Structural Investigation of Ground Dickite by X-ray Radial Distribution Function Analysis

Hojin Ryu, Kazumasa Sugiyama*, Fumio Saito* and Yoshio Waseda*

Division of Inorg. Mater., Korea Research Institute of Chemical Tech., Taejon 305-606, Korea
*Institute for Advanced Mater. Processing, Tohoku Univ., Sendai 980, Japan
(Received May 12, 1995)

A structural analysis of dickite prepared by dry grinding with different grinding time has been made by X-ray diffraction. The SiO_4 tetrahedra are found to remain unchanged in the ground dickite samples by analysing the radial distribution function (RDF). On the other hand, with an increase of the grinding time a change in oxygen coordination number around aluminum has been quantitatively confirmed. This variation may be attributed to the change of hydroxyl induced by the prolonged grinding.

Key words : RDF, Dickite, Disordered structure, Mechanochemistry

I. Introduction

R ecently the structural changes of various inorganic substances induced by a usual grinding technique have received much attention from the viewpoints not only of the better understanding of the mechanochemical effects but also of the relatively new method for producing several interesting materials.[1,2] In these regards, the structural behavior of various minerals relevant to the mechanical grinding process has been extensively studied, including their transformations and solid state reactions.[3]

Clay minerals, which are often used as raw materials for various ceramic products, are known to display strong mechanochemical effects and easily change from crystalline to noncrystalline state where they are subject to a long time grinding. In particular, kaolin minerals were reported to show pronounced mechanochemical effects.[4-6] However, their structural changes induced by grinding have not been fully elucidated yet, although some spectroscopic data were available.[6] This has led to an increasing demand for direct determination of the fundamental local ordering unit structure of ground kaolin minerals. In this study, we investigate the structure of dickite [$Al_2Si_2O_5(OH)_4$] with different times of grinding by applying radial distribution function analysis to measured X-ray scattering intensities, as commonly used for structural study of disordered systems such as liquids and glasses.

II. Experimental

A dickite sample used in this study was taken from Syokozan Mine of the Okayama Prefecture in Japan. The bulk dickite sample was firstly crushed in a stainless steel mortar and pestle for 60 minutes to obtain a powdered sample under 100 μm in size. A preliminary X-ray diffraction analysis indicates that the diffraction pattern of this powdered dickite agrees with the result compiled in the JCPDS card No. 19-770 and no significant structural change was detected at the stage of sample preparation. A further grinding experiments were carried out by a planetary mill equipped with a mill pot made of stainless steel. Stainless steel balls of 16 mm diameter were employed as grinding media. The powdered dickite samples of 3.5 g and the balls were charged in the mill pot and then ground under several dry atmospheric conditions with the duration of 30, 60, 120 and 240 minutes. Soapy feel of the starting powdered samples changed into rough feel with increment of the grinding time. This change happens commonly in prolonged grinding of clay minerals and suggests the aggregation of the ground fine minerals and a subsequent increase in particle size.[4,7] In addition, the color of the ground dickite samples, on the whole, changed slightly to black, indicating some contamination from stainless steel pot and balls.

X-ray diffraction profiles for the ground dickite samples were measured using *Mo Kα* radiation with a singly-bent pyrolytic graphite monochromator in a diffracted beam in the wave vector Q range from 5~150 nm^{-1}. Here, $Q=4\pi\sin\theta/\lambda$ where θ is the one half of the angle between incident and diffracted beams and λ is the wavelength of incident beam. After applying corrections for absorption, polarization, and Compton scattering[8] to the measured intensity data,[9] the X-ray scattering intensities were converted into electron units by the generalized Krogh-Moe-Norman method[10] with the density measured by the Archimedes method with toluene, and then the interference function i(Q) was obtained. In this work, observed intensity data at Q less than 5 nm^{-1} were smoothly ex-

trapolated to zero at $Q=0$ nm^{-1}. The effect of this extrapolation or truncation up to $Q=150$ nm^{-1} for the broad profiles observed in disordered system is known to make no critical contribution to the radial distribution function calculated from the interference function by the Fourier transformation.[11]

III. Data Processing

The method for analyzing the X-ray diffraction patterns of disordered systems containing more than one kind of atom is very common and has already been described in detail.[9,12,13] Consequently, only the essential features with a few equations necessary for data analysis are given below.

