Structural change of alkali feldspar by ball milling

Hiromi Nojiri, Masayuki Okuno, Hiroki Okudera, Tomoyuki Mizukami and Shoji Arai

Department of Earth Science, Graduate School of Science and Technology, Kanazawa University, Kanazawa 920-1192, Japan

The structural changes and amorphization of alkali feldspar by ball milling were investigated using X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, Raman spectroscopy, scanning electron microscopy (SEM), thermal analysis, particle size analysis, and specific surface area measurements. The Or77Ab23 alkali feldspar crystal has an Ab-rich lamella texture in Or-rich host crystals. The mean particle size decreased from ~67 μm to almost 3 μm after 50 h of ball milling. After 600 h of ball milling, the apparent mean particle size calculated from the observed particle size distribution increased prominently because of the agglomeration of small particles. It reached ~38 μm after 1200 h of ball milling. While the density variation was not consistent with that of the particle size, it was consistent with that of the crystallinity estimated from X-ray diffraction data. The FTIR and Raman spectra indicated breaking of the Si-O-Si or Al-O-Si bonds and the formation of defects and distortion of the TO4 (T = Si or Al) tetrahedra as a result of the milling. An increase in the intensity of luminescence with milling supported these results. XRD analysis revealed the sample that was ball milled for 1200-h was amorphous. However, the structure and properties of this amorphous phase were different from those of fused feldspar glass and had weak crystalline features. These amorphous materials were similar to those in the fault zone that were formed naturally and experimentally without melting. The Si-OH (or Al-OH) shoulders ν = 890 cm−1 in the FTIR spectra were formed by the chemical reaction between the broken Si-O-Si (or Al-O-Si) bonds and atmospheric water surrounding the 300-h milled samples. Because of this reaction, the surface and interior structure of the milled particles depended on the agglomeration and formation of defects formation resulting from the long milling time. XRD results of the milled samples indicated that grains with a larger amount of Ab-rich lamella structures were downsized more rapidly than the Or-rich host.

Keywords: Alkali feldspar, Lamella, Ball-milling, Structural change, Amorphization

INTRODUCTION

Feldspar is one of the primary rock-forming minerals in the Earth’s crust. Knowledge regarding the milling and deformation processes of feldspar minerals is important to understand the role of amorphous and powder materials in the fault zone (Yund et al., 1990; Ozawa and Takizawa, 2007; Janssen et al., 2010; Reches and Lockner, 2010) and sub-micron materials in the shear zone of the continental crust (Okuno and Willaime, 1985; Shigematsu et al., 2004; Fukuda et al., 2012). Janssen et al. (2010) found amorphous materials in core samples at the San Andreas Fault Observatory at Depth (SAOD), and this amorphous material was formed by comminution without melting and acted as a lubrication layer in the San Andreas Fault. Reches and Lockner (2010) reported that fine-grained rock powder lubrication plays an important role in fault weakening and earthquake instability. Okuno and Willaime (1985) investigated experimentally deformed sanidine crystals, analyzed the relationship between the deformations and slip systems, and also found sub-micron crystals in the shear zone. Shigematsu et al. (2004) and Fukuda et al. (2012) reported fine-grained feldspars of granitoid mylonite. Shigematsu et al. (2004) discovered that microvoids coalesce in fine-grained plagioclase layers, leading to the formation of a crush zone.

On the other hand, there have been many experimental grinding studies that have investigated structural and physical property changes of various minerals such as quartz, feldspar, kaolinite, and pyrophyllite. Sugiyama et al. (1994a, 1994b) investigated the amorphization of gibbsite, kaolinite, and pyrophyllite by mechanical grinding using X-ray radial distribution function analysis and reported that the SiO4 tetrahedra remain unchanged in both kaolinite and pyrophyllite. Sanches et al. (2004) reported amorphization and agglomeration during milling of anorthoclase; they also investigated recrystallization of
fine ground anorthoclase particles with consolidation by sintering. Kitatani (2003) investigated the structural changes of albite, anorthite, and sanidine by ball milling. He concluded that the small size and lower quantity of the crystalline phases remain even after extended milling based on the observed X-ray diffraction (XRD) profiles and Fourier transform infrared (FTIR) spectra.

