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# Study of Grinding Reaction of the System of Fine Particle Silica and Basic Zinc Carbonate by X-Ray Silicon K-Emission Band Spectra[1]

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Usefulness of X-ray emission spectrometry was demonstrated in a study of the grinding reaction of the system of fine particle silica and basic zinc carbonate. Si$K\alpha$ bands of the ground mixtures shifted toward the lower energy side relative to that of the fine particle silica, whearas Si$K\beta$ bands toward the opposite side. These band shifts were regarded as a measure of the reaction progress. The Si$K\beta$ band shift was shown more distinctly than the $K\alpha$ band shift and explained as come from a decrease in the $s$-character of the bond caused by the chemical bonding of the zinc atom with the fine particle silica. The $K\beta$ band shift was also correlated with the destabilization energy relative to the fine particle silica after C. G. Dodd and G. L. Glen. The band shifts indicated that the final product of this grinding reaction was amorphous zinc silicate-like compound. The correspondence of the X-ray band shifts with the infrared spectral shifts was also shown.

Solid structures of materials are distorted by a mechanical treatment such as grinding, rolling, or crushing.[2] This sort of structural distortions gives samples physicochemical activities and, when mixtures of more than two chemicals are subjected to such a mechanical treatment, chemical reactions occur in some cases.[3] The chemical state of each species in the ground mixture is not easily known. It can hardly be measured whether some species become chemically bounded or not.

X-Ray emission and absorption spectra originate in electronic process, so that, to a first approximation, they are not affected by physical states and reflect electronic structures of materials. Many studies have been made of the chemical effects on the X-ray spectra, particularly for third-period elements such as magnesium, aluminum, and silicon.[4] This paper describes an experimental application of X-ray emission spectra to studying amorphous ground mixtures of fine particle silica and basic zinc carbonate. A correspondence of the X-ray method with infrared spectroscopic method is also shown.

## Experimental

*Materials and Grinding Procedure.* Basic zinc carbonate was used in commercial grade. The samples of fine particle silica named Nipsil VN-3, Carplex ♯1120 and Aerosil were obtained from Nihon Silica Co. Ltd., Shionogi Seiyaku Co. Ltd., and Degussa Inc., respectively. Some properties of these kinds of silica were shown in Table 1. Amorphous zinc silicate was obtained from Kantoo Chemical Co., Ltd. Crystalline zinc silicate was prepared by heating amorphous zinc silicate for two hours at 950°C in an electric furnace. A mixture of 3 g of the basic zinc carbonate and 2 g of the fine particle silica was dry-ground in an automatic mortor for a desired time. The grinding process was monitored with the X-ray diffraction diagram of basic zinc carbonate in the ground mixture.

TABLE 1. SOME PROPERTIES OF FINE PARTICLE SILICA

| Fine particle silica | Particle size Å | Specific surface area m$^2$/g | pH |
|---|---|---|---|
| Nipsil VN-3 | 160 | 240 | 6.2 |
| Carplex ♯1120 | 100 | 110 | 10.5 |
| Aerosil | 200 | 200 | 4.0 |

*Apparatus and Measurements.* A Rigakudenki Geigerflex fluorescent X-ray spectrometer equipped with a type D9C constant potential X-ray generator and with a type KG5 goniometer was used for the X-ray emission measurements.

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1) Study on the Grinding Effect on the Mixtures. II. Part I of this series: G. Hashizume and K. Amita, *Kogyo Kagaku Zasshi*, **71**, 1379 (1968).

2) H. Takahashi and K. Tsutsumi, This Bulletin, **40**, 7 (1967); I. Motooka, G. Hashizume, and M. Kobayashi, *J. Phys. Chem.*, **73**, 3012 (1969); I. Motooka, *Dissertation*, Osaka Univ. (1969); G. B. Alexander, *J. Phys. Chem.*, **61**, (1957); H. Takahashi, This Bulletin, **31**, 275 (1958); *ibid.*, 235, 245, 252 (1959).

3) F. M. Acampora, A. S. Tompa, and N. O. Smith, *J. Chem. Phys.*, **24**, 1104 (1956); R. Rasch, *Ber. Deut. Keram. Ges.*, **40**, 635 (1963); G. Hashizume, *Dissertation*, Osaka City Univ. (1963).

