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Synthesis, characterization and gas sensing performance of aluminosilicate azide cancrinite

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Abstract. **The present investigation deals with synthesis and gas sensing performance of $Na_8[AlSiO_4]_6(N_3)_{2.4}(H_2O)_{4.6}$ cancrinite-based thick film. The product obtained was characterized by Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscope, thermogravimetric analysis and magic-angle spin nuclear magnetic resonance (MAS NMR). The crystal structure of the product was determined from X-ray powder diffraction data by applying Rietveld refinement. Refinement showed that azide cancrinite crystallize in the space group $P6_3$. Alternate arrangement of Si and Al atoms was confirmed by single intense peak of MAS NMR analysis. For the first time, this study reports the gas sensing performance of aluminosilicate azide cancrinite. The effect of annealing and operating temperature on gas sensing characteristic of azide cancrinite thick film is investigated systematically for various gases at different operating temperatures. This sensor was observed to be highly sensitive and selective to ammonia gas.**

Keywords. **Cancrinite; XRD; Rietveld refinement; thick film; gas sensing; thermal analysis.**

1. Introduction

Cancrinite, a type of zeolite, consists of parallel six-membered rings consisting of alternate AlO_4 and SiO_4 tetrahedra. The hexagonal symmetry is a result of stacking of such six-membered rings in an AB sequence. This stacking leads to large number of continuous channels, which are formed by twelve-membered rings of alternate AlO_4 and SiO_4 tetrahedra. It also contains small channels known as ε-cage, which are bounded by 5 six-membered and 6 four-membered rings. Cancrinite structure at high temperature was investigated by few researchers [1–5], according to their thermal study, cancrinite loses water almost at 898 K, and thereafter purely anhydrous cancrinite phase exists up to 1198 K [6]. Encapsulated anions start to decompose from 898 K, and mass loss occurs in the temperature range of 293–1373 K [7], whereas Sirbescu and Jenkins [8] have explored that mass loss in the temperature range of 1058–1623 K was observed in thermogravimetric analysis (TGA). Barrer *et al* [9] reported that decomposition of free sodium azide takes place at 548 K, and decomposition reaction is exothermic in nature. Decomposition of sodium azide incorporated into the zeolitic framework in a step-wise process [10]. The above cited results prompted that the effect of temperature on the structure of azide-enclathrated cancrinite could be studied.

Ammonia severely irritates the nose, throat and lungs. Symptoms may include burning sensations, coughing, wheezing, shortness of breath, headache and nausea. Overexposure may also cause effects on the central nervous system, including unconsciousness and convulsions. Vocal chords are particularly vulnerable to corrosive effects of high concentrations. Very high concentration of ammonia can even cause death of an animal [11]. Some of the researchers have reported some metal oxide materials [12–20], polyaniline [21], Nafion [22] and polypyrrole [23] thin film coatings, as an ammonia gas sensor, but no report is found with cancrinite as a gas sensor.

After extensive literature search, it was observed that cancrinite as a gas sensor is not yet reported, till date no efforts have been made to study sensing and thermal properties of aluminosilicate azide cancrinite. In continuation of our research work on the synthesis of cancrinite, we report herein the characterization, effect of temperature on IR frequencies, thermal analysis (TGA and DTA) and sensing property of azide-enclathrated aluminosilicate cancrinite.

2. Experimental

2.1 *Aluminosilicate azide cancrinite synthesis*

Aluminosilicate azide cancrinite was synthesized by using zeolite-A. A quantity of 2 g of zeolite-A, 7 g of sodium azide and 3.2 g sodium hydroxide was taken in a Teflon autoclave containing 20 ml distilled water. Then the reaction mixture was shaken vigorously to obtain homogeneity. After the reaction period, the product was washed with deionized water, and dried overnight at 373 K to remove the weekly adsorbed water.

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2.2 *Characterization*

The pure white crystalline aluminosilicate azide product obtained was characterized by different analytical techniques such as Fourier transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), scanning electron microscope (SEM), ^{23}Na and ^{29}Si magic-angle spin nuclear magnetic resonance (MAS NMR), thermogravimetric analysis (TGA) and differential thermal analysis (DTA).

