Journal of Sensor Technology, 2012, 2, 13-18
http://dx.doi.org/10.4236/jst.2012.21003 Published Online March 2012 (http://www.SciRP.org/journal/jst)

Structural Characterization of Nanocrystalline $La_{1-x}Sr_xCrO_3$ Thick Films for H_2S Gas Sensors

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Received November 14, 2011; revised December 6, 2011; accepted January 5, 2012

ABSTRACT

The nanocrystalline of $La_{1-x}Sr_xCrO_3$ (x = 0.0, 0.1, 0.2, 0.3 & 0.4) were prepared by sol-gel method and their crystal structures & morphology were characterized by X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM). XRD patterns indicate that the average particle size of the nanocrystalline $La_{0.7}Sr_{0.3}CrO_3$ in the range of 30 - 35 nm. The gas sensing properties were studied towards reducing gases like Ammonia gas (NH_3), liquefied petroleum gas (LPG), hydrogen sulphide (H_2S) and H_2 gas and it is observed that undoped $LaCrO_3$ shows response to H_2S gas at relatively high operating temperature 300˚C. The $La_{1-x}Sr_xCrO_3$ based sensor with x = 0.3 shows better sensitivity towards H_2S gas at an operating temperature 210˚C. The effect of Sr doping on sensitivity, response time and recovery time of the sensor in the presence of H_2S and other reducing gases were studied and discussed.

Keywords: $La_{1-x}Sr_xCrO_3$; H_2S Gas; Selectivity; Response & Recovery Time

1. Introduction

The sensors are required basically for measurement of physical quantities and for use of controlling some systems. Presently, the atmospheric pollution has become a global issue. Gases from auto and industrial exhausts are polluting the environment. In order to detect, measure and control these gases, one should know the amount and type of gases present in the ambient. Thus, the need to monitor and control these gases has led to the research and development of a wide variety of sensors using different materials and technologies. Gas sensitive resistors based on semiconducting oxides are simple and robust devices which owe their response to changes in charge-carrier concentration within a depletion layer at the solid-gas interface, in turn caused by a change in the surface density of electron trap states [1,2]. They raise interesting questions of surface chemistry: the effects are considered due either to change in the surface coverage of the adsorbed oxygen species, caused by a reaction with the gas, or to adsorption of a gas species generating a new surface trap state.

H_2S is a colourless, toxic, flammable and malodorous gas as sources from gasoline, natural gases, city sewage, volcanic gases and hot springs with smells like rotten eggs. It can also be produced from bacterial breakdown of organic matter or wastes produced by human and animal. Other sources are craft paper mills, tanneries and petroleum refineries. H_2S gas is badly harmful to human body and the environment. Meanwhile the type of oil and natural gas is correlative with the concentration of H_2S. The oil and natural gases mines can be found depending on the concentration of H_2S. Therefore, the detection and monitoring of H_2S are of high importance for both resource exploitation and human health. In the recent researchers, a number of semiconductor sensors have been found to be sensitive to H_2S including WO_3, In_2O_3, ZnO and a few pervoskite type materials [3-7].

The pervoskite oxides (ABO_3) were used as gas sensor materials for their stability in thermal and chemical atmospheres. Modifications in microstructure, processing parameters and also concentration of acceptor/donor dopant can vary the temperature coefficient of the resistance and conductivity of ABO_3 oxides. Sensors based on ABO_3-type complex oxide material, of rare earth elements have an outstanding merit of its high sensitive and selective characteristics. These characteristics can be controlled by selecting suitable A and B atoms or chemically doping A′ and B′ elements equivalent respectively to A and B into ABO_3 to obtain $A_xA'_{1-x}B_yB'_{1-y}O_3$ compound [8,9].

In the recent years, a number of semiconductor sensors have been found to be suitable for H_2S gas e.g. SnO_2, WO_3, In_2O_3, ZnO_2 and a few perovskite-type materials like $NdFeO_3$ and $NiFeO_4$ [10-13]. $LaCrO_3$ based com-

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pounds are usually synthesized by the traditional solid state reaction method, urea combustion method [14,15]. Sol-gel approach, as a classical method, has a lot of inherent merits with better homogeneity, higher purity, and lower temperature of preparation.

