

Aliovalent Yttrium added silver sulphate: a promising candidate for SO₂ gas sensor

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ABSTRACT

Optimum alio-valent doping with yttrium sulphate creating 7% vacancy concentration provided promising features from sensor application view. This provides a better option over green Silver Sulphate. The sensors fabricated with the modified sulphate based silver ion conducting solid electrolyte, silver-silver sulphate reference electrode and test gas (Pt) electrodes has been tested over the range of 50-1000 ppm SO₂ blended in constant oxygen-partial pressure and argon at 400°C. A promising sensor characteristic behaviour is exhibited by the modified electrolyte - solid solution of silver sulphate with yttrium. Copyright © 2012 VBRI Press.

Keywords: Electrochemical gas sensors, SO₂ detectors, fast ionic conductors, sulphate based solid electrolytes, galvanic sensors, environmental pollution etc.



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Introduction

Sulphate based Solid Electrolytes (SE) have attracted a great deal of attention[1] due to their high potential for applications in various devices that include sensors, batteries, thermal batteries, heart pace makers, smart windows *etc.*

Due to the rise of modernization and industrialization in order to facilitate a better lifestyle for people, unwanted pollutants has increased. Now-a-days the pollutants have caused sizeable destruction. Detection and monitoring the pollutants has become an objective worth aiming for in order to sustain healthy life on the planet. One of such harmful pollutants is sulphur dioxide, SO₂. It is a known pollutant and has been counter attacked by human being since a long time [2-4]. In earlier times it was detected by Gas Chromatography. These methodologies are obsolete and redundant now. In the present context of modernization, the detection techniques should be fast, automatic and electronically compatible for PC interface.

The pollutant SO₂ originates from the oxides of sulphur which are produced during coal combustion and burning of fossil fuels. Accumulation of these toxic species in the atmosphere is the cause of pollution resulting in its adverse effect on vegetation and marine life. For the purpose of monitoring and controlling environmental pollution a device is required that can measure *in situ* concentration of SO₂/SO₃. The present work proposes utilization of new materials that offers some advances in the Galvanic SO₂ Sensor having many salient features.

In earlier stages of development, gaseous reference electrode was used which was cumbersome to handle and

measurements interfering. The innovative solid reference electrode ($\text{Ag}+\text{Ag}_2\text{SO}_4$) [5-18] has proved advantageous over reference gas electrode. The quality performance of Solid State Electrochemical Gas Sensor (SSEGS) in terms of response time, thermodynamic stability, operating temperature, gas sensing ability, sensitivity and concentration range that is sensed has evoked interest [19]. The sensor configuration;

Test gas- cathode/solid electrolyte/reference anode has major performance dependence upon the solid electrolyte. The present work attempts to synthesize and study performance of optimum Y added solid solution of Ag_2SO_4 solid electrolyte followed by its utilization in galvanic SO_2 sensors [20-23]. 7 vacancy% creation in base Ag_2SO_4 solid electrolyte promotes optimum ionic conductivity. It is corresponding to 3.63 mole% of $\text{Y}_2(\text{SO}_4)_3$ in pure Ag_2SO_4 to form solid-solution. The prima-facie results indicate this material as a promising candidate as solid electrolyte for SO_2 electrochemical gas sensors. With $\text{Ag}+\text{Ag}_2\text{SO}_4$ reference electrode, when SO_2 partial pressure in test gas electrode varies from 50pp to 1000 ppm, emf of the sensor cell alters by 280 mV exhibiting reversal on alteration of SO_2 partial pressure.

Selection of solid electrolyte and reference electrode: Sulphate based solid electrolytes have attracted a great deal of attention because the SO_4^{2-} ion can equilibrate with SO_2/SO_3 in gas mixture and establish the cell reaction. The cell emf is given by Nernst equation;

$$E = \frac{-\delta G^{\circ}(T)}{2F} + \frac{RT}{2F} \ln \left(\frac{P_{\text{SO}_3} P_{\text{O}_2}^{\frac{1}{2}}}{a_{\text{Ag}_2\text{SO}_4}} \right)$$

Amongst the alkali sulphates, Ag_2SO_4 was found to be more suitable from the view of chemical compatibility and ionic conductivity properties. The silver-oxygen-sulphur system is unique in which silver and Ag_2SO_4 can coexist as equilibrium phase in contrast to usual situations where an oxide phase separates the metal from sulphate. Moreover, ionic properties of Ag_2SO_4 (electrical conductivity, ion migration enthalpy, ionic transference number) in different SO_2/SO_3 partial pressures are seen to be invariant. This is an essential feature that offers **stable** sensing performance.

