doi:10.1246/cl.2011.504
Published on the web April 20, 2011

Evidence of CO_2 Chemisorption at High Temperature in Lithium Gallate (Li_5GaO_4)

Tatiana Ávalos-Rendón and Heriberto Pfeiffer*
Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México,
Circuito Exterior s/n Cd. Universitaria, Del. Coyoacán, CP 04510, México DF, Mexico

(Received February 3, 2011; CL-110097; E-mail: pfeiffer@iim.unam.mx)

Li_5GaO_4 was tested as a possible CO_2 captor. Li_5GaO_4 was synthesized by solid-state reaction, structurally characterized, and then thermally treated under a CO_2 flow, from 30 to 900 °C, having the highest CO_2 chemisorption at around 709 °C. The results clearly showed that Li_5GaO_4 is able to trap CO_2 chemically in two different steps. The CO_2 quantity trapped was equal to $8.9\,\mathrm{mmol\,g^{-1}}$, which is considerably high in comparison to other ceramics.

The increase of carbon dioxide (CO_2) in the atmosphere is claimed to be one of the major contributors to the greenhouse effect and will result in serious global warming issues, such as melting icebergs in the polar regions, hotter summer and winters never seen before, all of them due to the global increment of temperature.[1–3]

In that sense, in the last years, different lithium ceramics have been proposed as possible CO_2 captors.[4–10] Among all these ceramics, Li_4SiO_4, Li_4TiO_4, $Li_6Zr_2O_7$, and Li_5AlO_4, seem to have the best theoretical and experimental CO_2 capture efficiencies.[7,8,10–15] In fact, in a recent paper Ávalos-Rendón et al.[11] proposed Li_5AlO_4 as a new CO_2 captor, and the results presented in that paper showed the highest experimental CO_2 absorption reported in the literature, up to now, for this kind of materials, $16.4\,\mathrm{mmol\,g^{-1}}$ (maximum CO_2 theoretical capacity, $19.8\,\mathrm{mmol\,g^{-1}}$).

On the other hand, lithium gallate (Li_5GaO_4) has been scarcely studied, and it has been mainly tested as a lithium ion conductor.[16,17] Additionally, it has to be pointed out that Li_5GaO_4 and Li_5AlO_4 are isostructural materials. It is important, as Li_5AlO_4 has been shown to be one of the best possible CO_2 captor ceramics.[11] Both ceramics have orthorhombic phases, where the cell parameters varied from 9.173, 9.094, and 9.202 Å to 9.087, 8.947, and 9.210 Å for Li_5GaO_4 and Li_5AlO_4, respectively.[18,19] Therefore, based on the high lithium content of Li_5GaO_4 and the fact that it is an isostructural material with Li_5AlO_4, the aim of this work was to study and demonstrate if Li_5GaO_4 is able to capture CO_2, through a similar mechanism to that reported previously for other lithium ceramics.

Li_5GaO_4 was synthesized by solid-state reaction using gallium oxide (Ga_2O_3, Aldrich) and lithium oxide (Li_2O, Aldrich) as reagents, where 30 wt % excess lithium oxide was used to prevent lithium sublimation. If this excess lithium was not added or added in smaller quantities, the Li_5GaO_4 was not correctly synthesized (see Supporting Information[27]). Powders were mechanically mixed and pressed. Then, a pellet was thermally treated at 500 °C for 24 h. Finally, the sample pellet was air-coolded and pulverized.

Figure 1 shows the XRD patterns of the Li_5GaO_4 sample synthesized by solid-state reaction and the same sample after the CO_2 chemisorption process (the second pattern is described later). As it can be seen, Li_2CO_3 was detected as a secondary phase (<8%). In fact, the presence of Li_2CO_3 may indicate certain reactivity between the Li_5GaO_4 and CO_2 or the reaction of the Li_2O added in excess, as lithium carbonate was not used as reagent, and it must be produced due to the CO_2 capture of Li_5GaO_4 from the environment. In addition, the N_2 adsorption–desorption isotherm was obtained, and then the surface area of this sample was estimated using the BET model. The surface area was equal to $1\,\mathrm{m^2\,g^{-1}}$. Although the surface area is considerably small, it is comparable with the other surface areas presented by different lithium ceramics used for CO_2 capture, where the surface areas usually do not exceed $3\,\mathrm{m^2\,g^{-1}}$.[20,21]

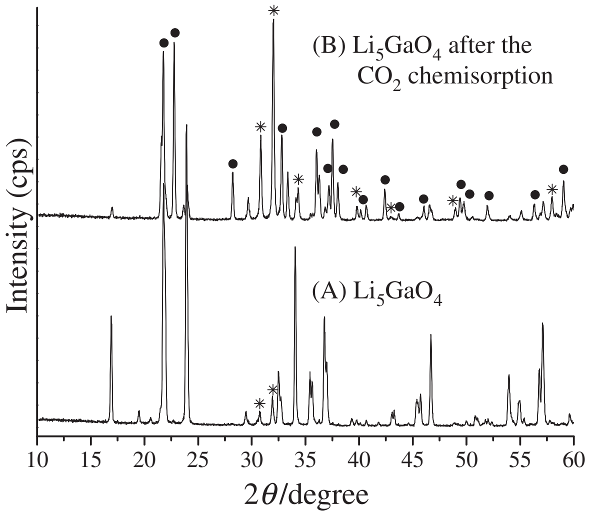

Figure 1. XRD patterns of the Li_5GaO_4 sample (A) and the Li_5GaO_4 sample after the CO_2 chemisorption process (B). Peaks labeled as ✳ and ● correspond to Li_2CO_3 (87-0728 JCPDS card) and $LiGaO_2$ (72-1640 JCPDS card) compounds, respectively.

