Preparation and Characterization of a New Tetrahedral Oxynitride Phase Cd$_{2-x}$GeO$_{4-x-3y}$N$_{2y}$

C. Louis dit Picard, O. Merdrignac, J. Guyader, and Y. Laurent

Laboratoire de Chimie des Matériaux, URA 1496 CNRS "Verres et Céramiques" Université de Rennes 1, Campus de Beaulieu, Avenue du Général Leclerc 35042 Rennes Cedex, France

A new oxynitride phase, Cd$_{2-x}$GeO$_{4-x-3y}$N$_{2y}$, with $0.9 \leq x \leq 1.5$ and $0.3 \leq y \leq 0.7$ has been prepared by reaction of gaseous ammonia on a "Cd–Ge–O" amorphous phase. Its composition depends on the synthesis conditions and more particularly on the starting ratio Cd/Ge. The amorphous precursor is obtained by coprecipitation of cadmium and germanium oxides and gives after heating in air the crystallized double oxide Cd$_2$GeO$_4$ with or without the CdO oxide phase, depending on the initial Cd/Ge ratio. The oxynitrides obtained after nitridation have been characterized by chemical analysis and X-ray diffraction. They present a tetrahedral structure derived from the wurtzite type with orthorhombic symmetry. The lattice parameters are $5.60 \leq a \leq 5.75$ Å, $6.80 \leq b \leq 6.85$ Å, and $c \approx 5.39$ Å. Electrical properties have been investigated and reveal that Cd$_X$GeO$_Y$N$_Z$-based thick films can be used as gas sensors. © 1995 Academic Press, Inc.

INTRODUCTION

In the past few years, the study of atmospheric pollutant detection by suitable sensors has developed rapidly. The goal is that the chosen device must be not only efficient and reliable, but also easy to use. In addition, it should have a low initial cost and a low utilization cost. It is known that electronic transport properties of semiconductors are sensitive to the physical factors to which these materials are subjected, such as temperature, pressure, light, and gaseous environment. Numerous field studies have been made, especially on oxides such as ZnO or SnO$_2$. We have started work on oxynitrides, particularly on Zn$_X$GeO$_Y$N$_Z$ screen-printed materials (1). NH$_3$ and H$_2$S detection investigations have revealed that Zn$_X$GeO$_Y$N$_Z$ is an excellent sensing material for these gases. However, its high electrical resistance (10^{10} Ω in air at 250°C) prevented the production of industrial devices at low cost. Thus, the objective was to find other MeGeON-based thick film gas sensors with appropriate resistance. Cd$_{2-x}$GeO$_{4-x-3y}$N$_{2y}$ compounds have been prepared by nitridation of an oxide precursor (2), as described for the Zn$_X$GeO$_Y$N$_Z$ phase in an earlier study (1). The films

exhibit good electrical characteristics and can be utilized for gas sensor applications. So, it would be interesting to understand the behavior and the properties of Cd$_{2-x}$GeO$_{4-x-3y}$N$_{2y}$ in correlation with the zinc and germanium oxynitride phases. This paper describes the preparation of materials of the general formula Cd$_{2-x}$GeO$_{4-x-3y}$N$_{2y}$ and their characterization by chemical and X-ray diffraction analyses.

EXPERIMENTAL PROCEDURE

A. Sample Preparation

Cadmium and germanium oxynitride powders were prepared by reaction of gaseous ammonia with cadmium germanate. Cadmium germanate was obtained by coprecipitation of cadmium and germanium oxides. First, both oxides, GeO$_2$ and CdO, were dissolved in water. The solution was made alkaline by the addition of ammonia at 90°C. The double hydroxide that precipitates was washed, separated by centrifugation, and oven-dried at 120°C. The nitridation of the sample was made under flowing ammonia (10 liter/hr) at 580°C. The heating rate was 20°C/min and the maximal temperature was maintained for 6 hr. Cooling occurred under flowing ammonia. The samples presented different chemical compositions, as will be apparent from the data given below.

B. Characterization

The oxynitride compounds were characterized by different techniques under the following experimental conditions:

Elemental analysis of oxygen and nitrogen was carried out by using LECO equipment (TC 436 analyzer and EF 400 furnace). Calibration was performed with CO$_2$ and N$_2$ gases.

