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Shock-induced transformation of sillimanite powders

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Shock recovery experiments were performed on sillimanite powders ($\leqslant 40\,\mu$m). Exposure of the material to high dynamic pressures revealed characteristic phase transformations. X-ray patterns showed the formation of a small amount of corundum (α-Al_2O_3) and infrared spectra indicated the formation of long-range disordered Al_2O_3 and SiO_2. No mullite was formed upon shock. The occurrence of long-range disordered Al_2O_3 and SiO_2 may be attributed to shock compression and pressure release expansion. The transformation process is favoured by the high shock temperatures.

1. Introduction

The aluminium silicates kyanite, andalusite, and sillimanite are valuable raw materials for the ceramic and refractory industries. Upon annealing, these transform into an equimolar mixture of mullite and silica. The latter phase appears X-ray amorphous (andalusite and sillimanite) or as cristobalite (kyanite).

Previous studies on the behaviour of andalusite single crystals and andalusite and kyanite powders being exposed to shock waves suggest that andalusite undergoes transformation into X-ray amorphous Al_2O_3 and SiO_2 at pressures above 300 kbar [1, 2]. No experimental studies on shocked kyanite and sillimanite single crystals are yet available. Stöffler [3] investigated shocked sillimanites of a garnet sillimanite schist from a suevite breccia from the Ries crater, Germany. Investigations on the shock behaviour of andalusite and kyanite powders were recently performed. The shocked andalusite powders undergo partial transformation into X-ray amorphous Al_2O_3 plus SiO_2 and into mullite. Neither X-ray patterns nor infrared spectra of the shocked kyanites yielded any evidence of possible high pressure or high temperature reaction [2].

The structures of kyanite, andalusite, sillimanite and mullite are characterized by chains of aluminum oxygen octahedra running parallel to the *c*-axis. There is a close structural relationship between andalusite–mullite and sillimanite–mullite. Relationships are more complicated between kyanite and mullite. It has been expected that the shock-induced deformation and transformation of minerals is highly structure controlled [4, 5]. The comparison of the shock behaviour of kyanite, andalusite, and sillimanite is therefore of interest for the interpretation of reaction mechanisms.

2. Experimental procedure

2.1. Sample

Yellow-brownish, dense, polycrystalline sillimanite material from Harcajuelo de la Sierra, Madrid, Spain was used for the experiments.

The X-ray phase determination showed that the material contained a small amount of muscovite. The same result could be deduced from the relatively high K_2O content (1.36 wt%) of the sample (Table I). The sillimanite raw material was ground in a tungsten carbide mill to a grain size fraction $\leqslant 40\,\mu$m. For pressure experiments the mineral powder was pressed into discs having a diameter of 13 mm and a thickness of 3 mm (see [2]).

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TABLE I Chemical composition of the sillimanite samples (wt %)

Sample	Measured values	Calculated values
SiO_2	38.61	37.08
Al_2O_3	58.17	62.92
TiO_2	0.06	–
Fe_2O_3	0.64	–
CaO	0.06	–
MgO	0.28	–
Na_2O	0.06	–
K_2O	1.36	–
Total	99.24	–

2.2. Shock experiments

Details on the shock experiments have recently been published (see Schneider *et al.* [2]). It has to be pointed out that the given pressures were those in armco steel at the boundary between the sample container and the sample (Table II, see [2]). The actual peak pressures in the samples were considerably lower.

2.3. Annealing of samples

The heating experiments on the shocked and unshocked sillimanite powders were carried out at 1400° C, the annealing time being 60 min in each case. The samples were immediately exposed to the annealing temperatures and quenched to room conditions after 60 min.

2.4. Methods of investigation

2.4.1. X-ray phase analysis

All samples were checked for phase transformations by means of X-ray powder diffractometry. A quantitative determination of mullite turned out to be difficult because of the close structural similarity between sillimanite and mullite, the small amount of the sample material available and the strong shock-induced line broadening of the X-ray reflections. However, the maxima of the diffraction bands include 1 2 0 and 2 1 0 reflections of sillimanite and mullite centre between the respective peaks of both aluminium silicates in a sillimanite–mullite phase mixture. Therefore, the angle separations $\Delta = 2\theta_{120} - 2\theta_{210}$ should give rough values for the extent of the high-temperature reaction.

