IRJSE International Research Journal of Science & Engineering
Int. Res. J. of Science & Engineering, 2018; Special Issue A2 : 230-236
ISSN: 2322-0015
SJIF Impact Factor 4.11
UGC Approved Journal No. 63628
RESEARCH ARTICLE **OPEN ACCESS**

Synthesis, Characterization and Gas sensing properties of Cu surface modified BaTiO3 thick films

Nahire SB[1], Patil GE[2], Jain GH[2], Gaikwad VB[3], Deshmukh Sushant B[4]

[1]Department of Physics, Arts, Science and Commerce College, Ozar (Mig) Nashik 422103, India 422 206,[2]Dept of Physics, SNJB's KKHAArts, SMGL Commerce & SPHJ Science College, Chandwad 423101, India,[3] Prin. Dept. of Chem. KTHM College , Nashik 422 005,[4]Department of Physics, JES College, Jalna 431203, India
Email: nahiresandip@gmail.com

Manuscript Details
Available online on http://www.irjse.in
ISSN: 2322-0015

Editor: Dr. Arvind Chavhan

Cite this article as:
Nahire SB, Patil GE, Jain GH , Gaikwad VB, Deshmukh Sushant B. Synthesis, Characterization and Gas sensing properties of Cu surface modified BaTiO3 thick films, *Int. Res. Journal of Science & Engineering*, January 2018; Special Issue A2: 230-236.

ABSTRACT

Barium titrate oxide ($BaTiO_3$) is synthesized by co-precipitation method with surface modification by Cu to improve the sensitivity and tailoring the operating temperature, when the surface modified thick films are exposed to H_2S. The thick film sensor is prepared by screen printing technique. Then $BaTiO_3$ thick films are surface-modified by Cu, using cupric acid. Influence of Cu on the film phase composition, microstructure and sensing characteristics is discussed. Dynamic response properties show that the operating temperature of the surface modified $BaTiO_3$ thick film is at 100 ^oC, which is about 250 ^oC for pure $BaTiO_3$. Response time of the sensor is about 10 s while recovery time is 30 s. The selectivity of the sensor elements for H_2S against different gases was also discussed.

Key words: Cu, BaTiO3 thick films, XRD

INTRODUCTION

Semiconductor metal oxides as gas sensing materials have been extensively studied for a long time due to their advantageous features, such as good sensitivity to the ambient conditions and simplicity in fabrication [1–3]. Nevertheless, there are still some critical limitations to be overcome for the commercial sensors based on particulate or thin-film semiconductor metal oxides, such as limited maximum sensitivity, high working

temperatures and lack of long-term stability. Recently, several groups reported the sensors based on semiconductor nanowires and nanoribbons. Barium titanate (BaTiO3) is a perovskite ferroelectric oxide, barium titanate (BaTiO3) have been extensively investigated, affording wide applications in devices such as thermistors [4], multilayer ceramic capacitors (MLCCs) [2], electro-optic devices [3], and dynamic random access memories (DRAM) [4]. Doped barium titanate has found wide application in semiconductors, positive temperature coefficient resistors, ultrasonic transducers, piezoelectric devices, and has become one of the most important ferroelectric ceramics. Large number of different dopants can be accommodated in the BaTiO3 lattice, therefore, doping of BaTiO3 ceramics is very important to obtain required characteristics for its applications in Hydrogen sulphide gas is harmful to human body and environment. The threshold limit value (TLV) defined for H2S is 10 ppm. Human exposure to H2S gas at level higher than 250 ppm are likely to result in neurobehavioral toxicity and may even cause death[6]. Metal oxide semiconductor gas sensors have advantageous features such as high response under ambient conditions, low cost and simplicity in fabrication [7, 8]. The sensor performance can be improved by increasing the porosity. The fundamental sensing mechanism of metal oxide based gas sensors relies on change in electrical conductivity due to the interaction process between the surface complex such as O-, O2- , H+ , OH+, reactive chemical species and the gas molecules to be detected [9]. Semiconductor BT is sensitive to many sets of gases and has high satisfactory stability, but it has some disadvantages, such as high working temperature of 400^{o}C–500 ^{0}C; poor gas selectivity and comparatively low response. Furthermore, it has also been reported that the gas response and selectivity of semi-conductive complex oxides can be influenced by dipping or doping. Some workers discovered that complex oxides exhibit good response to reducing gases [8,9]. Metal oxide gas sensors are stable at high temperature [8]. Sensing principle is based on the change in the electrical resistance of semiconductor oxide films when specific gas interacts with its surface [9]. Gas sensitivity, selectivity and durability are the most important sensor properties [10-11]. High gas sensitivity is the key factor in detecting gases at very low concentrations; for example, leakage of a harmful gas in a work environment should be detected as early as possible. It has been suggested that gas sensitivity can be enhanced by controlling the microstructure of thin films of the sensing material, e.g., dispersing small pores at the grain boundaries or decreasing the grain size [12,13]. Gas selectivity is another very important indicator that measures the ability of a sensor to precisely identify a specific gas in a mixture of a several gases [14]. To improve the gas selectivity, microstructure control and doping of hetero component are known to be effective, because active sites for particular gas species can be produced. $BaTiO_3$ has been mainly studied in bulk or thick film form as a material for gas sensing. Following this consideration, the aim of the present work is to study the gas sensing properties of $BaTiO_3$ materials surface modified in the solution $CuCl_2$.

