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Shock-induced transformations of andalusite and kyanite powders

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Exposure of andalusite and kyanite powders ($\leqslant 40\,\mu$m) to high dynamic pressures revealed a strongly different behaviour of the two materials against shock. While experiments on andalusite powders yielded characteristic shock-induced phase transformations, kyanite powders did not show any phase change upon release from shock compression. X-ray patterns and infra-red spectra proved the formation of 3/2-mullite from andalusite, and infra-red spectra also indicated the formation of long-range-disordered Al_2O_3 and SiO_2. While the formation of mullite must be associated with high (shock) temperatures, the formation of the $Al_2O_3 + SiO_2$ oxide mixture may be a (shock) pressure effect. The lack of temperature-induced transformations in kyanite may be explained by the lower porosity of the sample tablets as compared to those of andalusite. The absence of high-pressure transformations in kyanite is most probably due to its dense structure which is more resistant to shock waves than the more open andalusite structure.

1. Introduction

In the system Al_2O_3–SiO_2 the following four alumosilicate phases are known to exist: andalusite, kyanite, sillimanite, all of composition $Al_2SiO_5 = Al_2O_3 \cdot SiO_2$, and mullite, varying in composition from $2Al_2O_3 \cdot SiO_2$ (2/1-mullite) to $3Al_2O_3 \cdot 2SiO_2$ (3/2-mullite). Mullite of composition $Al_2O_3 \cdot SiO_2$ (1/1-mullite) has also been reported [1, 2], but its existence has not yet been definitely proved. At sufficiently high temperatures any of the Al_2SiO_5 phases transforms into a mixture of 3/2 mullite and SiO_2 (e.g. [3]).

Single crystals of andalusite, when exposed to shock waves creating dynamic pressures in excess of about 300 kbar (the method of pressure determination is given in Section 2.2), undergo transformation into X-ray amorphous γ-Al_2O_3 and SiO_2. The X-ray amorphous SiO_2 is believed to be a pressure release product of stishovite, the assumption being that stishovite is produced along with γ-Al_2O_3 when andalusite disproportionates upon shock compression [4]. A comparable reaction occurs when powdered samples of kyanite are subjected to static pressures of 160 kbar at temperatures near 1000° C [5].

This paper is concerned with possible phase transformations in powdered samples of andalusite and kyanite when subjected to dynamic pressures up to 620 kbar. Analogous experiments with powdered samples of sillimanite are in progress. Although the effect of experimentally produced shock waves on a variety of metallic and nonmetallic powders has been studied during the last few years ([6–9] and others), data on the shock behaviour of powdered alumosilicates are still scarce [10]. Powdered samples are expected to

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behave differently from single crystals, since their porosity has the effect of lowering the peak pressures and considerably increasing the peak temperatures [11].

Structural imperfections and diminution of grain size due to the shock process are the subject of further investigations and will not be considered in this paper.

2. Experimental details

2.1. Samples

Reddish brown andalusite crystals from Glomel (Côtes du Nord, France) were used for the investigation. This is the same material which is used as raw material by the refractory industry. The kyanite crystals, bluish-gray in colour, came from Minas Gerais (Brazil).

Quantitative X-ray phase analyses of the two samples showed that the only detectable impurity, quartz, was present in a concentration of less than 1 wt %. The chemical analyses are given in Table I. The andalusites and kyanites used for the high-pressure experiments were ground in a tungsten carbide mill to a grain size fraction of less than 40 μm and then pressed into discs having a diameter of 13 mm and a thickness of 3 mm.

2.2. Shock experiments

Details of the shock apparatus are given in Fig. 1. The experimental procedure is very similar of that used in single crystal experiments [12–14]: a flyer plate, accelerated by the detonation of high-explosive material, impacts the steel sample container. At the surface of the steel container a shock wave is produced which propagates through the container. Shock pressures are determined by means of the so-called pin method which measures free surface velocities. At the boundary between steel and mineral the shock wave splits into two independent waves, due to the different shock-wave resistances of the materials. After having travelled through the sample, the shock wave is reflected into the compressed andalusite or kyanite material at the near boundary between sample and steel container. At this moment the rarefaction wave travelling behind the shock wave has reached the sample, and therefore the reflected wave does not cause a pressure increase in the sample. The reflection of the shock wave back into the sample causes a considerable extension of the pressure pulse and a slow-down of the pressure release.