The electron RDF can be readily estimated by applying Fourier transformation to the interference function in electron units, $i(Q)$, which is directly obtained from experiment as follows;

$$i(Q) = \left[\frac{I_{eu}(Q)}{N} - \sum_{uc} f_j^2 \right] \Big/ f_e^2 \qquad (1)$$

$$RDF_{exp} = 2\pi^2 r \rho_e \sum_{uc} Z_j + \int_0^{Q_{max}} Q_i(Q) e^{-\alpha^2 Q^2} \sin(Qr) dQ \qquad (2)$$

where I_{eu}/N is the intensity of unmodified scattering in electron units per unit of composition, f_j and f_e are the atomic scattering factor and the average scattering factor per electron, respectively. The atomic scattering factors were taken from International Tables for X-ray Crystallography IV and corrected for anomalous dispersion.[14] ρ_e is the average number density of electron and Z_j is the atomic number of j-element. In this study, the chemical composition is considered to be $Al_2O_3 + 2SiO_2 + nH_2O$ and other chemical constituents were ignored. The amount of water molecule, here the number n, were estimated with the successive ignition values obtained from heating of 1423 K. The amount of impurity (metallic Fe) caused by the abrasion of mill pot and grinding media may be of the order 4.0 wt% at most, and its contribution to the X-ray diffraction patterns can be isolated from the halo patterns arising from the ground dickite samples because this crystalline impurity displays sharp Bragg diffraction peaks. The effect of such isolation to the final RDF results should be negligibly small. The term of $exp[-\alpha^2 Q^2]$ is a convergence factor, which is usually introduced to minimize the truncation error and weigh down the uncertainties in larger Q region. However, α is assumed to be zero in the present calculation of the experimental RDF, although this artificial parameter is known not to be critically selected.

On the other hand, the electron RDF can be calculated for particular distances r_{ij} and coordination numbers N_{ij} of i-j pairs using the following equation.

$$RDF_{cal} = \sum_{uc} \sum_i \frac{N_{ij}}{r_{ij}} \int_0^{Q_{max}} \left[\frac{f_i f_j}{f_e^2} e^{-\alpha^2 Q^2} \sin(Qr_{ij}) \sin(Qr) \right] dQ \qquad (3)$$

This equation, using the concept of pair functions, was originally employed by Mozzi and Warren[15] under the name of Pair Function Distribution (PFD). The correlation distance is readily determined from the position of the corresponding peak in the experimental RDF data. In addition, the coordination numbers can be estimated by finding the quantity of N_{ij} which will bring the calculated RDF using Eq. (3) to be best fitted with the experimental RDF. In this process, the value of $\alpha=0.05-0.08$ is employed on the basis of previous studies for various oxide glasses.[16] It should be, however, noted that the present approach by applying Eq. (3) is effective only for a few near-neighbor correlations such as Si-O, Al-O and O-O.

IV. Results and Discussion

Fig. 1 shows the X-ray scattering intensity patterns of the ground dickite samples. The basic intensity profiles of these samples appear to be not closer relation to the original dickite structure than the common disordered structure like glasses. However, a few small spikes are detected at $Q=7$, 14, 19, 24, 41 and 47 nm^{-1} in a sample ground for 30 min. This implies that a small amount of the original dickite structure still remains in the ground sample, although such peaks disappears by further grinding. Fig. 2 shows the reduced interference functions $Qi(Q)$ of the ground dickite samples with variation of the grinding time. The reason for the introduction of the factor Q
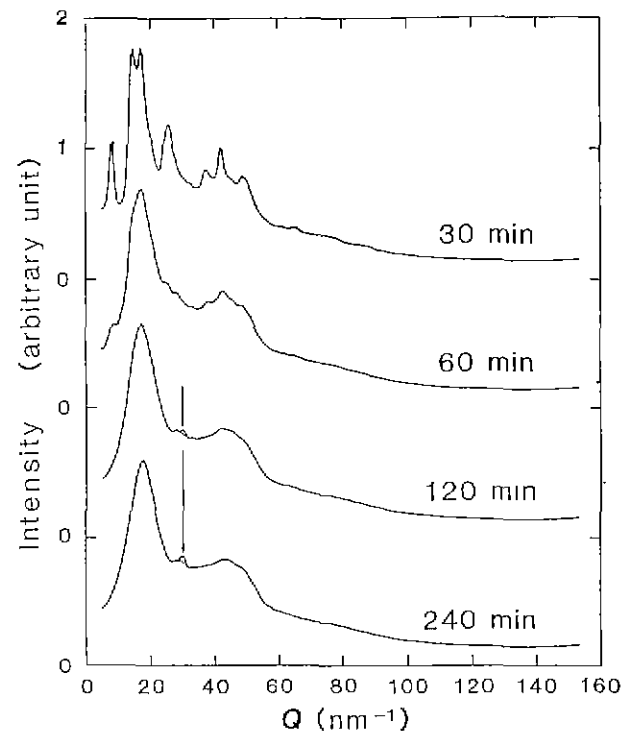