METHODOLOGY

Synthesis of BT and preparation of BT thick films: BaTiO3 fine submicron powders were prepared from $Ba(OH)_2$ and $TiCl_4$ using a co-precipitation process. The titanium precursor was slowly introduced in a strong basic $Ba(OH)_2$- NaOH aqueous solution (pH>13) kept at 100 ^{o}C. After 6 h ageing at 100 ^{o}C, the powder was washed with distilled water until Cl ions were completely removed from the supernatant. The powder was further annealed at 600 ^{o}C for 2 h. The details of preparation are described elsewhere [11]. The as-prepared powder, characterized by XRD, scanning electron microscopy, UV-visible spectroscopy. The XRD spectrum of as prepared powder confirmed the sub-microcrystalline perovskite phase. The thixotropic paste was formulated by mixing the fine powder of BT with a solution of ethyl cellulose (a temporary binder) in a mixture of organic solvents. The ratio of the inorganic to organic part was kept at 75:25 in formulating the paste. This paste was screen printed [12-13] on a glass substrate in a desired pattern. The films were fired at 550 ^{o}C for 30 min.

Preparation of Cu surface modified BT thick films: The screen is held at about a few mm above the substrate on a printing set up. The required paste is poured on the top surface of the stencil and squeegee

pushed the paste through the opening while it is passed from one end to the other. Any paste for electronic thick film passive component or sensing element contains at least two ingredients: an organic vehicle and functional material or active ingredient. The thick films of BT from as-prepared powders were surface modified with Cu by dipping of BT thick films in an aqueous solution of the copper chloride. In order to compare gas sensing performances, thick films were dipped for different interval timing as 5 min, 10 min, 15 min. 20 min and 30 min and referred respectively as CuBT1, CuBT2, CuBT3, CuBT4 and CuBT5. These films were dried at 100 °C, followed by firing at 550 °C for 30 min and then used for further characterization such as UV-visible spectroscopy, scanning electron microscopy, XRD and tested their gas sensing properties. After annealing, the concentration of Cu (mass %) on the surface of the films was determined by EDX. These surface modified films are termed as 'Cu-modified BT' (CuBT) films

RESULTS AND DISCUSSION

1. X-ray diffraction (XRD) analysis

Figures 1 and 2 shows the x-ray diffraction pattern of the samples modified with different Cu content of CuBT1, CuBT2, CuBT3, CuBT4 and CuBT5. It can be found that the positions and intensities of the diffraction peaks are similar and no secondary phases were observed. All the above patterns of XRD show the single phase tetragonal system and similar to that of standard pattern of JCPDS of pure $BaTiO_3$ [14]. It indicates that influence of CuO did not affect the structural properties.

