Nanostructure of CaMgSi₂O₆ (Diopside) and CaTiO₃ (Perovskite) Mechanically Activated in Carbon Dioxide

A. M. Kalinkin^a, V. N. Nevedomskii^b, and E. V. Kalinkina^a

^a Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials, Kola Scientific Center, Russian Academy of Sciences, ul. Fersmana 26a, Apatity, Murmansk oblast, 184209 Russia

^b Ioffe Physicotechnical Institute, Russian Academy of Sciences, Politekhnicheskaya ul. 26, St. Petersburg, 194021 Russia e-mail: kalinkin@chemy.kolasc.net.ru

Received April 5, 2007; in final form, September 3, 2007

Abstract—The micro- and nanostructure of materials resulting from mechanochemical interactions of natural diopside (CaMgSi₂O₆) and synthetic perovskite (CaTiO₃) with CO₂ have been studied by transmission electron microscopy (TEM) and high-resolution TEM. The results indicate that CO₂ absorption is accompanied by CO₂

"dissolution" in the form of CO_3^{2-} ions in the structurally disordered silicate or titanate matrix. The diopside activation product is a quasi-homogeneous amorphous carbonate–silicate phase. The mechanically activated perovskite is a nanocomposite consisting of CaTiO₃ nanocrystals embedded in a carbonated amorphous titanate matrix.

DOI: 10.1134/S0020168508060162

INTRODUCTION

Calcium- and magnesium-containing silicates are potential sorbents of emissions of carbon dioxide, the major component of green house gas [1-3]. They offer two important advantages. First, the reaction of CO₂ and silicates is an energetically favored process. For example, the standard Gibbs energy of the reaction

$$\frac{1}{2}CaMgSi_2O_6(diopside) + CO_2$$

= $\frac{1}{2}CaCO_3(calcite) + \frac{1}{2}MgCO_3(magnesite)$ (1)
+ SiO₂(α -quartz)

evaluated from reference data [4], is $\Delta_r G^0(1) = -(18.3 \pm 5.4)$ kJ/mol. In addition, silicates are widespread rockforming minerals, present in large amounts in mining dumps and metallurgical slags, i.e., near large CO₂ emission sources. One drawback of silicates as sorbents is the near-zero rate of their reactions with carbon dioxide under ordinary conditions. The reaction can be accelerated either by raising the temperature of direct carbonation (1) or by extracting alkaline-earth cations from the silicate into solution (by autoclaving in water at elevated pressures or by reacting with an acid), followed by carbonate formation [1–3]. At the same time, raising the temperature shifts equilibrium (1) to the left, and the gas pressure must be raised. Additional reagents (water, acid) add complexity to the process.

Recent work [5–7] has shown that the reactivity of silicates with CO_2 can be enhanced by mechanochemi-

cal means. During fine grinding in air or under mechanical activation (MA) conditions in carbon dioxide atmosphere, a number of calcium-containing minerals, such as diopside (CaMgSi₂O₆), titanite (CaTiSiO₅), and perovskite (CaTiO₃), display high affinity for carbon dioxide. Under the effect of mechanical processing, such minerals selectively absorb carbon dioxide in the form of carbonate ions from the gaseous environment, as confirmed by IR spectroscopy results. The mole frac-

tion of CO_3^{2-} ions resulting from the absorbed carbon dioxide may be comparable to that of calcium and/or magnesium. Two hypotheses were proposed as to the state of carbonate ions in mechanically activated silicates. According to one of them, silicates react with CO_2 to convert to carbonates, as represented by reaction (1). At the same time, in contrast to what might be expected, milling-induced quantitative carbon dioxide absorption is not accompanied by the appearance of xray diffraction (XRD) peaks from calcite, magnesite, or any other carbonates. Large amounts of carbon dioxide absorbed by carbonates do not lead to the formation of amorphous calcium carbonate and cannot be accounted for by CO_2 surface chemisorption [6–8].

The other hypothesis is that, during fine grinding, CO_2 is incorporated into the structurally disordered silicate (or titanate) matrix through homogeneous "dissolution" to form a glassy carbonate–silicate phase similar to those resulting from quenching of carbonate-containing silicate melts. IR spectroscopy, XRD, and high-resolution Si²⁹ NMR results [5–8] lend support to the latter hypothesis, but there is still no direct observa-

tional evidence that MA products have such a nano-structure.