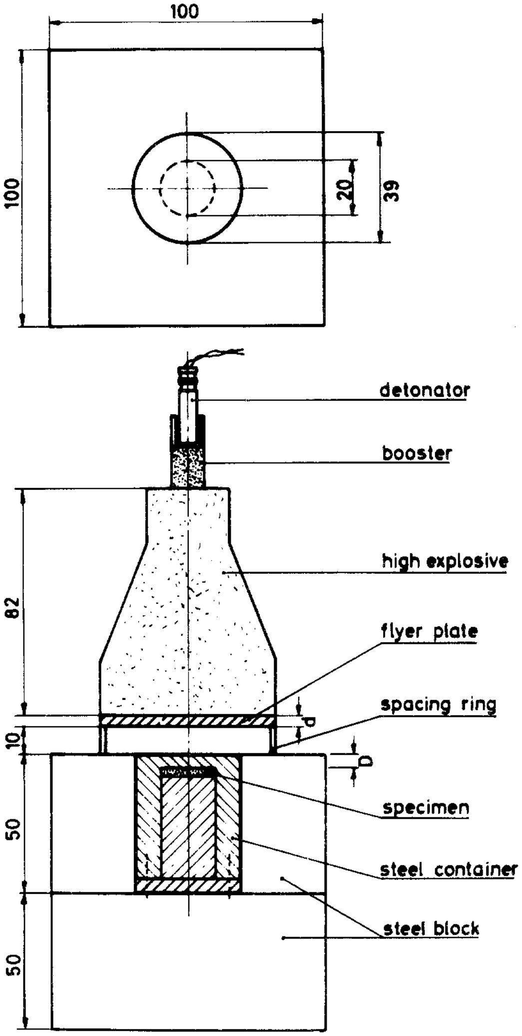

Figure 1 Shock recovery arrangement for mineral powders: plan and elevation. All dimensions in millimetres.

TABLE I Chemical composition of the alumosilicates used in the experimental studies (wt %)

	kyanite	andalusite
SiO_2	37.29	37.86
Al_2O_3	62.41	61.34
TiO_2	–	0.09
Fe_2O_3	0.19	0.46
CaO	–	0.02
MgO	0.04	0.10
Na_2O	0.04	0.04
K_2O	0.03	0.09

The peak pressures in the mineral itself can, in principle, be determined with the impedance method [15], using the Hugoniot curves of the container and sample materials. For kyanite, no Hugoniot data have as yet been published, and for andalusite such data are available only for single crystals and pressures ranging from 600 to

TABLE II Shock experiments

No. of shock experiment	Mineral involved	Peak pressure in Armco steel container [kbar]
1	kyanite	380
2	kyanite	465
3	kyanite	590
4	andalusite	280
5	andalusite	380
6	andalusite	465
7	andalusite	620

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

1200 kbar [16]. An equation has been published which would allow extrapolation of the Hugoniot curve for single crystal andalusite to lower pressures, [17], and there is also an equation for calculating pressures in porous material when the pressures in the corresponding single crystal are given. Since the extrapolation method does not take into account the phase transformation which probably occurs in the region of extrapolation [4], reliable results cannot be expected from this procedure. We therefore refrain from making such calculations. All pressures which are quoted in this paper in connection with the powdered andalusite and kyanite samples are pressures in Armco steel at the boundary between steel container and sample. The shock experiments are summarized in Table II.

2.3. Annealing of shocked and unshocked samples

The annealing experiments of the shocked and unshocked powders were performed in the hot zone of a voltage stabilized rhodium furnace. The temperatures were measured with a Pt–Pt/Rh(90/10) thermocouple to an accuracy of about ± 12° C. The following high-temperature runs were carried out: 1180, 1230, 1300, 1360, 1400 and 1435° C, the annealing time being 60 min in each case. The samples were immediately exposed to the annealing temperatures and were quenched to room temperature at the end of the experiments.