The amount of germanium was determined by atomic absorption (Varian SpectrAA10) while the amount of cadmium was obtained by using a complexometric procedure.
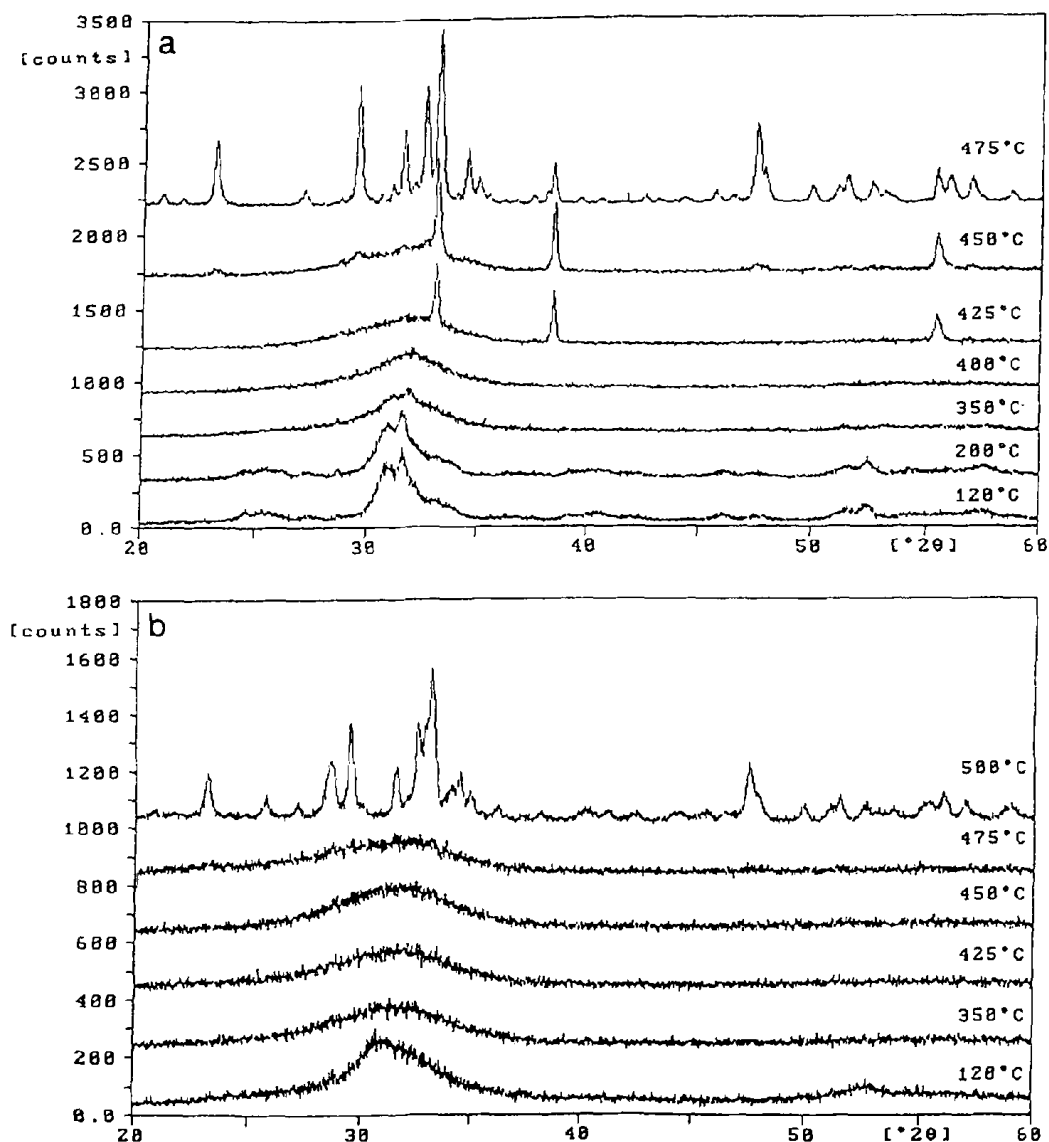
X-ray powder diffraction patterns were recorded with

FIG. 1. X-ray diffraction patterns of coprecipitated samples as a function of heating temperature (dwell time: 1 hr) (a) when the ratio Cd/Ge = 2; and (b) when the Cd/Ge ratio = 3.

a Philips PW 3710 mdp control generator equipped with an X-PERT goniometer system. A step size of 0.02° and a step time of 14 sec were used.