The structural change and amorphization of feldspar minerals resulting from meteoritic impact have also been studied extensively (Stöffler and Hornemann, 1972; Fritz et al., 2005).

Although there have been many studies on the milling of silicate minerals, details on the amorphous phase and the grinding processes of feldspar minerals have not been reported. Moreover, the results of milling experiments were not examined in relation to amorphous materials in fault zones. Therefore, the main purposes of this work are to provide precise information on structural changes, including the amorphization process in alkali feldspar by ball milling and the nanoscale structure of the amorphous phase using various analytical techniques, and to demonstrate similarities of our results with those of previous works.

**EXPERIMENTAL**

**Starting sample**

Single crystals of alkali feldspar with perthite lamella texture collected from India were used for the ball-milling experiments.

The average chemical composition [(K; 0.759, Na; 0.220), Al; 1.037, Si; 2.820, O; 8.000] was determined using a wavelength-dispersive X-ray fluorescent (XRF) spectrometer (Rigaku, System 3270). Standard samples from the Geological Survey of Japan, AIST, were used in this analysis, which showed that the alkali feldspar sample had an approximate composition of Or$_{77}$Ab$_{23}$. This sample showed distinctive cleavage at $\{001\}$ and consisted of pinkish and gray semi-transparent segments. The scanning electron microscope (SEM) image (Fig. 1) of the (001) plane of this sample shows a small lamella structure belonging to stringlet or string-type lamella identified by previous classification (Smith, 1974). On the other hand, we also measured Raman spectra from two different parts of the sample (Fig. 2). The Raman spectra from the gray and white regions of the SEM image were similar to those of low-albite and orthoclase, respectively (Freeman et al., 2008).

![Figure 1. SEM image of alkali feldspar sample with perthite lamella; deep gray regions correspond to Ab-rich feldspar and light gray regions correspond to Or-rich feldspar.](image1)

![Figure 2. Raman spectra of deep gray and light gray regions of the starting sample.](image2)

**Ball milling and SEM observation**

The alkali feldspar sample was coarsely milled using an agate mortar to obtain a starting powder (hereafter referred to as the 0-h sample). Extended milling was performed in a 1000-mL alumina ball-milling vessel. 150 g of air-dried starting powder and 1600 g of 20-mm diameter zirconia balls were placed in the alumina vessel and ground (100 rpm) under atmospheric conditions at room temperature for 1200 h. Approximately 1-g specimens were collected after 1, 2, 5, 10, 50, 150, 300, 600, and 1200 h of milling (hereafter referred to as the 1-h milled sample, 2-h milled sample, 5-h milled sample, and so on). The observed wear rate of the alumina ball mill, re-
ported by the manufacturer (Nikkato Ltd., Japan), was under 0.03 ppm/h. Therefore, contamination from the alumina vessel and zirconia ball did not have any distinct effect on this study. The 1200-h milled sample was heat treated at 200, 300, 400, 500, and 1000 °C to analyze the relaxation process. A scanning electron microscope (JEOL, JSM-5200 LV) was used to observe the microstructures of the milled samples at an accelerating voltage of 15 kV.

**Particle size measurement**

The particle size distribution and mean particle size of the milled alkali feldspar samples were measured using a laser-diffraction particle-size analyzer (Horiba, LA 920) with a 632.8 nm He-Ne laser. The particle diameter was in the range of 0.03–1000 µm. The mean particle size is denoted by \( D_{50} \), which represents 50% of the integrated particle size distribution.

**Surface area and density measurements**

The specific surface areas of the milled alkali feldspar samples were determined using the Brunauer-Emmett-Teller (BET) method with \( \text{N}_2 \) gas (Quantachrome, Quantasorb QS-11). The densities of the milled samples were measured at room temperature with a 5 cm\(^3\) pycnometer (SOGO LABORATORY GLASS WORKS CO.LTD).

