

Evaluation of the performance of a Silicate Based Thick Film Freon Gas Sensor Operating at 750 °C in Low Temperature Cofire Ceramics

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Abstract

Ceramic silicate sensors were evaluated to detect halogen gases. These gas sensors typically operate in the range from 650°C – 800°C. A low temperature cofire ceramic (LTCC) low power micro heater was developed which operates at 750°C to meet the heating requirements for these sensors. Four basic sensor materials were fabricated: Li_2SiO_3 , Na_2SiO_3 , K_2SiO_3 , and CaSiO_3 . The evaluation of the sensor material, operating temperature, bias voltage, as well as the description of the sensor behavior before and after the gas is present was performed. The sensor with a composition of 51.5% CaSiO_3 + 48.5% Li_2SiO_3 demonstrated the best results, including a stable current and response to R-134A Freon gas.

Key words: Gas sensor, Silicate based sensors, LTCC.

Introduction

Hydrofluorocarbons (HFCs) are considered one of the best substitutes for reducing stratospheric ozone loss because of their short lifetime and lack of Cl. In the United States, HFC-134a is used in mobile air conditioning and in residential, commercial and industrial refrigeration systems growing rapidly with an atmospheric lifetime of about 12 years [1]. The prior art of sensors for detecting gases has utilized a number of different detection principles [2, 3]. Prior art positive ion emission and surface depletion layer detectors have very low sensitivity to HFCs. One way to increase their sensitivity to HFCs is to increase the sensor operating temperature. However, this has the adverse effect of significantly shortening the life of the sensor, increase the power consumption, and greatly increasing its sensitivity to other gases, particularly to chlorinated and/or brominated gases and, as a result, unwanted interference signal are sometimes generated making difficult to discern the presence of the gas of immediate interest [4].

Proper operation of cooling systems can be maintained using compact portable sensors that detect small amounts of refrigerant gases and have long life expectancy [5, 6]. The portable refrigeration leak detectors presented are based on heated element type sensors which consist of a sensing ceramic element that is fabricated on one side of the substrate and a heater on the opposite side using a Low Temperature Co-fired ceramic (LTCC) as the substrate material. After the sensor is heated up, an

equilibrium concentration of both anion and cation vacancies will occur. Since the number of vacancies (and therefore reaction of sites), is a function of temperature, the higher the temperature, the greater the number of vacancies. Upon reaction of the sensor with the halogen species (because of a higher thermodynamic free energy of reaction) an oxygen vacancy must be annihilated to maintain electrical charge partial neutrality of the remaining ceramic silicate, resulting in a change of current flow that can be measured to determine the presence of the gas. Four basic sensor materials were tested (Li_2SiO_3 , Na_2SiO_3 , K_2SiO_3 , and CaSiO_3) as well as several combinations between them. The evaluation of the sensor size, operating temperature, bias voltage, and electrodes size is presented. The analysis for the sensor includes the modeling of the sensor as a resistor and the reactivity analysis between the materials and the gas using Gibbs free energy.

Sensor Design and Fabrication

The sensor element as well as the heater element were placed in opposite sites of the LTCC substrate using thick film technology. The assembly is presented in Figure 1.

