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Preparation and characterization of $AlVO_4$ compound

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$AlVO_4$ is a relatively new sensor material derived from V_2O_5/Al_2O_3 mixtures to selectively detect NO and NO_2 gases. Previous studies carried out in order to determine its structural, absorptive and sensory properties indicate that the $AlVO_4$ is not the only single phase. This work deals with the synthesis of the compound by the ceramic and the nitrate decomposition methods, and by the sol gel route. The Rietveld refinement of the compound was carried out in order to determine its crystal structure. Single phase of $AlVO_4$ was successfully obtained via the nitrate decomposition and the sol gel methods. Thereafter, films prepared by the sol gel route were deposited on alumina and $Si/SiO_2/Pt$ substrates and characterized by SEM and X-ray diffraction. The electric characterization of the $AlVO_4$ on alumina substrate film is also presented. © *2004 Kluwer Academic Publishers*

1. Introduction

Thin films of mixed oxides are becoming more important for the electronic industry applications such as gas sensors [1]. Mixtures of V_2O_5 and Al_2O_3 and the pure $AlVO_4$ have been considered for the detection of nitrogen oxides, namely NO and NO_2, with good sensibility and selectivity. In particular, the sensor properties of the V_2O_5-Al_2O_3 mixture has been studied [2, 3] singling out the V^{4+} ions as the main centers to adsorb the NO_x. Some routes have been developed for the preparation of $AlVO_4$, both as bulk and thin film, but the synthesis and preparation of $AlVO_4$ present some open questions: (i) the exact structure of $AlVO_4$ is unknown although it is considered to be isostructural with $FeVO_4$; (ii) it is necessary to use high temperature (∼1400°C) for the solid state reaction between Al_2O_3 and V_2O_5 in order to prepare the compound; (iii) $AlVO_4$ has a peritectic decomposition at 700°C; (iv) thin films of $AlVO_4$, prepared using the sol-gel processing are not single phase because Al_2O_3 and Al—V—O spinel phase are present as spurious phases [4].

The aim of this work is to prepare the $AlVO_4$ single phase compound both as bulk, by the ceramic method and the thermal decomposition of nitrates, and as thin film by the sol-gel route. The crystal structure of $AlVO_4$ compound and a detailed structural characterization of the phases present during the growth processing have been carried out. The resistivity, as a function of temperature of the film grown on alumina, was measured. The construction of a prototype of sensor is in progress.

2. Preparation methods

2.1. Standard ceramic method

The standard ceramic method initially was used to prepare the $AlVO_4$. A mixture of Al_2O_3 and V_2O_5 was weighed in the molar ratio 1:1. Table I shows the chemical and physical properties of the reagents used.

The oxide powders were milled to decrease the grain size and to increase the reactivity. The mixture was heat treated at 450°C during 8 h. The resulting powder shows only the peaks corresponding to the Al_2O_3 and V_2O_5,

TABLE I Chemical and physical properties of oxides for preparation of $AlVO_4$

Compound	Formula weight	Melting point (°C)	Boiling point (°C)
V_2O_5	181,88	690	1750
α-Al_2O_3	2101,96	2015	2980
$Al(NO_3)_3 9H_2O$	375.13	73.5	150 (decomposes)

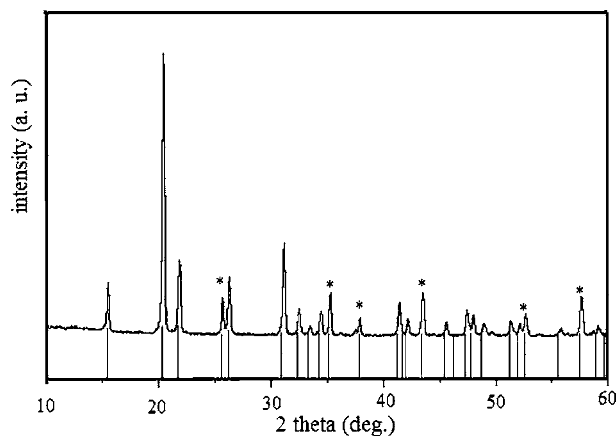

Figure 1 X-ray diffraction spectrum of the mixture of Al_2O_3 and V_2O_5 after 8 h of thermal treatment at 450°C (* indicates the peaks corresponding to Al_2O_3; unmarked peaks correspond to V_2O_5).

indicating the low reactivity of the oxides at this temperature (see Fig. 1). The powder was milled again and a thermal treatment, every time at higher temperature, was performed. Thermal treatments were subsequently applied at 500, 550, 600 and 650°C. X-ray diffraction spectra indicated that the reaction between oxides has not taken place. Additionally, a thermal treatment at 700°C resulted in the fusion of the mixture. Similar results were obtained when the molar ratio of the oxides have been changed to 1:2 and 2:1.