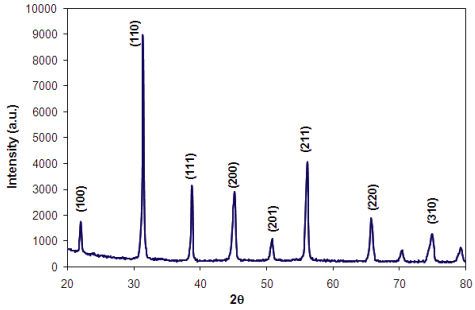


Fig. 1: X-ray diffraction pattern of pure BT

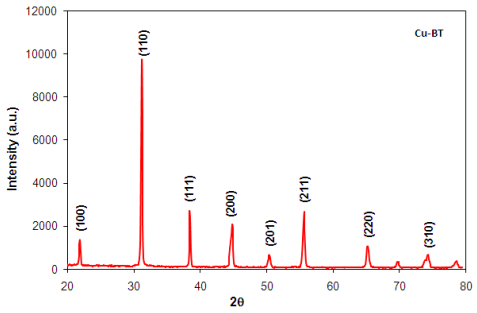
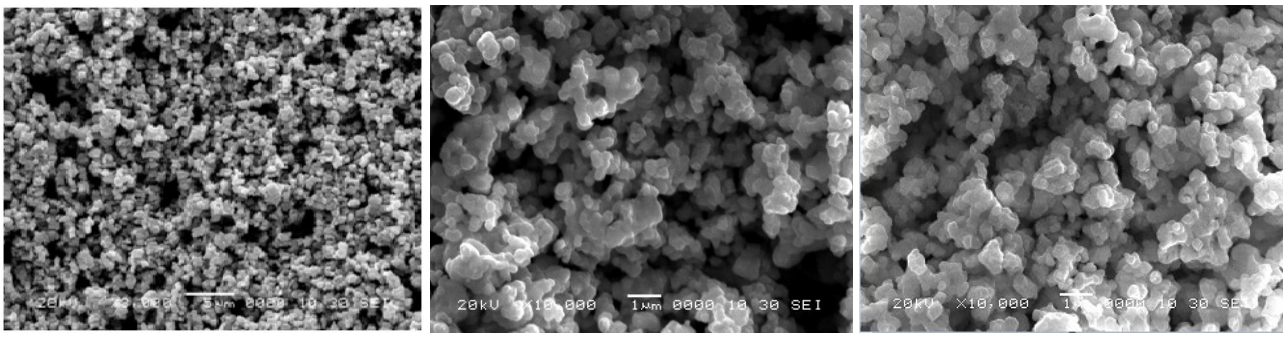
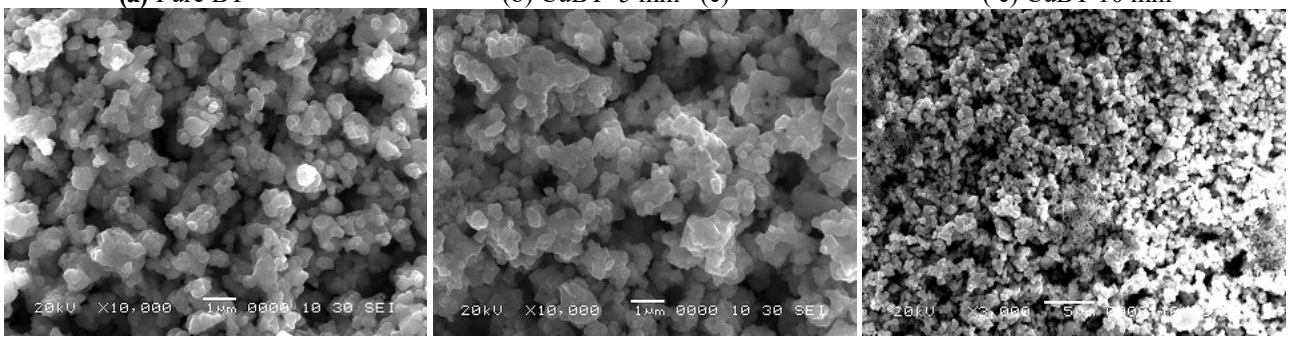