Experimental

Materials preparation

The initial ingredients Ag, Ag_2SO_4 and $\text{Y}_2(\text{SO}_4)_3$ with 99.999% purity (SIGMA ALDRICH) of appropriate mole fraction compositions were thoroughly mixed under GR grade acetone followed by slow cooling of the melt in a translucent silica quartz tube with cooling rate $1.5^{\circ}\text{C}/\text{min}$. The silica quartz ampoules offer minimal optical decomposition of silver sulphate. Silver powder and Ag_2SO_4 in 2: 1 weight ratio was thoroughly mixed under acetone to form solid reference electrode. A system of $(100-x)\text{Ag}_2\text{SO}_4:(x) \text{Y}_2(\text{SO}_4)_3$ has been prepared for $x=0, 1.53, 2.56, 3.63$ and 4.72 mole% that creates vacancies concentration 0%, 3%, 5%, 7% and 9% respectively as a monovalent Ag^+ is replaced by a trivalent Y^{3+} . In coulombic charge balancing, vacancies are created by formula

$\text{Ag}_{2-3x}\text{Y}_x\text{SO}_4$ [24]. These vacancies are anticipated to support ion migration process enhancing its suitability as SE.

Cell assembly

The cell with configuration

$\text{Ag}+\text{Ag}_2\text{SO}_4/\text{new electrolyte}/\text{Pt}, \text{SO}_2(\text{g}), \text{O}_2(\text{g})$ (I) was fabricated by simultaneously pressing the reference electrode and electrolyte. On other side, Pt powder was sprinkled to derive electrical contact.

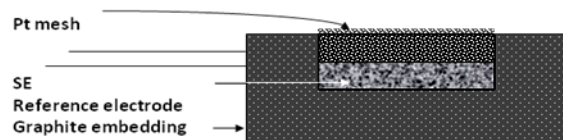


Fig. 1. Cell assembly with isolation of reference electrode by graphite embedding.

With this material as SE, the cell was fabricated with configuration (I). The cell was embedded in graphite (see **Fig. 1**) using a dia-punch of higher diameter so that it seal the reference electrode from gaseous environment and helps derive electrical connection from reference electrode. This cell was mounted in a specially designed Sensor Probe fabricated using silica quartz tube. The gas blending of SO_2 , O_2 , and Ar with different concentrations ranging from 50 ppm to 1000 ppm of SO_2 at fixed O_2 , was obtained using Teledyne Hasting's (USA) mass flow controllers. All gases used were ultra high pure (99.9% purity) and procured from local suppliers. Gas compositions with 0.21 oxygen partial pressure environment was prepared so that $\text{SO}_2+\frac{1}{2}\text{O}_2=\text{SO}_3$ reaction kinematics has resemblance with ambient. Ar and O_2 flows are adjusted in SLPM (Standard Liter Per Minute) while SO_2 has been controlled in SCCM (Standard Cubic Centimeter per Minute) to obtain suitable mixture of SO_2 concentration. Gas compositions of 50 and 1000 ppm were obtained by controlling gas flow meter for 0.21 SLPM O_2 , 0.79 SLPM Ar, (i) 50.1 SCCM SO_2 and (ii) 1001 SCCM SO_2 respectively.

Characterization

The prepared samples were characterized by X-ray powder diffraction (XRD) (Phillips PW 170 diffractometer attached with PW 1710 controlling unit) and scanning electron microscope (SEM (Cambridge Mark-III Stereo-scan electron microscope)). SEM studies were carried out on all five systems. DSC and IR studies for entire series were also conducted. For electrical characterization samples were prepared in the form of circular discs of 9mm diameter and 2mm thickness by pressing the powder with the help of SS die-punch and hydraulic press. The pellets were sintered at 500°C for 24 hrs. For electrical characterization of the specimen pellet a good ohmic contact was ensured by using quality silver paint on to both opposite parallel surfaces of pellet followed by baking at 200°C for 2 hrs. The ionic transference number of the specimen was measured by

Wagner's DC polarization method at 400°C to ensure ionic contribution using Keithley 617 Electrometer. **Fig. 2** depicts the schematic diagram of the experimental setup used for sensor characterization. Test gas with 21% oxygen and known concentration of SO₂ alongwith balancing non-interfering Ag is allowed to flow across so that it serves as 'gas electrode'. At 440 °C, the cell emf has been recorded for different SO₂ concentrations.