In this present paper, synthesis of nanocrystalline $La_{1-x}Sr_xCrO_3$ powder by a simple chemical route has been reported. The gas sensing properties of nanocrystalline $La_{1-x}Sr_xCrO_3$ (x = 0.0, 0.1, 0.2, 0.3 & 0.4) are reported and the gas sensor based on the nanocrystalline $La_{0.7}Sr_{0.3}CrO_3$ material shows good sensitivity and selectivity to the H_2S gas.

2. Experimental Details

2.1. Material Synthesis

The $La_{1-x}Sr_xCrO_3$ (x = 0.0, 0.1, 0.2, 0.3 & 0.4) were synthesized by sol-gel method using poly ethylene glycol as a solvent. $La(NO_3)_3{\cdot}6H_2O$, $Sr(NO_3)_2$, $Cr(NO_3)_3{\cdot}9H_2O$ and citrate acid (all analytically pure) were firstly dissolved in ion free water at 80˚C for 2 h. Then ethylene glycol was added under constant stirring to obtain a homogene- ous and stable sol. The solution was further heated in pressure vessel at about 140˚C for 14 h. During this reac- tion transparent solution was transform into a gel state with very high viscosity. The material was then heated in a furnace at 350˚C for 3 h and a violent combustion was occurs which spontaneously propagates until all the gel was burnt out to form a loose powder. The powder was then calcined at 800˚C for 6 h in order to improve the crystallinity of materials.

2.2. Characterization of Samples

The synthesized samples were characterized by powder XRD using a Siemens D 5000 diffractometer .The XRD data were recorded by using Cu Kα radiation (1.5406 Å). The intensity data were collected over a 2θ range of 10˚ - 70˚. The average crystallite size of the samples was estimated with the help of Scherrer equation using the diffraction intensity of all prominent lines. TEM examination of the synthesized powder was performed using an H-800 electron microscope.

2.3. Measurement of Sensing Characteristics

For gas sensing properties, the calcined powder was then mixed with 2% PVA (polyvinyl alcohol) as a binder and 5% ethanol as a solvent; the resulting paste was coated onto an Al_2O_3 tube provided with platinum wires as electrodes at each end. The Al_2O_3 tube was about 8 mm in length, 2 mm in external diameter and 1.6 mm in internal diameter**.** A small Ni-Cr alloy coil was placed inside the tube to serve as a heater, which provided operating temperatures from 50˚C - 350˚C. The temperature was controlled by adjusting the heating power. Finally, the sensor was sintered at 600˚C for 1 h so that the PVA decomposes and strength of the element markedly increases. The different test gases are injected into the specimen chamber through an inlet. The sensing performance of the sensors was examined using the "flow gas sensing system".

The gas sensing studies were carried out on a static gas sensing system under normal laboratory conditions. The electrical resistance of thick films in air (R_a) and in the presence of H_2S (R_g) was measured to evaluate the Sensitivity (S) and is given by the relation,

$$\text{Sensitivity}(S) = \left|\frac{R_a - R_g}{R_a}\right| = \frac{\Delta R}{R_a} \quad (1)$$

where R_a is the resistance of the $La_{1-x}Sr_xCrO_3$ thick films in air and R_g is the resistance of the $La_{1-x}Sr_xCrO_3$ thick films in H_2S atmosphere. The response of the sensor for H_2S was tested in the presence of other gases so that the selectivity can be determined. The response and recovery time of the sensor was measured.

3. Results and Discussion

3.1. X-Ray Diffraction Study

The XRD patterns of the precursor powders $LaCrO_3$ and $La_{0.7}Sr_{0.3}CrO_3$ calcined at 800˚C for 6 h are shown in **Figure 1**. **Figure 1(a)**, shows the XRD pattern of $LaCrO_3$, which is in good agreement with XRD results previously reported in the literature [16]. All the diffraction peaks of the phases are indexed as perovskite-type with tetragonal structure. The diffraction data is good agreement with JCPD card of $LaCrO_3$ (JCPDS No.24-1016). **Figure 1(b)**, shows the XRD pattern of $La_{0.7}Sr_{0.3}CrO_3$ nanomaterial, which indicates that ions Sr^{2+} partially substitute for ions La^{3+} in the $LaCrO_3$ crystal lattice. The ionic radii of Sr^{2+} (1.21 Å) are very close to that of La^{3+} and Sr is incorporated into the $LaCrO_3$ lattice at the La site. The mean crystallite sizes (D) of $La_{0.7}Sr_{0.3}CrO_3$ powder was deduced from half height width of XRD peaks based on the Scherer's equation, $t = 0.9\lambda/\beta\cos\theta$, where t is the average size of the particles, λ is wavelength of X-ray radiation, β the full width at half maximum of the diffracted peak and θ is the angle of diffraction [17]. Extremely broad reflections are observed indicating nanosized particle nature of the material obtained. The average particle size of the nanocrystalline $La_{0.7}Sr_{0.3}CrO_3$ according to the scherrer formula was in the range of 30 - 35 nm.