**Thermal analysis**

Thermogravimetric (TG) measurements were conducted on 10 mg of the 1200-h milled sample at up to 1100 °C, using a differential thermal balance (Rigaku, Thermoplus TG 8120) at a heating rate of 10 °C/min. The temperature was held at 1100 °C for 1 h before cooling. \( \text{Al}_2\text{O}_3 \) powder was used as a standard reference.

**X-ray diffraction analysis**

XRD measurements were performed using an X-ray powder diffractometer (Rigaku, RINT 2200) with monochromated CuK\( \alpha \) radiation. Measurements were performed for fixed periods of 10 s with the step scanning method in 0.02° increments in the range 2\( \theta \) = 2–90°. The acceleration voltage and current were 40 kV and 30 mA, respectively.

**Fourier transform infrared (FTIR) spectroscopy**

The milled powder samples and the heat-treated powder samples were mixed with spectroscopic-grade KBr and pressed into 3.0-mm diameter discs for transmission infrared spectroscopic measurements. FTIR absorption spectra were measured using a spectrometer (JASCO, FT-IR 610V) with a ceramic source and a triglycine sulfate (TGS) detector in the range of \( \nu = 400-4000 \) cm\(^{-1}\) at a spectral resolution of 4 cm\(^{-1}\), with 100 scans collected for each sample.

**Raman spectroscopy**

Raman spectra of the milled feldspar specimens were measured using a Raman microspectrometer (Horiba-Jobin Yvon, Lab RAM HR-800), with excitation using the \( \nu = 514.05 \) nm line (green) of an \( \text{Ar}^+ \) laser. The Raman scattered light was collected in the 180° scattering geometry. Spectra were accumulated in the range of \( \nu = 200-3000 \) cm\(^{-1}\) with a resolution of 0.5 cm\(^{-1}\) and a collection time of \( 2 \times 10 \) s.

**RESULTS**

**Particle size and surface area**

The observed particle size distributions of the milled feldspars are shown in Figure 3a. The \( D_{50} \) variation of the

![Figure 3](image-url). Change in particle size distribution and mean particle size \( (D_{50}) \). (a) Particle size distribution of milled feldspar samples. (b) Mean particle size \( (D_{50}) \) of the milled feldspar samples as a function of milling time.
milled feldspars as a function of milling time is shown in Figure 3b. The mean particle size decreased rapidly during the first 5 h of milling. Between 5 and 50 h, the particle size decreased slowly with milling time; it was almost constant (~3 μm) from 50 to 600 h. However, after 1200 h of milling, the particle size distribution exhibited two maxima around 20 and 100 μm, and the mean particle size increased to approximately 38 μm. The variation of specific surface areas of the milled feldspars is shown in Figure 4. The surface area increased rapidly during the first 5 h of milling, and then increased between 5 and 150 h. After over 150 h of milling, the specific surface area became almost constant at approximately 11 m$^2$/g.

**Density measurement**

The densities of the milled feldspars are shown in Figure 5. The density decreased from 2.58 to 2.47 Mg/m$^3$ after 150 h of milling. After 300 h, the density remained almost constant at 2.39–2.41 Mg/m$^3$. The estimated error

---

**Figure 4.** Specific surface area of milled feldspar samples as a function of milling time.

**Figure 5.** Density of milled feldspar samples as a function of milling time.

**Figure 6.** SEM images of milled feldspar samples.
was ±0.1 Mg/cm³.

SEM observations

SEM images of the milled samples are shown in Figure 6. They indicate particle size reduction followed by particle agglomeration to diameters of approximately several micrometers with milling. The samples milled for the 150-h, 600-h, and 1200-h samples included sub-micron particles.

Thermal analysis

The TG profile of the sample milled for 1200 h is shown in Figure 7. Continuous weight loss (~0.16 mg/100°C, ~8% of total loss) was observed up to 500 °C and almost no weight loss was observed between 500 °C and 1100 °C.