RESULTS AND DISCUSSION

The precursor obtained by coprecipitation in aqueous solution is an amorphous "Cd–Ge–O" phase of variable composition depending on the initial Cd/Ge ratio. To determine the optimum crystallization temperature, samples were heated for 1 hr in air at different temperatures (Fig. 1). The diagram of the sample coprecipitated at 475°C consisted of the crystallized phases CdO and Cd$_2$GeO$_4$

when the ratio Cd/Ge = 3. The CdO phase crystallizes at 425°C (Fig. 1a). When Cd/Ge = 2, the diagram of the coprecipitate shows the Cd$_2$GeO$_4$ phase at a temperature of 500°C (Fig. 1b); the 475°C sample still consists of an amorphous phase.

The temperature and pH conditions used during precipitation yielded a coprecipitate with a specific area on the order of 70 to 90 m^2/g. The evolution of the specific area of the samples upon drying in air at different temperatures is reported in Fig. 2.

The precursor used for the nitridation is only dried at 120°C in air. Crystallized Cd$_2$GeO$_4$ does not react with ammonia to give the oxynitride compound. Nor can it be
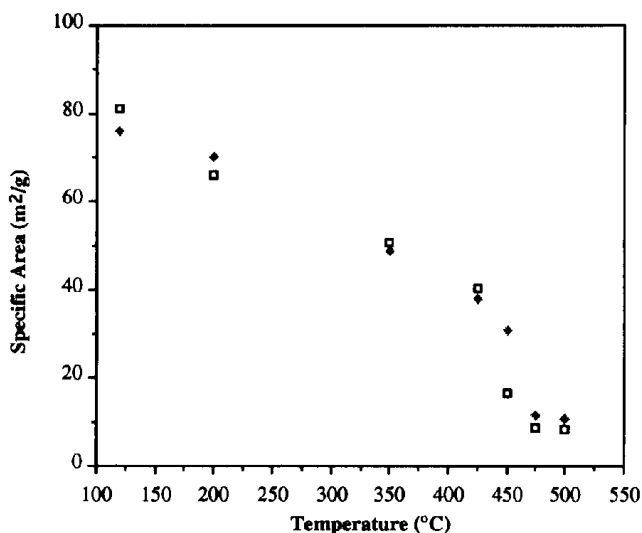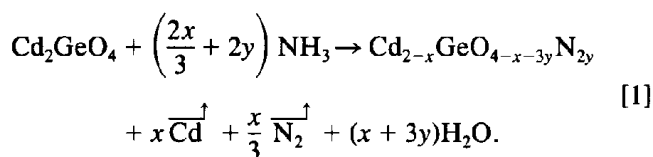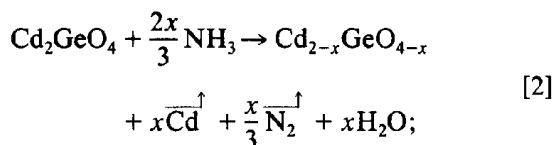
FIG. 2. Specific area of the coprecipitated samples as a function of heating temperature (maintained 1 hr): ($\square$) Data from the powders prepared with Cd/Ge = 2; ($\blacklozenge$) data from the samples with Cd/Ge = 3.

obtained by direct reaction between ammonia and the commercial oxides CdO and GeO_2. It must be prepared by heating the amorphous Cd–Ge–O phase at 580°C under flowing ammonia. The global reaction with a Cd/Ge ratio of 2 is described as follows (note that the precursor is written Cd_2GeO_4 for simplification):

$$Cd_2GeO_4 + \left(\frac{2x}{3} + 2y\right) NH_3 \rightarrow Cd_{2-x}GeO_{4-x-3y}N_{2y}$$
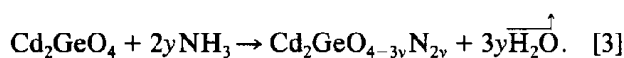$$+ x\overline{Cd}^{\uparrow} + \frac{x}{3}\overline{N_2}^{\uparrow} + (x + 3y)H_2O. \quad [1]$$