4) D. M. Koffman and S. H. Moll, *Advance X-ray Anal.*, **9**, 323 (1966); E. W. White and G. V. Gibbs, *Amer. Mineral.*, **54**, 931 (1969); N. D. Savchenko, P. V. Gel, and V. P. Tsvetkov, *Ukr. Fiz. Zh.*, **15**, 835 (1970); C. G. Dodd and G. L. Glen, *J. Appl. Phys.*, **39**, 5377 (1968); G. Widch, "Soft X-Ray Band Spectra and the Electronic Structure of Metals and Materials," ed. by D. J. Fabian, Academic Press, London and New York (1968); D. W. Fischer and W. L. Baun, *Advance X-Ray Anal.*, **10**, 374 (1966).

The chromium target of Philips PW2164 X-ray tube operated at 50 kV and 40 mA was used for the excitation. The silicon K-emission spectra were analyzed with a flat crystal of EDDT cut for its (020) plane (2$d$=8.808 Å). The detector was a cylindrical gas flow proportional counter with a 2 $\mu$ thick polypropyrene film, where counting gas was a 90% argon-10% methane mixture and a voltage of 1920 V was applied. A pulse height analyzer was used for improving peak-to-background ratios. The X-Ray chamber was kept vacuum of less than $10^{-2}$ mmHg during the measurements. Two Soller collimators were used. Each of the entrance collimator of 100 mm long and the receiving collimator of 30 mm long had a 0.15 mm vane spacing. The band profiles of the silicon K-emission spectra were measured by counting X-ray intensities at every 1/100° (2$\theta$) for $K\alpha$ and 5/100° (2$\theta$) for $K\beta$ band. Instrumental drifts including that by a temperature change were monitored by measuring a standard fine particle silica for every five samples.

The X-ray diffraction diagrams were recorded with a Geigerflex X-ray diffractometer. Nickel-filtered copper $K\alpha$ line excited at 40 kV and 10 mA was used with a scanning speed of 1° (2$\theta$) per min, a divergence slit of 1°, and a receiving slit of 3 mm.

Infrared spectra were measured with a spectrometer type DS-403G (Japan Spectroscopic Co., Ltd.) equipped with grating monochrometers. The ground products were suspended in liquid paraffin and held between two potassium bromide plates for the measurements.

## Results

The X-ray diffraction diagrams of the ground mixtures are shown in Fig. 1 in which diffraction peaks corresponded to those for basic zinc carbonate. The crystalline structure of the basic zinc carbonate seems distorted with an increase of grinding time, and the ground mixture becomes wholly amorphous after about 300 hours' grinding. In the early stages of the grinding treatment, however, the intensities of the diffraction peak at 35.9° (2 $\theta$) increase as shown in Fig. 2. But it is not evident that these changes of the diffraction diagrams are correlated with some grinding reactions. The X-ray diffraction diagrams may not give further information about any grinding reactions.

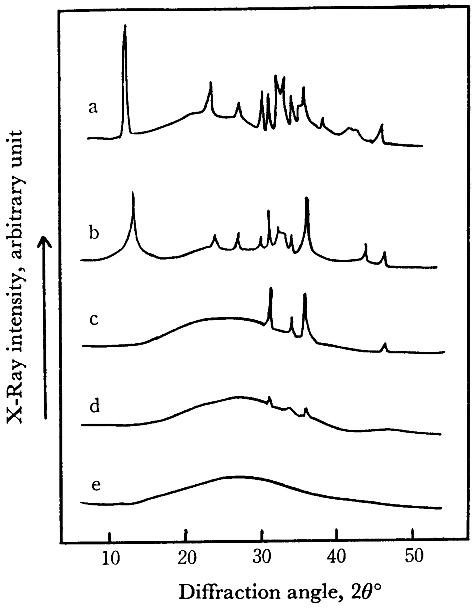

Fig. 1. X-ray diffraction diagrams of the ground mixtures of the fine particle silica and the basic zinc carbonate. Diagrams from a to e correspond to the grinding times for 0, 24, 90, 300, and 600 hr, respectively.