2.4. Methods of analysis

2.4.1. Chemical analysis

Chemical analyses of the samples were performed with an X-ray fluorescence spectrometer (Rigaku 3064 Dataflex).

2.4.2. X-ray phase analysis

All samples were checked for possible phase transformations by means of a recording X-ray powder diffractometer (Philips PW 1060). The amount of mullite was determined quantitatively by comparing the relative X-ray line intensities of andalusite and mullite in the samples with the corresponding intensity ratios obtained from standards which had been prepared by admixing the pure components in known proportions. For both andalusite and mullite the integrated intensities of the (1 2 0)–(2 1 0) double peaks were taken.

2.4.3. Infra-red phase analysis

Infra-red spectra (from 4000 to 200 cm^{-1}) were recorded on a Beckman spectrometer model 4250 in order to determine both crystalline and X-ray amorphous compounds formed by the shock process. About 2 mg of the sample was finely powdered together with about 200 mg RbI and the resulting mixture was pressed into pellets of 13 mm diameter at a pressure of 7 kbar. RbI was chosen because of its extended transmission range as compared to KBr or KI.

2.4.4. Scanning electron microscopy

Scanning electron microscopic studies of the shock-loaded powder samples were carried out on a Cambridge Stereoscan S 600 instrument.

3. Results

3.1. Shock-induced phase transformations

3.1.1. Andalusite

For samples shocked with pressures up to 280 kbar, the X-ray patterns and the infra-red spectra do not show any changes which can be interpreted in terms of the formation of new phases. At a shock-loading of the powder samples to pressures higher than 280 kbar, the X-ray diagrams contain some faint and broad reflections which may be attributed to structurally imperfect and extremely fine-grained (grain size < 1000 Å) 3/2-mullite. With the degree of shock-loading the amount of mullite increases (Fig. 2). This can also be seen from the infra-red spectra (Fig. 3).

While X-ray studies do not give any hint of the existence of additional phases, the infra-red spectra do show new and prominent absorption bands centred near 1100 and 470 cm^{-1} (Fig. 3). These are the wave numbers of the Si–O stretching and the O–Si–O angle deformation modes of silica glass [18–21]. The ratios of the intensities of these silica bands to the main mullite band near 1200 cm^{-1} are higher than those observed for an equimolar mixture of silica and mullite such as

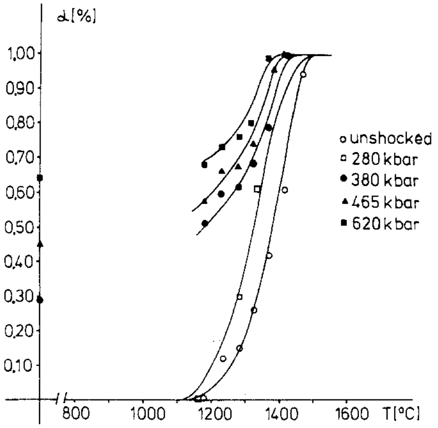

Figure 2 Extent of reaction (α) of unshocked and shocked andalusite powders (≤ 40 μm) to 3/2-mullite versus annealing temperatures. The shock pressures are those calculated for the steel container.

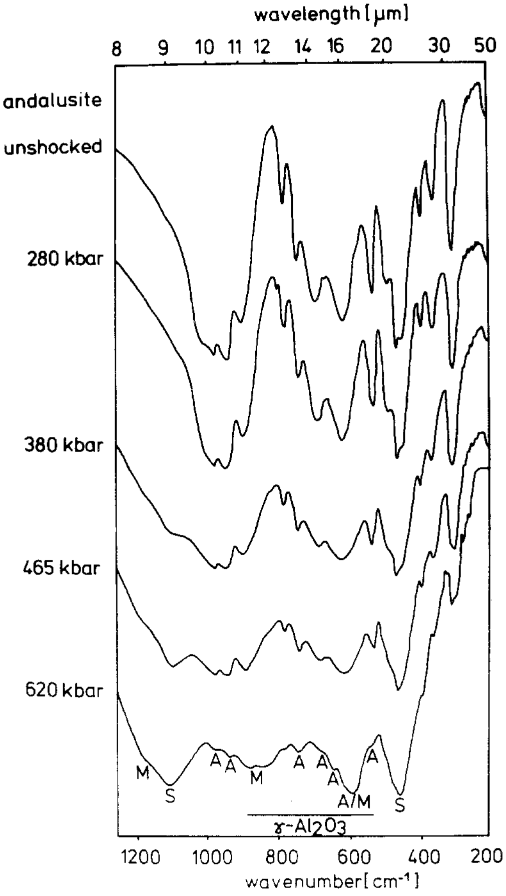

Figure 3 Infra-red transmission curves of unshocked and shocked andalusite powders. The shock pressures are those calculated for the steel container.