2.2. Thermal decomposition of nitrates method

The $Al(NO_3)_3 \cdot 9H_2O$ was chosen because it decomposes at 150°C, as indicated in Table I. A 1:1 molar mixture of V_2O_5 and $Al(NO_3)_3 \cdot 9H_2O$ was finely mixed in a mortar. The mixture was then heat treated at 250°C for one hour to separate the H_2O and NO_2 formed by the decomposition of the nitrate. The powder was milled and heat treated again till the reaction was complete. This reaction begins at 550°C and is complete at 650°C: after every thermal treatment the powders were ground; two thermal treatments at 650°C, every one of 24 h, were enough to obtain an almost single phase compound (see Fig. 2).

2.3. Preparation of $AlVO_4$ by sol-gel method

Sol gel was chosen to prepare $AlVO_4$ thin films because it is a relatively simple technique and a good control of the chemical composition is always possible.

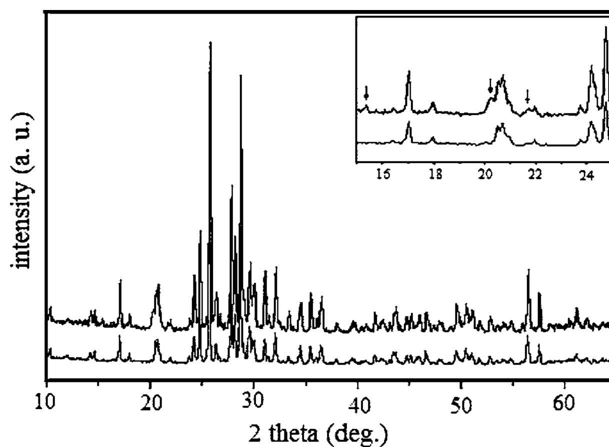

Figure 2 X-ray diffraction spectra of $AlVO_4$ prepared by the decomposition of nitrate route: (a) after different thermal treatments up to 650°C and (b) a thermal treatment at 650°C during 24 h. The inset shows the region between 17 and 25° in which the arrows indicated the peaks attributed to V_2O_5.

A solution of 0.88 M of $VO(O^iPr)_3$ and $Al(O^iPr)_3$ in toluene were refluxed during four hours in nitrogen atmosphere. The inert atmosphere is necessary due to the extreme sensibility of the solution to the humidity that could initiate the hydrolysis process. 4.49 g of $Al(O^iPr)_3$ were dissolved in 25 ml of toluene. 5.32 g of $VO(O^iPr)_3$ were added to the solution with stirring in a glove box. The solution was transferred to a three-necked flask and refluxed for 4 h. The solution changes from clear yellow to dark green during the refluxing due to vanadium reduction from V^{5+} to V^{4+}. Afterwards, the solution is transferred to a flask and cooled to room temperature.

0.2 ml of an hydrolyzing solution, prepared with 1 M H_2O and isopropyl alcohol and added drop by drop to 12 ml of the solution of Al—V—O, is enough to induce a gelation of the whole solution. The gel was dried in air for several hours to obtain a dark brown powder. The structure of this powder is amorphous, as indicated by X-ray diffraction. In order to obtain crystalline $AlVO_4$ the powder was heat-treated at 650°C for 8 h. Fig. 3 shows the diffraction spectrum of the treated powder, where only $AlVO_4$ is the phase present.

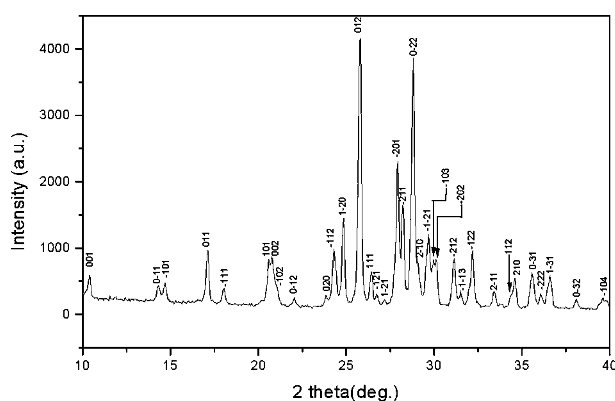

Figure 3 X-ray diffraction spectrum of the $AlVO_4$ powder obtained by the sol-gel route.