TABLE II Shock experiments on sillimanite powders

Experiment number	Peak pressure in Armco steel container (container shock pressure) (kbar)
1	280
2	380
3	460
4	540
5	620

Explosive: composition B (TNT/Hexagen = 40/60)

2.4.2. Chemical analysis

The chemical bulk analysis of the sillimanite raw material was carried out with an X-ray fluorescence spectrometer.

2.4.3. Infrared spectroscopy

Infrared spectra were recorded from shocked and unshocked samples and also from the heat-treated material in a wavenumber range from 4000 to 250 cm^{-1}. Details of the preparation techniques are given in Schneider *et al.* [2].

2.4.4. Scanning electron microscopy

Scanning electron microscopic pictures were taken from 2 shocked sillimanite powders.

3. Results

3.1. Shock-induced phase transformations

No phase transformation could be detected either by means of X-ray diffraction techniques or by infrared spectroscopy up to a container shock pressure of about 380 kbar. Infrared spectra taken from samples submitted to container shock pressures $\geqslant$ 380 kbar show new broad absorption bands near 1075 and 470 cm^{-1} (Fig. 1). The intensity of these bands increases with the degree of shock loading. The bands centred at 1075 and 470 cm^{-1} can be assigned to Si–O stretching and O–Si–O angle deformation of an X-ray amorphous SiO_2 phase. The amount of silica phase is much higher than would result from simple thermal decomposition of sillimanite to mullite plus silica. This might be explained by the conclusion that "free" long-range disordered SiO_2 was formed during the shock process. Phases enriched with Al_2O_3 must occur if SiO_2 is a shock decomposition product. The following reaction is supposed to take place during shock loading: sillimanite → aluminum oxide + silica.

Some more observations may account for this suggestion: The spectrum of the "620 kbar" sample leached with HF solution (Fig. 1) is very similar to that of unshocked sillimanite. However, there are some important differences, especially

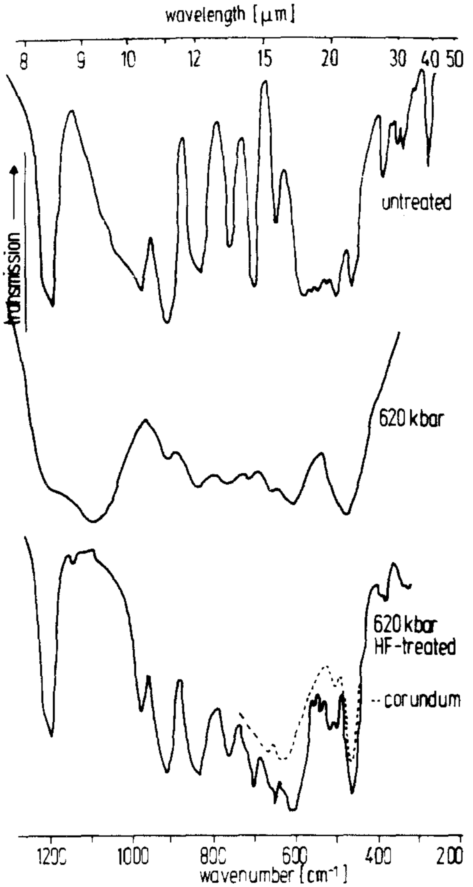

Figure 1 Infrared transmission curves of unshocked and shocked sillimanite powders. The HF treated sample contains only sillimanite and corundum and no long-range disordered Al_2O_3 or SiO_2 phases. The pressures are those calculated for the steel container.

in the range 600 to 400 cm^{-1}. In this region, untreated sillimanite is characterized by a broad and strong absorption group with peaks centred at 490 and 455 cm^{-1}. The HF treated "620 kbar" sillimanite has a prominent band at 452 cm^{-1} and some peaks of low intensity at about 490 and 600 cm^{-1}. Probably these differences can be attributed to the presence of a small amount of corundum in the shocked sample (Fig. 1). X-ray patterns of the "620 kbar" and of the HF treated "620 kbar" samples stress the formation of α-Al_2O_3.