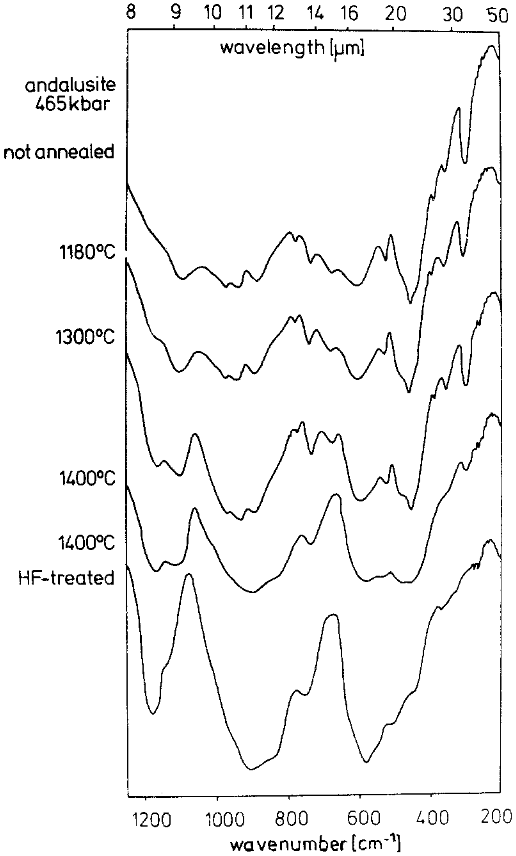

Figure 4 Infra-red transmission curves of andalusite powders shocked to 465 kbar. The sample was subsequently annealed at different temperatures. The shock pressure refers to the value calculated for the steel container. The HF-treated sample contains only 3/2-mullite and no long-range-disordered Al_2O_3 or SiO_2 phases.

would result, for example, from the purely thermal decomposition of andalusite. See also Fig. 4 which shows the spectra of the thermal decomposition products of an andalusite sample shocked at 480 kbar.

We therefore conclude that additional long-range-disordered* SiO_2 was formed by the shock process. For stoichiometric reasons the remaining phases must then be enriched in Al_2O_3. By analogy with the shock-induced transformation of single crystal andalusite, one may expect the formation of a long-range-disordered Al_2O_3 [4]. Such material is known to exhibit only a broad absorption region extending from about 900 to 550 cm^{-1} [22] which prevents its detection when other compounds also absorb in this region, as is the case here. Scanning electron micrographs of the highly (≥ 380 kbar)

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* We prefer the term "long-range-disordered" over the commonly used but imprecise "short-range-ordered".

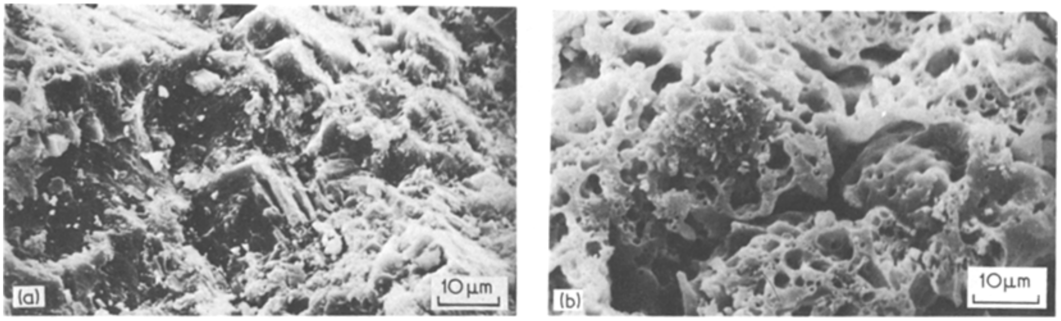

Figure 5 Scanning electron micrograph of andalusite powder: (a) unshocked, (b) shock-loaded up to 620 kbar. The shock pressure refers to the value calculated for the steel container.