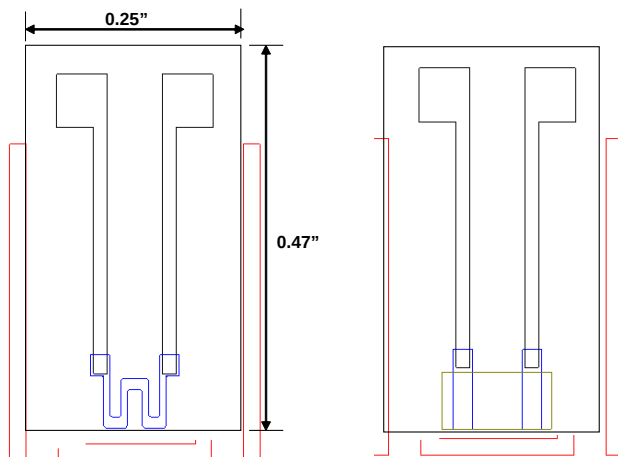


Figure 1. Heater (L) and Sensor (R) Design

The substrate was fabricated out of three layers of Heraeus CL91-8242 (Heraloc) that exhibits minimum shrinkage on firing and was compatible with the inks for all the elements. The total thickness for the substrate after the lamination and firing processes is approximately 270 μm . The heater side contains a heating element and conductive leads. The heater was placed on the substrate using Platinum (Heraeus CL 11-5100) in a serpentine shape with chamfered corners to prevent the occurrence of current crowding. The electrodes were printed with Heraeus C4740 which contains Ag and 1% Pt. The heater was double printed but the electrodes and leads were single printed due to the surface density of this layer is not as important. The electrodes and leads thickness after firing are 10 and 8 μm respectively.

The sensor side contains three elements: the sensor, electrodes, and leads. The final sensor was designed as a square element, and the final electrodes (Heraeus C4740) and leads (Heraeus CL 11-5100) were designed as two parallel lines. The leads are used to apply the bias voltage required to form the depletion region as well as to measure the current flow when the sensor detects the gas presence. After an analysis between the sensor working mechanism, the gas and previous effort, the selected inks for the sensor were: Potassium Silicate (K_2SiO_3), Lithium silicate (Li_2SiO_3), Sodium Silicate (Na_2SiO_3), and Calcium Silicate (CaSiO_3). The selected inks were not available commercially were fabricated in the facilities of Heraeus Company at Conshohocken, PA following all the requirements for ink fabrication (particle size, organic media and viscosity, etc.). The final viscosities for K_2SiO_3 , Li_2SiO_3 , Na_2SiO_3 , and CaSiO_3 were 335, 314, 346, and 298 kcps respectively.

Experimental Results

During the test of the sensor a graph of current versus time was obtained. A typical sensor behavior showing a sensor tested multiple times is presented in Figure 2.

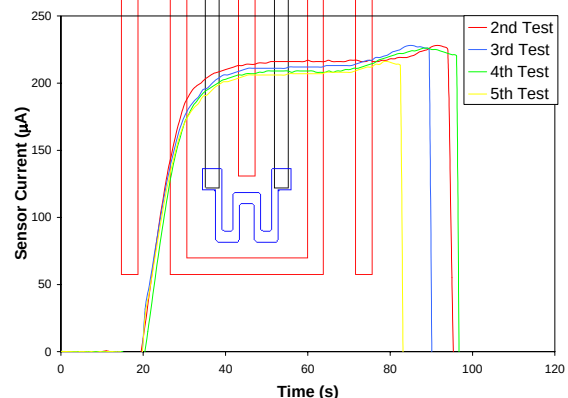


Figure 2. Sensor Behavior: Multiple tests

Once the sensor is at the operating temperature and bias voltage established the current increases until stability is achieved. After this, the gas is placed in the chamber and the response can be observed as an increase in current until the sensor is turned off. The first test was not included due to the extended time to achieve a stable current (charge movement due to the “diode effect”). After the first test, the time to reach a stable current is reduced approximately 10 times due to the previous movement of positive and negative charges, resulting in minimal ion migration. Additionally, during the first test there is an initial peak in current that disappears during multiple testing of the sensor. The peak in current is due to inherent defects, and impurities within the sensor that are swept out during the first testing and disappear during multiple testing.

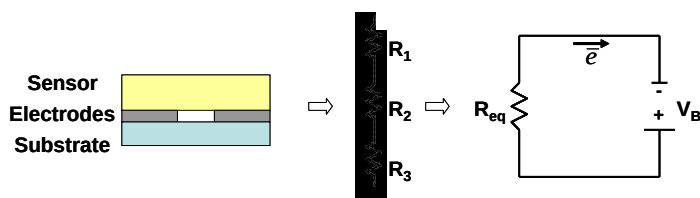
Sensor Analysis before gas

The sensor inks fabricated were tested individually to determine the stable current and the time to reach stabilization. The sensors were tested at 690°C and 3V. Every sensor was tested 5 times and the results for stable current and the time to reach stabilization are presented in Table 1.