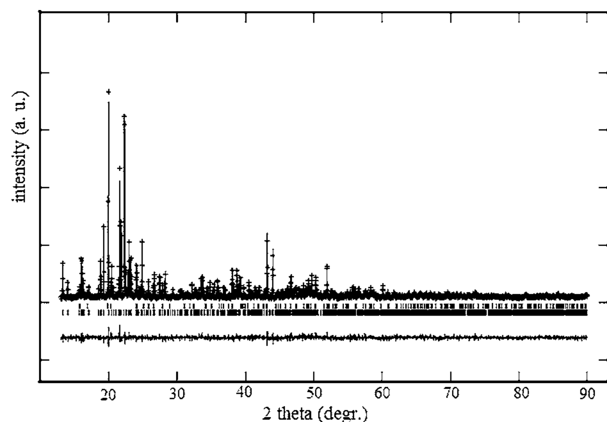

Figure 4 Experimental and refined spectra along with the difference curve obtained by Rietveld refinement using the GSAS program.

3. Crystal structure

A diffraction spectrum of $AlVO_4$ was obtained using synchrotron radiation, located in Daresbury (England) using the high-resolution 2.3 line at angular dispersion. The spectrum was obtained at a wavelength of 1.2 Å between 6° and 90° using a step of 0.015° with a record time of 1 s/step.

The Rietveld refinement was applied to obtain the structure of $AlVO_4$, using the Silicon Graphics version of the GSAS program [5]. The $AlFeO_4$ (triclinic, space group $P\bar{1}$), assumed to be isostructural with $AlVO_4$, was used as the initial model [6] for the refinement, with cell parameter taken from the spectrum of the powder obtained using X-ray diffraction (Cu K_α radiation). The unit cell contains 3 different positions for aluminium and for vanadium and 12 for the oxygen. Fig. 4 shows the experimental and refined spectra along with the difference curve. The total number of reflections is 1646, a very high number due to the low symmetry of the structure. The structure parameters are reported in Table II.

There were no restrictions imposed on the atomic positions during the refinement. Table III shows the refined atomic positions and the thermal isotropic parameters. It is possible to visualize the structure of $AlVO_4$ with these parameters in Fig. 5: the aluminium has two octahedral and one bipyramidal trigonal coordination; the vanadium presents tetrahedral coordination. The bipyramidal trigonal coordination of the aluminium is quite unusual because it has been only observed in metallorganic compounds.

4. $AlVO_4$ thin film

4.1. Deposition

To study the film characteristics, the deposition was made on alumina and on $Si/SiO_2/Pt$ substrates. The X-ray diffraction spectrum of the alumina substrate, before the deposition of the film, indicated that a small amount of the spinel structure was present. A detailed

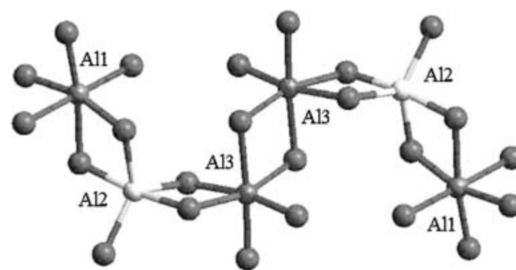

Figure 5 Sequence of Al1-Al2-Al3-Al3-Al2-Al1 of the $AlVO_4$ crystal structure.

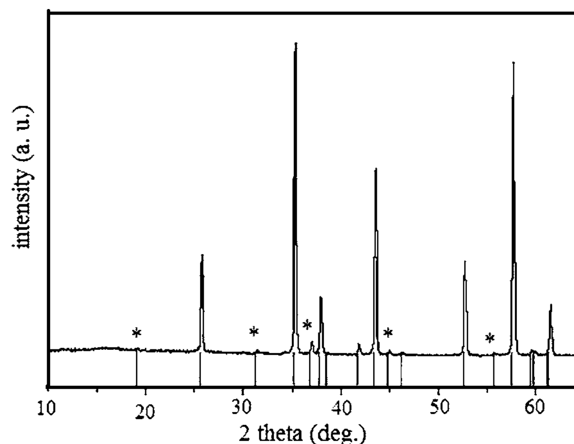

Figure 6 X-ray diffraction spectrum of the alumina substrate prior to the deposition of the film with the peaks (*) corresponding to $MgAl_2O_4$ spinel.

analysis showed that the peaks correspond to $MgAl_2O_4$. These peaks should correspond to the ones present in the spectrum obtained in [4], and attributed to the spinel phase of Al—V—O (see Fig. 6).