Fig. 2: X-ray diffraction pattern of CuBT4 sample



(a) Pure BT (b) CuBT 5 min (c) (c) CuBT 10 min



(d) CuBT 15 min (e) CuBT 20 min (f) CuBT 30 min

Table 1: Quantitative elemental composition of pure BT and surface modified Cu-BT thick films.

Element	Pure BT mass %	CuBT1 mass %	CuBT 2 mass %	CuBT3 mass %	CuBT4 mass %	CuBT5 mass %
O	16.38	15.89	15.35	15.81	15.66	14.34
Ti	12.04	10.74	9.31	10.10	9.75	6.90
Ba	71.58	72.09	72.72	70.87	70.17	74.61
Cu	-	1.28	2.62	3.21	3.41	4.64
Total	100	100	100	100	100	100

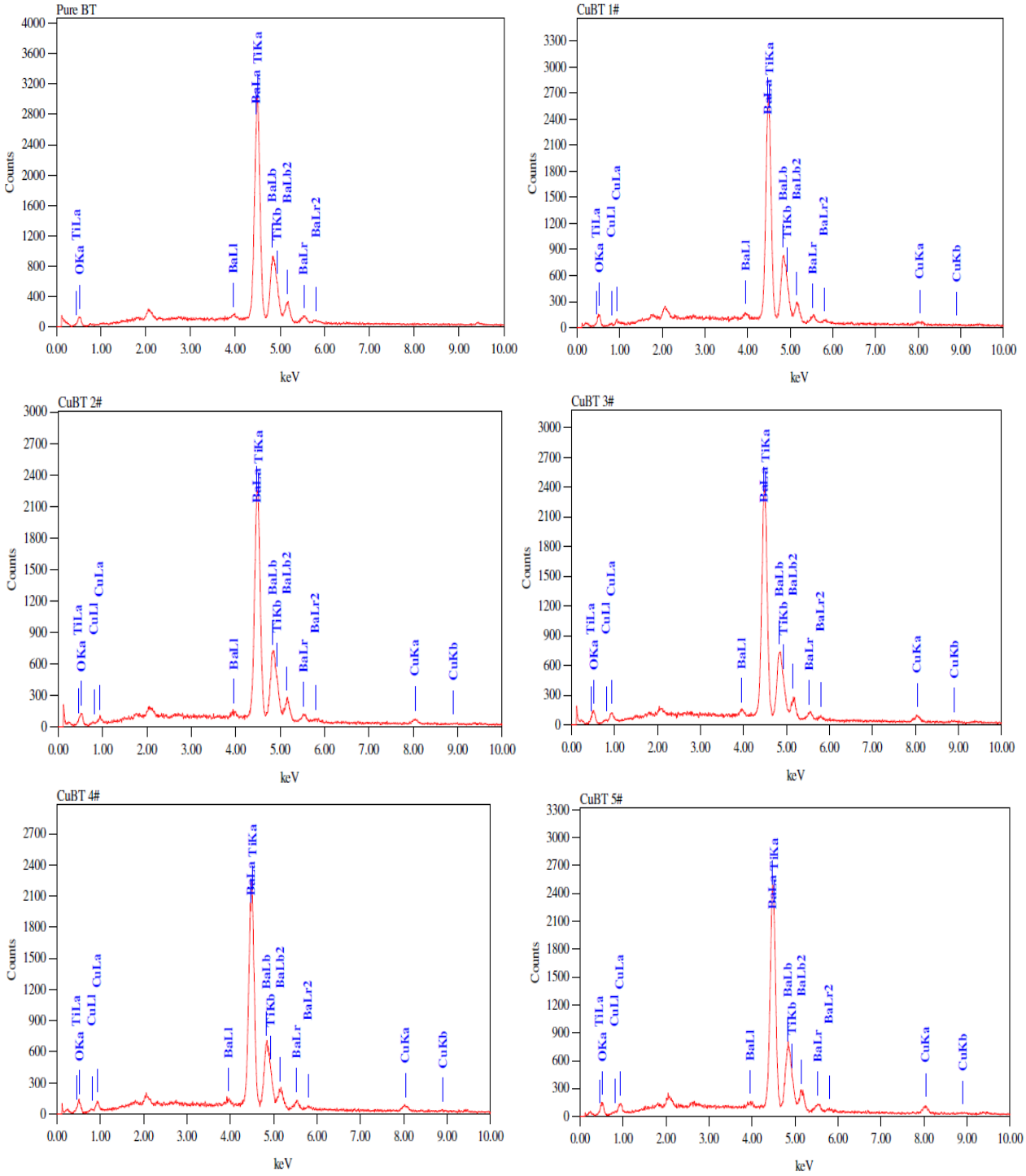


Fig.4 (a-f): EDX spectra of pure BT and surface modified by Cu BT thick films

3.2 Surface morphology by SEM and elemental composition by EDX analysis

The microstructure with surface morphology and the composition analysis were investigated using scanning electron microscope (SEM) with energy dispersion X-ray spectroscope attached. The compositional analysis was carried out at different spots on the samples. The SEM images of pure BT and surface modified BT thick films are shown in Fig. 3. From the SEM micrographs it is clear that grain distribution was uniform with porosity throughout the samples surface. The surface modified porous films which can be advantageous for gas sensing (Fig. 3(b-f)). The top surface of the sensors modified from Cu Fig. 3 (b-f) looks more porous compared to that pure BT.