2.3 *Thermal study*

Primarily FT-IR spectroscopy was applied to study the structural changes in product, and decomposition process of azide (N_3^-) anion by recording spectra at various temperatures. For FT-IR analysis KBr pellet technique was used. To prepare KBr disc, 2 mg sample was homogeneously mixed with 80 mg of KBr, and spectra were recorded on Shimadzu IRAffinity spectrometer. The thermal behavior of the cancrinite was examined within the temperature range of room temperature to 853 K. The MAS NMR of ^{23}Na, and ^{29}Si nuclei analysis was carried out on a Bruker solid-state MAS NMR spectrometer DSX 300. The X-ray powder diffraction data were recorded over the range of 5–80°2θ with CuKα radiation for $5<2\theta<90°$ using diffractometer operating in θ–θ geometry (step width 0.017°2θ, sample time 1 s per step).

The thermal stability of the product was studied by TGA using Metlor Toledo instrument at a heating rate of 10°C min^{-1}, in the temperature range of room temperature to 1296 K. DTA curve was also recorded at the same heating rate as well as temperature range. The SEM image was taken on a JEOL JEM-6360A model, equipped with JEOL JEC_560 auto-carbon coater SEM, to study the crystal morphology.

2.4 *Thick film preparation*

The paste of synthesized aluminosilicate azide cancrinite was prepared by mixing its fine powder with ethyl cellulose, which acts as temporary binder, and in a mixture of organic solvents, i.e., 2 butoxyethanol and terpineol. These materials were mixed in appropriate proportions. The films were prepared on glass substrate by using screen printing followed by drying under tungsten filament lamp. Dried films were fired at 400°C for definite time.

The steady gas sensing system had been applied for testing the sensing property of the product films towards the different gases (figure 1). Sensitivity can be simply defined as,

$$S = \frac{R_a - R_g}{R_a} = \frac{\Delta R}{R_a},$$

where R_a is the resistance of cancrinite film in the presence of test gas and R_g the resistance of cancrinite film in dry air.

3. Results and discussion

3.1 *Effect of temperature on wavenumber of azide cancrinite*

Figure 2 shows the FT-IR spectrum of azide-enclathrated aluminosilicate cancrinite. The FT-IR spectrum shows three kind of vibrations [24–27], such as ν_{as} (Al–O–Si) (asymmetric stretching vibrations) at about 1005 cm^{-1}, ν_s (Al–O–Si) (symmetric stretching vibrations) from 508 to 682 cm^{-1} and δ (O–T–O) (bending vibration) at 429 and 462 cm^{-1}. Apart from these vibrations, strong and well-pronounced absorption band appears at 2069 cm^{-1}, whose presence confirms the enclathration of azide anion inside the framework of cancrinite. These wavenumbers clearly show the formation of framework with enclathration of azide anion. The accommodation of water molecule in cancrinite framework is confirmed by broad band (3100 to 3600 cm^{-1}) and bending mode at 1650 cm^{-1}.

FT-IR study of cancrinite [7,28] and azide zeolite [10] materials at various temperatures is very rarely observed in literature. The behaviour of the product during its heating throughout the temperature range is shown in figure 2a–f.