The alumina substrate was immersed in boiling isopropanol and dried on a hot plate at 100°C. The deposition of the film was performed using spin coating technique. The refluxed solution of Al—V—O were diluted with ^{i}PrOH in the ratio 1:5 and syringed on the substrate through a 0.2 μm PTFE filter. The spinning speed was 6000 rpm for one minute and then, the film was allowed to dry and heat-treated at 650°C for 20 min. The electron micrograph of the film is shown in the Fig. 7 where it is possible to observe an uncovered part of the substrate. The grain size is smaller than 1 μm. The film is homogeneous and does not present cracks. The X-ray diffraction indicated that the deposited film showed only the peaks corresponding to the $AlVO_4$. In Fig. 8, the spectrum of the substrate, before and after the deposition, is compared with that of $AlVO_4$ prepared via nitrate decomposition.

The deposition of the films on $Si/SiO_2/Pt$ substrates follows the same procedure as the deposited ones on alumina. The film is formed by non-connected crystallites with elongated shape. This fact could be due to the low interaction between the film and the metallic

TABLE II Refinement data and cell parameters of the $AlVO_4$ structure

a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å^3)	Z	Reflections	R_p	R_{wp}
6.538 (2)	7.756 (3)	9.131 (3)	96.17 (7)	107.23 (8)	101.40 (9)	426.63 (7)	2	1646	0.087	0.112

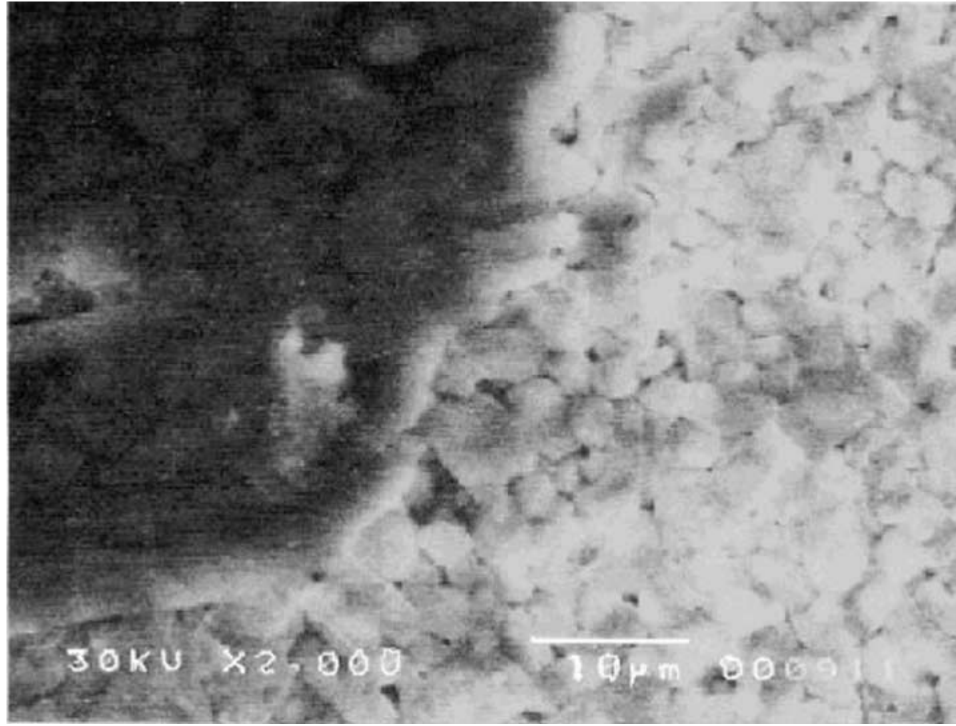

Figure 7 SEM micrograph of the $AlVO_4$ film deposited on alumina substrate. The darker part corresponds to the film.

substrate that produces the aggregation of the particles of $AlVO_4$ during the thermal treatment. As shown in the Fig. 9, the mean dimensions of the grains are around $1\times3\ \mu m^2$.