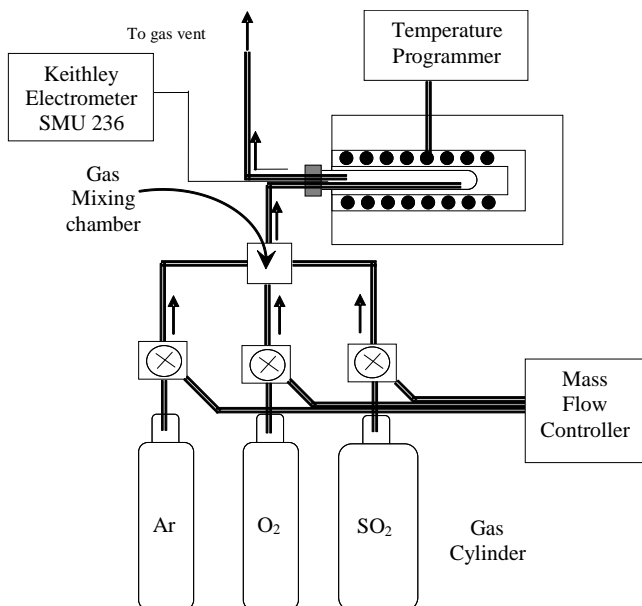


Fig. 2. Schematic representation of the experimental setup for study of sensor characteristics.

Results and discussion

XRD

The XRD pattern for all five systems was obtained at room temperature. Up to $x=3.63$ mole%, the lines corresponding to the guest cation is absent. While a small intensity for Y₂(SO₄)₃ starts appearing for $x=4.72$ mole% concentrations and above. This indicates that up to $x=3.63$ mole% Y forms solid solution with Ag₂SO₄. The data corresponding to only two systems for $x=0$ (JCPDS), $x=3.63$ mole% (Experimental) is presented in **Table 1**.

Table 1. Comparison of experimental and JCPDS data for (96.37)Ag₂SO₄:(3.63) Y₂(SO₄)₃.

S. No	d	I/I_0	d	I/I_0	$[hkl]$	Phase
	$x=3.63$ mole%		JCPDS Data			
1	3.1826	78	3.177	70	[040]	Ag ₂ SO ₄
2	2.8723	10	2.873	10	[311]	Ag ₂ SO ₄
3	2.6529	65	2.644	90	[022]	Ag ₂ SO ₄
4	2.4276	39	2.421	30	[331]	Ag ₂ SO ₄
5	1.9706	10	1.980	11	[242]	Ag ₂ SO ₄
6	1.9286	44	1.926	30	[351]	Ag ₂ SO ₄

A comparison of experimental ' d ' values and relative " I/I_0 " with those of JCPDS data reveals that with addition of Y₂(SO₄)₃, the experimental d values are slightly deviated from JCPDS data of β -Ag₂SO₄. These small deviations in experimental d values of β -Ag₂SO₄ may be attributed to replacement of Ag⁺ by Y³⁺. The absence of any line corresponding to pure Y₂(SO₄)₃ may be attributed to the partial replacement of Ag⁺ by wrong sized Y³⁺. The absence of any new line rules out the formation of any intermediate phase. This supports formation of solid solution up to $x=3.63$ mole%.

SEM

A photograph for $x=0$, 3.63 and 4.72 mole% have been presented in **Fig. 3**. A close look reveals that morphology for $x=0$ and $x=3.63$ mole % is identical supporting to the formation of solid solution. However, a small cluster of new material appears in the surface morphology of material for $x=4.72$ mole% which grows for higher doping concentrations. The micro photographs representing the surface morphology of pure and Y substituted Ag₂SO₄ reveal that, doping up to $x=3.63$ mole% improves grain to grain contacts thereby improving mechanical properties of the material.

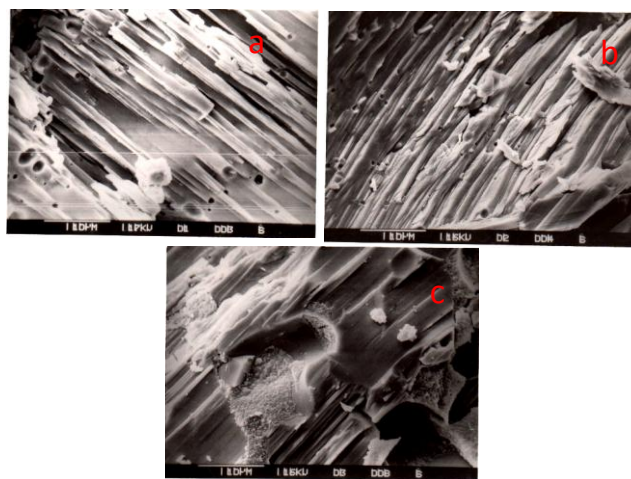


Fig. 3. Scanning Electron Microscopy photographs for (a) $x=0$, (b) $x=3.63$, (c) $x=4.72$ mole%.