Fig. 1. X-ray scattering intensity patterns of ground dickite samples as a function of the grinding time, obtained by *Mo* *K*α radiation.

is to complement the resolution of the small oscillating behavior observed in the large Q region. The general feature of the reduced interference function Qi(Q) for these samples is very close to those of oxide melt and glasses.[1] These basic profiles observed in the present four samples imply that a considerable fraction of the local ordering unit structures, such as SiO_4 tetrahedra, remains although its distribution appears to be different with the grinding time. It may also be noted that their oscillating behavior slightly differs from the metallic melt and glass cases where the damping behavior of the function Qi(Q) is rapid and monotonic.

The RDFs of the ground dickite samples are shown in Fig. 3, which correspond to the Fourier transform of the Qi(Q) functions in Fig. 2. In this calculation, a few small spikes found in a sample ground for 30 min are included, because the essential profile of Qi(Q) seems to be the one similar to the typical disordered system. The general features of the RDFs are again found to be almost independent on the grinding time, although the damping behavior of RDFs in the larger distance of r has some relevance to the increment of the grinding time. The first peak in the RDFs of all ground samples appears almost completely resolved and the subsequent oscillations are reduced so as to converge to the average number density value at larger values of r. This behavior of RDFs is consistent with the contrast between the narrow distribution of local ordering unit structures and a loss of positional correlation at a few near-neighbor distances away from any starting point. Information of such local ordering unit structures could be obtained by fitting the respective peaks by the pair function method.

Original crystalline dickite is known to have the two-layered structure, in which a sheet of octahedrally coordinated aluminum is linked with tetrahedrally coordinated silicon sheet. For convenience of discussing the
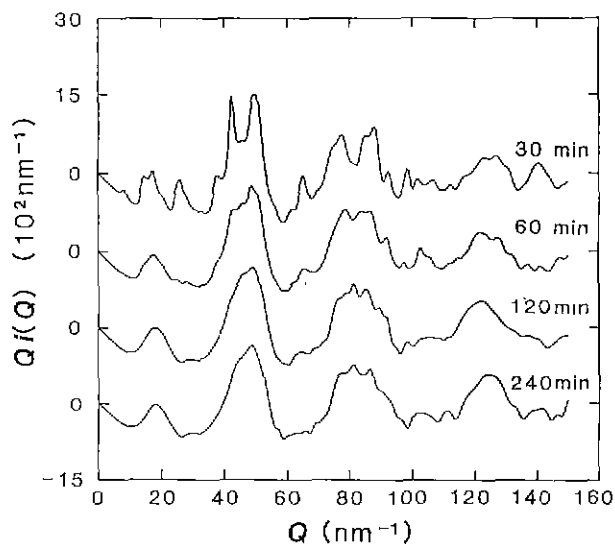
structural features of ground dickite, several interatomic distances in crystalline dickite are calculated and their averaged values are shown in Fig. 3.[17] Taking into account these atomic pairs of crystalline dickite, it is probably reasonable to identify the first peak at around 0.16 nm with both Si-O and Al-O contribution and second one around 0.26 nm with O-O pairs. The peak around 0.32 nm corresponds to the mixed correlation of several atomic pairs such as Si-Si, Si-Al and Al-Al pairs. It is worth mentioning that the first correlation peaks at around 0.16 nm of the sample ground for 30 min shows distinct shoulder at larger r region, and this shoulder disappears with the increment of grinding time. This variation clearly indicates some kind of change in local ordering unit structure is caused by the strong mechanochemical effects, which may be clarified by analyzing experimental RDFs with the pair function method as follows.