3.2. Surface Morphology

The TEM specimens were prepared by placing microdrops of colloid solutions on a carbon film supported by

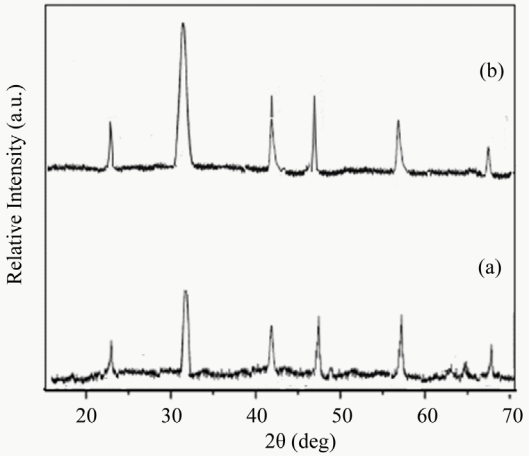

Figure 1. XRD spectra of (a) $LaCrO_3$; (b) $La_{1-x}Sr_xCrO_3$ calcined at 800˚C.

a copper grid. The TEM images of the nanocrystalline $La_{0.7}Sr_{0.3}CrO_3$ calcinated at 800˚C is shown in **Figure 2**. It indicates the presence of $La_{0.7}Sr_{0.3}CrO_3$ nanoparticles with 30 - 50 nm size which form spherical type of oriental aggregation, agglomeration and polymeric linkage throughout the region.

3.3. Gas Sensing Characteristics

Electrical characterization of samples $La_{1-x}Sr_xCrO_3$ (x = 0.1, 0.2, 0.3 & 0.4) synthesized by sol-gel method and calcinied at 800˚C has been carried out in a gas test chamber. The resistance of the films was measured by using Equation (1). The resistance of the films decreased upon exposure to H_2S gas. **Figure 3** shows gas sensing response of H_2S gas, at different operating temperatures (50˚C - 400˚C) for thick films of pure $LaCrO_3$. It is observed that response for pure $LaCrO_3$ is obtained at high operating temperature 350˚C, than decreases as increase in operating temperature. At a low operating temperature, the low response can be expected because the gas molecules do not have enough thermal energy to react with the surface adsorbed oxygen species. As the temperature increases, the thermal energy obtained was high enough to overcome the potential barrier, and a significant increase in electron concentration resulted from the sensing reaction. The response of semiconductor oxide gas sensor to the presence of a given gas depends on the speed of the chemical reaction on the surface of the grains and the speed of diffusion of the gas molecules to that surface which are activation processes, and the activation energy of the chemical reaction is higher. In this case, at low temperatures the sensor response is restricted by the speed of the chemical reaction, and at higher temperatures (above 350˚C) it is restricted by the speed of diffusion of gas molecules. At some intermediate temperature (at 350˚C), the speed, values of the two processes be-

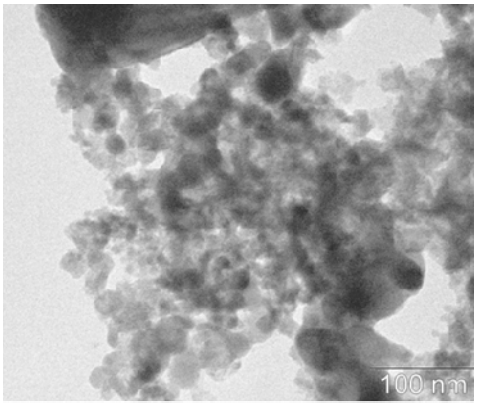

Figure 2. TEM micrograph of $La_{0.7}Sr_{0.3}CrO_3$ calcined at 800˚C.