DSC & IR

Differential Scanning Calorimetric (DSC) and Infra Red (IR) studies were carried out on all samples. It was observed that for $x=0$, 1.53, 2.56, 3.63 mole % the DSC isotherms, transition temperature, enthalpy etc remained same. The Infra red spectrums are also identical for $x=0$, 1.53, 2.56, 3.63 mole% leaving the frequency nodes unchanged remains same. A DSC isotherm and IR spectrum for the sample $x=0$ are depicted in **Fig. 4**. **Table 2** indicates wave number and transmittance nodes. It clearly shows a negligible change for concentrations up to 3.63 mole %.

Electrical properties

The measurement of ionic transport number by Wagner's DC polarization technique indicates ionic conductivity which remains invariant on account of Y substitution. The

real and imaginary parts of impedance were measured as a parametric function of frequency in the range from 5 Hz to 13 MHz and temperature from 450 to 150°C during cooling cycle using computer controlled hp 4192A If impedance analyzer. The temperature of the furnace was controlled using PID temperature controller. The bulk resistance in the Complex Impedance plot along with dimensions of the specimens was explored to obtain electrical conductivity. The temperature dependence of the electrical conductivity obeyed Arrhenius equation;

$$(\sigma T) = (\sigma T)_0 \exp\left(\frac{-E_g}{2kT}\right)$$

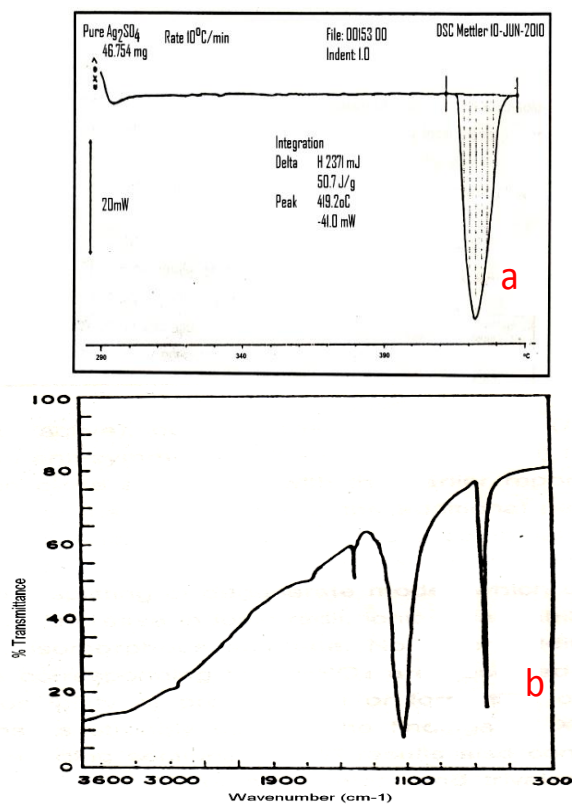


Fig. 4. (a) DSC isotherm for $x=0$ (b) Infra Red Spectrum for $x=0$.

Table 2. Concentration dependent wave number comparison for $x=0, 1.53, 2.56, 3.63$.

Wave no/ $x=$	0	1.53	2.56	3.63
v_1	983	988	988	988
v_2	466	470	470	470
v_3	1123	1125	1128	1129
v_4	619	617	617	617

The concentration (mole % or vacancy %) dependent conductivity in orthorhombic at 220°C and hexagonal at 440°C phase has been presented in Fig 5. The Optimum composition $x=3.63$ mole% that corresponds to 7% vacancy concentration offers highest ionic conductivity. The activation enthalpy for ion migration obtained from slope in Arrhenius plot is also found to be moderate for 7% vacancy concentration. Therefore the corresponding molar

composition for $x=3.63$ mole% can be explored for its utilization in SO₂ gas sensor. In balancing charge, a pair of vacancy which is created helps offering a possible vacant site for ion migration. The number of vacant sites exceeding number of mobile cations generates probability of ion migration through possible modest potential barrier. This may result in increase in ionic conductivity making the material with $x=3.63$ mole% suitable to be used for sensor application. The temperature and concentration dependent conductivity of the Ag₂SO₄ doped with Y system indicates that doping improves the conductivity of pure Ag₂SO₄ and at 7% vacancy concentration it offers optimum ionic conductivity.