Table 1. Results for Pure Materials before Gas

Sensor Material	Stable Current (μA)	Time for Stabilization (s)
100% K_2SiO_3	250	37
100% Na_2SiO_3	255	25
100% CaSiO_3	258	35
100% Li_2SiO_3	206	31

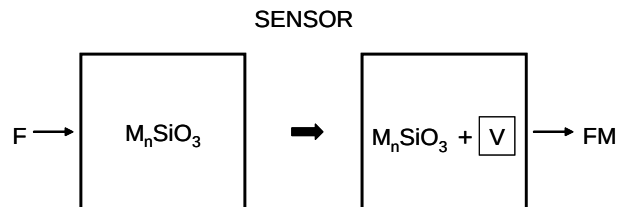
The material with the highest stable current or baseline corresponds to CaSiO_3 follow by Na_2SiO_3 , K_2SiO_3 and finally Li_2SiO_3 . These results were compared with values calculated through a resistor model of the sensor. The model with the equivalent resistant as well as a cross sectional view of the sensor, electrodes and substrate is presented in Figure 3.

**Figure 3. Sensor Modeling as a Resistor**

The equivalent resistance is calculated adding $R_1 + R_2 + R_3$ that correspond to the resistance for the sensor, electrodes and substrate respectively. The resistance for every component is calculated using the resistivity, length and cross sectional area. Both, calculated and experimental results have the same trend. However, the sensor with 100% Na_2SiO_3 showed high instability and stop responding during the second test in most of the cases.

Sensor Reaction to the Gas

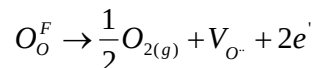
In order to calculate the Gibbs free energy (ΔG), it is necessary to define the reactions between the silicates and the halogen gas. After the depletion region is formed and the positive and negative charges within the sensor are in equilibrium, the halogen gas is put in contact with the sensor. Due to the high temperature, the gas will dissociate separating the F atoms that will react with the sensor material. In order to write the general reaction M will represent the cation (+) from the sensor material (K, Li, Na or Ca) and F is the anion (-) from the halogen gas. Due to its higher thermodynamic free energy of reaction F will react with M creating a vacancy in the sensor material. This can be seen schematically in Figure 4.

**Figure 4. Reaction between M - X**

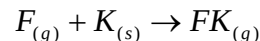
The subscript n is 2 for K, Li, and Na and 1 for Ca. The general reaction will be:



For the vacancy notation the subscript means the type of site occupied and the superscript means the excess charge associated with the site. In this case there is the removal of a cation from a cation site to produce a cation vacancy leaving excess negative charge (') associated with the surrounding anions. The sensor material is no longer balanced and therefore it is necessary to create an oxygen vacancy to maintain the balance:



The reactant is oxygen, where the anion (superscript) will leave an oxygen site (subscript). In the products there is the oxygen and the oxygen vacancy that will generate the electrons to produce the current that will be the measure of the gas presence. In order to find the most reactive sensor material, the Gibbs free energy was calculated using the reaction between the sensor materials and F. The reaction between F and K has two reactants: atomic F in gas state (g) and K in solid state (s). The product is FK in gas state (g):



Similarly reactions were used for the other silicates. The results for the Gibbs free energy calculations between the sensor material and F are presented in Table 2.

Table 2. Reactivity between sensor and gas

Elements	ΔG (KJ/mol)
F - K	-410
F - Li	-432
F - Na	-377
F - Ca	-380

All reactions have negative values for Gibbs free energy meaning that the sensor materials will react spontaneously with the gas, in agreement with the fact that all sensor materials tested respond to the

gas presence. Additionally, Gibbs free energy values show that the first material that reacts with the gas is Li_2SiO_3 follow by K_2SiO_3 , CaSiO_3 , and finally Na_2SiO_3 , also in agreement with the experimental time in which the sensor respond to the gas: 0.7 s, 1.0 s, 1.2 s and 1.3 s for Li_2SiO_3 , K_2SiO_3 , CaSiO_3 , and Na_2SiO_3 respectively.

Surface Diffusion

After the sensor reaches its stable current and the gas runs into the chamber the first reaction between the gas and the sensor occurs with the cations at the sensor surface. This corresponds to the surface diffusion that is observed in the sensor response linearly. The correlation for the surface diffusion is as follows:

$$I(t) = I_s + s \cdot t \quad (0 \leq t \leq 8)$$

Where:

$I(t)$: Current as function of time

I_s : Stable current

s : Slope

t : Time that the gas is in contact within the sensor.