The quantitative elemental composition of the pure and Cu modified BT films was analysed using an energy dispersive spectrometer and atomic percentage (mass %) of Ba, Ti, O and Cu are represented in Table 1. All samples were observed to be oxygen deficient. Also, the films dipped in Cu were observed to be most oxygen deficient than the pure BT film. It is clear from Table 1 that the mass % of Cu goes on increasing and mass % of oxygen goes on decreasing with the dipping time.

3.2.2 Optical properties by UV-visible spectroscopy

UV-visible absorption spectra were used to estimate the band gap of BT and surface modified BT thick films. The spectra were obtained using a UV-VIS spectrometer (UV-2500PC, SHIMADZU). Fig. 4 shows variation of absorbance with wavelength for samples pure BT, CuBT1, CuBT2, CuBT3, CuBT4 and CuBT5. The absorption at higher wavelengths in the visible region is low and at wavelength 350-410 nm an intense absorption can be seen for modified samples.

The value of absorption coefficient (α) is of the order of 10^3 cm^{-1}. The band gap of the films corresponding to samples pure BT, CuBT1, CuBT2, CuBT3, CuBT4 and CuBT5. were calculated by plotting the graph of $(\alpha h\nu)^2$ verses hν using the relation,

$$\alpha h\nu = A\,(h\nu - Eg)^n, \qquad (2)$$

where α is absorption coefficient, A is constant, Eg is band gap energy, hν is photon energy and n is constant.

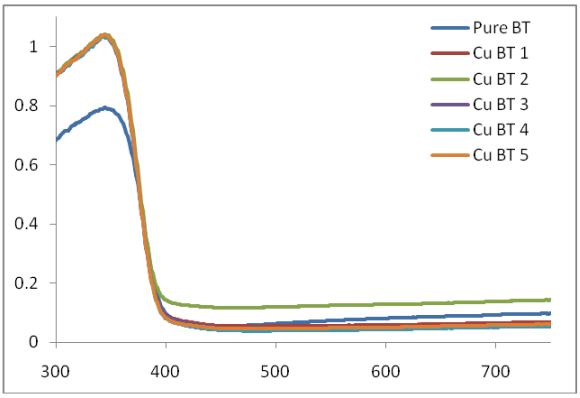


Fig. 5: Variation of absorbance with the wavelength for pure BT, CuBT1, CuBT2, CuBT3, CuBT4 and CuBT5.