XRD analysis

XRD patterns of the milled feldspars are shown in Figure 8a. The XRD pattern of the 0-h sample consisted of some peak shapes that were significantly different from those for the 10-h milled sample. This difference may be explained as follows. Prior to milling (0 h), the mean particle size was quite large (~70 μm in diameter) and the particle size distribution was wide (approximately 0.5–100 μm). Therefore, the 0-h sample might have included large crystal particles. On the other hand, the samples milled for 10 h and more were well ground and had similar patterns without intensity spikes and broadening of peaks. Therefore, the peak intensities decreased and the background intensity increased smoothly with milling time. After 1200 h of milling, the intensities of the originally sharp diffraction peaks for the feldspar crystal were reduced, leaving only a broad halo pattern centered at approximately 2θ = 27.0°. Enlarged XRD patterns of samples in the 2θ range of 27.4–28.6° are shown in Figure 8b. Precise analysis of these XRD profiles revealed that the 002 and 040 diffraction peaks were located at almost the same 2θ position for each milled sample and appeared to be a single peak. This peak could be resolved as diffractions from the Or-rich and Ab-rich portions of each sample. The peak intensity of XRD profiles from the region with the Ab-rich lamella decreased more rapidly with milling than that of the Or-rich host.
FTIR spectra

FTIR spectra of the milled alkali feldspar and that of fused alkali feldspar glass in the wavenumber range of \( \nu = 400-4000 \text{ cm}^{-1} \) are shown in Figure 9. Absorption bands of the 0-h sample were observed at \( \nu = 1145, 1110, 1051, 1010, 768, 728, 648, 585, 538, 467, \) and 428 cm\(^{-1}\). According to the results of Iishi et al. (1971), these bands were assigned as follows. The bands at \( \nu = 1145 \) and 1110 cm\(^{-1}\), and at \( \nu = 1051 \) and 1010 cm\(^{-1}\) were assigned to Si-O and Al-O stretching vibrations, respectively. The bands at \( \nu = 768 \) and 728 cm\(^{-1}\) were assigned to Si-Si and Al-Si stretching vibrations, respectively. The bands at \( \nu = 648 \) and 585 cm\(^{-1}\) were assigned to O-Si-O and O-Al-O bending vibrations, and those at \( \nu = 538 \) and 467 cm\(^{-1}\) were assigned to coupling between O-Si-O deformation and K-O stretching vibrations. The band at \( \nu = 428 \) cm\(^{-1}\) was assigned to Si-O-Si deformation.

The absorption bands became lower and broader with milling time, especially above 600 h where broadening of the bands was significant. The spectrum of the sample milled for 1200 h indicated an amorphous state.

The prominent absorption around \( \nu = 900-1600 \text{ cm}^{-1} \) for the 0-h sample had two maxima at approximately \( \nu = 1050 \) and 1145 cm\(^{-1}\). The absorbance maximum at \( \nu = 1145 \) cm\(^{-1}\) decreased with milling. The width of this intense band also decreased rapidly up through 150 h of milling. Above 600 h of milling, this band became just a shoulder. The intensity of the Si-Si and Si-Al stretching bands around \( \nu = 700-800 \text{ cm}^{-1} \) decreased significantly after milling for 150 and 300 h.

On the other hand, for samples that were milled for 300 h or longer, a new band was observed at approximately \( \nu = 890 \text{ cm}^{-1} \), which could be assigned to Si-OH or Al-OH vibration (Wood et al., 1983). The intensity of this band became larger with milling time. The FTIR spectra of the milled samples also showed a small band at around 1600 cm\(^{-1}\) and a broad band at around 3500 cm\(^{-1}\).

The FTIR spectra of the 1200-h milled samples that were then heat treated at 200, 300, 400, 500, and 1000 °C are shown in Figure 10. The Si(Al)-OH stretching band at around \( \nu = 890 \text{ cm}^{-1} \) disappeared with heat treatment at 500 °C. The band intensities at around 1650 cm\(^{-1}\) and 3500 cm\(^{-1}\) also decreased. However, weak intensity remained in the spectra even for the sample that was heat treated at 1000 °C.

