [2, 3]. Among the solution processing routes recently the hydrothermal processes has been proposed to be an effective method for synthesizing fine ceramic powders [4-7]. In general the hydrothermal process progressed in closed system at high auto generous pressure. By the benefit of closed system with high pressure the required temperature for preparing ceramic powder can be greatly reduced because of enhanced reactivity of reactive species and fine particles with high sinter ability can be obtained [8-9] The synthesis by hydrothermal route is interesting as the sub micrometer $BaTiO_3$ particles obtained via this route under moderate conditions have exact stoichometry ,homogeneity & uniform size distribution.

Thermodynamic and kinetics of hydrothermal synthesis of $BaTiO_3$ is investigated by many researchers [10-12]. Hert[11] reported the kinetics of $BaTiO_3$ proposing the in situ transformation mechanism for hydrothermal conversion of TiO_2 to $BaTiO_3$. While using $Ba(OH)_2$ and particulate TiO_2 as precursors he found that the rate determining step at high concentration of $Ba(OH)_2$ is the topo chemical reaction of Ba^{2+} with TiO_2 at the interface whereas at low concentration of $Ba(OH)_2$ the diffusion of Ba^{2+} through the $BaTiO_3$ product layer limits the reaction rate. He found that particle size of $BaTiO_3$ is inversely proportional to initial concentration of $Ba(OH)_2$[12]

It is well known that the semiconducting Barium titanate forming oxygen vacancy or by donar dopping with the trivalent ions such as lathanium , antimony , yttrium etc on the barium site. To maintain the purity of barium titanate the concentration of donar dopant should be very low. For dopping ionic radii is the major parameter which decide substitution site. La^{3+} ionic radii is 1.15 A^o. This is very suitable for the barium site because Ba^{2+} ionic radii is 1.35 A^o and not on Ti site because Ti ionic raddi is 0.68A^o. Lanthanum produce N-type semiconductor. [13]

It is well known that the gas sensing reactions occurs at the surface of the metal oxide based sensors. Sensitivity of metal oxide sensor is concerned with various factors like chemical components ,surface modification, temperature ,humidity and microstructure of layer etc So we have modified the surface of the thick film of the material by dipping method.

EXPERIMENTAL

Material Preparation

$Ba(OH)_2$ .8 H_2O (Merck make) is used as Barium precursor, $LaNO_3$. $6H_2O$ (alpha aesar) is used as lanthanum precursor while TiO_2 (¬ 25 nm. Sigma Aldrich make) are used as Ti precursor . All precursors added in to Teflon vessel along with doubled distilled water to maintain the equimolar amount of Ba and Ti the Barium to titanium ratio is kept one (Ba:Ti=1) and lanthanum 0.3,0.5,1.0 mole percentage is added . No mineraliser such as NaOH or KOH is used to adjust the pH. The concentration of Ba used where the alkalinity of $Ba(OH)_2$ aqueous solution is sufficient for the precipitation of $BaTiO_3$. The pH of the solution at this concentration of Ba is in the range 9 -10. The reaction is performed in an autoclave at autogenous pressure. At 100 ^oC the reaction is carried out for 48 h in Teflon vessel . Heating is carried out in laboratory Oven. After obtaining the product is washed with double distilled water to remove the $BaCO_3$. The product is dried overnight at the same temperature in furnace. The powdered samples are characterised using X-ray diffraction (XRD), FTIR, Scanning electron microscopy (SEM) techniques.

Thick film preparation

The nanocrystalline $BaLaTiO_3$ powder was ball milled to ensure the sufficiently fine particle size. The thixotropic paste was formulated by mixing the fine powder of nanocrystalline $BaLaTiO_3$ material with a ethyl cellulose (a temporary binder) in a organic solvents such as butyl cellulose, butyl carbitol acetate and terpineol, etc. The ratio of the inorganic to organic part was kept at 75:25(volume) in formulating the paste. This paste was screen-printed (Deore et al., 2013; Patil et al., 2007) on a glass substrate in a desired pattern (1.5cm × 0.5cm). The films were dried under infrared radiation for 45 minutes to remove the organic vehicle and then fired at a temperature of 550°C, constant firing for 30 min at the peak temperature and then to attain the room temperature in a muffle furnace. The range of thicknesses of the films was observed in the range from 65 to 75 mm. The reproducibility in thickness of the films was possible by maintaining the proper rheology and thixotropy of the paste.