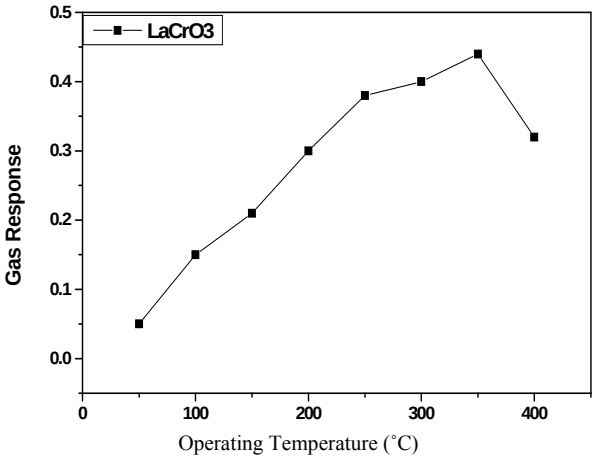

Figure 3. H_2S gas response vs operating temperatures for $LaCrO_3$ calcined at 800˚C.

come equal, and at that point the sensor response reaches its maximum [18].

Thus, the pure $LaCrO_3$ shows response towards H_2S gas at high operating temperature 350˚C, which is rather high and practically inconvenient in view of commercial standards. Therefore, efforts were made to modify the $LaCrO_3$ based sensors by doping with Sr, so as to be operated at lower operating temperatures with high sensitivity and selectivity. **Figure 4** shows gas sensing response of H_2S gas, for thick films of pure $LaCrO_3$ doped with different concentrations of Sr. From the figure it is clear that the response values of every doped sample apparently increased with increasing the operating temperature. In this figure, it is observed that the $La_{0.7}Sr_{0.3}CrO_3$ thick film had the largest sensing response at an operating temperature 210˚C. It is indicating that Sr doping can greatly improve the sensitivity of $LaCrO_3$ based sensor towards H_2S gas. We know that the semiconductor oxide gas sensors can detect different gases by changing the conductivity of their surface due to the reaction of the reducing gases with adsorbed oxygen. Sr doping in La-

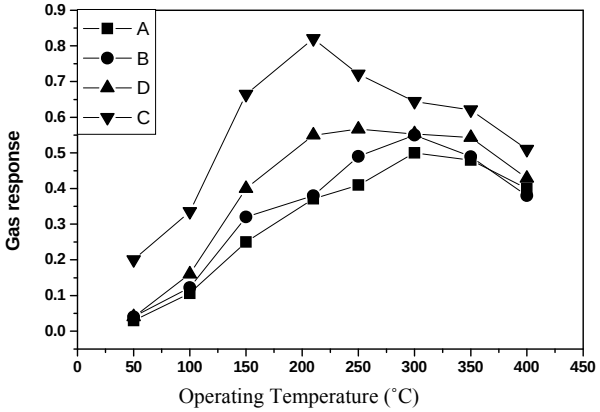

Figure 4. H_2S gas response vs operating temperatures for (A) $La_{0.9}Sr_{0.1}CrO_3$, (B) $La_{0.8}Sr_{0.2}CrO_3$; (C) $La_{0.7}Sr_{0.3}CrO_3$ & (D) $La_{0.6}Sr_{0.4}CrO_3$ calcined at 800˚C.

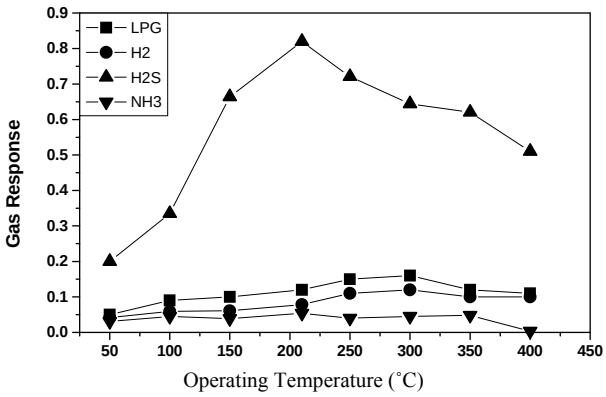

Figure 5. Cross sensitivity vs operating temperatures for different reducing gases for $La_{0.7}Sr_{0.3}CrO_3$.