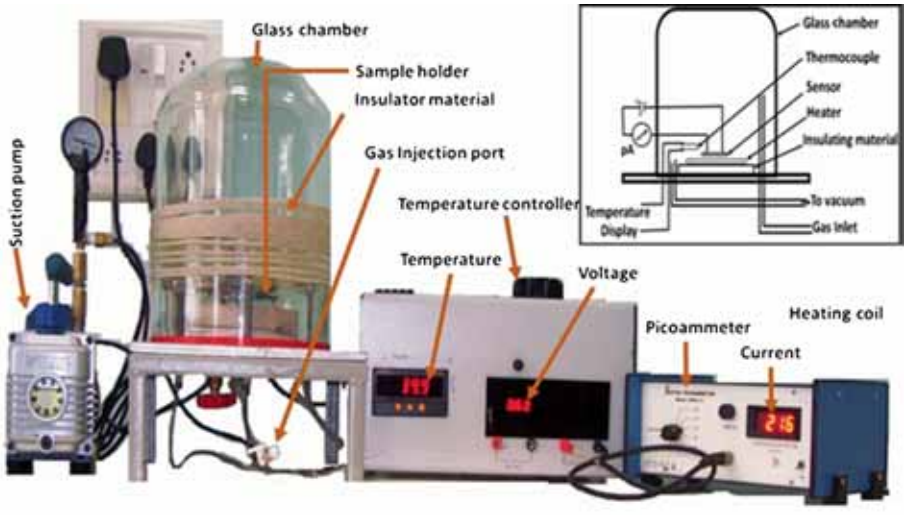

Figure 1. Steady gas sensing system photograph with block diagram.

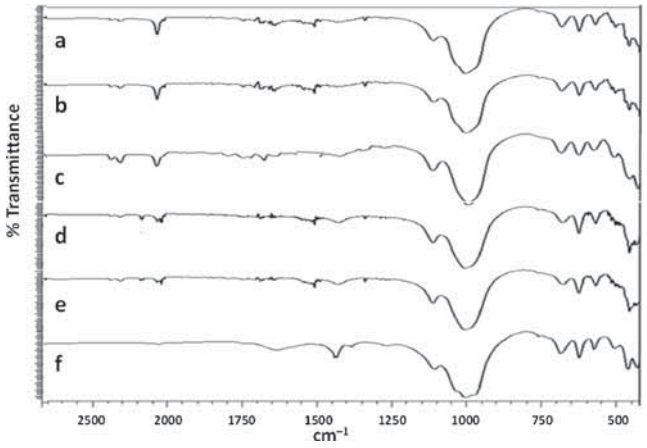

Figure 2. IR spectra of aluminosilicate azide cancrinite after heat treatment at various temperatures: (a) room temperature, (b) 473, (c) 673, (d) 23, (e) 843 and (f) 853 K.

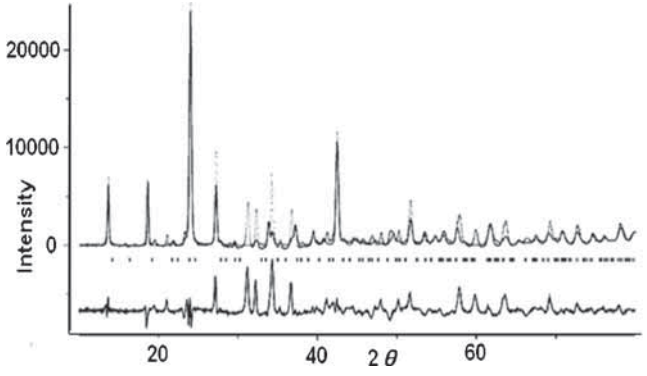

Figure 3. X-ray powder diffraction profile for aluminosilicate azide cancrinite ($Na_8[AlSiO_4]_6(N_3)_{2.4}(H_2O)_{4.6}$).

Spectra in figure 2a–f show gradual decrease in the intensity of the peak at 2069 cm^{-1}, same peak also shifts gradually from 2069 to 2065 cm^{-1} (towards lower frequency) with increase in temperature. The asymmetric stretching vibration at 1005 cm^{-1} also shifts to lower wavenumber as temperature increases. In the last spectrum (f) of figure 2, peak at 2065 cm^{-1} has completely disappeared, which shows the decomposition of enclathrated azide (N_3^-) anion. These IR spectra give the idea about structural change with temperature.