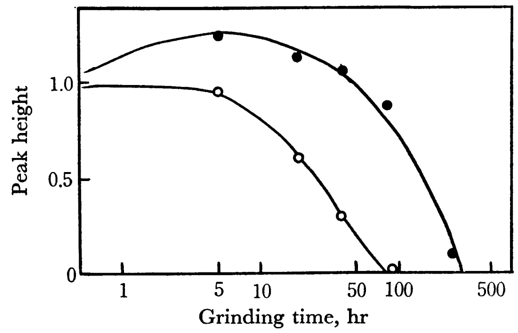

Fig. 2. Variation of diffraction peaks with the grinding time. The peak heights are the relative value to a non-treated mixture of the fine particle silica and the basic zinc carbonate.
●: Peak at 35.9° (2$\theta$)
○: Peak at 12.4° (2$\theta$)

*X-Ray Emission Spectra.* The Si K-emission spectra of the fine particle silica and the zinc silicate are shown in Fig. 3. In these spectra, both the $K\alpha$ and the $K\beta$ bands are normalized in such a way that each maximum is made as taking a uint intensity. When compared with those for the fine particle silica, the $K\alpha$ band of the zinc silicate shifts toward the lower energy side, whearas the $K\beta$ band toward the higher energy side. Any differences among the K-emission spectra of Nipsil VN-3, Aerosil and, Carplex ♯1120 were not observed in this experiment. A satellite band, $K\beta'$, at the lower energy side of the main $K\beta$ band also shifted, but its intensity was too weak to be studied. Although the $K\alpha$ band was also accompanied by some satellite bands, the resolving power of the instrument was not satisfactory and it was difficult to determine their pre-

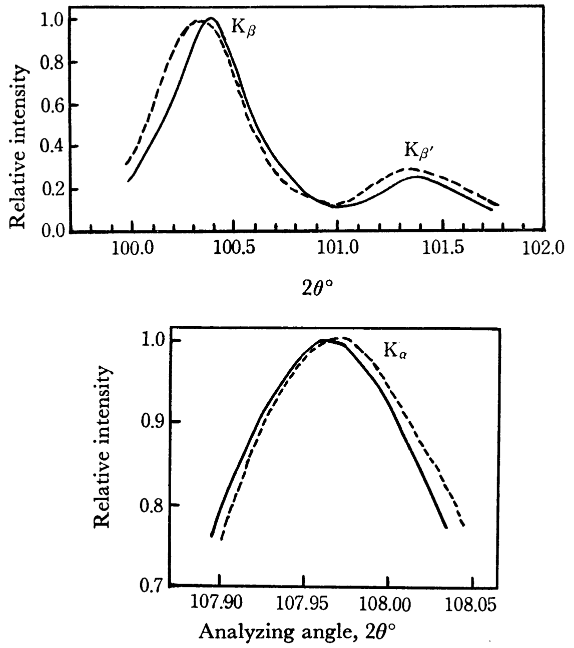

Fig. 3. Silicon K-emission spectra: Solid and dashed lines show spectra of fine particle silica and zinc silicate, respectively. The peak heights are normalized.

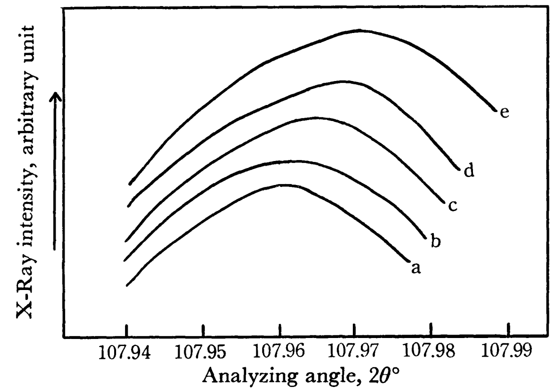

Fig. 4. Variation of Si$K\alpha$ bands of the ground mixtures of the fine particle silica and the basic zinc carbonate with the grinding treatment. Spectra from a to e correspond to the grinding times of 0, 46, 93, 160, and 610 hr, respectively.