Raman spectra

Raman spectra of the milled alkali feldspar are shown in Figure 11. The spectra of the powder samples were similar to that of orthoclase (Freeman et al., 2008). The spectrum of the 1200-h milled sample could not be observed...
Structural change of alkali feldspar by ball milling clearly owing to intense luminescence. According to the results of Freeman et al. (2008), the observed Raman bands were assigned as follows. The Raman bands in the $\nu = 450$–520 cm$^{-1}$ region belonged to the breathing modes of the four-membered rings of the TO$_4$ (T = Al or Si) tetrahedra. The bands below $\nu = 400$ cm$^{-1}$ corresponded to the rotational/translational modes of the four-membered rings and cage/shear modes, respectively. The Raman bands in the $\nu = 700$–900 cm$^{-1}$ region were assigned to the deformation modes of the TO$_4$ tetrahedra. Bands in the $\nu = 900$–1200 cm$^{-1}$ region were assigned to the vibrational stretching modes of the TO$_4$ tetrahedra. The Raman band attributed to Si(Al)-OH at around $\nu = 900$ cm$^{-1}$ could not be detected clearly.

All band intensities decreased and their shapes broadened with milling time. The variations of the Raman band intensities in the $\nu = 400$–1200 cm$^{-1}$ region as a function of milling time are shown in Figure 12a. The intensities of the $\nu = 447$ cm$^{-1}$, 469 cm$^{-1}$, and 507 cm$^{-1}$ bands decreased significantly after 600 h of milling and were very weak in the 1200-h milled sample. However, the intensity of bands at higher wavenumbers decreased more slowly than those with low wavenumbers (Fig. 12b). For example, the band intensity at $\nu = 1120$ cm$^{-1}$ was detectable, even after 1200-h of milling. On the other hand, the intensities of the bands around $\nu = 400$–520 cm$^{-1}$ decreased more rapidly. The bands around $\nu = 450$–520 cm$^{-1}$ were related to medium-range structures such as the tetrahedral network and the ring structure of the tetrahedra, whereas the bands around $\nu = 1000$–1200 cm$^{-1}$ are related to medium-range structures such as the tetrahedral network and the ring structure of the tetrahedra, whereas the bands around $\nu = 1000$–1200 cm$^{-1}$
were related to the vibration in a tetrahedron or between neighboring tetrahedra. The sample milled for 1200 h showed no clear Raman spectrum owing to strong luminescence. The intensities of luminescence were estimated based on observed intensities at $\nu = 2000 \text{ cm}^{-1}$, which increased with milling time (Fig. 13).

**DISCUSSION**

**Variation of particle size and surface area with milling**

The mean particle size decreased to $\sim 3 \mu m$ after 50 h of milling and then became almost constant with further milling for up to 600 h. Kanda (2006) reported that a large amount of energy was required for further reduction of particle size owing to the increase in surface energy with particle size reduction during mechanical milling. In this study, the particle size distributions and SEM images of the milled samples suggested that the milled small particles formed large agglomerates after more than the 600 h of milling. This was why the apparent mean particle size first decreased and then increased to $\sim 36 \mu m$ after 1200 h of milling. It was also the reason for the significant change in the particle size distribution, with two maxima centered around 20 $\mu m$ and 100 $\mu m$. On the other hand, the results of TG measurements and the FTIR spectrum for the 1200-h milled sample indicated that the well milled sample absorbed water in the form of Si(Al)-OH as well as water molecules. Therefore, we conclude that agglomeration was accelerated because of the large surface energy of the fine particles and the absorbed water. Generally, particles with extremely high surface energy tend to agglomerate to reduce their surface energy. For example, similar agglomeration was also reported in milling experiments of antigorite and fused silica (Bishop et al., 2008; Iwao et al., 2010). On the other hand, the specific area of the milled sample became almost constant after 150 h of milling; our results also showed an initial decrease followed by a prominent increase in apparent particle size by agglomeration after 600 h of milling.

In contrast, the density became almost constant after 300 h of milling, indicating that the density decreased even after the surface area reached a maximum value. The transition of the crystals to an amorphous state by milling was probably responsible for this density decrease. We will discuss this amorphization in detail in the next section.