In this paper, we report our findings on the microand nanostructure of materials resulting from mechanochemical interactions of natural diopside (CaMgSi₂O₆) and synthetic perovskite (CaTiO₃) with CO₂. The materials were characterized in detail by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM).

EXPERIMENTAL

Perovskite, CaTiO₃, was synthesized mechanochemically [9]. A stoichiometric mixture of rutile TiO₂ and reagent-grade calcium carbonate was ground in an AGO-2 planetary mill [10] at 60 g for 5 min. The ball-to-powder weight ratio was 20 : 1. The ground material was pressed into disks, which were then heattreated for 4 h at 1200°. According to XRD and chemical analysis data, the resultant material was crystalline calcium titanate, CaTiO₃.

MA of the perovskite in a CO₂ atmosphere was performed in the AGO-2 under similar conditions, at a ball-to-sample weight ratio of 20:1. The initial sample weight was 10 g. After loading the sample and balls, the vessel was purged for 2 min with a slow stream of carbon dioxide, which was delivered from a cylinder through a drying column filled with calcined calcium chloride. CO₂ displaced the air from the vessel, since its density is 1.5 times higher. Every 2 min of MA, positive mixing was performed, and then the vessel was refilled with CO₂. The perovskite was activated in carbon dioxide for a total of 30 min. The CO₂ content of the samples was determined volumetrically [11] using an AN-7529 analyzer. A weighed portion of the sample was calcined at 1200°C, and the released carbon dioxide was absorbed by a strontium chloride solution in an electrochemical cell, raising the solution acidity. The solution was then neutralized by passing an electric current through the cell as a result of the reduction of hydrogen ions. The CO₂ content was evaluated from the quantity of electricity needed for neutralization.

In studies of natural diopside (nominal composition CaMgSi₂O₆), we used the same sample as earlier [12]. According to chemical analysis and atomic absorption data, its composition was (wt %) SiO₂, 49.70 \pm 0.08; CaO, 24.50 \pm 0.05; MgO, 16.10 \pm 0.05; Al₂O₃, 1.34 \pm 0.05; FeO, 2.88 \pm 0.05; TiO₂, 0.48 \pm 0.05; Na₂O, 0.43 \pm 0.05; K₂O, 0.19 \pm 0.02; and MnO, 0.08 \pm 0.02. The diopside was activated in a 75T-DRM vibratory mill for 65 h at a nearly atmospheric carbon dioxide pressure. As a result, the mineral was fully amorphized and adsorbed the maximum possible amount of CO₂ under the conditions of this study.

XRD patterns were collected on a DRON-2 powder diffractometer (Cu K_{α} radiation). IR spectra were measured on a UR-20 spectrometer using potassium bro-

mide disks. The specific surfaces of the MA perovskite and diopside samples were 5.1 ± 0.2 and 3.4 ± 0.1 m²/g, as determined by temperature-programmed nitrogen desorption measurements using a Micromeritics Flow-Sorb II 2300 instrument. Scanning electron microscopic (SEM) images were obtained on a Supra 50 VP, and TEM images were obtained on a JEOL JEM-2100F. The specimens were dispersed in ethanol by agitation for 10 min and then applied to collodion film and dried for 5–12 h.

RESULTS AND DISCUSSION

MA of diopside. As mentioned above, MA under the conditions of this study caused diopside to fully amorphize. Accordingly, its XRD pattern showed a broad halo (Fig. 1a, scan 2). The CO₂ content of the MA diopside was 21.3 ± 0.8 wt %. The carbon dioxide absorbed during mechanical processing is present in the diopside sample in the from of carbonate ions, as evidenced by the strong, split v₃ band around 1500 cm⁻¹,

due to the antisymmetric stretching mode of the CO_3^{2-} ion (Fig. 1b, spectrum 2). The reasons for the splitting of this band were discussed elsewhere [6].

From SEM data (Fig. 2), we obtained the following particle size distribution: 0–0.2 μ m (17.0%), 0.2–1.0 μ m (78.0%), 1.0–2.0 μ m (4.5%), 2–5 μ m (0.5%). From the specific surface and density ($d \approx 3 \text{ g/cm}^3$) of the diopside, the average particle size must be 0.39 ± 0.02 μ m, in reasonable agreement with the SEM data.

Dispersing the powder in ethanol insured partial disaggregation, as evidenced by TEM images, which showed ultrafine particles one to two orders of magnitude smaller (Fig. 3a) than those observed by SEM (Fig. 2). More detailed information about the particle microstructure is provided by HRTEM (Fig. 4c). Note that no marked inhomogeneities were detected in the bulk of MA diopside particles. The particles had smooth (melted) surfaces, with no sharp edges. The boundary between two overlapping particles was rather easy to discern (Fig. 4a).