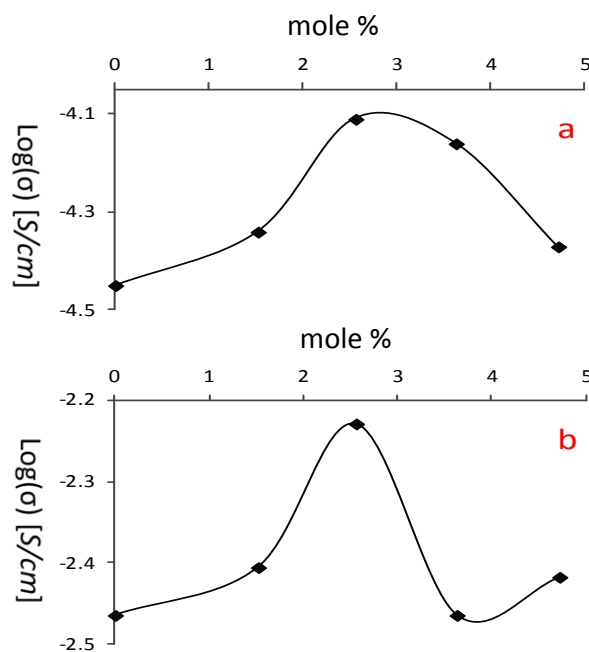


Fig 5. (a) Doping concentration dependent conductivity at 220°C (b) Doping concentration dependent conductivity at 440°C.

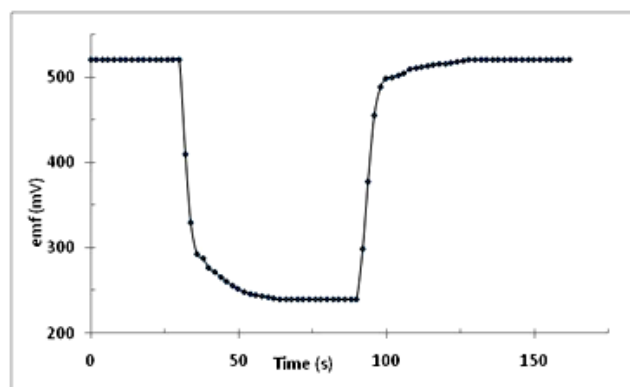


Fig. 6. Variation of emf with time for swapping of SO₂ concentration from 50 to 1000 ppm.

The optimum material (96.37)Ag₂SO₄:(3.63) Y₂(SO₄)₃ offers better electrical conductivity in both orthorhombic and hexagonal phase of silver sulphate. The active species for electrochemical reaction is SO₃ and not SO₂. To ensure equilibrium over conversion of SO₂ to SO₃, the gas mixture was passed through platinum mesh – the well known

catalyst – at 400°C [19, 25-27]. The time dependence of emf toggling when SO₂ concentration switched from 50 to 1000 ppm at various temperatures has been depicted in Fig. 6. A sensor formed by utilizing (96.37)Ag₂SO₄:(3.63)Y₂(SO₄)₃ solid solution offers a good sensor option. Sensor emf toggling between 520 mV to 240 mV was observed for shuffling of SO₂ gas concentration from 50 ppm to 1000 ppm. A response time of 22 seconds is observed. The prima-facie sensor characterization indicates promising sensor behavior.

Conclusion

The present study demonstrates that Y substituted Ag₂SO₄ that results in vacancy concentration up to 7% forms solid solution and enhances ionic conductivity which may be attributed to additional creation of energetically accessible optimum vacancies that support ion migration. Doping up to $x=3.63$ mole% improves grain to grain contacts resulting into mechanical integrity. For $x \leq 3.63$ mole%, it seems to form solid solution as no other phase is detected in X-ray, SEM, DSC and IR analysis. Transport number measured for all samples exhibits that the doping concentration does not alter ionic transference number. Thus, it offers enhanced suitability as electrolyte for SO₂ gas sensors over pure Ag₂SO₄. A simple test of varying SO₂ gas concentration from 50 to 1000 ppm shows a change in cell potential by 280mV at 440°C. This sensor characteristics behavior exhibits reproducibility.

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