CrO_3 promotes the deviation from stoichiometry and enhances the surface defect. A large surface defect concentration creates more active surface states for adsorbed oxygen [19,20].

Selectivity or specificity is defined as the ability of a sensor to respond to certain gas in the presence of other gases. **Figure 5** shows the selectivity of $La_{0.7}Sr_{0.3}CrO_3$ for different gases. It is clear from the figure that $La_{0.7}Sr_{0.3}CrO_3$ sample is more selective to H_2S gas at 210˚C against all other tested gases viz: NH_3, LPG and H_2. As easily seen, the $La_{0.7}Sr_{0.3}CrO_3$ was most selective to H_2S among the gases tested, while it was least selective to NH_3.

The sensor selects a particular gas at a particular temperature. Thus by setting the temperature, one can use the sensor for particular gas detection. The same sensor could be used for the detection of different gases by operating it at particular temperature for a typical gas. This can be attributed to different chemical reactivity's of different gases on the sensor surface. Different gases have different energies for adsorption, desorption, and reaction on the metal oxide surface, and therefore the response of the sensor at different temperatures would depend on the gas being sensed. The amount of oxygen adsorbed (O_2^-, O^-, O^{2-}) on the sensor surface goes on increasing with an increase in temperature, reaches to the maximum and then decreases with a further increase in operating temperature. The response to the gas to be detected follows the same behavior. When a reducing gas comes in contact with the sensor surface, it gets oxidized. The rate of oxidation would be the function of the amount of adsorbed oxygen on the surface and the type of gas to be detected. The larger the rate of oxidation, the larger would be the number of electrons released, and in turn the larger would be the gas response. At higher temperatures, the amount of oxygen adsorbed would be smaller, leading to a slower rate of reduction of a target gas and, therefore, the smaller gas response.

Figure 6 depicts the variation of sensitivity of $La_{0.7}Sr_{0.3}CrO_3$ sample with H_2S gas concentrations at 210˚C temperature. It is clear from the figure that the gas response goes on increasing linearly with gas concentration up to 200 ppm and saturated beyond it. The rate of increase in gas response was relatively larger up to 200 ppm. It is observed that as the concentration of H_2S gas increases, the average sensitivity increases linearly in the beginning and later it becomes saturated. The linear relationship between sensitivity and gas concentration may be attributed to the availability of sufficient number of sensing sites. The low concentration implies a lower surface coverage of gas molecules, resulting in a lower surface reaction between the surface adsorbed oxygen species and the gas molecules. The increase in H_2S gas concentration increases the surface reaction due to a large surface coverage. Further on increasing the H_2S gas concentration, the surface reaction does not increase and eventually saturation takes place. Thus, the maximum sensitivity was obtained at higher concentration of H_2S gas, *i.e.*, 200 ppm.

The response and recovery time is an important parameter, used for characterizing sensors. It is defined as the time required to reach 90% of the final change in voltage or resistance, when the gas is turned on or off, respectively. The response and recovery times of $La_{0.7}Sr_{0.3}CrO_3$ sample is represented in **Figure 7**. The response was quick (~20 s) to 200 ppm of H_2S while the recovery was moderate (~60 s). The quick response may be due to faster oxidation of gas. Its high volatility explains its quick response .The large recovery time would be due to lower operating temperature. At lower temperature O_2^- species is more prominently adsorbed on the surface and thus it is less reactive as compared to other species of oxygen, O^- and O^2.

The long-term stability is another important factor for gas sensors. The stability of the $La_{0.7}Sr_{0.3}CrO_3$ nanocrystalline based sensor was studied in the presence of 200 ppm H_2S gas for fifty day at 210˚C. Repeated experi-

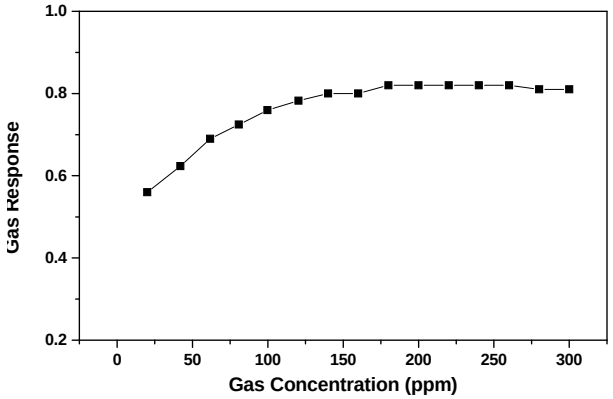

Figure 6. Gas response of $La_{0.7}Sr_{0.3}CrO_3$ to H_2S gas of different concentration at an operating temperature 210˚C.