An essential factor in this equation is the slope due to the stable current is constant for every sensor and the time that the gas is in contact within the sensor is a predefined value due to the sensor is a portable device. In order to compare the surface diffusion in the different sensor materials the slope for the sensor response to the gas was determined. The results for the slope during the surface diffusion for every sensor material are presented in Table 3.

Table 3. Sensor Response to Gas

Sensor Material	Surface Diffusion Slope ($\mu\text{A/s}$)
100% K_2SiO_3	0.5
100% Na_2SiO_3	1.3
100% CaSiO_3	0.7
100% Li_2SiO_3	1.6

It is observed that the silicate with the highest slope for the response to the gas is Li_2SiO_3 , follow by Na_2SiO_3 , CaSiO_3 and finally K_2SiO_3 . Once again, due to the fluorine (F) atoms will react with potassium, sodium, lithium or calcium atoms due to the higher thermodynamic free energy of reaction. Therefore, knowing the number of atoms that will react there should be a direct relation between them and slope for the current response. The number of atoms was calculated using the mass, Avogadro's number, and the atomic mass. The results are presented in Table 4.

Table 4. Number of Atoms

Element	Number of Atoms
K	3.05E+18
Li	1.07E+19
Na	5.86E+18
Ca	3.24E+18

As it was expected there is a direct relation between the number of cations within the sensor and the slope for the sensor response. The number of atoms at the surface depends at the bulk number of atoms showing that the silicate with highest number of atoms has the highest slope for the sensor response.

Operating Temperature Effect

A critical factor in the sensor response is the operating temperature. Since the sensor operates through a diffusion mechanism where vacancies are the key, it is known that the process is temperature dependant. However, since the sensor is desired to be a portable device and the heater is the source for the temperature, for practical purposes, the operating temperature should be as low as possible to reduce the power applied to the heater. The ideal temperature to assure the maximum number of vacancies should be 90% of the melting temperature. Since most of the sensors that temperature is higher than the auto-ignition temperature, the highest operating temperature was selected below the auto-ignition temperature for the gas and the lowest operating temperature was obtained directly from the $\text{KF-LiF-K}_2\text{SiO}_3\text{-Li}_2\text{SiO}_3$ phase diagram. The three operating temperatures tested are: 690°C, 600°C, and 540°C. Different sensors were tested and the average for small and large sensors with 56% K_2SiO_3 + 44% Li_2SiO_3 at 3V are presented Table 5.

Table 5. Operating Temperature Results

Operating Temperature (°C)	Stable Current (μA)	Time for Stabilization (s)	Surface Diffusion Slope ($\mu\text{A/s}$)
690	264	31	0.72
600	55	31	0.47
540	14	33	0.28

The critical effect of the operating temperature on the sensor behavior is observed. The sensor response as well as the stable current is directly proportional to the operating temperature. It was also observed that even when the sensor responds at the lowest temperature there is a noise effect on the response. The depletion region stabilization is inversely proportional to the operating temperature which is in agreement with the movement of the ions within the sensor is also a temperature dependent process. Additionally, the

resistance versus the inverse of temperature was plot and is presented in Figure 5. It is observed a linear relation for the resistance and the inverse of the temperature showing the conductivity effect within the sensor.

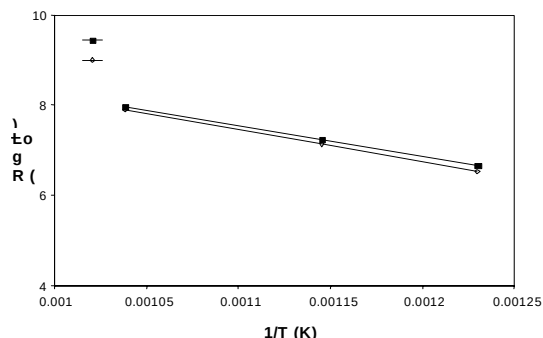


Figure 5. Operating Temperature Effect

SEM pictures for the 56%K₂SiO₃ + 44% Li₂SiO₃ after testing are presented in Figure 6. Cracks are observed on the sample tested at 690°C that is in agreement with the failure of this sample during the fifth test due to burning of the sensor.