**Structural change and amorphization by milling**

We examined the decrease in peak intensities and the broadening of the peak profiles with milling time in the XRD patterns (Fig. 8a). The XRD pattern of the 1200-h milled sample had almost no crystalline peaks, indicating that the alkali feldspar was almost totally transformed into the amorphous phase by the 1200-h milling process. Sánchez et al. (2004) also studied the effect of grinding on feldspar and obtained an almost amorphous phase after only 2 h of grinding using a planetary ball mill. Although their results suggest that the planetary ball mill is more effective for grinding, their 1-h and 2-h grinding samples showed distinctive iron contamination. In our study, in order to investigate in detail the amorphization process of alkali feldspar with milling, the proportion of the crystalline peak area with respect to the total profile area was calculated in the 2$\theta$ range of 10–60°. The crystalline peak area was estimated by subtracting the background area from the total profile area (Shimoda et al., 2004); this value is defined as the crystallinity (Fig. 14). The crystallinity decreased abruptly after 10 h of milling and then decreased gradually with further milling to almost zero at 1200 h. This variation in crystallinity indicated that the alkali feldspar was gradually transformed to the amorphous phase by over 10 h of milling. The trend was similar to that for the density, which suggests that the density variation was also dependent on amorphization by milling.

The density of the 1200-h milled sample ($\sim 2.39 \text{ Mg/m}^3$) was similar to that of shock-induced (38 GPa) orthoclase glass [2.40 $\text{ Mg/m}^3$; Okuno (2003)], which is larger than that of fused orthoclase glass [2.36 $\text{ Mg/m}^3$; Okuno (2003)]. Shock-induced feldspar glass has some properties in common with feldspar crystal, such as en-
thalpy (Geisinger et al., 1986); therefore, the 1200-h milled sample could also have properties that were similar to those of shock-induced feldspar glass. On the other hand, the position of a broad halo pattern centered at approximately 2θ = 27.0° was larger than that observed for fused alkali feldspar glass (2θ = 24.6°). This diffraction peak of the amorphous phase is called as the First Sharp Diffraction Peak (FSDP). We calculated the value $q_1 (= 4\pi \sin \theta /\lambda)$ from the position of the FSDP; from $q_1$, the mean cell distance ($d_m = 2\pi /q_1$) was calculated. Tan and Ardnt (1999) showed a linear relationship between the SiO$_2$ glass density and $q_1$; they also reported the value of $d_m$ may be related to the size of the intermediate-order structure of SiO$_2$ glass such as the four- or six-membered rings of SiO$_4$ tetrahedra. The calculated $q_1$ and $d_m$ values (1.904 and 3.298, respectively) of the 1200-h milled sample were larger and smaller than those (1.780 and 3.530, respectively) of fused alkali feldspar glass, respectively, which might be an indication that the 1200-h sample had an amorphous-like structure with small rings of TO$_4$ tetrahedra such as a 4-membered ring, which is the basic unit of the feldspar structure. These facts are consistent with the structural difference of the 1200-h sample and fused glass as well as structural preservation of the crystalline phase in the sample.

The SEM image of the non-milled sample (Fig. 1) and the Raman microspectra (Fig. 2) showed an Ab-rich lamella texture in this alkaline feldspar. The peak intensity of the XRD profile from the Ab-rich lamella segment decreased more rapidly than the Or-rich host (Fig. 8b), suggesting that the milling energy was probably concentrated at the Ab-rich lamella and was down-sized rapidly. However, the mechanism of energy concentration was unclear. Also, the thickness of the Ab-rich lamella was on the micrometer scale, therefore Ab-rich lamella crystals were easily milled to a powder with micrometer dimensions. Kitatani (2003) reported structural change of albite and sanidine by mechanical milling, whose variations in crystallinities with milling were similar; he also observed similar variations in their FTIR spectra. His results support ours on the effect of the lamella structure on milling behavior.