Since the resolution of the first peak in RDFs is not good enough to separate two correlations of Si-O and Al-O pairs, the most feasible values for oxygen coordination number were estimated by reproducing the experimental data using the pair function distribution equation. Then, the estimated interatomic distances and coordination numbers of the first three correlations are summarized in Table 1. The dotted lines in Fig. 3 are an example of calculated RDF using the case of the ground dickite for
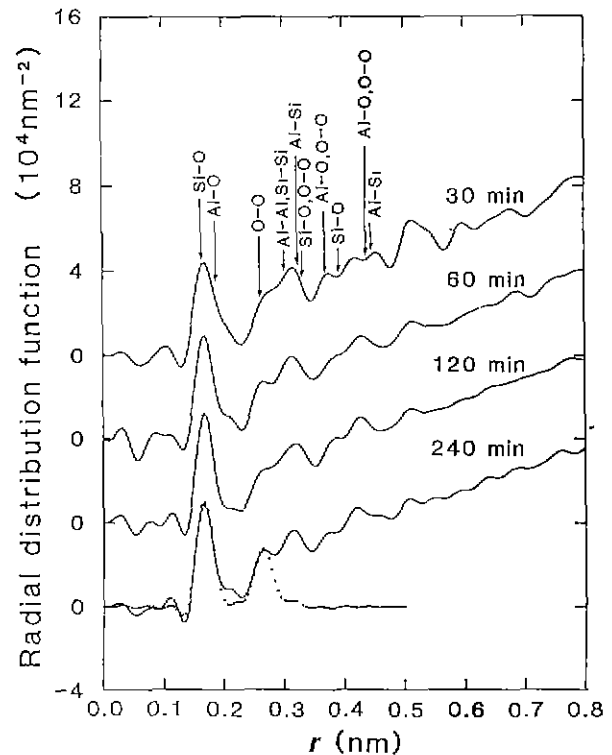
Fig. 3. Electron radial distribution functions (RDFs) for ground dickite samples as a function of grinding time. The solid line is the experimental data and the dotted line is an example of the calculated sum of a few pair functions. The arrows indicate positions of some pairs observed in crystalline dickite.[17]

Fig. 2. Reduced interference function of Qi(Q) of ground dickite samples as a function of grinding time.

Table 1. Comparision of Distance (r) and Coordination Number (N) for the Ground Dickite Samples Determined in this Work. The Variations of r and N are of the order of 0.002 and 0.2, Respectively.

Grinding time (min)	Si-O		Al-O		O-O		Density
	r (nm)	N (atom)	r (nm)	N (atom)	r (nm)	N (atom)	(g/cm^3)
30	0.162	4.0	0.187	4.9	0.266	5.5	2.33
60	0.162	4.0	0.184	4.4	0.265	5.8	2.28
120	0.162	4.0	0.181	4.1	0.266	5.8	2.26
240	0.162	4.0	0.180	4.0	0.266	5.7	2.21

240 min. The number of oxygens around silicon in the present ground dickite samples are confirmed to be four. Thus, the SiO_4 tetrahedra remain unchanged as the local ordering unit structures in the present ground samples. The number of Al-O pairs around Al estimated here decreases with the increment of the grinding time and the interatomic distances follow this change. Therefore, it is plausible to consider that the breakdown of such sheets of coordination polyhedra results in a more loose local structure around aluminum. Dehydration may occur simultaneously, which changes the original $Al(OH)_4O_2$ coordination to AlO_4, as shown in a formation of meta-kaolin by heating.[18] This variation could be well consistent with the results of magic-angle-spinning nuclear magnetic resonance (MAS-NMR), suggesting the development of tetrahedally coordinated aluminum with the progress of grinding.[6] The easy dehydration reaction at relatively low temperature of ground dickite samples detected in TG-DTA analysis, also explicitly indicates the local change around aluminum.

The structural information of the ground dickite samples obtained in this work is insufficient to build up the full structural model of the ground dickite. Nevertheless, the present study could shows that the prolonged dry grinding of crystalline dickite readily induces a structural breakdown, resulting from the change in role of hydroxyl towards the reduction of the oxygen coordination number around aluminum. It would be useful to carry out some further structural studies using energy dispersive X-ray diffraction facility in order to get more precise information on the aluminium distribution and the role of hydroxyl.