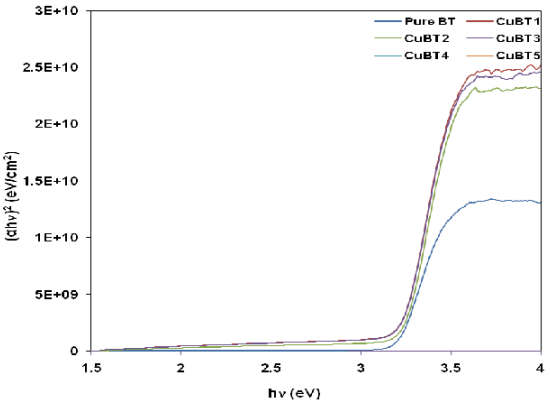


Fig. 6: Plot of the $(\alpha h\nu)^2$ verses photon energy (hν)

The value of n is 1/2 or 2 depending on presence of the allowed direct and indirect transitions. The variation of $(\alpha h\nu)^2$ with hν, shown in Fig. 5, has a straight line portion indicating that the transition involved is direct [15]. The direct band gap, determined by extrapolating the straight line portion to the energy axis to $(\alpha h\nu)^2 = 0$, is found to be 3.20 eV for pure BT. The intercepts on energy axis gives the value of band gap energy for all the modified samples and found to be 3.2210 to 3.2434 as given in Table 4. Notably, the band gaps of all CuBT films were larger than that of the pure BT thick film. There is only slight change observed in band gap energy for samples with increasing dipping time of BT thick films in Cu.

Table 2: Band gap energy pure and modified BT thick films.

Sample	Band gap (eV)
Pure BT	3.20
NBT1	3.2210
NBT2	3.2215
NBT3	3.2321
NBT4	3.2445
NBT5	3.2434

3.2. Electrical conductivity

Fig. 7 represents the variation of conductivity with temperature for the pure $BaTiO_3$ and CUBT films. The legends suffixed 5, and 15' are the graphs for the conductivities of the films in the air ambient, while legends suffixed '10, 30 and 20 are the graphs for conductivities of the films in the H_2S gas ambient. It is clear from the graphs that the conductivity is varying approximately linearly with temperature for all films. The conductivity of CuBT films was observed to be increased.

3.3. Temperature dependence of sensitivity of pure and modified BT thick films to H_2S Gas sensing properties of pure and modified BT thick films

The sensor was placed in a gas test chamber, exposed to gases. The properties of the investigated sensor were determined by the measurements of sensitivity S. This parameter was defined as the ratio of sensor electrical conductance in air (Ia) to that containing detected gas (Ig) [15]. The sensitivity depends on factors, such as morphology, dopants and their concentrations, thickness of film and operating temperatures. We tested sensitivity of pure BT and Cu surface modified BT thick films towards various reducing and oxidizing gases, such as H_2S, H_2, CO_2, CO, liquid petroleum gas, Cl_2, NH_3 and ethanol vapors. All the samples showed maximum sensitivity to H_2S gas. Fig. 8 shows the sensitivity of the pure BT, CuBT1, CuBT2, CuBT3, CuBT4 and CuBT5 sensor element as a function of operating temperature to H_2S gas for 100 ppm. It is seen that the sensitivity changes significantly with the operating temperature. It increases with increasing temperature and reaches a maximum at around 250 °C for pure BT. It has been observed in the present investigation that increasing the dipping time of the BT thick films in $CuCl_2$ solution and thereby increasing the Cu coating on surface improves the sensor sensitivity quite significantly. For modified thick film (CuBT3) a remarkable sensitivity towards H_2S gas is observed at 150 °C operating temperature. It is found that in comparison to CuBT1, CuBT2, CuBT3, CuBT4 and CuBT5shows highest sensitivity towards H_2S gas. Selectivity or specificity is defined as the ability of a sensor respond to a certain (target) gas in the presence of other gases [15]. Fig. 9 the shows a histogram of pur BT and CuBT3 selectivity towards 100 ppm of H_2S and 1000 ppm of other test gases such as H_2, CO_2, CO, liquid petroleum gas, Cl_2, NH_3 and ethanol vapors at 150 °C.