Some of the MA diopside particles contained inclusions about 10 nm in size—no more than one inclusion in a relatively large particle on the order of $0.5-1 \,\mu\text{m}$ in size. One inclusion is seen in Fig. 4b. Presumably, the inclusions are either diopside nanocrystals or iron particles originating from the mill material.

On the whole, the diopside activated in CO_2 has a homogeneous microstructure, with no microstructural features, as evidenced by HRTEM images (Fig. 4c) and selected area diffraction (SAD) patterns, characteristic of amorphous structure (Fig. 5a).

MA of perovskite. According to XRD data, mechanical processing of the perovskite sample in CO_2 produced less structural imperfections in comparison with diopside (Fig. 1a, scans 3, 4). The carbon dioxide content of the MA perovskite was determined to be



Fig. 1. (a) XRD patterns and (b) IR spectra of (1, 2) diopside and (3, 4) perovskite (1, 3) before and (2, 4) after MA in carbon dioxide.



Fig. 2. SEM images of MA diopside.



Fig. 3. TEM images of MA (a) diopside and (b) perovskite dispersed in ethanol and then applied to collodion film.

INORGANIC MATERIALS Vol. 44 No. 6 2008



Fig. 4. TEM images of MA (a–c) diopside and (d–f) perovskite.

 11.6 ± 0.5 wt %. Like in the case of diopside, carbon dioxide was present in the form of carbonate groups (Fig. 1b, spectrum 4).

After dispersing the powder in ethanol and applying it to collodion film, the medium and large perovskite and diopside particles (and aggregates) ranged in size from 0.2 to 2.0 μ m (Fig. 3). At the same time, as seen

in Fig. 3 the perovskite sample contained far more ultrafine particles. Note that the average particle size of the perovskite evaluated from its specific surface and density ($d \approx 4$ g/cm³) was 0.44 ± 0.02 µm.

As seen in Fig. 4, the perovskite and diopside samples differ in particle microstructure even on a length

INORGANIC MATERIALS Vol. 44 No. 6 2008



Fig. 5. SAD patterns of the MA (a) diopside and (b) perovskite particles shown in Figs. 4a and 4d, respectively.

scale of 500 nm. The MA perovskite particles have ragged edges and contain well-defined inhomogeneities. The boundary between two overlapping particles is difficult to discern.

More detailed TEM images (Fig. 4e) demonstrate that the sample contains structured inclusions in the form of rather heavy particles (dark areas in the micrograph) embedded in a low-Z amorphous matrix. From TEM data, we obtained the following size distribution for the structured inclusions: 0-5 nm (15%), 5-10 nm (35%), 10–15 nm (43%), 15–20 nm (7%). It is of interest to compare the size of the crystalline perovskite inclusions with the size of coherently scattering domains (CSDs) evaluated from the width of diffraction lines (Fig. 1). Peak broadening was analyzed using the approximation method [13]. The crystallite size and microstress were determined from the 121 and 242 reflections using Gaussian lineshapes. The integral linewidth β is then related to the crystallite size D and microstress $\Delta d/d$ by

$$(\beta \cos \theta)^2 = (\lambda/D)^2 + [4(\Delta d/d)\sin \theta]^2,$$

where λ is the x-ray wavelength, and θ is the diffraction angle. In this way, the average CSD size was determined to be 18 ± 3 nm, in good agreement with the above TEM data.

The SAD pattern of the MA perovskite sample (Fig. 5b) is characteristic of polycrystalline material, with no preferred orientation. The diffraction spots are consistent with the orthorhombic structure of $CaTiO_3$ [14] (PDF, no. 42-423).

The HRTEM image of MA perovskite particles in Fig. 4f (particle edges) demonstrates that the matrix is structurally disordered and contains crystalline inclusions 3 nm and more in diameter. Figure 6 shows the HRTEM image of the delineated area in Fig. 4f. The



Fig. 6. HRTEM image of MA perovskite (delineated area in Fig. 4f, 13.2-nm field of view).

atomic rows are well seen, with a spacing of 2.7 Å (marked by arrows), which corresponds to the (121) plane.