The surface modification was done by dipping method using the above thick films. For the surface modification we select the stannous chloride (Merck). The prepared films were dipped in the different concentration (1 %, 2%, 3 %) solution of Stannous chloride with varying the dipping time (5 min, 10 min, 20 min 25 min).

RESULT AND DISCUSSION

X- Ray Diffraction (XRD)

In order to understand the structural properties of nano $BaLaTiO_3$: BTL material the X-ray diffraction study was undertaken. The X-ray diffraction analysis of $BaLaTiO_3$: BTL were carried out Cu_ka radiation. The intensity data were collected over a 2θ range of 20-80 ^{0}

Fig. 1 shows XRD pattern of Nanocrystalline BTL material . The observed diffraction peaks of $BaLaTiO_3$ are well matched with JCDPS reported data of $BaLaTiO_3$ The sharp peaks of XRD are corresponds to standard cubic $BaLaTiO_3$ Phase. A very small diffraction peak is observed at 2θ= 25 & 28 ^{o}. The samples contain some $BaCO_3$ impurities probably formed by the dissolution of atmospheric CO_2 in alkaline solution. This type of impurities are normal in the hydrothermal synthesis of $BaTiO_3$ unless a great care is taken to ensure that the precursors and the reaction environment are free from CO_2 [14] The higher peak intensities of an XRD pattern is due to the better crystallinity with preferred orientation along the (110) direction.The average crystallite size was calculated from XRD data based on Debye Scherer's formula equation [15]

$$D = 0.9 \lambda / \beta \cos \theta$$

Where

D = Average crystallite size

β = Broadening of the diffraction line measured at half maximum intensity (FWHM)

λ = Wavelength of X-ray radiation

θ = Bragg's angle

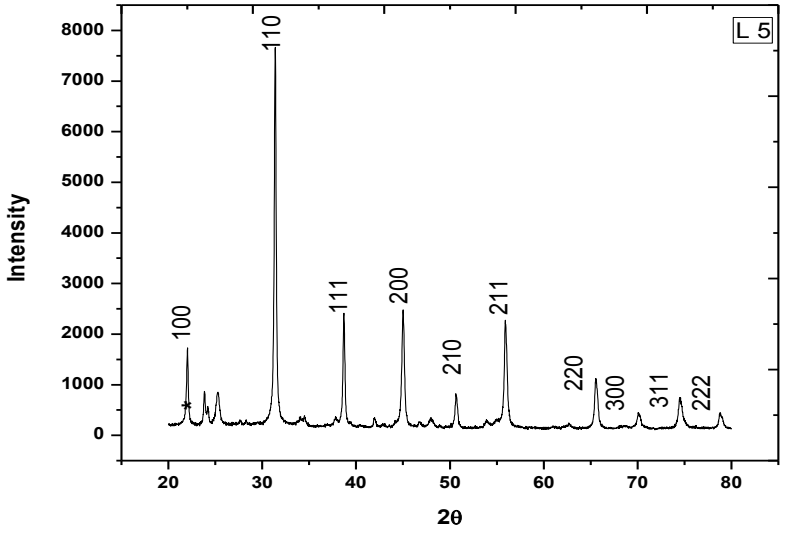

Fig.1 XRD pattern of nanocrystalline $BaLaTiO_3$

Fig 2(a) and (b) shows SEM images of the surface of $BaLaTiO_3$ and surface modified $BaLaTiO_3$ surface is highly porous