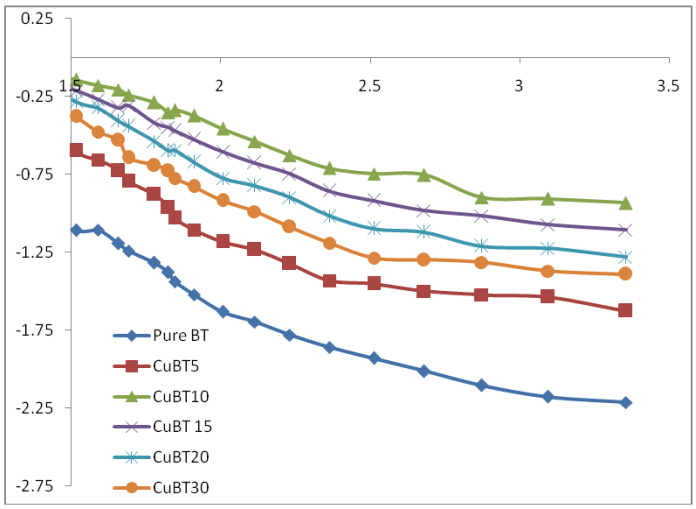


Fig 7 : Variation of electrical conductivity with temperature

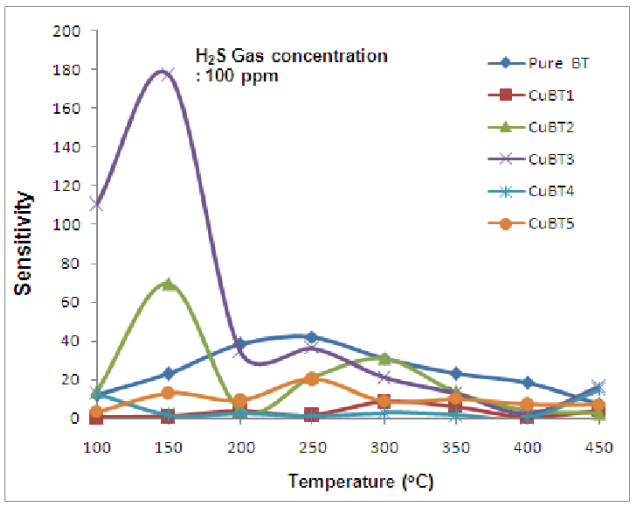
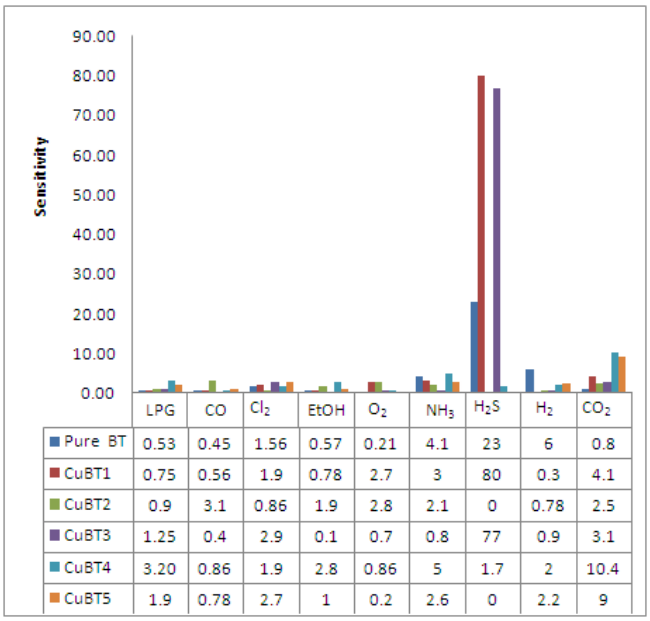