3.2 *Structure refinement*

Rietveld refinement method was used to refine crystal structure of synthesized cancrinite. Figure 3 shows the XRD pattern of aluminosilicate azide cancrinite. In aluminosilicate azide cancrinite, refinement was performed on considering aluminosilicate cancrinite as a starting model in a space group $P6_3$. The crystallographic data and experimental conditions for the structure refinement of product are given in table 1. Atomic positional parameters are listed in table 2, and selected geometrical data are given in table 3. Framework atoms aluminium and silicon were placed at (1/4, 0, 1/2) and (1/4, 1/2, 0) sites, respectively, while framework oxygen atoms (O1 to O5) were at different sites (table 2). Sodium atoms were refined at two different positions with occupancy factor 0.5, one of the nitrogen at (0,0, $\approx$ 0.61) position and another nitrogen on (0,0, $\approx$ 0.75) position.

Table 1. Crystallographic data and experimental conditions for the structure refinement of aluminosilicate azide cancrinite.

Cancrinite	Azide-CAN
Temperature	20°C
Space group	$P6_3$
Wavelength (Å)	1.5405
Formula unit	$Z = 1$
Cell parameter (Å)	$a = 12.5899$
	$c = 5.1424$
Density	2.821
Data collection	
2θ range (°)	10–80
Step size (2θ°)	0.017
Sample time (s per data point)	1s
Number of variables	76
Agreement factors	
R_{wp}	0.0962
R_p	0.0709

Table 2. Fractional coordinates and equivalent displacement parameters of aluminosilicate azide cancrinite.

Atom	Site	x	y	z
$Na_8[AlSiO_4]_6(N_3)_{2.4}(H_2O)_{4.6}$				
Si	6c	0.0939	0.4200	0.2020
Al	6c	0.0750	0.6600	0.2500
O1	6c	0.2012	0.4040	0.3352
O2	6c	0.9930	0.6856	0.5000
O3	6c	1.0075	0.3653	0.4611
O4	6c	0.1164	0.5518	0.2718
Na1	2b	0.3300	0.6600	0.3701
O5	6c	0.3030	0.6460	0.8160
Na2	6c	0.0355	0.2176	0.5668
N1	2a	0.0000	0.0000	0.6100
N2	2a	0.0000	0.0000	0.7500

In aluminosilicate azide cancrinite the unit cell parameters are $a = 12.5899$ Å and $c = 5.1424$ Å. The average Al–O bond distance is 1.7371 Å and Si–O is 1.61029 Å. The average T–O bond distance between tetrahedrally coordinated framework atoms (T) and oxygen is found to be 1.6736 Å, while the average T–O–T bond angle is found to be (Al–O–Si) = 137.101°. The O–T–O tetrahedral angles are distorted from their regular tetrahedral geometry, the detailed bond distances and bond angles are summarized in table 3.

3.3 *MAS NMR spectroscopy*

MAS NMR results for azide cancrinite of the product shows single resonance line. In aluminosilicate azide cancrinite ^{29}Si

Table 3. Selected derived bond distances and bond angles for aluminosilicate azide cancrinite.

Bond distances	(Å)	Bond angles	(°)
$Na_8[AlSiO_4]_6(N_3)_{2.4}(H_2O)_{4.6}$			
Al–O1	1.73863(14)	Si–O1	1.61457(12)
Al–O2	1.77640(16)	Si–O2	1.60958(13)
Al–O3	1.74822(20)	Si–O3	1.63828(18)
Al–O4	1.68818(14)	Si–O4	1.57876(12)
Average	1.73710		1.61029
Al–Na1	3.26930(26)	Si–Na1	3.11950(24)
Al–Na1	3.33293(27	Si–Na1	3.24065(25)
Al–Na1	3.20936(26)	Si–Na1	3.18336(25)
Al–Na2	2.70951(20)	Si–Na2	2.94616(24)
O1–Na1	2.79701(23)	O2–Na2	2.64776(30)
O1–Na1	2.90672(24)	O4–Na1	2.38322(19)
O1–Na1	2.90629(24)	O4–Na1	2.49112(20)
O1–Na2	2.52605(18)	O4–Na1	2.38747(19)
Na1–O5	2.8646(4)	Na1–O5	2.3156(4)
Na1–O5	2.3118(4)	Na1–O5	2.8787(4)
Na1–O5	2.8676(4)	Na1–O5	2.3292(4)
Na2–N	2.55553(21)		
Na2–N	2.71447(20)		
Na2–N	3.02271(22)		
O1–Al–O2	87.973(3)	O1–Si–O2	115.866(3)
O1–Al–O3	124.348(0)	O1–Si–O3	91.350(7)
O1–Al–O4	106.879(1)	O1–Si–O4	108.244(3)
Si–O1–Al	138.893(6)		
Si–O2–Al	122.242(5)		
Si–O4–Al	150.168(2)		
Average	137.101		