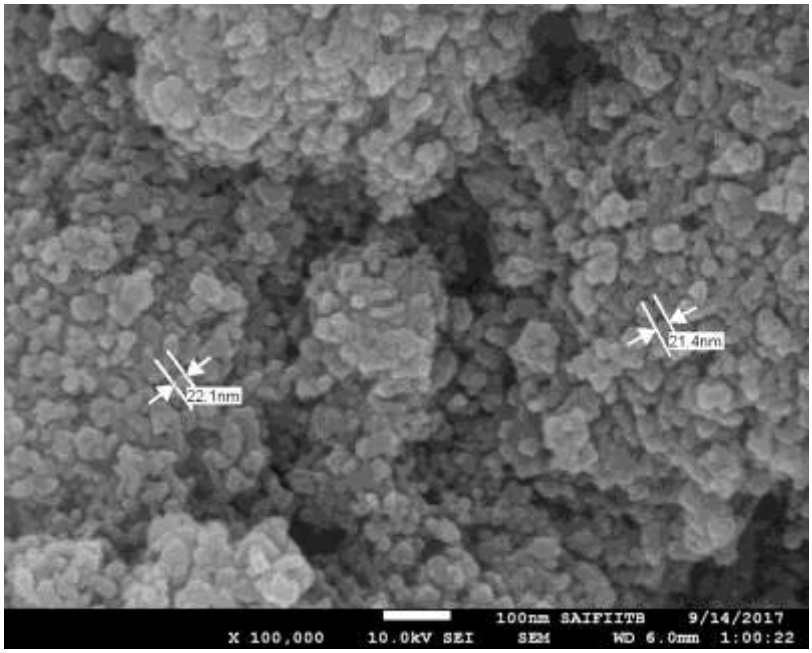

Fig 2 (a): SEM images $BaLaTiO_3$

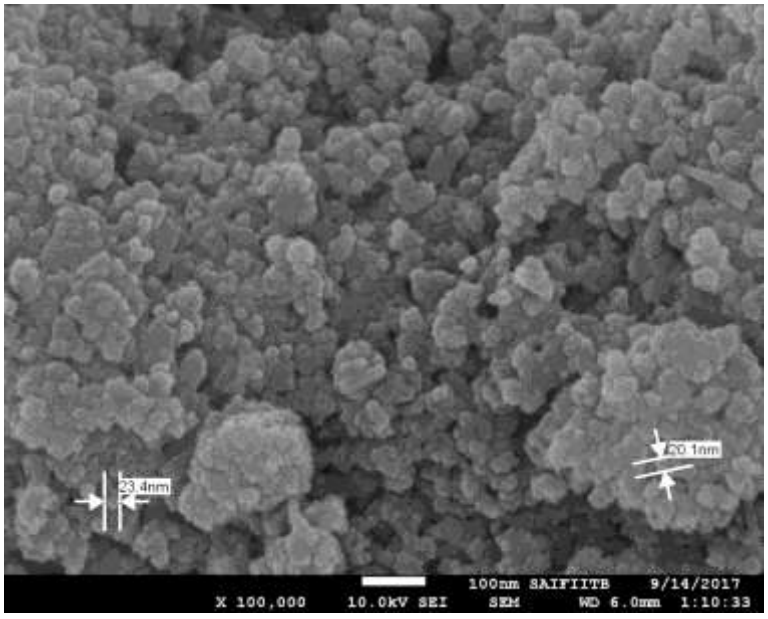

Fig 2 (b): SEM images Sn dipping 20 min 2% $BaLaTiO_3$

GAS SENSING PROPERTIES

Gas sensing performance of nano $BaLaTiO_3$ thick film

The gas sensing performance of usual and nano *BaLaTiO3* thick films was studied by using static gas sensing system [16]. The conductance of thick films was measured as a function of temperature in air as well as in CO, NH_3 ,H_2S, LPG, CO_2, H_2, SO_2 etc. gases atmosphere. The operating temperature was varied from 50°C to 450°C. From the measured conductance in air as well as in gases atmosphere, the gas response was determined at particular operating temperature using

the equation (1) (Gaikwad et al., 2009).