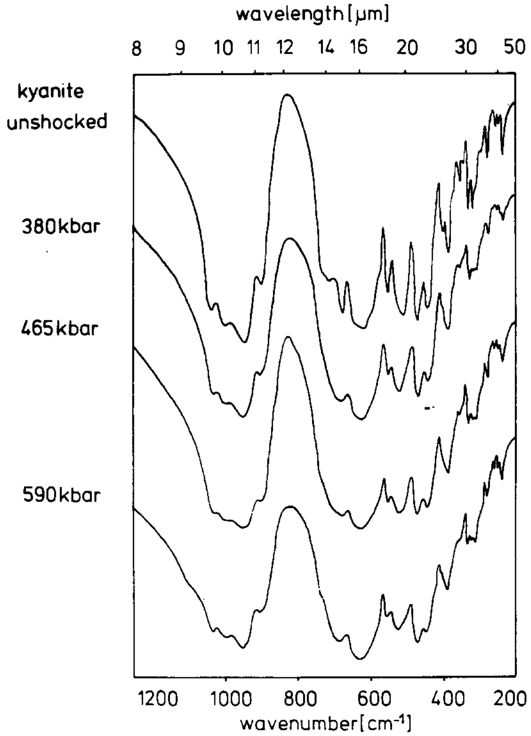

Figure 6 Infra-red transmission curves of unshocked and shocked kyanite powders. The shock pressures are those calculated for the steel container.

shock-treated samples differ appreciably from those of the untreated material and look as if the samples had been partly fused or at least strongly sintered (Fig. 5a and b).

3.1.2. Kyanite

Neither X-ray patterns nor infra-red spectra of the shocked kyanites yielded any evidence for possible pressure- or temperature-produced phases. Only the infra-red spectrum of the highest shock-loaded sample (590 kbar) shows a slight shoulder near 1100 cm^{-1} which may be assigned to the Si–O stretching mode of long-range-disordered SiO_2 (Fig. 6). Although there is some evidence, from line broadening in the X-ray diagrams, of plastic deformation and volume compression of the material, the scanning electron micrographs taken from shocked and unshocked kyanites prove that there is no dramatic change in grain morphology (Fig. 7a and b).

3.2. Thermal behaviour of shocked and unshocked samples

3.2.1. Andalusites

The shocked andalusites, consisting of the newly formed Al_2O_3 and SiO_2 phases, of residual

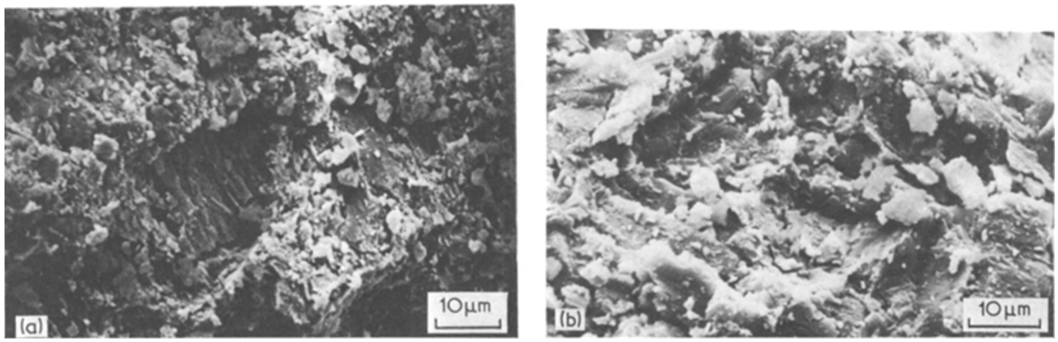

Figure 7 Scanning electron micrograph of kyanite powder: (a) unshocked, (b) shock-loaded up to 590 kbar. The shock pressure refers to the value calculated for the steel container.