Acknowledgements

References

1. H. J. Ryu, E. Kasai and F. Saito, 'Effect of Mixed Grinding of Kaolinite-Gibbsite Mixture on Formation of Mullite," J. Min. & Met. Inst. Japan, Met. Trans., 108[3], 221-226 (1992).

2. H. J. Ryu, E. Kasai, K. Sugiyama and F. Saito, "Effect of Dry Grinding using a Planetary Ball Mill on the Crystal Structure and Superconductivity in the $YBa_2Cu_3O_x$ Ceramics", Proceedings of Fourth International Symposium on Advanced Nuclear Energy Research-Roles and Direction of Materials Science in Nuclear Technology-, Ibaraki, Japan, Feb., 94-99 (1992).

3. S. A. Mishirky and S. Yariv, "Some Effects of Grinding Kaolinite with Calcined Kaolinite," Clay Science, 4, 213-224 (1974).

4. H. Takahashi, 'Effects of Dry Grinding on Kaolin Minerals. I. Kaolinite," Chem. Soc. Japan, 32, 235-245 (1959).

5. H. Takahashi, "Effects of Dry Grinding on Kaolin Minerals. II. Kibushi-clay," Chem. Soc. Japan, 32, 245-251 (1959).

6. H. Kodama, L. S. Kotlyar and J. A. Ripmeester, "Quantification of Crystalline and Noncrystalline Material in Ground Kaolinite by X-ray Powder Diffraction, Infrared, Solid-state Nuclear Magnetic Resonance, and Chemical-dissolution Analyses," Clays & Clay Miner., 37, 364-370 (1989).

7. H. J. Ryu, E. Kasai and F. Saito. "Effect of Mixed Grinding of Kaolinite-Gibbsite Mixture on Formation of Mullite," J. Min. & Met. Inst. Japan, 108[3], 221-226 (1992).

8. D. T. Cromer, 'Compton Scattering Factors for Aspherical Free Atoms," J. Chem. Phys., 50[11], 4857-4859 (1969).

9. Y. Waseda, The Structure of Non-Crystalline Materials, pp. 1-326, McGrew-Hill New York, 1980.

10. C. N. J. Wagner, "Direct Methods for the Determination of Atomic-scale Structure of Amorphous Solids (X-ray, Electron, and Neutron Scattering*)," J. Non-Cryst. Solids, 31, 1-40 (1978).

11. E. Matsubara, Y. Waseda, K. Inomata and S. Hashimoto, "X-ray Structural Study of Ferromagnetic Vitreous $0.5La_{0.7}Sr_{0.3}MnO_3 0.5B_2O_3$," Z. Naturforsch, 44a, 723-725 (1989).

12. E. Matsubara, Y. Waseda, M. Ashizuka and E. Ishida, 'Structural Study of Binary Phosphate Glasses with MgO, ZnO and CaO by X-ray Diffraction," J. Non-Cryst. Solids, 103, 117-124 (1988).

13. B. E. Warren, X-ray Diffraction, pp. 116-151, Addison-Wesley Pub. Co. Massachusetts, 1969.

14. International Tables for X-ray Crystallography Vol. IV, pp. 71-102, Kynoch Press. Birmingham, 1974.

15. R. L. Mozzi and B. E. Warren. "The Structure of Vitreous Silica,' J. Appl. Crystallog., 2, 164-172 (1969).

16. K. Sugiyama, E. Matsubara, I. K. Suh, Y. Waseda and J. M. Toguri, "Determination of the Structural Parameters of Local Ordering in Oxide Melts and Glasses from X-

ray Diffraction Data," *Sci. Rep. Res. Inst. Tohoku Univ.*, **A34**, 143 (1988).

17. P. R. Suitch and R. A. Young, "Atom Positions in Highly Ordered Kaolinite," *Clays & Clay Miner.*, **31**, 357-366 (1983).

18. K. Sugiyama, H. J. Ryu and Y. Waseda, "Local Ordering Structure of Meta-kaolinite and Meta-dickite by the X-ray Radial Distribution Function Analysis," *J. Mater. Sci.*, **28**, 2783-2788 (1993).