DOI 10.5162/IMCS2018/P1GS.12

Crystal Structure and CO_2 Sensing Properties of Rare-earth oxycarbonates

T. Suzuki[1,3], F. Lauxmann[2], A. Sackmann[1], A. Staerz[1], U. Weimar[1], C. Berthold[2], N. Barsan[1]
[1] Institute of Physical Chemistry, University of Tübingen, Tübingen, Germany
[2] Applied Mineralogy, University of Tübingen, Tübingen, Germany
[3] Corporate R&D Headquarters, Fujielectric Co. Ltd., Tokyo, Japan
takuya.suzuki@ipc.uni-tuebingen.de

Abstract

Rare-earth oxycarbonates $Ln_2O_2CO_3$ (Ln = rare-earth element) are promising materials for chemoresistive CO_2 gas sensors. The previous works singled out monoclinic $La_2O_2CO_3$ as the best performing member of this family of materials. However, the monoclinic structure is metastable and could be transformed into the hexagonal phase. To date there is no clear evidence about the sensing properties of hexagonal structure. In this work we are attempting to study the issues of thermal stability and CO_2 sensing performance for both structure. To do so, we synthesized monoclinic and hexagonal $La_2O_2CO_3$ by using two different preparation routes. Our investigations are indicating that both structures are sensitive to CO_2 gas to the same degree, but the resistivity of the hexagonal $La_2O_2CO_3$ is higher and the monoclinic structure may transform also under typical measurement conditions at least partially into the hexagonal structure which significantly influences the electrical properties and thereby the characteristics of the sensor.

Key words: gas sensor, CO_2, oxycarbonate, structure, XRD

Introduction

CO_2 sensing is relevant not only in the conventional field of environmental safety, such as building and parking area management, but also in the agricultural and food businesses. The standard current technology is mainly NDIR, which is expensive, bulky, and hard to install. Obtaining low cost, simple and good performaning chemoresistive CO_2 gas sensors has the potential to be a game changer. Rare-earth oxycarbonates have been proposed as promising chemoresistive materials for CO_2 sensors [1-5]. The already published results indicate monoclinic $La_2O_2CO_3$ as the most suitable for material for CO_2 sensors. There are no reports about the sensing properties of the more thermally stable hexagonal $La_2O_2CO_3$. Because the monoclinic structure is metastable and could be transformed into the hexagonal one it is very important to find out more about the stability and sensing properties of both structures.

Sensor Fabrication

Rare-earth oxycarbonates were formed from the hydroxides in many of previous works [1-4]. We synthesized La-oxycarbonates through two different routes as shown in Fig.1. One was from La hydroxide (*Route#1*) and the other was from La oxalate hydrate (*Route#2*). The precursors, La-hydroxide (99.9%, Aldrich) and La-oxalate hydrate (99.99%, Aldrich), were kept heated at 450°C in air for 18 hours. The two synthesis routes resulted in the two different structures of the La-oxycarbonate as confirmed by XRD (see results presented in Table 1.)

The obtained powders were mixed with appropriate solvents and the resulting pastes were screen printed onto alumina substrates provided with Pt interdigitated electrodes and Pt heaters substrates. After the deposition of the sensing layers the substrates were heated at 450°C in laboratory air for 10 minutes.

Sensing Properties and Stability

The initial CO_2 sensing properties of both sensor materials were measured in a background of humid air (50% relative humidity at 20°C) and at an operation temperature of 300°C. In order to test the stability, a week long aging process was performed in humid air and under periodic exposure to CO_2 in the range 300 to 3000ppm at an operation temperature of 350°C. After aging the CO_2 sensing properties were measured again in the same condition as for the initial characterization. The results of the initial and final characterization are shown in Fig.2. The initial resistance of the sensor from La-hydroxide was much higher than that from La-oxalate hydrate, and the initial sensor signals of both samples were almost the same level. The resistance of the sensor from La oxalate hydrate increased up to the same level as the sensor from La hydroxide after aging. On the other hand, the resistance of the sensor from La hydroxide remained unchanged.

