Crystal Structure and CO₂ Sensing Properties of Rare-earth oxycarbonates

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Abstract

Rare-earth oxycarbonates Ln₂O₂CO₃ (Ln = rare-earth element) are promising materials for chemoresistive CO₂ gas sensors. The previous works singled out monoclinic La₂O₂CO₃ 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 CO₂ sensing performance for both structure. To do so, we synthesized monoclinic and hexagonal La₂O₂CO₃ by using two different preparation routes. Our investigations are indicating that both structures are sensitive to CO₂ gas to the same degree, but the resistivity of the hexagonal La₂O₂CO₃ 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, CO₂, oxycarbonate, structure, XRD

Introduction

CO₂ 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 performing chemoresistive CO₂ gas sensors has the potential to be a game changer. Rare-earth oxycarbonates have been proposed as promising chemoresistive materials for CO₂ sensors [1-5]. The already published results indicate monoclinic La₂O₂CO₃ as the most suitable for material for CO₂ sensors. There are no reports about the sensing properties of the more thermally stable hexagonal La₂O₂CO₃. 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 CO₂ 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 CO₂ in the range 300 to 3000ppm at an operation temperature of 350°C. After aging the CO₂ 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$_2$O$_2$CO$_3$ and hexagonal La$_2$O$_2$CO$_3$ separately and revealed that both of them are sensitive to CO$_2$ gas to the same degree and that the hexagonal La$_2$O$_2$CO$_3$ is more stable than monoclinic La$_2$O$_2$CO$_3$.

References


Table 1: The results of XRD.

<table>
<thead>
<tr>
<th>Starting material</th>
<th>Initial</th>
<th>After aging</th>
</tr>
</thead>
<tbody>
<tr>
<td>La hydroxide</td>
<td>hexagonal La$_2$O$_2$CO$_3$</td>
<td>hexagonal La$_2$O$_2$CO$_3$</td>
</tr>
<tr>
<td>La oxalate</td>
<td>monoclinic La$_2$O$_2$CO$_3$ + hexagonal La$_2$O$_2$CO$_3$</td>
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Fig. 1. Synthetic routes. “H” or “C” on the axes indicates the number of hydrogen or carbon atom in each compound respectively.

Fig. 2. Sensor resistance vs CO$_2$ concentration