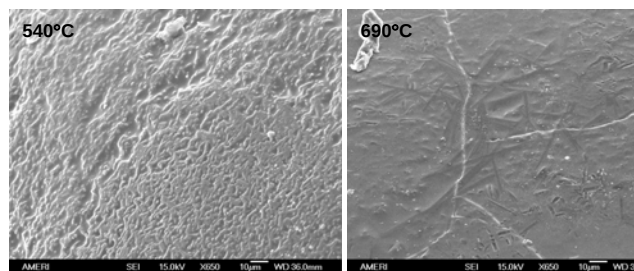


Figure 6. Operating Temperature Effect (SEM)

Bias Voltage Effect

Five bias voltages were selected for testing: 5V, 4V, 3V, and 2V. The results for the small sensor with 56%K₂SiO₃ + 44%Li₂SiO₃ at 690°C are presented in Table 6.

Table 6. Bias Voltage Results

Bias Voltage (V)	Stable Current (μA)	Time for Stabilization (s)	Surface Diffusion Slope (μA/s)
5	372	32	0.76
4	321	25	0.69
3	235	31	0.58
2	166	28	0.54

It is observed that there is a direct relation between the applied bias voltage and the sensor response as well as the stable current. When the bias voltage increases 1V the stable current increases 68 μA approximately. There is not a linear relation for the slope in the sensor response for every voltage increase. It was also observed that when the bias

voltage increases the sensor life reduces showing cracks on the sensor surface.

Testing of Compounds

In addition to the pure materials several combinations between them were tested. The best results were obtained for the combinations obtained from 3 phase diagrams: (KF-LiF-K₂SiO₃-Li₂SiO₃), (LiF-CaF₂-Li₂SiO₃-CaSiO₃), and (LiF-NaF-Li₂SiO₃-Na₂SiO₃). It was found that the sensor with the best behavior including stable current, sensor response to the gas and sensor life is the sensor with 51.5%CaSiO₃ + 48.5%Li₂SiO₃.

Finally, the selectivity of the sensor was evaluated using Gibbs free energy between the halogen and chlorine. The comparison for the results between the sensor material and the two halogen gases can be seen in Figure 7.

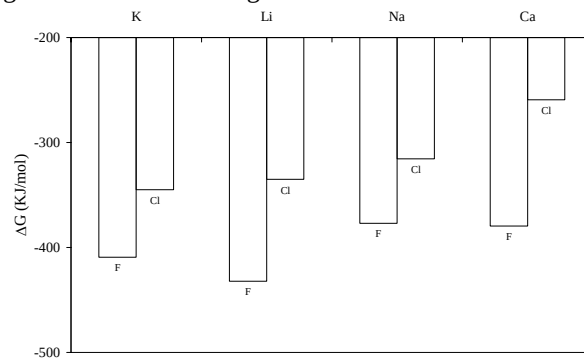


Figure 7. Sensor reaction with F and Cl

The sensor material reacts with both fluorine and chlorine due to the negative values for the Gibbs free energy. However, all sensor materials will react faster with F than Cl.

Conclusions

1. It is possible to fabricate a heated ceramic sensor to detect leaks of halogen gases using K₂SiO₃, Li₂SiO₃, Na₂SiO₃, and CaSiO₃ inks using techniques from microelectronics assembly including LTCC and thick film technology.
2. The stable current was calculated through resistor modeling of the sensor and determining the equivalent resistance for the sensor, electrodes and substrate. The calculations for the stable current were compared with the experimental results and agreement was found between the calculated and experimental values.
3. The Gibbs free energy analysis between the sensor and the gas were done utilizing the chemical reactions between the sensor and the gas. The calculations show the reactivity between the sensor and the gas is in agreement with the experimental results. Similarly, the calculated results are in

agreement with the time that the sensor takes to detect the gas.

4. The stable current and response to the gas have a direct relationship with the sensor material, sensor thickness, operating temperature, and bias voltage

5. Comparing the results for the different materials as well as the different parameters evaluated it was concluded that the sensor with the best behavior including stable current, sensor response to the gas and sensor life is the sensor with $51.5\%\text{CaSiO}_3 + 48.5\%\text{Li}_2\text{SiO}_3$.

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