The XRD investigation of the sensors after the full sensing properties assessment, including aging, indicated that the hexagonal structure remained unchanged but the monoclinic structure was partly transformed during aging into the hexagonal structure (see Table 1). These results are in correlation with the sensing properties and give important hints for the manufacturing of those kind of sensors.

Conclusions

We have succeeded in synthesizing monoclinic $La_2O_2CO_3$ and hexagonal $La_2O_2CO_3$ separately and revealed that both of them are sensitive to CO_2 gas to the same degree and that the hexagonal $La_2O_2CO_3$ is more stable than monoclinic $La_2O_2CO_3$.

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Table.1: The results of XRD.

Starting material	Initial	After aging
La hydroxide	hexagonal $La_2O_2CO_3$	hexagonal $La_2O_2CO_3$
La oxalate	monoclinic $La_2O_2CO_3$	monoclinic + hexagonal

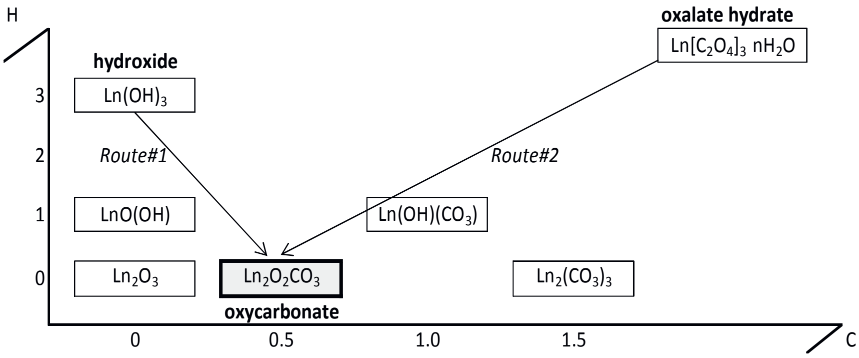
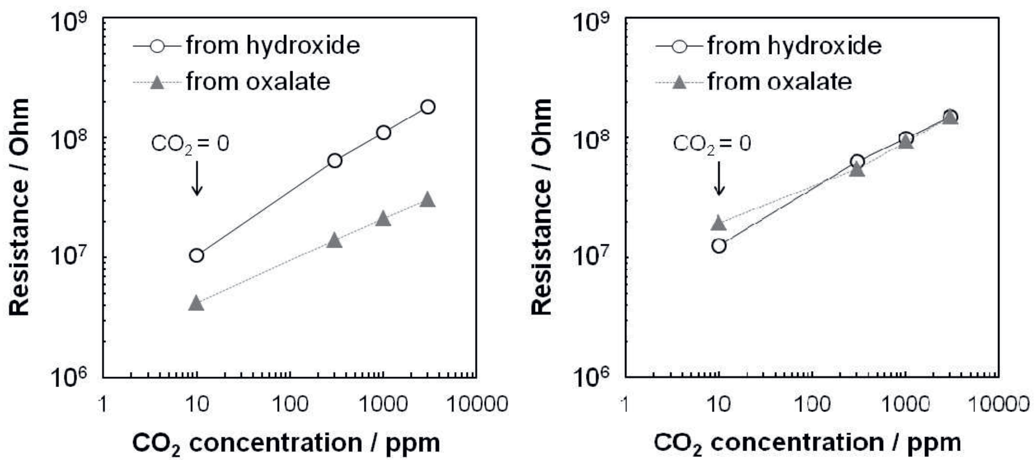


Fig.1.Synthetic routes. "H" or "C" on the axes indicates the number of hydrogen or carbon atom in each compound respectively.



(a) Initial *(b) After aging*

Fig.2. Sensor resistance vs CO_2 concentration