Once the Li_5GaO_4 was characterized, the material was thermally treated under a CO_2 flow to analyze if this material can function as CO_2 captor (CO_2 flow used was equal to $60\,\mathrm{mL\,min^{-1}}$). If Li_5GaO_4 were able to react with CO_2, one of the following reactions may occur:

$$2Li_5GaO_4 + 5CO_2 \rightarrow 5Li_2CO_3 + Ga_2O_3 \quad (1)$$

$$2Li_5GaO_4 + 4CO_2 \rightarrow 4Li_2CO_3 + 2LiGaO_2 \quad (2)$$

where the reaction would be similar to those observed for other lithium ceramics,[7,10–12] in which lithium carbonate is produced in addition to a residual compound, Ga_2O_3 or $LiGaO_2$ in these cases. For this reaction, the maximum theoretical CO_2 capacity on Li_5GaO_4 corresponds to 14.8 (reaction 1) or $11.8\,\mathrm{mmol\,g^{-1}}$ (reaction 2). These are smaller CO_2 absorption capacities, in comparison to the isostructural aluminium ceramic (Li_5AlO_4).

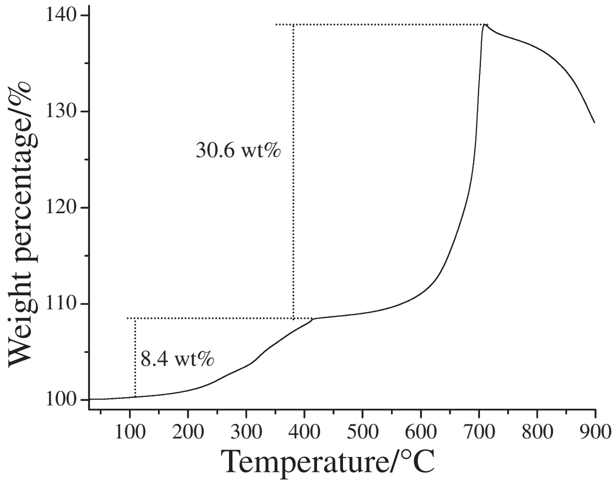

Figure 2. Dynamic thermogram analysis of the Li_5GaO_4 sample in a CO_2 flow.

Of course, this variation is simply due to the mass differences between the metal structural elements, gallium and aluminium. Therefore, the CO_2 absorption capacity of Li_5GaO_4 can be considered high among lithium ceramics and among other materials proposed for CO_2 capture.[11,22]

Figure 2 presents the Li_5GaO_4 dynamic thermogram, where it is very clear that two different processes took place. First, between 112 and 418 °C an initial weight increment of 8.4 wt % was produced. Then, the thermogram presented a very slight increment of weight, until 568 °C, where a remarkable increment of weight was produced. Between 568 and 709 °C the sample gained 30.6 wt %. Then, the total final increment observed was equal to 39 wt %.

According to this result, Li_5GaO_4 seems to capture CO_2 in a very similar way to that observed for other lithium ceramics (Li_2O, Li_5AlO_4, Na_2ZrO_3, and Li_2CuO_2) presenting this reaction mechanism:[6,11,12,23,24] First, at low temperatures, a superficial reaction is produced. At this moment, an external lithium carbonate shell is formed over the surface of the ceramic particles. Then, when the temperature is increased sufficiently and the alkaline diffusion is activated, in this case lithium, the reaction continues through the bulk of the material, completing the CO_2 capture. For Li_5GaO_4, an identical reaction mechanism can be described. The superficial reaction corresponds to the first increment of weight observed between 112 and 418 °C. Later, at temperatures equal or higher than 568 °C the lithium diffusion should be activated and the process continued through the Li_5GaO_4 bulk. Finally, it can be seen in Figure 2 that at temperatures higher than 715 °C, the desorption process is activated. This is in good agreement with the Li_2CO_3 melting point (720 °C). In order to corroborate the reaction mechanism, the Li_5GaO_4 sample after CO_2 capture was characterized by XRD (Figure 1B). As it can be seen, different compounds were detected; Li_2CO_3, $LiGaO_2$, and Li_5GaO_4. This result confirms that CO_2 is being trapped chemically, producing Li_2CO_3 and $LiGaO_2$ as products. Therefore, the reaction mechanism must correspond to that proposed in reaction 2.