4.2. Electrical characterization

Gas sensors based on semiconductor metallic oxides are devices that change their electrical conductivity with the composition of the surrounding atmosphere. These sensors have the advantage of the low fabrication costs and low dimensions. A first trial was performed in order to characterize the film in air, between room temperature and 150°C. The used technique was the four points method in the constant current method [7], measuring the difference of potential. The substrate with the film was fixed to a holder with a thermocouple; a current of 1 nA was applied.

TABLE III Atomic positions of the Al, V and O obtained by the Rietveld refinement

	x/a	y/b	z/c	$U_{iso} * 100$
Al1	0.745 (2)	0.695 (1)	0.406 (1)	2.4 (3)
Al2	0.461 (1)	0.881 (1)	0.2122 (9)	1.3 (2)
Al3	0.963 (1)	0.309 (1)	0.0074 (9)	1.2 (2)
V1	0.001 (8)	0.9953 (6)	0.2552 (6)	2.2 (2)
V2	0.1933 (9)	0.5997 (6)	0.3445 (5)	2.1 (2)
V3	0.5162 (8)	0.2985 (6)	0.1248 (6)	2.0 (2)
O1	0.638 (2)	0.491 (2)	0.254 (2)	2.2 (5)
O2	0.255 (2)	0.429 (2)	0.424 (2)	2.0 (5)
O3	0.046 (2)	0.699 (2)	0.429 (2)	1.8 (5)
O4	0.158 (2)	0.093 (2)	0.430 (2)	2.9 (5)
O5	0.466 (2)	0.750 (2)	0.366 (2)	1.5 (5)
O6	0.753 (3)	0.867 (2)	0.270 (2)	2.9 (6)
O7	0.520 (2)	0.120 (2)	0.218 (1)	1.9 (5)
O8	0.355 (2)	0.731 (2)	0.027 (2)	1.0 (5)
O9	0.253 (3)	0.297 (2)	0.033 (2)	2.5 (5)
O10	0.049 (2)	0.519 (2)	0.140 (2)	2.0 (6)
O11	0.162 (3)	0.868 (2)	0.174 (2)	3.1 (6)
O12	0.947 (2)	0.146 (2)	0.138 (2)	2.2 (5)

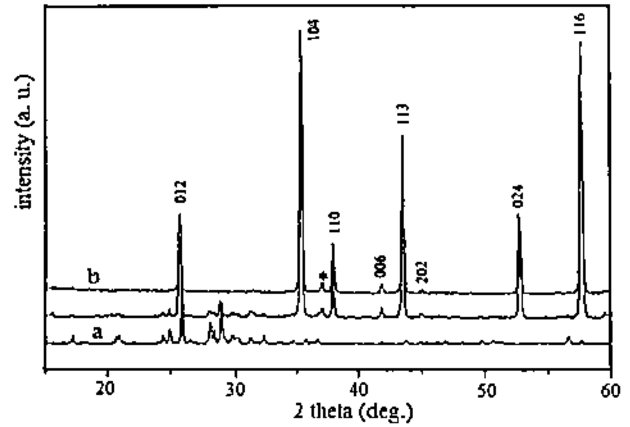

Figure 8 Comparison of the X-ray diffraction patterns of: (a) $AlVO_4$ prepared via nitrates; (middle) alumina substrate after the deposition of the $AlVO_4$ film, and (b) before the deposition.

The thermal coefficient resistivity, α, is defined as:

$$\alpha = (1/\rho)(\mathrm{d}\rho/\mathrm{d}T) \qquad (1)$$

hence:

$$\ln \rho = -(1/\alpha T). \qquad (2)$$

The experimental results for $AlVO_4$ on an alumina substrate are shown in the Fig. 10. The resistivity of $AlVO_4$ at room temperature was found to be $1.04 \times 10^4\ \Omega$ cm. The resistivity coefficient is $\alpha = -2.9099 \times 10^{-3}{}^\circ C^{-1}$ and the activation energy is $E_a = 0.11$ eV.