CONCLUSIONS

The present results lend support to earlier conclusions as to the mechanochemical interaction between CO_2 and calcium-containing minerals. Milling-induced extensive incorporation of CO_2 molecules into the particle bulk is accompanied by CO_2 dissolution in the form of CO_3^{2-} ions in the structurally disordered silicate or titanate matrix, with no mechanochemical conversion of the silicate or titanate to a distinct carbonate phase. The MA diopside is a quasi-homogeneous amorphous carbonate–silicate phase consisting of nanoclusters, i.e., structural elements with no translational symmetry [15]. The MA perovskite is a nanocomposite consisting of CaTiO₃ nanocrystals embedded in a carbonated amorphous titanate matrix.

ACKNOWLEDGMENTS

We are grateful to V.I. Putlyaev for his assistance in taking the scanning electron microscopic images.

This work was supported by the Russian Foundation for Basic Research (grant no. 06-03-32198), the Leading Scientific Schools Program (grant no. NSh-4383.2006.03), and the Materials Research and Diagnostics in High Technologies Regional TsKP.

REFERENCES

- Seifritz, W.,CO₂ Disposal by Means of Silicates, *Nature*, 1990, vol. 345, no. 6275, p. 486.
- Lackner, K.S., Wendt, C.H., Butt, D.P., et al., Carbon Dioxide Disposal in Carbonate Minerals, *Energy*, 1995, vol. 20, no. 11, pp. 1153–1170.
- Huijgen, W.J.J., Witkamp, G.J., and Comans, R.N.J., Mineral CO₂ Sequestration by Steel Slag Carbonation, *Environ. Sci. Technol.*, 2005, vol. 39, no. 24, pp. 9676– 9682.
- Termicheskie konstanty veshchestv. Spravochnik (Thermal Constants of Substances: A Handbook), Glushko, V.P., Ed., Moscow: VINITI, 1968–1979.
- 5. Kalinkina, E.V., Kalinkin, A.M., Forsling, W., and Makarov, V.N., Sorption of Atmospheric Carbon Diox-

ide and Structural Changes of Ca and Mg Silicate Minerals during Grinding: I. Diopside, *Int. J. Miner. Process.*, 2001, vol. 61, no. 4, pp. 273–288.

- Kalinkin, A.M., Politov, A.A., Boldyrev, V.V., et al., Study of Mechanical Activation of Diopside in a CO₂ Atmosphere, *J. Mater. Synt. Process.*, 2002, vol. 10, no. 1, pp. 59–65.
- Kalinkin, A.M., Kalinkina, E.V., and Vasil'eva, T.N., Effect of Mechanical Activation on the Reactivity of Sphene, *Kolloidn. Zh.*, 2004, vol. 66, no. 2, pp. 190–197.
- Kalinkin, A.M., Kalinkina, E.V., Zalkind, O.A., and Makarova, T.I., Chemical Interaction of Calcium Oxide and Calcium Hydroxide with CO₂ during Mechanical Activation, *Neorg. Mater.*, 2005, vol. 41, no. 10, pp. 1218–1224 [*Inorg. Mater.* (Engl. Transl.), vol. 41, no. 10, pp. 1073–1079].
- Avvakumov, E.G. and Pushnyakova, V.A., Mechanochemical Synthesis of Mixed Oxides, *Khim. Tekhnol.*, 2002, no. 5, pp. 6–17.
- Avvakumov, E.G., Mekhanicheskie metody aktivatsii khimicheskikh protsessov (Mechanical Activation of Chemical Processes), Novosibirsk: Nauka, 1986.
- 11. Dymov, A.M., *Tekhnicheskii analiz* (Technical Analysis), Moscow: Metallurgiya, 1964.
- Kalinkin, A.M., Politov, A.A., Kalinkina, E.V., et al., Mechanochemical Interaction of Calcium Carbonate with Diopside and Amorphous Silica, *Khim. Interesah Ustoich. Razvit.*, 2006, vol. 14, pp. 357–367.
- 13. Iveronova, V.I. and Revkevich, G.P., *Teoriya rasseyaniya rentgenovskikh luchei* (Theory of X-ray Scattering), Moscow: Mosk. Gos. Univ., 1978, p. 129.
- Bragg, W. and Claringbull, G.F., Crystal Structures of Minerals, vol. 4 of The Crystalline State, Bragg, W., Ed., London: Bell, 1965.
- 15. Glezer, A.M., Amorphous and Nanocrystalline Structures: Similarities, Dissimilarities, and Mutual Transitions, *Ross. Khim. Zh.*, 2002, vol. 46, no. 5, pp. 57–63.