resonance line appears at $\delta = -86.859$ pm. The single resonance line in the spectrum confirms strictly alternating order of Si and Al framework atoms with Si/Al ratio of 1.0. The chemical shift value gets influenced by local structural factors and distinguishes between the structures. Aluminosilicate azide cancrinite framework consists of SiO_4 as well as AlO_4 tetrahedra, and the resonance line appears at −86.859 pm.

^{23}Na MAS NMR of cancrinite shows single resonance line in the spectrum. Owing to spherical symmetry of the field gradient at the sodium sites, single environment around sodium atoms results, and gives single line in the spectrum. MAS NMR spectrum shows narrow bands due to highly symmetrical environment.

3.4 *Thermal analysis*

Thermal investigation was carried out by using TGA and DTS at the heating rate of 10°C min^{-1} from 313 to 1296 K. The ∼5% weight loss over the range of 373–503 K was assigned to decomposition of water molecules accommodated into the cancrinite framework and adsorbed water molecules, whereas ∼2% weight loss at 873–1023 K was assigned to decomposition of azide anion encapsulated into the framework.

3.5 *Scanning electron microscopy*

Unlike sodalite, which shows cubic morphology in the SEM picture, SEM image of the cancrinite shows well-shaped hexagonal needle structure. The observed crystal morphology supports for the hexagonal structure and unit cell parameters. Some of the crystals show longer needle-like shapes, ranging between 10 and 25 μm.

3.6 *Gas sensing performance*

Sensing property of the product was examined by using 'steady gas sensing system'. Azide aluminosilicate cancrinite showed appreciable sensing properties. Experiments were performed by using 100 p.p.m. concentration of gases, whereas while studying the effect of gas concentration on sensitivity, gas concentration was varied from 50 to 150 p.p.m.

In the aluminosilicate cancrinite cage, Na^+ cation exists as attached to oxygen in the cage and when it comes in contact with ammonia, it forms a bonding with ammonia. This bonding weakens the Na^+–O–CAN framework, which facilitates Na^+ mobility from one place to another [29,30]. Although Na^+–NH_3 interaction takes place, there is a possibility of another interaction which affects the sensitivity that needs to be taken into account. Oxygen attached to sodium interacts with ammonia gas to produce free electrons. These free electrons affect current flow through circuit.

3.6a *Response of materials towards various gases*: Sensitivity of azide cancrinite was observed towards various gases at room temperature and from the results it is clear that the aluminosilicate azide cancrinite film showed highest response towards ammonia gas (figure 4). As shown in figure 4, the response towards gases gradually increases with temperature up to their respective maxima and decreased further although the temperature is increased. Figure 4 shows the histogram of selectivity of azide cancrinite thick film to various gases at room temperature. The film showed highest selectivity for ammonia gas against all other gases: CO_2, Cl_2, CO, H_2S, H_2 and LPG.