The following mechanism can be proposed for this reaction as the most probable one. Two phenomena are superposed:

—the volatilization of cadmium,

$$Cd_2GeO_4 + \frac{2x}{3}NH_3 \rightarrow Cd_{2-x}GeO_{4-x}$$
$$+ x\overline{Cd}^{\uparrow} + \frac{x}{3}\overline{N_2}^{\uparrow} + xH_2O; \quad [2]$$

—the substitution of oxygen by nitrogen,

$$Cd_2GeO_4 + 2yNH_3 \rightarrow Cd_2GeO_{4-3y}N_{2y} + 3y\overline{H_2O}^{\uparrow}. \quad [3]$$

The relative rates of reactions [2] and [3] depend on the temperature and on the time of the reactions. They

also depend on the ammonia flow rate, and the weight and the disposition of the original powders. A modification of these parameters leads to crystallization of GeO_2 or Cd_2GeO_4 oxides. For example, under our conditions, the weight of the sample must be on the order of 1 g. For smaller weights, the GeO_2 phase is observed in the sample after nitridation. The presence of this crystallized phase may be due to the volatilization of cadmium, which occurs during the nitridation. On the other hand, with higher weights, the nitridation is not complete and the sample contains the crystallized Cd_2GeO_4 double oxide. However, when the last two parameters (ammonia flow rate and precursor weight) are kept constant, two phenomena can be observed:

1. The cadmium weight percent decreases with temperature and reaction time (between 6 and 24 hr).
2. The nitrogen content depends mainly on the reaction time.

The evolution of cadmium and nitrogen weight percents in the oxynitride samples is reported in Table 1.

Chemical analysis data of some $Cd_xGeO_yN_Z$ compounds are reported in Table 2. We define rates to express the change in the cadmium and nitrogen contents as

$$T_{Cd}(\%) = \frac{x}{2} \times 100$$

$$T_N(\%) = \frac{z}{2} \times 100,$$

where T_{Cd} represents the cadmium content of the sample as nitridation progresses, relative to the initial cadmium content in Cd_2GeO_4, and T_N represents the ratio of the nitrogen content of the sample (as nitrogen is substituted for oxygen during the reaction under ammonia) to the nitrogen content of $CdGeN_2$.

Although it does not correlate with the material content of the unit cell, this notation allows the cadmium and nitrogen contents to be studied apart from the germanium content. The evolution of the nitrogen and cadmium con-

TABLE 1

Weight Percents of Cadmium and Nitrogen Determined as a Function of Heating Time by Chemical Analysis in $Cd_xGeO_yN_Z$ Samples Prepared at 580°C

	Time (hr)				
	6	10	15	24	CdGeN$_2$
(wt%)Cd	52.1	44.6	36.7	37	52.7
(wt%)N	6.2	9.4	9.5	7.0	13.1

TABLE 2
Specimen Preparation Conditions and Analytical Results

Sample number	Chemical composition	Specific area of the precursor (m²/g)	Heating temperature (°C)	Heating time (hour)	Specific area of $Cd_xGeO_yN_Z$ (m²/g)	N/O	(wt%) Cd	(wt%) N	VEC valence electron concentration	Cd rate (%)	N rate (%)
1	$Cd_{0.83}GeO_{0.87}N_{1.31}$	60	580	6	6	1.51	48.2	9.5	4.34	41.3	65.3
2	$Cd_{0.92}GeO_{0.84}N_{1.38}$	70	580	6	15	1.64	47.4	8.9	4.29	45.9	69.2
3	$Cd_{0.92}GeO_{1.03}N_{1.26}$	70	580	6	15	1.22	49.2	8.4	4.35	46.0	63.0
4	$Cd_{0.94}GeO_{1.03}N_{1.27}$	71	580	6	16	1.23	51.0	8.6	4.34	46.7	63.5
5	$Cd_{0.96}GeO_{1.19}N_{1.18}$	70	580	6	17	0.99	49.0	7.5	4.37	48.0	59.0
6	$Cd_{0.98}GeO_{0.92}N_{1.37}$	—	580	6	12	1.48	50.3	8.8	4.29	49.0	68.5
7	$Cd_{1.00}GeO_{1.05}N_{1.29}$	56	580	6	—	1.23	55.3	8.8	4.32	50.0	64.5
8	$Cd_{1.07}GeO_{1.54}N_{1.02}$	—	580	6	12	0.66	52.1	6.2	4.42	53.5	51.0
9	$Cd_{0.70}GeO_{0.93}N_{1.18}$	56	580	10	18	1.26	44.6	9.4	4.43	34.8	58.8
10	$Cd_{0.58}GeO_{0.76}N_{1.21}$	56	580	15	21	1.58	36.7	9.5	4.44	29.0	60.5
11	$Cd_{0.54}GeO_{1.30}N_{0.83}$	70	580	24	—	0.64	37.0	7.0	4.64	27.0	41.5
12	$Cd_{0.53}GeO_{1.42}N_{0.74}$	78	600	6	—	0.52	38.6	6.7	4.68	26.7	37.1