Sugiyama et al. (1994a) investigated amorphization of kaolinite and pyrophyllite via mechanical grinding by analyzing their X-ray radial distribution functions. They reported that the SiO$_4$ tetrahedra remain unchanged during the amorphization process. However, they did not report the structural changes and amorphization in detail. Through X-ray radial distribution function analysis alone, it might have been difficult to discuss the molecular structure and its changes with milling. Therefore, it is important for us to analyze the structural change and amorphization of alkali feldspar resulting from milling with FTIR and Raman spectroscopic data as well as X-ray diffraction data.

As it is difficult to analyze milling-induced changes in molecular structure using powder X-ray diffraction, we will focus our discussion in this section on structural change and amorphization based on FTIR and Raman spectroscopic data. The observed sharpening of the FTIR band around $\nu = 900-1600$ cm$^{-1}$ as a result of milling might be a direct indication of the breakdown of Si-O-Si and Al-O-Si linkages on the surface of particles, which corresponded to the reduction in particle size, because this breakdown might have caused a decrease in the strain of the TO$_4$ tetrahedra. This was also consistent with the intensity decrease of the absorption bands of Si-Si and Al-Si around $\nu = 700-800$ cm$^{-1}$. However, the position of the band at $\nu = 1050$ cm$^{-1}$ did not change distinctly with milling, indicating that milling did not change the T-O distance, which was consistent with the X-ray radial distribution analysis results of ground kaolinite previously reported by Sugiyama (1994a).

We also observed an additional FTIR band at about $\nu = 890$ cm$^{-1}$ as a shoulder band in the samples that were milled for 300-1200 h. The formation of this shoulder band could be explained by the chemical reaction between the broken Si(Al)-O-Si bonds and atmospheric water (Matsuoka, 2006; Bishop et al., 2008). This band was located at a lower wavenumber than the Si-OH band ($\nu = 900$ cm$^{-1}$; Wood et al., 1989) and may include contributions from Al-OH. The intensity of this band for the 1200-h milled sample decreased after heat treatment and completely disappeared after treatment at 500 °C, which suggests that this band was due to surface and internal T-OH bonds. The intensities of the bands at $\nu = 1650$ and 3500 cm$^{-1}$ were also decreased by heat treatment, but the bands remained even after heating at 500 °C. The internal and surface water molecules were also responsible for these absorption bands. They might also explain the trends of TG curves as follows. The ~ 6% decrease in the 1200-h sample’s weight at room temperature to its value after heat treatment at 300 °C might have been caused by molecular water; the ~ 2% decrease between heat treatments at 300 °C and 500 °C might have been caused by the T-OH group. The residual intensities of the samples treated at 500 °C and 1000 °C might have been due to molecular water absorbed after heat treatment.

The sample milled for 1200 h showed no sharp absorption band in Figure 9, indicating that it had a random structure such as that of amorphous matter. However, the spectrum showed some differences compared to that of fused glass. For example, the position of the T-O stretching band for the 1200-h milled sample ($\nu = 1035$ cm$^{-1}$)
was higher than that of fused glass (about $v = 1008 \text{ cm}^{-1}$) and the bandwidth was smaller. These facts suggest that the 1200-h milled sample might have retained some features of the feldspar structure such as four-membered rings of TO$_4$ tetrahedra, which was consistent with the observed density and FSDP position data of this sample, as described earlier.

The wave number-dependent variation of the Raman intensity can be explained as follows. The bands under $v = 450$-500 cm$^{-1}$ were related to long- and medium-range structures such as the tetrahedral network and the large ring structure of the tetrahedra, whereas the bands around $v = 1000$-1200 cm$^{-1}$ were related to the vibration in a tetrahedron or between neighboring tetrahedra. Therefore, this variation in intensity suggests that large-scale structures such as the high-membered rings of TO$_4$ tetrahedra in the feldspar structure were more easily broken than smaller structural units. These variations of Raman intensity (Fig. 12a) were consistent with the variation of crystallinity estimated from the XRD data. The intensity variation of the band at $v = 1000$-1200 cm$^{-1}$ (Fig. 12b) indicated that molecules such as TO$_4$ tetrahedra were not broken easily. This result was consistent with the results for ground kaolinite and pyrophyllite shown by Sugiyama (1994a). They also reported that the SiO$_2$ tetrahedra remained unchanged in grinding experiments.