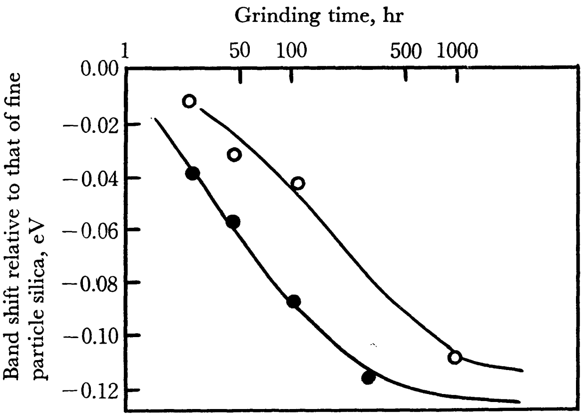

Fig. 5. Si$K\alpha$ band shifts with the grinding treatment
●: System of Nipsil VN-3 or Aerosil and basic zinc carbonate
○: System of Carplex #1120 and basic zinc carbonate

cise band profiles and positions. Therefore, only the main $K\alpha$ and $K\beta$ bands were used for the present study.

The $K\alpha$ bands of the ground mixtures measured at the various stages of the grinding treatment are shown in Fig. 4 in which the peak maxima are illustrated. The shifts of the $K\alpha$ band of the ground mixture from that of the fine particle silica are expressed in electron volts and plotted against the grinding time as shown in Fig. 5. The $K\alpha$ band shifts are not so large that each electron volt value plotted lacks accuracy. However, a distinct difference can be seen in the reactivities of Nipsil VN-3 or Aerosil and Carplex #1120. This fact would become more evident in the measurement of the Si$K\beta$ bands showing relatively large spectral shifts.

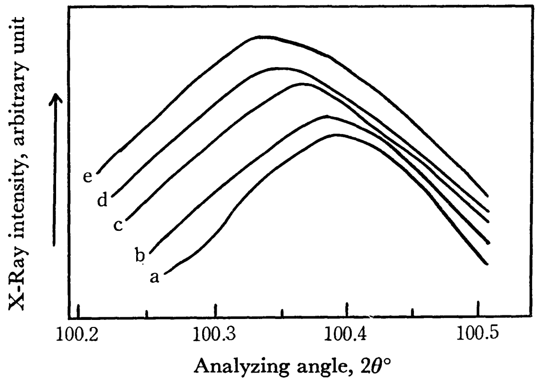

Fig. 6. Variation of Si$K\beta$ bands of the ground mixtures of the fine particle silica and the basic zinc carbonate with the grinding treatment. Spectra from a to e correspond to the grinding time of 0, 46, 93, 160, and 610 hr, respectively.

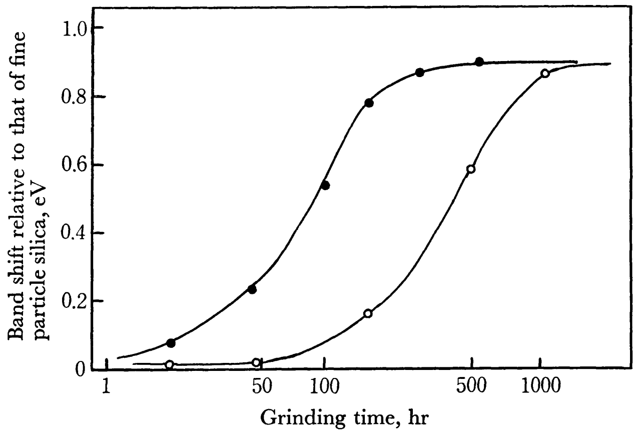

Fig. 7. Si$K\beta$ band shifts with the grinding treatment.
●: System of Nipsil VN-3 or Aerosil and basic zinc carbonate
○: System of Carplex #1120 and basic zinc carbonate

Figure 6 shows the Si$K\beta$ bands of the ground mixtures near the peak maxima measured at the various stages of the grinding treatment. A plot of the spectral shifts against the grinding time is also shown in Fig. 7 in which the $K\beta$ band shifts are increased about one order of magnitude compared with the $K\alpha$ band shifts. Figure 7 indicates that the grinding reaction of Nipsil VN-3 or Aerosil with the basic zinc carbonate proceeds for about 300 hr. Thereafter, the rates of this reaction become very small and finally not appreciable after about 500 hr. On the other hand, Carplex #1120 reacts quite late as the final state is obtained with more than 1,000 hr of the grinding treatment.