$$S = (G_{gas} - G_{air}) / (G_{air}) \quad \text{eq. 1}$$

where

G_{air} conductance of thick film in air

G_{gas} *conductance* of thick film in gas

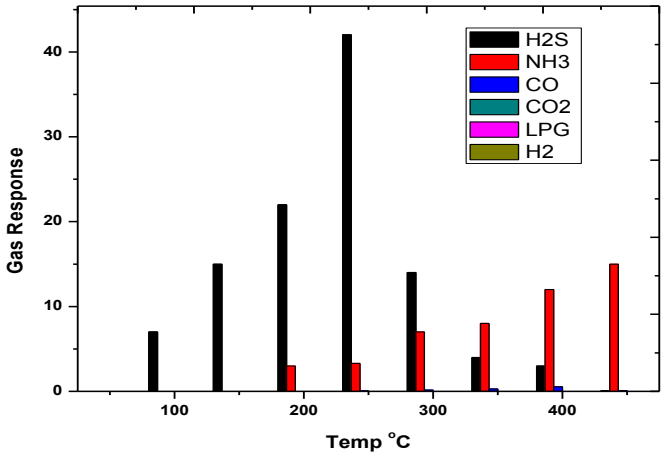

Fig. 3(a) Variation of different gases response $BaLaTiO_3$

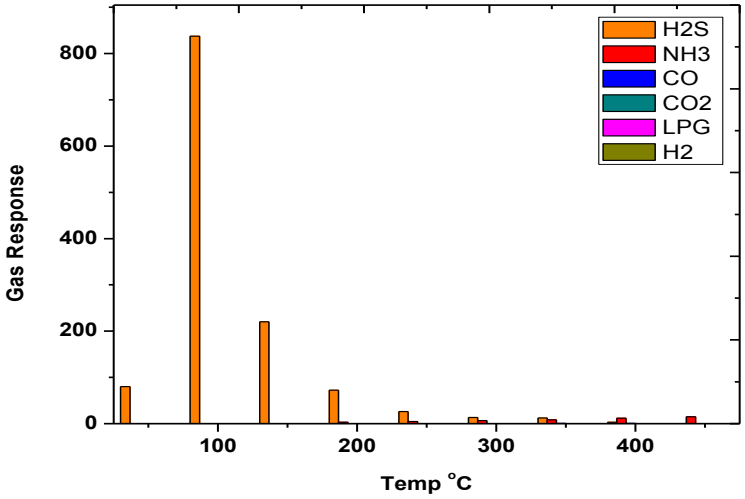

Fig. 3 (b) Variation of different gases response Surface modified $BaLaTiO_3$

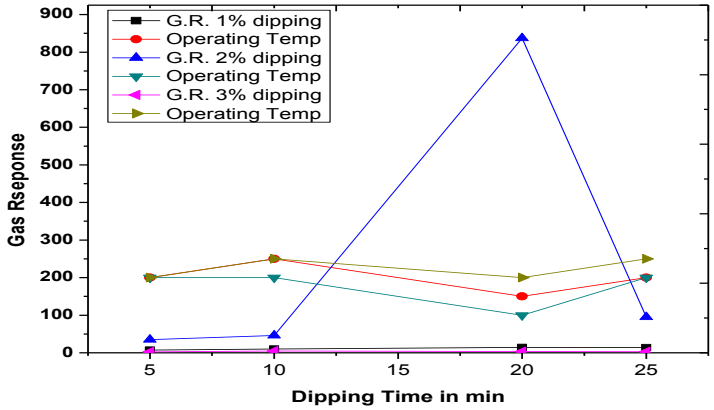

Fig. 3(c) H_2S Gas Response at various dipping percentage and time

Figure 3 (a) shows the variation in the gas response of nano BaLaTiO3 film for the gases viz: CO, NH_3 ,H_2S, LPG, CO_2, H_2, etc. as the function of operating temperatures . The nano BaLaTiO3 film shows the highest response to H_2S gas at 250°C. The response goes on increasing with increase in operating temperature, attains its maximum (at 250°C) and then decreases with a further increase in operating temperature. Figure 3 (b) shows the variation in the gas response of surface modified films(2% sn dipping 20 min) for the different gases as function of operating temperature, it is noticeable that the operating temperature of modified film shows maximum response at 100 ^{0}C and gas response is also increases 837. As the H2S is flammable gas so the low temperature performance is important. Figure 3 (c) shows the variation in response with different percentage of Sn and dipping time

H_2S gas sensing mechanism of $BaTiO_3$ nanostructures thick film control

The gas sensing mechanism of the semiconductor-based sensors predominantly depends on the surface of the sensing materials. We believe that the electrons from the valence band of $BaLaTiO_3$ get excited at higher temperature (250° C) and are available for interaction with other species such as H_2S and O_2. The O_2 adsorbed on the surface of $BaLaTiO_3$ nanostructures has a direct effect on the electrical conductance of gas sensing. The thermally excited electrons from the conduction band of $BaTiO_3$ nanostructures are consumed by the adsorbed O_2 molecules to form a reduced O_2^-species as shown in equation (2). The quantity of oxygen adsorbed on the sensor surface depends on particle size and specific surface area of the sensor material [14]. The surface area of nanosized $BaLaTiO_3$ is expected to be high and large concentration of atmospheric oxygen is expected to be adsorbed on its surface. Thus, after the thermal excitation of $BaLaTiO_3$ nanostructures, the amount of O_2^- species is available extensively.

$$O(gas) + 2e^- \rightarrow O_{2(ads)}^- \qquad (2)$$

Further, the O_2^-species react with H_2S (reducing gas) to generate H_2O and SO_2 with release of electrons back in the valence band of nanostructures as shown in equation (3). Since, the temperature is maintained at 250° C, the retained electrons in the valence band of $BaLaTiO_3$ nanaostrutures are excited back to the conduction band increasing the electrical conductivity. Thus, the gas response of this BaTiO3 nanaostruture based sensor depends directly on the number of $O_{2(ads)}^-$ species formed.

$$2H_2S_{ads} + 3O_{2(ads)}^- \rightarrow 2H_2O + 2SO_2 + 6e^- \qquad (3)$$

As the exposure of H_2S gas is stopped, the conductivity of sensor decreases as a result of decrease in the electrical conductivity of $BaLaTiO_3$ film. The decrease in electrical conductivity of BaLaTiO3 film is due to absence of reaction process mentioned in equation 3 as H2S gas is unavailable for reaction. The detailed mechanism is represented in Figure 4. It can be opined that the working temperature of the sensor is dependent on the band gap of the semiconductor used for gas sensing.