On the other hand, the variation of the luminescence intensity with milling time (Fig. 13) was similar to that for the crystallinity with milling time, suggesting that the luminescence originated from defects, such as dislocations in small particles formed by milling (Leoni et al., 2004), in addition to dangling bonds at grain surfaces (Pizani et al., 2008). This type of high luminescence was observed in ground SiO$_2$ glass (Pizani et al., 2008; Iwao et al., 2010).

The results obtained in this study provide important information to understand the feldspar formation process without melting, the physical properties of amorphous materials in the fault zone (Ozawa and Takizawa, 2007; Janssen et al., 2010), and fault weakening and earthquake instability by powder lubrication (Reches and Lockner) because the experimental slip velocity of 10-60 mm/s (Reches and Lockner) was approximately consistent with the ball–milling experiment. The results may also indicate a possibility that the small ground crystals in the shear zone that were found in experimentally deformed sanidine (Okuno and Willaime; 1985) have low density and characteristics of the amorphous state.

**CONCLUSIONS**

The structural changes in ball-milled alkali feldspar with Ab-rich perthite lamella were investigated using XRD measurements, FTIR spectroscopy, and Raman spectroscopy. The structural changes and amorphization of alkali feldspar as a result of ball milling are summarized as follows.

The mean particle size decreased to ~3 μm after the samples were milled for 50 h and then became almost constant. However, after 1200 h of milling, the particle size increased by agglomeration. The surface area of the milled samples became constant after 150 h of milling. These changes with milling preceded those of the particle density. However, the crystallinity of the milled samples determined from the XRD data revealed a variation similar to that of the density. Therefore, the change in density with milling is considered to be dependent on the crystallinity and distortion of the structure, as well as the particle size.

The intensity of the XRD peaks decreased with milling, although the peak patterns and positions were similar up to 600 h of milling. The principle FTIR and Raman spectral features also showed changes that were similar to those observed in the XRD patterns. The alkali feldspar crystal transformed completely to the amorphous state after 1200 h of milling. However, the density of the 1200-h milled sample (2.39 M g/m$^3$) was larger than that of fused glass [(2.36 M g/m$^3$; Okuno (2003)]. The FTIR spectrum of the 1200-h milled sample showed some differences from that of fused glass and some similarities to that of the alkali feldspar crystal, which indicate that the 1200-h milled sample might have some properties similar to those of the crystalline feldspar phase. These results provide important information to aid the understanding of the feldspar formation process without melting, the physical properties of amorphous materials in the fault zone, and the small ground crystals in the shear zone. Precise analysis of the XRD patterns indicated that the intensity of Ab-rich lamella particles decreased more rapidly by milling than that of the Or-rich host, which might be due to the micrometer-order size and shape of the Ab-rich feldspar lamella.

The Si(Al)-OH FTIR absorption shoulder ($v = 890$ cm$^{-1}$) was formed by the chemical reaction between the broken Si(Al)-O-Si bonds and atmospheric water for the samples that were milled for over 300 h. This reaction band caused for surface and interior of milled particles. In addition, samples milled for over 10 h showed distinct water absorption bands around $v = 1500$ and 3500 cm$^{-1}$, and the intensity of these bands increased with milling.
ACKNOWLEDGMENTS

We would like to thank Professor M. Kawano and the reviewer for their insightful and constructive comments. The authors would like to give special thanks to Dr. J. Muto of Tohoku University for assisting with SEM imaging, Dr. K. Koizumi of Society of Gem & Precious Metal for the wavelength-dispersive XRF measurements, Dr. T. Ishiguro of Toyama Industrial Technology Center for specific surface area measurements, and Mr. N. Sasaki of the Industrial Research Institute of Ishikawa Prefecture for particle size measurements.

REFERENCES


Manuscript received November 22, 2012
Manuscript accepted July 4, 2013
Published online September 27, 2013
Manuscript handled by Motoharu Kawano