tents of the oxynitride versus the time of reaction at 580°C is presented in Fig. 3. Cadmium and nitrogen contents change rapidly at the beginning of the reaction. The nitrogen content reaches a maximum after 6 hr. Beyond 15 hr, this grade decreases, due to the volatilization of cadmium. As a result, the domain of existence of cadmium and germanium oxynitrides is limited in time for a reaction temperature of 580°C on one hand, and in temperature (between 580 and 600°C) on the other hand.

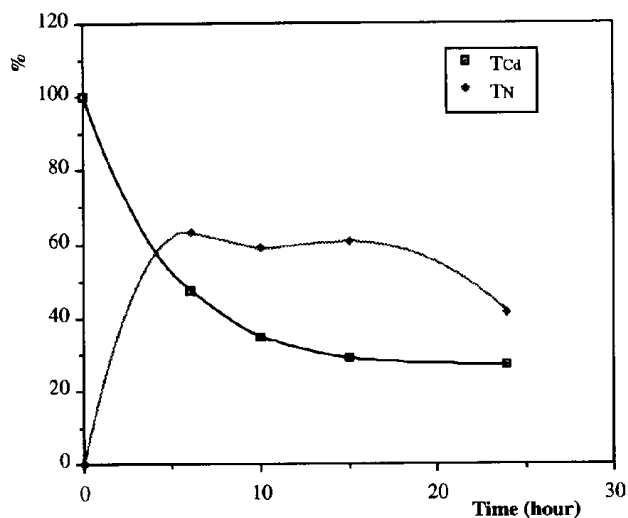Figure 4 presents all the possible compositions between cadmium, germanium, oxygen, and nitrogen, with their usual valences. This diagram is constructed by using variables u and v:

—the anionic ratio along the X-axis is such that

$$nitrogen\ number = 4u$$

$$oxygen\ number = 6(10 - u);$$

—the cationic ratio along the Y-axis is such that

$$germanium\ number = 3v$$

$$cadmium\ number = 6(10 - v).$$

The values of the valence electron concentration (VEC) are also reported in Fig. 4 (VEC = number of valence electrons/number of elements). Dots mark the phase composition we have prepared. For all these compounds, the VEC is contained in values 4 to 4.8. Therefore, according to Parthe's rules (3), they are defect tetrahedral structure compounds characteristic of the adamantine structure type.

The Cd–Ge–O–N system has a large range of compositions and the formulation can be defined, according to our experiments, as

$$Cd_{2-x}GeO_{4-x-3y}N_{2y}\ with\ 0.9 \le x \le 1.5\ and\ 0.3 \le y \le 0.7.$$
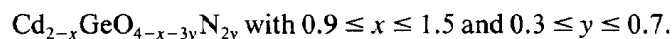
The chemical data of these two extreme phases, called CdGeON A and CdGeON B, are listed in Table 3.