*Infrared Spectra.* Infrared spectrometry also provided useful information about the grinding reaction. This is demonstrated in Fig. 8. With increasing the grinding time, the stretching absorption band of Si–O

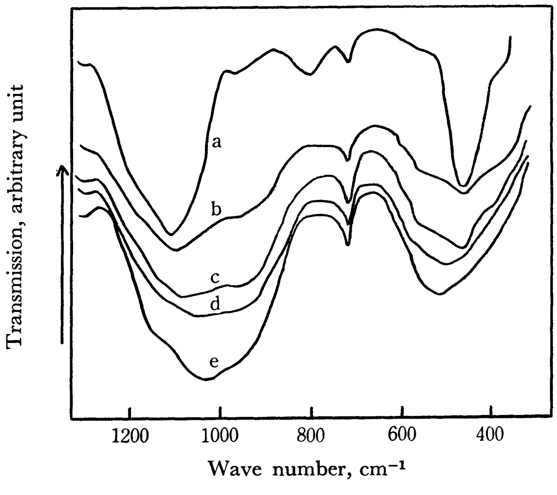

Fig. 8. Infrared spectra of the ground mixtures of the fine particle silica and the basic zinc carbonate. Spectra from a to e correspond to the grinding time of 0, 46, 93, 166, and 610 hr, respectively.

bond shifts toward the lower energy side and the bending one toward the opposite side. Although this figure represents the reaction system of Nipsil VN-3 and the basic zinc carbonate, the same was true for the case of the other samples of the fine particle silica.

## Discussion

White and Gibbs found a correlation between the mean Si–O bond lengths of various silicate minerals and their Si*Kβ* band shifts from the Si*Kβ* band of quartz.[5] They used quartz as a standard sample for the determination of wavelength shifts, whereas fine particle silica was used for the same purpose in the present measurement. However no differences in wavelength of the Si*Kβ* bands were observed between the fine particle silica and quartz in the present measurement, so that values of Si*Kβ* band shifts in their report may be regarded as in the same scale as in the present study.

Thus the variation of the mean Si–O bond length can be correlated with the time of the grinding treatment as shown in Fig. 9, in which their data were adopted in such a way that the linear correlation coefficient should be 0.85.[5] The mean Si–O bond length is also correlated with the mean coordination number of oxygen as reported by Brown and Gibbs.[6] The increase in the oxygen coordination number corresponds to the less *s*-character in a bond as a result of the withdrawal of the electrons on oxygen when zinc atom comes to make a chemical bond with silica.

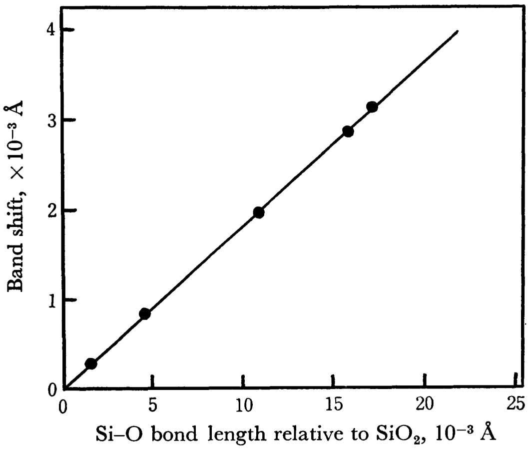

Fig. 9. Relation between Si*Kβ* band shifts and Si–O bond lengths of the ground mixtures of the fine particle silica and the basic zinc carbonate. A correlation coefficient is 0.85 after White and Gibbs.[5]

The situation is also reflected in the infrared absorption spectra, because an increase in the oxygen coordination number causes a variation in O–Si–O bond angle. The bending absorption bands shift toward the higher energy side with increasing the grinding time in Fig. 8. If the zinc atoms are, in fact, chemically bound with the oxygen atoms in silica, the shifts in the infrared absorption bands may be compared with those in the Si*Kβ* X-ray bands. Although the infrared absorption band in Fig. 8 is composed of more than two single bands, its absorption position in wave number was, for convenience, graphically determined as shown in Fig. 10. Figure 11 is a plot of the shifts in the bending absorption bands relative to the fine particle silica against those of the Si*Kβ* bands. A linear relationship is evident between the two spectroscopic measurements. This suggests that these variations in the individual spectrum result from the same chemical effects as mentioned above.