3.6b *Effect of operating temperature*: In this study, experiments were performed against different operating temperatures in order to investigate the effect of the operating temperature on sensing property of $Na_8[AlSiO_4]_6(N_3)_{2.4}(H_2O)_{4.6}$ (aluminosilicate azide cancrinite) thick film. It is observed that the sensitivity was found to increase from 100 to 200°C and further decreased up to 450°C. It showed the maximum sensitivity 127.14 to 100 p.p.m. of ammonia gas at annealing temperature of 400°C. Response at different temperatures is shown in figure 4. Sensitivity at various temperatures for ammonia gas was examined, which revealed utmost response at 473 K and at 100 p.p.m. ammonia gas concentration. The aluminosilicate azide cancrinite film showed the highest response towards ammonia gas at 200°C (figure 4). Operating

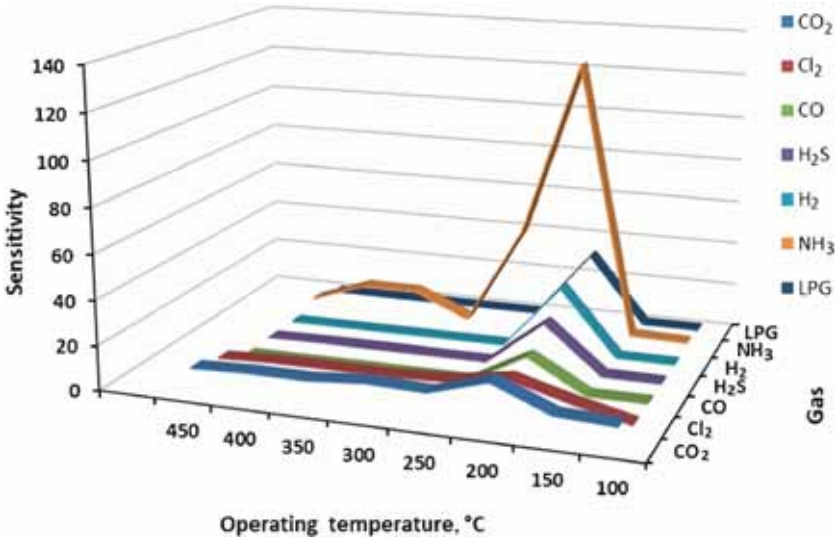

Figure 4. The response of azide cancrinite film to various gases as a function of temperature.

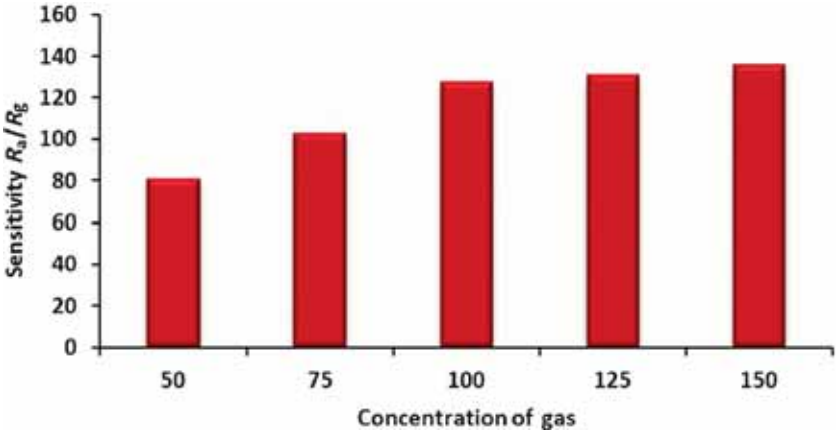

Figure 5. Effect of gas concentration on sensitivity.

temperature study was carried out at the gas concentration of 100 p.p.m.

3.6c *Effect of concentration of ammonia gas*: Glass chamber having a capacity of 10 liters was used in steady-state gas sensing system. Quantities of 0.5, 0.75, 1 and 1.5 ml gas was injected into the glass chamber so as to get 50, 75, 100 and 150 p.p.m. gas concentrations, respectively. Gas concentration variation experiment showed very interesting results, i.e., the largest response to ammonia gas was observed to be 135.83 at 150 p.p.m.. From figure 5 it is clear that response towards the ammonia gas increased with the concentration. Gas concentration variation study was carried out from 50 to150 p.p.m..

3.6d *Effect of annealing temperature*: Figure 6 depicts the effect of annealing temperature of aluminosilicate azide cancrinite film on response towards ammonia gas. Film annealed at 400°C showed best response at 200°C. This study was carried out by keeping constant gas concentration as 100 p.p.m..