FIG. 3. Time dependence of cadmium and nitrogen contents (respectively, T_{Cd} and T_N) of $Cd_xGeO_yN_Z$ samples prepared at 580°C under 10 liter/hr ammonia flow.
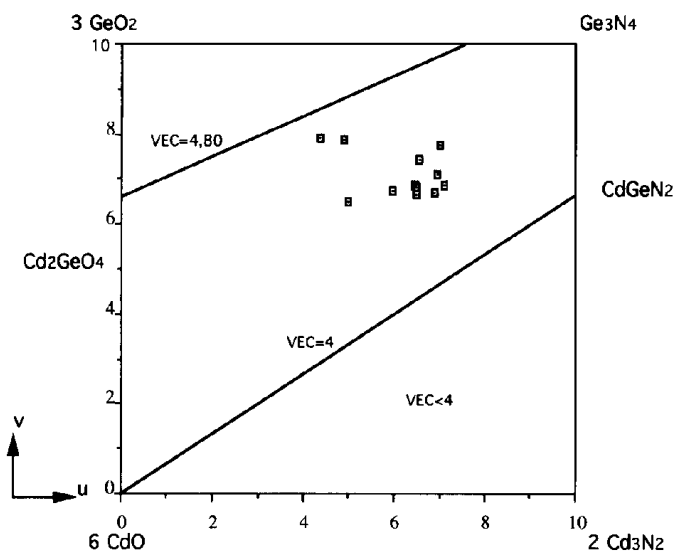
FIG. 4. Composition of the samples $Cd_XGeO_YN_Z$ prepared (Table 2) (VEC is the valence electron concentration).

The CdGeON A phase is obtained using a precursor with Cd/Ge > 2, and the CdGeON B type is prepared with a precursor without an excess of cadmium (Cd/Ge = 2).

The $Cd_XGeO_YN_Z$ phases present a tetrahedral structure derived from the wurtzite type as $Zn_ZGeO_YN_Z$ (1). All the $Cd_XGeO_YN_Z$ powder X-ray diffraction patterns were indexed in an orthorhombic unit cell similar to that of $Mn_{1+x}GeN_2O_x$ ($0 \leq x \leq 0.14$) (4). All the observed lines of the diffraction pattern were indexed (Table 4) and the parameters obtained are:

CdGeON A

$a_0 = 5.756(8)$ Å, $b_0 = 6.805(8)$ Å, $c_0 = 5.395(8)$ Å

CdGeON B

$a_0 = 5.613(2)$ Å, $b_0 = 6.847(2)$ Å, $c_0 = 5.393(2)$ Å.

TABLE 3

Chemical Composition of the Two Limit Phases CdGeON A and CdGeON B: $Cd_{2-x}GeO_{4-x-3y}N_{2y}$ and their Cadmium and Nitrogen Amounts (wt%)

	CdGeON A	CdGeON B
$Cd_{2-x}GeO_{4-x-3y}N_{2y}$	$Cd_{0.94}GeO_{1.03}N_{1.27}$	$Cd_{0.53}GeO_{1.42}N_{0.74}$
x	1.06	1.465
y	0.635	0.371
(wt%) Cd	51	38.6
(wt%) N	8.6	6.7

The crystal structure can be described as an adamantine type, where Cd and Ge fill half of the tetrahedral sites of the anionic atom arrangement.

The cations are distributed in an orderly fashion. This order is indicated by the presence of superstructure peaks on the X-ray diffraction diagram in comparison with the hexagonal structure type (Fig. 5). This is the structure type of nitrides such as $BeSiN_2$ (5), $MgSiN_2$ (6, 7), $MgGeN_2$ (6), $MnSiN_2$ (8, 9), $MnGeN_2$ (8, 10), and $ZnGeN_2$ (11–13). In these compounds, cations are ordered so that the crystalline symmetry is no longer hexagonal, as in wurtzite, but orthorhombic.

In $Cd_XGeO_YN_Z$ compounds, the crystalline symmetry is then orthorhombic, and the unit cell derives from the wurtzite unit cell according to the relations:

$$a_0 \approx a_h\sqrt{3}, \quad b_0 \approx 2a_h, \quad c_0 \approx c_h.$$

The order of evolution between the two extreme phases CdGeON A and CdGeON B shows a variation in the parameters a_0 and b_0:

$$5.60 \text{ Å} \leq a_0 \leq 5.75 \text{ Å}$$

$$6.80 \text{ Å} \leq b_0 \leq 6.85 \text{ Å}.$$

The value of c_0 is constant. The a_0/b_0 ratio values obtained for CdGeON A and CdGeON B (respectively, 0.846 and 0.820) also point out this evolution: they are effectively smaller than the value of 0.866 obtained for an hexagonal unit cell, i.e., one in which the cations are disordered. In fact, the Cd–Ge–O–N system presents a defect tetrahedral structure similar to that described in the Zn–Ge–O–N system (1). The measured density values of all $Cd_XGeO_YN_Z$ compounds are smaller than those calculated from the chemical composition. Thus, the chemical composition, taking the density into account, is reported for each compound in Table 5. Therefore, $Cd_XGeO_YN_Z$ compounds present deficiencies in both the cationic and the anionic lattices.