Summarizing, Li_5GaO_4 was synthesized and characterized. Then, the CO_2 absorption capacity was evaluated dynamically in a thermobalance with a CO_2 flow. The results clearly showed that Li_5GaO_4 would be considered as an alternative for CO_2 absorption. Li_5GaO_4 absorbs CO_2 in a wide range of temperatures, and the final weight increment observed in this sample was equal to 39 wt %, which corresponds to a CO_2 capture of 8.9 mmol g^{-1}. If this material is compared to other lithium ceramics, only Li_5AlO_4 has presented a higher experimental CO_2 absorption.[11] On the other hand, if these results are compared with the CO_2 absorption reported for other inorganic materials,[22,25,26] such as hydrotalcites, activated carbons, earth-alkaline oxides (CaO mainly), zeolites, and organic–inorganic hybrids, it is still a good result. In general, activated carbons, zeolites, and organic–inorganic hybrid materials adsorb CO_2 between 200 and 400 °C, having the best efficiencies of ca. 6 mmol g^{-1}. Hydrotalcites absorb CO_2 at higher temperatures (450–800 °C), but their efficiencies are very poor, 2 mmol g^{-1} maximum. Finally, CaO is one of the best CO_2 captors (theoretical capacity, 17.8 mmol g^{-1}). It absorbs CO_2 between 400 and 880 °C, and the experimental efficiency has reached up to 12 mmol g^{-1}.

This work was financially supported by the projects 179-2009 ICyT-DF and IN100609-PAPIIT. Furthermore, T. Ávalos-Rendón thanks CONACYT for financial support.

References and Notes

1 S. Pacala, R. Socolow, *Science* **2004**, *305*, 968.
2 G. Puxty, R. Rowland, A. Allport, Q. Yang, M. Bown, R. Burns, M. Maeder, M. Attalla, *Environ. Sci. Technol.* **2009**, *43*, 6427.
3 C. S. Song, *Catal. Today* **2006**, *115*, 2.
4 K. Nakagawa, T. Ohashi, *J. Electrochem. Soc.* **1998**, *145*, 1344.
5 K.-H. Choi, Y. Korai, I. Mochida, *Chem. Lett.* **2003**, *32*, 924.
6 L. M. Palacios-Romero, H. Pfeiffer, *Chem. Lett.* **2008**, *37*, 862.
7 H. Pfeiffer, P. Bosch, *Chem. Mater.* **2005**, *17*, 1704.
8 X.-S. Yin, M. Song, Q.-H. Zhang, J.-G. Yu, *Ind. Eng. Chem. Res.* **2010**, *49*, 6593.
9 E. Ochoa-Fernández, M. Rønning, T. Grande, D. Chen, *Chem. Mater.* **2006**, *18*, 6037.
10 B. N. Nair, R. P. Burwood, V. J. Goh, K. Nakagawa, T. Yamaguchi, *Prog. Mater. Sci.* **2009**, *54*, 511.
11 T. Ávalos-Rendón, J. Casa-Madrid, H. Pfeiffer, *J. Phys. Chem. A* **2009**, *113*, 6919.
12 H. A. Mosqueda, C. Vazquez, P. Bosch, H. Pfeiffer, *Chem. Mater.* **2006**, *18*, 2307.
13 N. Togashi, T. Okumura, K. Oh-ishi, *J. Ceram. Soc. Jpn.* **2007**, *115*, 324.
14 M. Kato, K. Nakagawa, K. Essaki, Y. Maezawa, S. Takeda, R. Kogo, Y. Hagiwara, *Int. J. Appl. Ceram. Technol.* **2005**, *2*, 467.
15 C. Gauer, W. Heschel, *J. Mater. Sci.* **2006**, *41*, 2405.
16 T. Esaka, M. Greenblatt, *Solid State Ionics* **1986**, *21*, 255.
17 A. D. Robertson, A. R. West, A. G. Ritchie, *Solid State Ionics* **1997**, *104*, 1.
18 F. Stewner, R. Hoppe, *Z. Anorg. Allg. Chem.* **1971**, *380*, 241.
19 F. Stewner, R. Hoppe, *Acta Crystallogr., Sect. B* **1971**, *27*, 616.
20 V. L. Mejía-Trejo, E. Fregoso-Israel, H. Pfeiffer, *Chem. Mater.* **2008**, *20*, 7171.
21 R. Rodríguez-Mosqueda, H. Pfeiffer, *J. Phys. Chem. A* **2010**, *114*, 4535.
22 S. Choi, J. H. Drese, C. W. Jones, *ChemSusChem* **2009**, *2*, 796.
23 I. Alcérreca-Corte, E. Fregoso-Israel, H. Pfeiffer, *J. Phys. Chem. C* **2008**, *112*, 6520.
24 Y. Matsukura, T. Okumura, R. Kobayashi, K. Oh-ishi, *Chem. Lett.* **2010**, *39*, 966.
25 Q. Wang, J. Luo, Z. Zhong, A. Borgna, *Energy Environ. Sci.* **2011**, *4*, 42.
26 D. M. D'Alessandro, B. Smit, J. R. Long, *Angew. Chem.* **2010**, *49*, 6058.
27 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.