Furthermore, previous experimental studies on the shock-induced transformation of andalusite powders [2] and single crystals [1] support the hypothesis of a shock-produced decomposition of sillimanite to aluminium oxide plus silica. The data for naturally shocked sillimanite from gneisses of the Ries crater, Germany, published by Stöffler [3] can be interpreted in an analogous way.

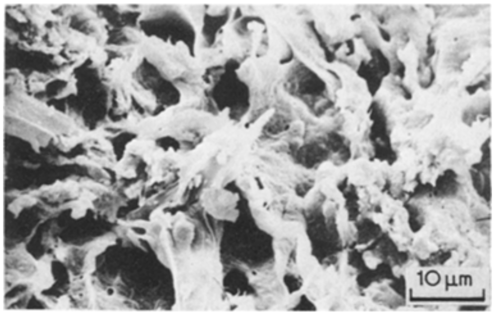

Figure 2 Scanning electron micrograph of sillimanite powder shock-loaded up to 380 kbar. The shock pressure refers to the value calculated for the steel container.

Stereo electron micrographs show that part of the material must have been in a plastic state during the shock event at high pressures. At "380 kbar", separate aggregates of sillimanite are still visible (Fig. 2), whereas at "620 kbar" the material forms a compact but porous "cake" (Fig. 3).

3.2. Thermal behaviour of the samples

An estimation of the extent of the mullite formation was carried out by means of the angle separation $\Delta = 2\theta_{210} - 2\theta_{120}$ (see above). In Table III values of shocked and unshocked sillimanites and of corresponding samples annealed at 1400° C are listed. Apparently, the data of the shocked but not heat-treated powders only slightly decrease indicating no significant transformation of sillimanite to mullite plus silica. This interpretation is reinforced by the infrared pattern of the HF treated "620 kbar" sample which shows the typical features of sillimanite (Fig. 1). On the other hand, there is a clear decrease in Δ-values

Figure 3 Scanning electron micrograph of sillimanite powder shock-loaded up to 620 kbar. The shock pressure refers to the value calculated for the steel container.

TABLE III Angle separation $\Delta = 2\theta_{210} - 2\theta_{120}$ of unshocked and shocked samples annealed at different temperatures

Container shock pressure (kbar)	Not annealed	Annealed at 1400° C
unshocked	0.391	0.340
280	0.375	0.270
380	0.338	0.285
460	0.354	0.215
540	0.331	0.179
620	nd	0.163

Reference material: $\Delta = 0.16$ sillimanite heat treated 180 min at 1600° C

nd = not determined, the shock pressures are those calculated for the steel container (see Table II)

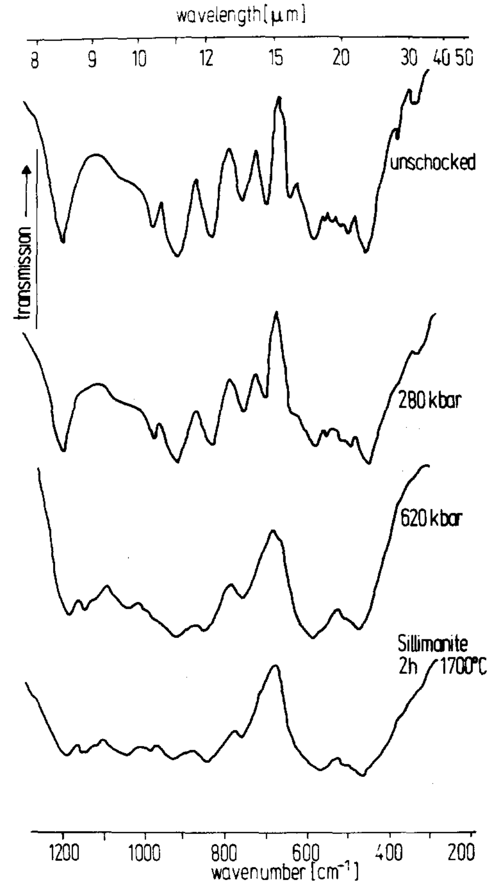

Figure 4 Infrared transmission curves of some shock-loaded sillimanite powders. The samples were subsequently annealed for 60 min to 1400° C. The shock pressure refers to the value calculated for the steel container. The last curve (sillimanite, 2 h, 1700° C) is made from an unshocked reference sample.