For comparison, the H_2S sensing properties of the azide cancrinite films at different annealing temperatures were also studied under identical experimental conditions. The annealing temperature is one of the important parameters for gas sensing material and designing of sensors [31]. A sufficient degree of crystallinity is required to attain electronic parameters necessary for gas sensing application. The dependence of sensitivity of prepared azide cancrinite to 100 p.p.m. ammonia was studied at annealing temperature 400°C.

3.6e *I–V characteristics*: Most important electrical property such as *I–V* characteristics was also studied for cancrinite film. *I–V* characteristics were observed to be

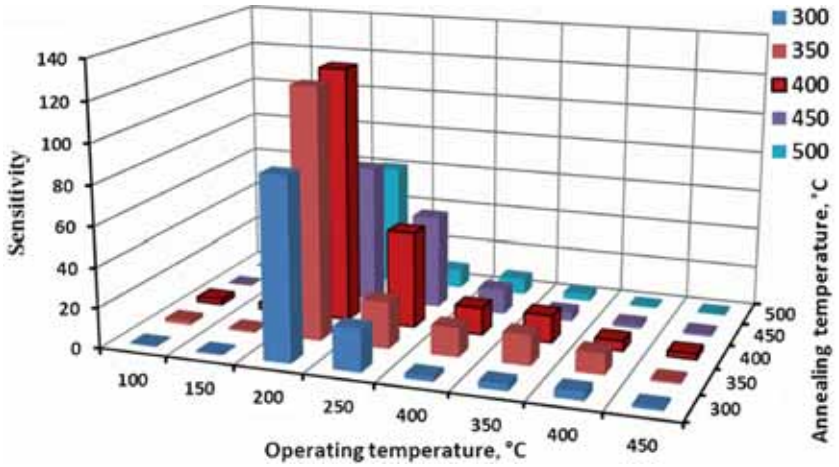

Figure 6. Effect of annealing temperature on gas response.

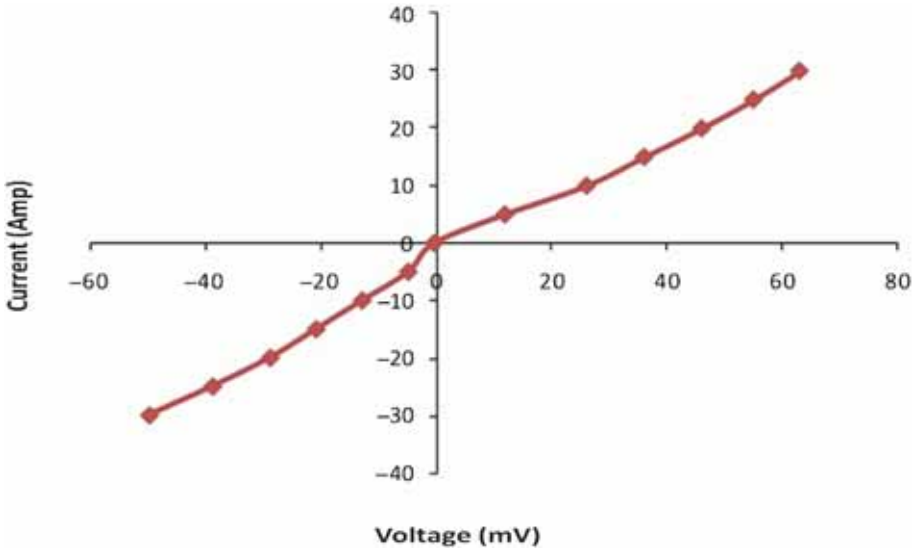

Figure 7. *I–V* characteristics of aluminosilicate azide cancrinite film.

symmetrical in nature, indicating Ohmic nature of silver contacts as shown in figure 7. Results revealed that cancrinite film can be used as a gas sensor.