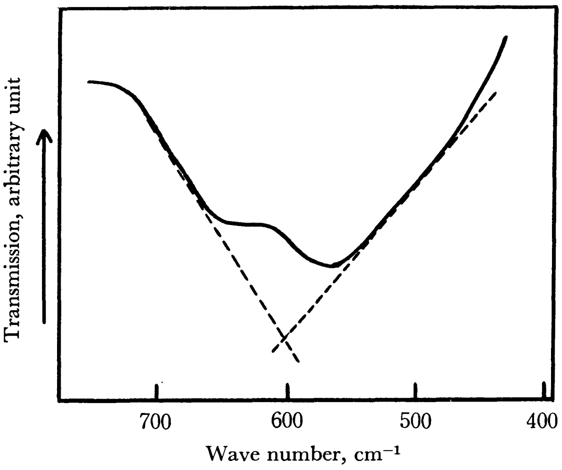

Fig. 10. Graphical method for the determination of infrared band position. Wave number at which two dashed lines intersect is adopted, for convenience, as a band position.

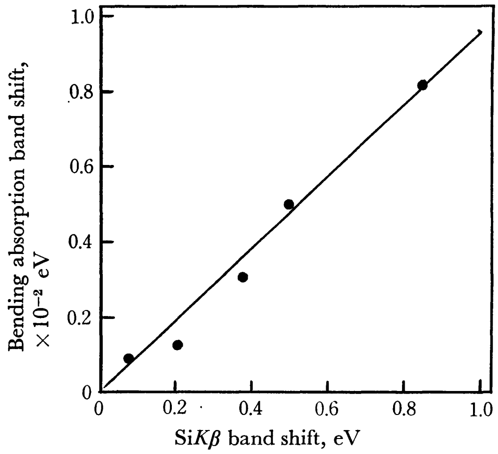

Fig. 11. Relation between X-ray Si*Kβ* band shifts and infrared bending absorption band shifts relative to that of fine particle silica.

Cauchois[7] and Fischer[8] assumed the Si*Kβ* bands of the oxides of magnesium, aluminum, and silicon to be due to the crossover transitions which originate from the anion or oxygen and terminate in the metal ion. Their assumption gives a relatively easy interpretation of the influence of zinc atoms on the Si–O bond. As the zinc atoms come to make chemical bonds with the oxygen atoms which are nearly tetrahedrally coordinated around the silicon atom, the Si–O bond will

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5) E. W. White and G. V. Gibbs, *Amer. Mineral.*, **52**, 985 (1967).

6) G. E. Brown and G. V. Gibbs, *ibid.*, **54**, 1528 (1969).

7) Y. Cauchois, "Soft X-Ray Band Spectra and the Electronic Structure of Metals and Materials," ed. by D. J. Fabian, Academic Press, London and New York (1968).

8) D. W. Fischer, *Advance X-Ray Anal.* **14**, 159 (1970).

become more ionic. This increase in ionic character corresponds to a decrease in the *s*-character of Si–O bond, which causes the Si$K\beta$ bands to shift toward the higher energy side. The interpretation of the $K\alpha$ band shifts are perhaps more complicated because the band shifts are so small that only a slight change in the 1*s* orbital of silicon influences the band shifts.

Table 2. Destabilization of Si–O bond by grinding treatment

| Grinding time hr | Si$K\beta$ band shift[a) ] $-10^{-4}$ Å | Destabilization energy[a)] eV | kcal/mol |
|---|---|---|---|
| 0 | 0 | — | — |
| 19 | 3.0 | 0.08 | 1.8 |
| 46 | 8.4 | 0.23 | 5.3 |
| 93 | 19.7 | 0.54 | 12.4 |
| 160 | 28.6 | 0.78 | 17.9 |
| 280 | 31.5 | 0.86 | 19.8 |
| 610 | 33.0 | 0.90 | 20.7 |
| Amorphous zinc silicate | 33.0 | 0.90 | 20.7 |
| Crystalline zinc silicate | 37.5 | 1.02 | 23.5 |