Compounds having a tetrahedral structure are of interest because some of them have semiconducting properties. Thus the semiconducting properties of the phases of the Zn–Ge–O–N system (n-type, gap ~2.7 eV) have been used in gas adsorption studies. These oxynitrides strongly chemisorb oxygen, which acts as an electron-acceptor trap and modifies the electrical resistance of the samples.

The electrical properties of the Cd–Ge–O–N system compounds, described above, are now investigated. The first results show, in comparison with the Zn–Ge–O–N phase:

—a considerable decrease in the electrical resistance. The measured values of identical samples are:

TABLE 4
X-Ray Powder Diffraction Data of $Cd_XGeO_YN_Z$: (a) CdGeON A, (b) CdGeON B (λ= 1.5406 Å)

(a)				(b)			
h k l	d_{calc} (Å)	d_{obs} (Å)	I_{obs} (%)	h k l	d_{calc} (Å)	d_{obs} (Å)	I_{obs} (%)
1 2 0	2.929	2.934	32	1 2 0	2.923	2.932	35
2 0 0	2.878	2.897	14	2 0 0	2.806	2.789	24
0 0 2	2.697	2.696	84	0 0 2	2.696	2.691	59
1 2 1	2.574	2.577	100	1 2 1	2.569	2.574	100
2 0 1	2.539	2.547	25	2 0 1	2.489	2.483	29
1 2 2	1.984	1.985	18	1 2 2	1.982	1.981	11
2 0 2	1.968	1.965	5	2 0 2	1.944	1.943	7
0 4 0	1.701	1.701	10	0 4 0	1.712	1.720	7
3 2 0	1.671	1.670	7	3 2 0	1.642	1.640	12
1 2 3	1.532	1.531	22	1 2 3	1.531	1.531	15
0 4 2	1.439	1.440	8	0 4 2	1.445	1.449	6
3 2 2	1.421	1.418	12	3 2 2	1.402	1.413	8
0 0 4	1.349	1.350	2	0 0 4	1.348	1.346	4

R_{ZnGeON} (air) $\approx 10^9 \, \Omega$, R_{CdGeON} (air) $\approx 10^6 \, \Omega$

R_{ZnGeON} (N_2) $\approx 10^6 \, \Omega$, R_{CdGeON} (N_2) $\approx 10^4 \, \Omega$.

This is due to the fact that Cd and Zn belong to the same group (12) of the periodic table, but Cd has a higher atomic number than Zn so that it is more electropositive than Zn.

—the same behavior toward oxygen and gases since the two families of compounds have the same tetrahedral structure with many deficiencies as well.

Feasibility studies are now in progress on a working scale model, in order to use compounds of the Cd-Ge-O-N system as sensor materials for the detection of NH_3 and H_2S gases. Experiments are being developed on the detection of NO_x and SO_x.

CONCLUSION

This study was intended to produce new oxynitride materials which could be fit for use as gas sensors. We have prepared $Cd_XGeO_YN_Z$ compounds by reaction of NH_3 with an amorphous precursor Cd-Ge-O. This precursor is obtained by coprecipitation in aqueous solution and its nature influences the nitridation reaction. The $Cd_XGeO_YN_Z$ phase has a defect tetrahedral structure with orthorhombic crystalline symmetry. It should be mentioned that the $Cd_XGeO_YN_Z$ phase cannot be obtained by reaction of NH_3 with a mixture of CdO and GeO_2 oxides or with a Cd_2GeO_4 crystallized germanate. These compounds present promising semiconducting properties. Gas sensing experiments are now in progress to investigate feasibility.