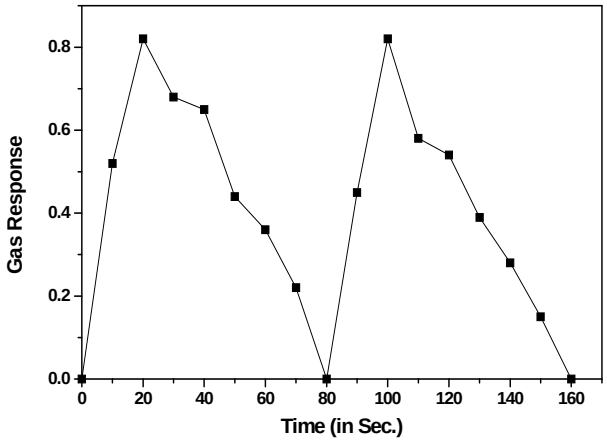

Figure 7. The response and recovery characteristics to 300 ppm H_2S gas of $La_{0.7}Sr_{0.3}CrO_3$.

ments were carried out and it was observed that both $La_{0.7}Sr_{0.3}CrO_3$ sensor showed good response performance even after 50 days (shown in **Figure 8**). It is observed that its resistance is stable except for a small variation for first ten days. This indicates that the present nanocrystalline $La_{0.7}Sr_{0.3}CrO_3$ sensor can be effectively used as H_2S gas sensor.

4. Conclusion

In this work the $La_{0.7}Sr_{0.3}CrO_3$ have been presented as suitable semiconductor materials for selective H_2S detection. The XRD pattern of $La_{0.7}Sr_{0.3}CrO_3$ shows perovskite-type with tetragonal structure. The results revealed that the particle size is in the range of 30 - 35 nm for $La_{0.7}Sr_{0.3}CrO_3$ with good crystallinity. From the results obtained, pure $LaCrO_3$ showed low response to H_2S gas. Sr doped $LaCrO_3$ thick films were found to be high sensitive for H_2S gas. Among all other synthesized samples $La_{0.7}Sr_{0.3}CrO_3$ thick film was found to be optimum and showed highest response to H_2S gas at 210˚C. The sensor shows high degree of selectivity towards H_2S gas than

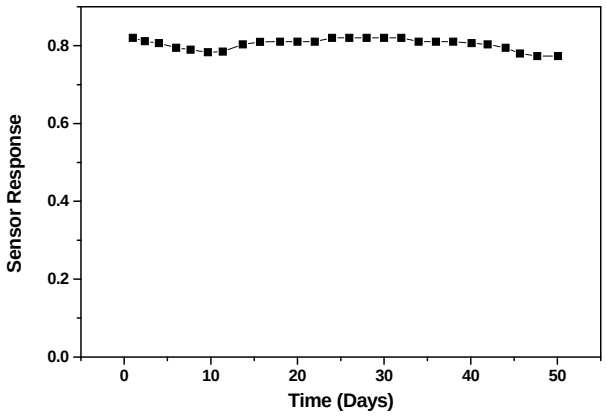

Figure 8. The stability characteristics of $La_{0.7}Sr_{0.3}CrO_3$ sensor towards H_2S gas.

other reducing gases. Also this sensor showed very rapid response and recovery to H_2S gas. Over long exposure it was observed that sensor exhibited a good stability and repeatability as gas sensor with consistent pattern and response magnitude.

5. Acknowledgements

The authors are also indebted to Principal, Dr.M.S Ali, Principal, Prof Ram Meghe College of Engineering & Management, Badnera-Amravati, India for his kind cooperation during this research work. The authors are thankful to University Grants Commission (UGC), New Delhi for providing financial support for this work.

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