a) Relative to Nipsil VN-3 or Aerosil

Another estimation was given by Dodd and Glen[9] that the Si–O bond is stable in the structure of α-quartz, the Si$K\beta$ band of which appears in the lowest energy position of all the silicate structures. Thus the Si$K\beta$ band shift of a certain silicate toward the higher energy side from that of α-quartz is a measure of the degree of Si–O bond destabilization relative to the Si–O bond of α-quartz. This estimation is readily accepted as a measure of the grinding reaction process, because it is not difficult to consider that the ground products are in metastable higher energy states in the sense of chemical bonding. The destabilizations of the ground mixtures relative to the fine particle silica were thus calculated from the X-ray shifts in Table 2 together with those of the synthetic amorphous zinc silicate and the crystalline zinc silicate. This table indicates that the final state in the ground product may result in amorphous zinc silicate and further reaction does not occur by the more grinding treatment. This phenomenon discriminates the grinding reaction or, more generally, the mechanical treatment from the ordinary thermal reaction in which the entire rearrangement of each species take place and the final crystalline product is obtained. This is summarized schematically in Fig. 12.

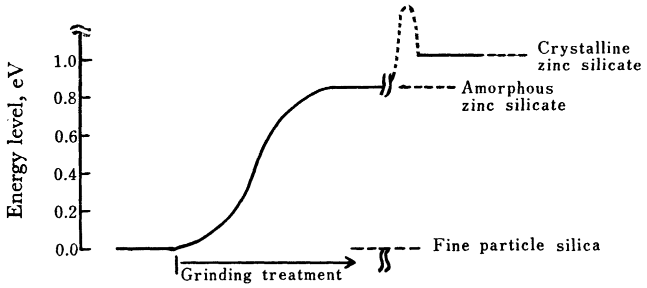

Fig. 12. Schematic illustration of the destabilization of the Si–O bond in fine particle silica.

Table 3. Half width of Si$K\beta$ band of ground mixture

| Grinding time hr | Half width[a)] Å | eV |
|---|---|---|
| 0 | 0.0225 | 6.03 |
| 19 | 0.0250 | 6.79 |
| 46 | 0.0271 | 7.35 |
| 160 | 0.0271 | 7.35 |
| 610 | 0.0281 | 7.62 |
| Amorphous zinc silicate | 0.0278 | 7.54 |
| Crystalline zinc silicate | 0.0263 | 7.15 |

a) The precision of the measured values should be taken as better than two significant figures, although three are reported in this column.

Further information is obtained with the changes of the Si$K\beta$ band width which are shown in Table 3. The half widths of the crystalline and amorphous zinc silicate are broader than that of the fine particle silica. However, the Si$K\beta$ band widths of the ground mixtures rapidly approach to that of the amorphous zinc silicate whose width is broader furthermore than that of the crystalline zinc silicate. It is notable that, even in the early stages of the grinding reaction, considerable band broadening occurs. On the other hand, considerable band shifts can not be seen in these stages as indicated in Fig. 5 and Fig. 7. Thus even in the early stages of the grinding treatment, chemical reaction may occur to a considerable extent, and with increasing the grinding time, the reaction more thoroughly. Hence the grinding reaction in the early stages of the treatment differs merely in the extent and not in the quality from that of the last stage of the treatment. The Si$K\alpha$ bands did not show so distinct a change in the band widths as seen in the $K\beta$ bands.

Roughly speaking, the changes in the X-ray diffraction diagram correspond to the progress in the grinding reaction described by means of Si$K$-emission spectral shifts in the cases of Nipsil VN-3 and Aerosil but not in the case of Carplex ♯1120. The surface acidity is critical to the difference of the reactivities of these three kinds of fine particle silica, as seen from Table 1.

## Conclusion

The X-ray Si$K$ spectra gave useful information about the grinding reaction in which the products are usually amorphous. The $K\beta$ band shifts changed depending on the grinding time which caused the corresponding decrease in the *s*-character in the Si–O bonds. The band shifts indicated that the final product in the reaction between the fine particle silica and the basic zinc carbonate was amorphous zinc silicate-like compound which was in a metastable higher energy state relative to the fine particle silica. The infrared spectra also provided useful information about this reaction but the X-ray spectroscopic method was superior to the former because the latter gave direct reflections of electronic structures.

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[9] C. G. Dodd and G. L. Glen, *Amer. Mineral.*, **54**, 1299 (1969).