of the heat-treated samples with the degree of shock loading. The decrease of angle separation values Δ has to be correlated to an increasing decomposition of sillimanite to mullite plus silica. Infrared patterns of the shocked and later on heat-treated samples yielded a continuous change from sillimanite ("280 kbar" sample) to mullite ("620 kbar" sample). In an earlier paper Stöffler [3] suggested that "... the infrared absorption behaviour leads to the conclusion that the long-range order of sillimanite is highly disturbed by shock ... and a transformation of this phase into mullite ... may be achieved at unusually low temperatures". It could possibly be concluded that the activation energy of the high temperature transformation of sillimanite into mullite is lowered due to shock produced lattice defects. Moreover, part of the mullite may be formed by the reaction between SiO_2 and Al_2O_3, both being products of the shock event (see also [2]).

4. Conclusion

Essentially the same conclusions may be drawn from recent investigations on sillimanite as from previous studies on andalusite powders: sillimanite powders submitted to high dynamic pressure decompose to long-range disordered Al_2O_3, and long-range disordered SiO_2. Hugoniot-data on andalusite and sillimanite and on SiO_2 and Al_2O_3 [6, 7] (Fig. 5) suggest that both aluminium silicates disproportionate into stishovite plus corundum at shock pressures above 700 kbar. Shock recovery experiments on andalusite single crystals [1] and on andalusite [2] and sillimanite powders (this investigation) yielded a transformation into Al_2O_3 plus SiO_2 at considerably lower shock pressures.

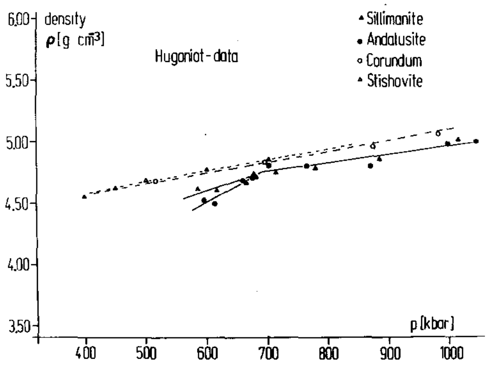

Figure 5 Hugoniot curves of an adalusite, sillimanite, corundum and stishovite in a density versus pressure plot (after Birch [6]).

In a previous paper on the shock behaviour of andalusite single crystals this discrepancy was explained by a partial decomposition of andalusite into γ-Al_2O_3 plus six-coordinated SiO_2 between ~ 360 and 550 kbar (stage I), complete transformation of andalusite into an isochemical mixture of α-Al_2O_3, γ-Al_2O_3 and SiO_2 between ~ 550 and 700 kbar (stage II), and the formation of the high pressure phases corundum and stishovite above ~ 700 kbar (stage III, [1]). The stishovite type SiO_2 phase probably being present under shock compression, decomposes into a long-range disordered material upon pressure release.

No mullite can be detected in samples recovered from shock loading. The absence of mullite must not in each case be interpreted as caused by low temperatures. A reason might be the K_2O content (1.36 wt %) in the sillimanite sample being much higher than in the andalusite (0.04 wt %) and kyanite samples (0.03 wt %) investigated [2]. Extended alkali content can prevent the formation of mullite in favour of a decomposition into corundum and a silica melt [8]. For kyanite, this has been demonstrated by Saalfeld [9]. A heat-induced decomposition of sillimanite into corundum plus silica has also been described by Gypesova and Durovic [10]. The intensive "sintering" of the material as observed on scanning electron micrographs may account for relatively high shock temperatures.

In our previous study on andalusite we suggested that the occurrence of long-range disordered Al_2O_3 and SiO_2 should mainly be attributed to shock compression and pressure release expansion, and not to a temperature effect. It is an interesting observation that the shock transformation of andalusite and sillimanite powders takes place at relatively low pressures, especially if it is taken into account that the "sample pressure" must be much lower than the "container pressure" which we always have to refer on (see above). We suppose that the shock temperatures being high in porous materials may make possible a surmounting of the activation energy of the reactions under consideration at lower peak pressures, than in the case of the single crystal. High temperatures may also accelerate the reaction kinetics. As a consequence, the overdrive of reaction conditions [1, 11] may decrease.

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