4. Conclusion

Hydrothermal method was effectively applied for synthesis of aluminosilicate azide cancrinite. Effect of temperature on azide anion was successfully investigated by monitoring decomposition process of intracage N_3^- anion using FT-IR spectroscopy. The thick film azide aluminosilicate cancrinite can be prepared by screen printing method. In addition to this study, we also successfully employed steady gas sensing system to cancrinite film and studied gas sensing properties of synthesized material. From the results obtained, $Na_8[AlSiO_4]_6(N_3)_{2.4}(H_2O)_{4.6}$, cancrinite film shows better response for ammonia gas.

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References

[1] Solodukhin A V and Kobyakov I B 1983 *Zh. Tekh. Fiz.* **53** 158
[2] Hassan I 1996 *Can. Mineral.* **34** 893
[3] Hassan I 1996 *Mineral. Mag.* **60** 949
[4] Weller M T and Kenyon N J 2004 *Stud. Surf. Sci. Catal.* **154** 1349
[5] Hassan I, Antao S M and Parise J B 2006 *Am. Mineral.* **91** 1117

[6] Hassan I, Antao S M and Parise J B 2006 *Am. Mineral.* **91** 1117

[7] Ogorodova L P, Mel'chakova L V, Vigasina M F, Olysich L V and Pekov I V 2009 *Geokhimiya* **3** 275

[8] Sirbescu M and Jenkins D M 1999 *Am. Mineral.* **84** 1850

[9] Barrer R M, Daniels E A and Madigan G A 1976 *J. Chem. Soc. Dalton Trans.* **75** 1805

[10] Hannus I, Tasi G, Kiricsi I, Nagy J B, Foster H and Fejes P 1995 *Thermochemica Acta* **249** 285

[11] Fine G F, Cavanagh L M, Afonja A and Binions R 2010 *Sensors* **10** 5469

[12] Nanto H, Minami T and Takata S 1986 *J. Appl. Phys.* **60** 482

[13] Wang X, Miura N and Yamazoe N 2000 *Sens. Actuat. B-Chem.* **66** 74

[14] Karunagaran B, Uthirakumar P, Chung S J, Velumani S and Suh E K 2007 *Mater. Charact.* **58** 680

[15] Zakrzewska K 2001 *Thin Solid Films* **391** 229

[16] Sberveglieri G 1995 *Sens. Actuat. B* **23** 103

[17] Clifford P K and Tuma D T 1983 *Sens. Actuat.* **3** 233

[18] Srivastava R K, Lal P, Dwivedi R and Srivastatva S K 1994 *Sens. Actuat. B* **21** 213

[19] Huebner H P and Drost S 1991 *Sens. Actuat. B* **4** 463

[20] Imawan C, Solzbacher F, Steffes H and Obermeier E 2000 *Sens. Actuat. B* **64** 193

[21] Chabukswar V V, Pethkar S and Athawale A A 2001 *Sens. Actuat. B* **77** 657

[22] Raimundo I M and Narayanaswamy R 2001 *Sens. Actuat. B* **74** 60

[23] Lahdesaki I, Lewenstam A and Ivaska A 1996 *Talanta* **43** 125

[24] Farmer V C 1974 *Monograph* (London: Mineralogical Society) **4** p 344

[25] Flanigen E M, Khatami H and Szymanski H A 1971 *Adv. Chem. Ser.: Molecular Sieve Zeolites* **16** 201

[26] Henderson C M B and Taylor D 1977 *Spectrochim. Acta* **33A** 283

[27] Moenke H 1962 *Mineralspektren* (Berlin: Akademie-Verlag)

[28] Olysych L V, Vigasina M F, Ogorodova L P, Pekov I V and Chukanov N V 2011 *Geokhimiya* **49** 772

[29] Zheng Y, Mullen M R, Wang J and Dutta P K 2014 *Sens. Actuat. B: Chem.* **193** 542

[30] Gellens L R, Mortier W J and Uytterhoeven J B 1981 *Zeolites* **1** 85

[31] Kotsikau D, Ivanovskaya M, Orlik D and Falasconi M 2004 *Sens. Actuat. B: Chem.* **101** 1