Fig. 8: Variation of sensitivity of pure and modified BT thick films with operating temperature



	LPG	CO	Cl_2	EtOH	O_2	NH_3	H_2S	H_2	CO_2
Pure BT	0.53	0.45	1.56	0.57	0.21	4.1	23	6	0.8
CuBT1	0.75	0.56	1.9	0.78	2.7	3	80	0.3	4.1
CuBT2	0.9	3.1	0.86	1.9	2.8	2.1	0	0.78	2.5
CuBT3	1.25	0.4	2.9	0.1	0.7	0.8	77	0.9	3.1
CuBT4	3.20	0.86	1.9	2.8	0.86	5	1.7	2	10.4
CuBT5	1.9	0.78	2.7	1	0.2	2.6	0	2.2	9

Fig. 9: Selectivity pure and modified BT thick films.

CONCLUSION

1. Pure BT. thick films were prepared by screen printing technique
2. Pure BT thick film showed maximum sensitivity to H_2S at 250°C for 100 ppm concentration.
3. Cu surface modified BT thick films were prepared by dipping pure Fe2O3 thick films in a 0.1M aqueous solution of cupric chloride for different intervals of dipping time of 5, 10, 20, 30 and 45 min.
4. SEM images of the films reveal surface morphology of the film. The grains found loosely connected with narrow size distribution which may be because of the final thermal treatment performed at 550 °C.
5. Elemental analysis shows that the film with dipping time 30 min is more oxygen (21.17) deficient and at the same time it is the one having highest wt% of Cr (8.34).
6. The surface-modified BT sensor showed larger sensitivity to H_2S gas (100 ppm) at 150°C.
7. Cu on the surface of the film shifts the reactivity of film from higher operating temperature to lower operating temperature.
8. Cu modified BT thick film with dipping time 20 minutes showed notable gas response (26.3458) to ethanol (300 ppm) at 350 oC as well as to H2S (gas response = 7.86) at same temperature.
9. The sensor showed good selectivity to H_2S against LPG, NH_3, H_2, CO, CO_2 and Cl_2.

Conflicts of interest: The authors stated that no conflicts of interest.

REFERENCES

1. Hennings D, Klee M, Waser R. Adv Mater 1991;3:334–40.
2. Mori M, Kineri T, Kadono K, Sakaguchi T, Miya M,Wakabayashi H, Tsuchiya T. J Am Ceram Soc 1995;78:2391–4.
3. Kingon AI, Streiffer SK, Basceri C, Summerfelt SR. MRS Bull 1996;21:46–52.
4. Nowotny J, Rekas M. Solid State Ionics 1991;49:135–54.
5. Buscaglia MT, V. Buscaglia, M. Viviani, P. Nanni, M. Hanuskova, "Influence of Foreign Ions on the Crystal Structure of BaTiO3", J. Eur. Ceram. Soc., 20 (2000) 1997–2007.
6. Kasap S, Capper P. Thick Films, Springer Handbook of Electronic and Photonic Materials, 2006.
7. Toan NN, Saukko S, Lantto V. Physica B 2003;327:279.
8. Wang, Yee SS, Carey WP. Sens Actuat B 1995; 24:454.
9. Dayan NJ, Karekar RN, Aiyer RC, Sainkar SR. J Mater Sci 1997;8:277.
10. Reddy MHM, Chandarkar AN. Thin Solid Films 1999;349: 260.
11. Jain GH, Patil, L.A. Gas sensing properties of Cu and Cr activated BST thick films 2006 Bulletin of Materials Science 29(4) 403-411
12. Shinde SD, Patil GE, Kajale DD, Gaikwad VB and Jain GH. International Journal on Smart Sensing and Intelligent System Vol. 5, No. 1, March 2012, pp. 57-70.
13. Chavan DN, Gaikwad VB, Kajale DD, Patil Ganesh E, Jain GH, Journal of Sensors, Volume 2011, Article ID 824215, 8 pages doi:10.1155/2011/824215.