andalusite, and in some cases also of mullite, produce 3/2-mullite when annealed at temperatures of 1180° C or higher, the rate of transformation increasing with rise in temperature. Similar results have been obtained by Stöffler [23], when carrying out annealing experiments on naturally shocked sillimanites of sillimanite gneisses from the Ries crater (Germany). The high temperature transformation curves of andalusite as determined by means of quantitative X-ray techniques are presented in Fig. 2. It can be seen that with increasing shock pressures the transformation curves are shifted towards lower temperatures. Two kinds of transformation curves can be distinguished: those of the unshocked and the 280 kbar andalusites which were free of mullite before annealing, and those of the samples shocked at 380 kbar or more, which contained significant amounts of mullite to start with.

3.2.2. Kyanite

Contrary to the thermal behaviour of the shocked andalusites, the transformation curves of even highly shocked samples differ little from those of the unshocked samples, the only difference being a slight displacement towards lower transformation temperatures (Fig. 8). In particular, there is no mullite in any of the unheated samples.

4. Discussion

Shock wave treatment of andalusite powders leads to transformation into a mixture of long-range-disordered Al_2O_3, long-range-disordered SiO_2, and mullite. It is a general problem in examining post-shock products to determine whether these were formed by dynamic pressure processes or by temperature effects or both. In considering pressure effects, one has to keep in mind that after passage of the shock wave the material undergoes a re-expansion which can lead to a final density even lower than that of the untreated material.

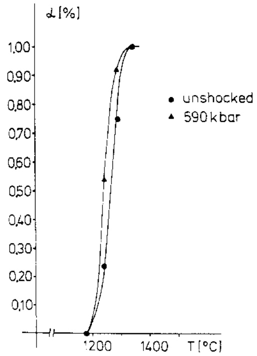

Figure 8 Extent of reaction (α) of unshocked and shocked (590 kbar) kyanite powders ($\leqslant 40\,\mu m$) to 3/2-mullite versus annealing temperatures. The shock pressure refers to the value calculated for the steel container.

The Al_2O_3 and SiO_2 oxide mixture is believed to be the result of pressure release of initially formed stishovite and γ-Al_2O_3, with temperature effects playing at most a secondary role. The reasons for this assumption are the following: (i) the phases in question have never been observed as thermal decomposition products of andalusite; (ii) the phases have been observed, however, after shock treatment of single crystal andalusite [4], where shock temperatures are too low to explain oxide formation by thermal shock effects (according to McQueen *et al.* [17] the shock temperatures at 570 kbar are approximately 700° C); (iii) the possible formation of an *in situ* high-pressure stishovite plus γ-Al_2O_3 would be thermodynamically feasible, because it is accompanied by a volume decrease of about 16%.

Mullite, on the other hand, is a typical high temperature phase which is never formed by pressure alone. Its formation must be a consequence of the elevated shock temperature, whether it is formed directly from andalusite or by reaction of γ-Al_2O_3 and SiO_2. Formation from andalusite would require temperatures in excess of 1250° C [24], whereas formation from the oxide mixture could take place at temperatures near 1000° C [25]. Contrary to this behaviour, single crystals of andalusite, shocked up to the same pressure range, do not show any transformation into mullite [4]. This may be a consequence of the dependence of the shock temperature on the porosity of the sample: calculations by Wackerle [26] on quartz single crystals and by Ahrens and Gregson [27] on quartz sandstones have shown that at 200 kbar the shock temperatures are 200 and 1500° C, respectively.

A striking point in our investigations is the different shock behaviour of andalusite and kyanite powders: while andalusite powders undergo distinct phase changes under shock, kyanite powders, when submitted to similar peak pressures, do not show any detectable phase transformations. The lack of high pressure transformations in kyanite may be due to the densely packed kyanite structure which is expected to be more resistant to shock waves. The absence of high-temperature transformations in kyanite may be explained by the different porosities of the sample tablets: the fibrous kyanite crystals are more closely packed than the granular andalusite crystallites, and therefore the shock temperatures are expected to be lower for the kyanite than for the more porous andalusite samples. It has been demonstrated in our laboratory that the porosity of kyanite pellets is lower than that of the andalusite pellets by several per cent.

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