The thermal energy required for the excitation of electron in such semiconductors will depend on the energy difference between the valence band and the conduction band (band gap). Hence, after surface modification by dipping of the BaLaTiO3 film there could be decreasing the band gap of such materials and so lowering the working temperature of gas sensors. In other words, altering the band gap of the semiconductors by dipping or quantum confinement effect could be vital in obtaining desired sensing properties at various temperatures.

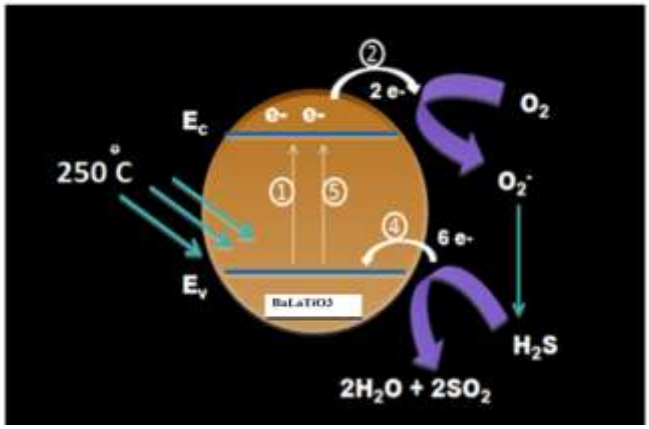

Figure 4 Gas Sensing Mechanism

Percent Selectivity : It is ability of a sensor to respond to certain gases in presence of other gases . the % selectivity of one gas over other is defined as the ratio of maximum response of other gas to maximum response to target gas at optimum temperature. Figure 5(a) shows % selectivity of sensor

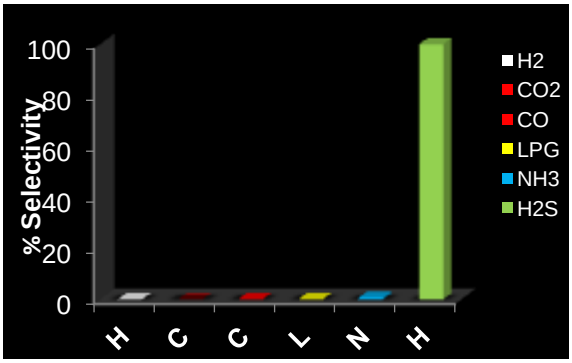

Figure 5(a) % selectivity

Response & Recovery Time: The sensor works with quick response and fast recovery Figure 5(b) shows response and recovery time of the sensor.

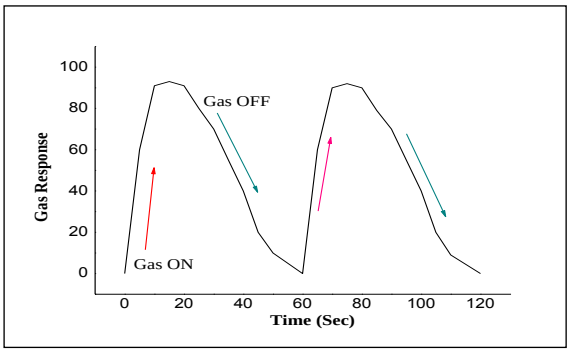

Figure 5(b) Respones and recovery time

CONCLUSIONS

i. Nanocrystalline *$BaLaTiO_3$* material was synthesised by hydrothermal method
ii. XRD analysis confirmed the prepared material was pure *$BaLaTiO_3$* with the crystallite size varying from 31 – 50 nm.
iii. the nano *$BaLaTiO_3$* thick film shows the highest response to the H_2S gas at the operating temperature 250°C and observed to be highly selective to H_2S gas
iv. The surface modified Nanocrystalline $BaLaTiO_3$ nanomaterial is excellent potential candidate for gas sensors at lower temperature (100°C) and lower concentration as compare to the Nanocrystalline Lanthanum dope Barium titanate ($BaLaTiO_3$) .

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