

Siderite, FeCO₃Jun WANG¹, Terutoshi SAKAKURA¹, Nobuo ISHIZAWA^{*1}, Hiromi EBA²¹Ceramics Research Laboratory, Nagoya Institute of Technology,
Asahigaoka, Tajimi, Gifu 507-0071 Japan²Tokyo City University, Tamazutsumi, Setagaya-ku, Tokyo 158-8557 Japan**Introduction**

Carbon dioxide is a greenhouse gas as it transmits visible light while it absorbs the infrared and near-infrared strongly. This is the reason why the increase of carbon dioxide in Earth's atmosphere is considered a potential culprit in the global warming. In order to solve problems about the greenhouse effect, attentions have been drawn to a battery system utilizing carbon dioxide and ferrous waste [1].

Iron (II) carbonate (FeCO₃) has a mineral name siderite occurring as primary gangue mineral in many hydrothermal vein deposits and in some high-temperature metasomatic ore deposits. The concentration of carbon dioxide in atmosphere and the formation of siderite were closely related with each other on the early Earth [2].

Siderite is paramagnetic at ambient conditions and undergoes an antiferromagnetic phase transition at about 40 K. It also has a pressure-induced magnetic transition. The decarbonation of siderite results in the formation of iron oxides like FeO, Fe₂O₃ and Fe₃O₄ at elevated temperatures. This kinetic process depends strongly on the atmospheric circumstance and has not been well resolved till now [3]. The present study was undertaken in order to obtain a clue to clarify the mechanism of decarbonation of siderite and related compounds through the single-crystal electron density distribution analysis in association with other high-temperature diffraction experiments using the laboratory X-ray source.

Experimental

Crystals were grown by the hydrothermal method. Synchrotron diffraction experiments were carried out using the horizontal-type four-circle diffractometer at the beamline 14A, PF-KEK [4]. Vertically-polarized X-rays were monochromatized with the Si (111) double crystal monochromator. The wavelength of the X-rays was calibrated using the Si standard crystal to be 0.680213 Å. The eight-channel avalanche photodiode detector was used for the photon counting [5]. Neither absorbers nor attenuators were used owing to the wide dynamic range of the detector with linearity up to 10⁸ counts per second. Data were collected for a crystal (FeCO₃_1_10) of about 50 micron in size at room temperature. The self-consistent values of the f1 and f2 components of the atomic scattering factors were taken from the table given by National Institute of Standards and Technology [6].

Siderite has long been assumed to be a member of the rhombohedral structural family with the space group *R*-3*c* as well as the other well-known carbonate minerals like

rhodochrosite (MnCO₃), calcite (CaCO₃), and magnesite (MgCO₃). The present study on the sample (FeCO₃_1_10), however, observed several reflections which broke the symmetry of the space group *R*-3*c*. For example, the six equivalent reflections in the {344} group which should be extinct in *R*-3*c* in the primitive rhombohedral setting had the following *F* and $\sigma(F)$ values:

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i>	$\sigma(F)$
-4	-4	-3	2.21	2.95
-3	-4	-4	4.75	1.27
-4	-3	-4	<u>17.13</u>	0.65
4	4	3	3.32	1.90
4	3	4	<u>15.53</u>	0.74
3	4	4	0.00	0.00

This table clearly shows that the 434 reflection and its Friedel counterpart have significant intensities as underlined.

A provisional refinement of the structure assuming *R*-3*c* converged to *R*1=1.95% for 298 independent reflections with *F* > 4 $\sigma(F)$. A significant compilation of residual electrons was observed at about 0.5 Å apart from Fe(II), suggesting a possible manifestation of the localized Fe 3*d* electrons. Detailed analysis is in progress.

This study was supported by Grants-in-Aid for Scientific Research No. 22360272 from the Japan Society for the Promotion of Science.

References

- [1] H. Chen, J. Wang, Y. Li, J. Gao, *Challenges of Power Engineering & Environment Vol. 1*, 978-981. Springer (2007)
- [2] H. Ohmoto, Y. Watanabe & K. Kumazawa, *Nature* **429**, 395-399 (2004).
- [3] P. K. Gallagher, S. St. J. Warne, *Thermochimica Acta* **43**, 253-267 (1981).
- [4] Y. Satow, & Y. Iitaka, *Rev. Sci. Instrum.* **60**, 2390-2393 (1989).
- [5] S. Kishimoto, N. Ishizawa & T. P. Vaalsta, *Rev. Sci. Instrum.* **69**, 384-391(1998).
- [6] C. T. Chantler, K. Olsen, R. A. Dragoset, J. Chang, A. R. Kishore, S. A. Kotochigova, D. S. Zucker; The National Institute of Standards and Technology, USA, <http://www.nist.gov/physlab/data/> (2010).

* ishizawa@nitech.ac.jp