TABLE 5
$Cd_XGeO_YN_N$ Compositions and Analytical Results

Sample number	Chemical composition	d_{exp} (g/cm³)	d_{calc} (g/cm³)	Chemical composition taking the density into account
1	$Cd_{0.83}GeO_{0.87}N_{1.31}$	5.86	6.21	$Cd_{0.72}Ge_{0.87}□_{0.41}O_{0.75}N_{1.13}□_{0.12}$
2	$Cd_{0.92}GeO_{0.84}N_{1.38}$	5.52	6.97	$Cd_{0.65}Ge_{0.71}□_{0.64}O_{0.60}N_{0.98}□_{0.42}$
3	$Cd_{0.92}GeO_{1.03}N_{1.26}$	5.23	6.68	$Cd_{0.63}Ge_{0.68}□_{0.69}O_{0.70}N_{0.86}□_{0.44}$
4	$Cd_{0.94}GeO_{1.03}N_{1.27}$	5.75	6.49	$Cd_{0.73}Ge_{0.78}□_{0.49}O_{0.80}N_{0.99}□_{0.21}$
5	$Cd_{0.96}GeO_{1.19}N_{1.18}$	5.71	6.97	$Cd_{0.61}Ge_{0.64}□_{0.74}O_{0.76}N_{0.76}□_{0.48}$
7	$Cd_{1.00}GeO_{1.05}N_{1.29}$	5.28	6.55	$Cd_{0.68}Ge_{0.68}□_{0.64}O_{0.72}N_{0.88}□_{0.40}$
9	$Cd_{0.70}GeO_{0.93}N_{1.18}$	5.10	5.62	$Cd_{0.60}Ge_{0.86}□_{0.54}O_{0.80}N_{1.01}□_{0.19}$
10	$Cd_{0.58}GeO_{0.76}N_{1.21}$	5.11	5.72	$Cd_{0.52}Ge_{0.90}□_{0.58}O_{0.69}N_{1.08}□_{0.22}$
11	$Cd_{0.54}GeO_{1.30}N_{0.83}$	4.45	5.29	$Cd_{0.43}Ge_{0.79}□_{0.78}O_{1.02}N_{0.65}□_{0.32}$
12	$Cd_{0.53}GeO_{1.42}N_{0.74}$	4.34	4.98	$Cd_{0.43}Ge_{0.80}□_{0.76}O_{1.14}N_{0.59}□_{0.26}$

REFERENCES

1. D. Jamois, Thesis No. 840, Rennes, France, 1992.
2. C. Louis dit Picard, O. Merdrignac, J. Guyader, P. Verdier, Y. Laurent, and J. Razafindrakoto, French Patent 94 10841, September 1994.
3. E. Parthe, in "Crystal Chemistry of Tetrahedral Structures," p. 46. Gordon & Breach, New York, 1964.
4. M. Maunaye, J. Guyader, Y. Laurent, and J. Lang, *Rev. Chim. Miner.* **11**, 92 (1974).
5. P. Eckerlin, *Z. Anorg. Allg. Chem.* **353**, 225 (1967).
6. J. David, Y. Laurent, and J. Lang, *Bull. Soc. Fr. Mineral. Cristallogr.* **93**, 153 (1970).
7. M. Wintenberger, F. Tcheou, J. David, and J. Lang, *Z. Naturforsch. B* **35**, 604 (1980).
8. M. Maunaye, R. Marchand, J. Guyader, Y. Laurent, and J. Lang, *Bull. Soc. Fr. Mineral. Cristallogr.* **94**, 561 (1971).
9. M. Wintenberger, R. Marchand, and M. Maunaye, *Solid State Commun.* **21**, 733 (1977).
10. M. Wintenberger, J. Guyader, and M. Maunaye, *Solid State Commun.* **11**, 1458 (1972).
11. P. Bacher, G. Roult, M. Ghers, O. Merdrignac, J. Guyader, and Y. Laurent, *Mater. Chem. Phys.* **21**, 223 (1989).
12. M. Maunaye, P. L'Haridon, Y. Laurent, and J. Lang, *Bull. Soc. Fr. Mineral. Cristallogr.* **94**, 3 (1971).
13. M. Wintenberger, M. Maunaye, and Y. Laurent, *Mater. Res. Bull.* **8**, 1049 (1973).