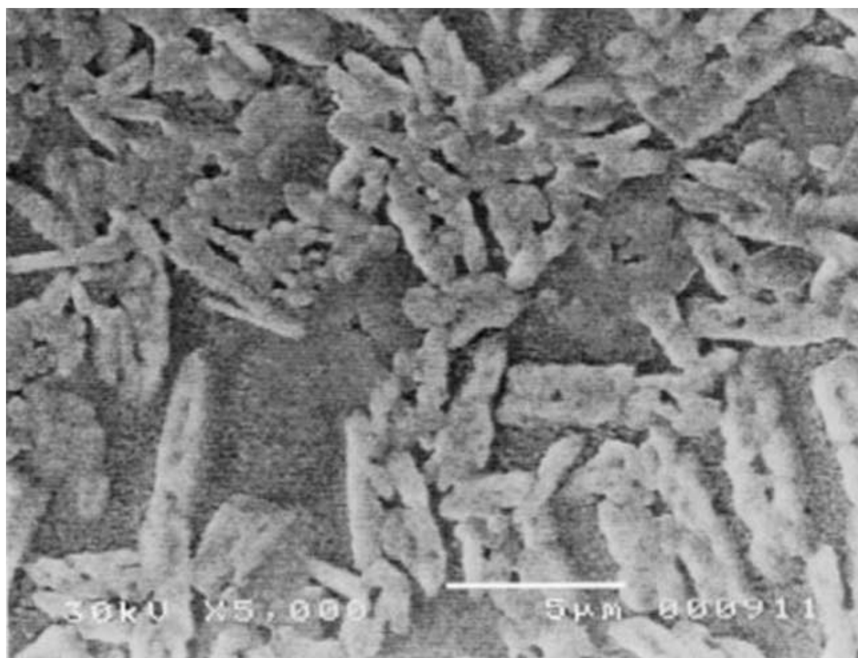

Figure 9 SEM micrograph of $AlVO_4$ film deposited on $Si/SiO_2/Pt$ substrate.

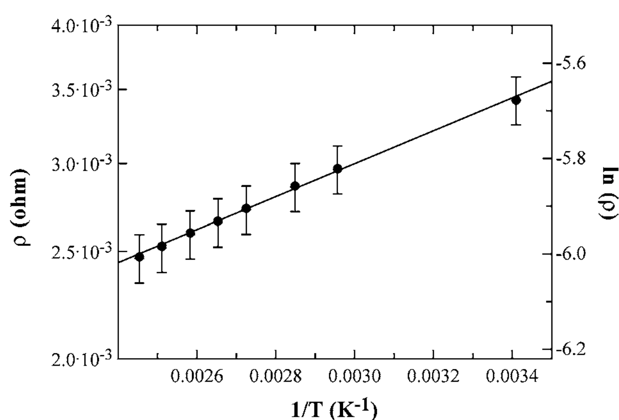

Figure 10 Plot of the resistivity, $\ln(\rho)$, of the $AlVO_4$ film deposited on alumina substrate as a function of the temperature, $1/T$.

5. Conclusions

Different preparation methods to obtain single phase $AlVO_4$ compound are reported, as a first step to determine whether or not the $AlVO_4$ single phase is responsible for its high sensibility to nitrogen oxides. Although the ceramic method is the most utilized to prepared mixed oxides, the low reactivity of aluminium oxide prevents the formation of the pure $AlVO_4$. Decomposition of nitrates and the sol gel methods are used to prepare $AlVO_4$ a Rietveld refinement was performed on single phase powders in order to determine the crystal structure.

Single phase films were obtained as long as deposited on alumina or on $Si/SiO_2/Pt$ substrates as observed by SEM and XRD. The electrical characteristics of the $AlVO_4$ thin film on alumina substrate are: a resistivity of 1.04×10^4 Ωcm at room temperature, a temperature resistivity coefficient of $-2.9099 \times 10^{-3}{}^{\circ}C^{-1}$ and an activation energy of 0.11 eV.

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References

1. Y. SHIMISU and M. EGASHIRA, *MRS Bull.* **24** (1999) 18.
2. T. ISHIHARA, K. SHIOKAWA, K. EGUCHI and H. ARAI, *Sensors and Actuators* **19** (1989) 259.
3. K. ZAKRZEWSKA, *Thin Solid Films* **391** (2001) 229.
4. B. LEYER, H. SCHMELZ, H. GÖBEL, H. MEIXNER, T. SCHERG and H. KNÖZINGER, *ibid.* **310** (1997) 228.
5. A. C. LARSON and R. B. VON DREELE, GSAS Programme, Los Alamos National Laboratory, NM87545 USA (1995).
6. B. ROBERTSON and E. KOSTINER, *J. Solid State Chem.* **4** (1972) 29.
7. L. J. VAN DER PAW, *Philips Res. Rep.* **13** (1958/9) 1.

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