

The high-temperature transformation of andalusite (Al_2SiO_5) into 3/2-mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$) and vitreous silica (SiO_2)

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SUMMARY. The high-temperature transformation of andalusite (Al_2SiO_5) into 3/2-mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$) plus vitreous silica (SiO_2) has been studied within the temperature interval from 1300 to 1600 °C by means of X-ray powder and single-crystal techniques and by infrared spectroscopy. Results are interpreted in terms of a topotactic transformation in which (011) and (0 $\bar{1}$ 1) planes of andalusite transform into (20 $\bar{1}$) and (201) planes of 3/2-mullite; in this way the *a*- and *b*-axes of the two phases are interchanged. From the structural and orientational relationship between the andalusite and 3/2-mullite lattices it is concluded that the aluminium-oxygen octahedral chains, running in both structures parallel to the crystallographic *c*-axis, are preserved during phase transformation.

THE system Al_2O_3 - SiO_2 is of great interest for mineralogical studies. It contains four compounds occurring in nature: andalusite, sillimanite, kyanite, and mullite. The first three have the chemical composition Al_2SiO_5 and are common minerals in metamorphic rocks. Mullite occurs very rarely in natural rocks, but is an important phase in ceramics and other refractory products. It has a varying chemical composition, which is generally accepted to range from $2\text{Al}_2\text{O}_3\cdot \text{SiO}_2$ to $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$. Konopicky and Patzak (1974) even describe the occurrence of a 1/1-mullite ($\text{Al}_2\text{O}_3\cdot \text{SiO}_2$).

The crystal structures of andalusite, sillimanite, and mullite, which are important for the understanding of the thermal decomposition of andalu-

site, have been determined by Taylor (1928, 1929), Burnham and Buerger (1961), Burnham (1963), and Sadanaga *et al.* (1962). All three structures are characterized by chains of aluminium-oxygen octahedra, which run parallel to the *c*-axes. In andalusite individual octahedral chains are linked by silicon-oxygen tetrahedra and by aluminium-oxygen bipyramids (fig. 1*a*). In sillimanite neighbouring octahedral chains are linked by tetrahedral

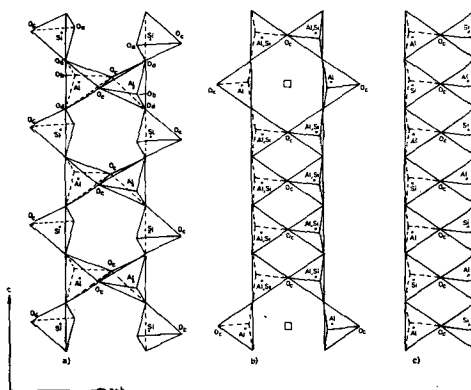


FIG. 1. Tetrahedral chains in andalusite, mullite, and sillimanite; (a) modified tetrahedral Zweier-Doppelkette in andalusite, the O_c -atoms that point 'outward' are symmetrically equivalent to those that form the shared edge of the bipyramids; (b) mixture of tetrahedral Einer-Doppelkette and tetrahedral Zweier-Doppelkette in mullite, □ indicates a vacancy; (c) tetrahedral Einer-Doppelkette in sillimanite.

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TABLE I. Lattice constants and space groups of andalusite, sillimanite, 2/1-mullite, and 3/2-mullite compared with the results of this investigation

	andalusite		sillimanite	2/1-mullite	3/2-mullite	
$a[\text{\AA}]$	7.7942(2)*	7.800	7.4856(6)†	7.583(2)‡	7.5456§	7.550
$b[\text{\AA}]$	7.8985(2)	7.903	7.6738(3)	7.681(2)	7.6898	7.706
$c[\text{\AA}]$	5.559(2)	5.560	5.7698(8)	2.8854(5)	2.8842	2.888
Space group	<i>Pnmm</i>		<i>Pbnm</i>	<i>Pbam</i>	<i>Pbam</i>	

* Burnham and Buerger, 1961.

† Burnham, 1963.

‡ Sadanaga *et al.*, 1962.

§ JPDC-card (number: 15-776).

|| This work.

Einer-Doppelketten (AlSiO_6 chains) parallel to c , in which the periodicity is doubled due to Si-Al cation ordering (fig. 1c). In 2/1-mullite the same tetrahedral Einer-Doppelketten as in sillimanite exist but with two alterations: the c lattice constant of 2/1-mullite is reduced to half the value of sillimanite because of Si-Al cation disorder within the tetrahedral Einer-Doppelketten; furthermore, the sequence of the Einer-Doppelketten is disturbed as shown in fig. 1b. The disturbance occurs statistically, and on the average every fifth pair of tetrahedra is misorientated with respect to the Einer-Doppelketten. The centres of such tetrahedra are occupied by aluminium atoms. No structure refinement of 3/2-mullite has yet been published; however, it is quite reasonable to assume a structure similar to that of 2/1-mullite, but with an O_c -oxygen (fig. 1b) deficit of 1:8 instead of 1:5.

Under atmospheric pressure and at high temperatures, andalusite and sillimanite transform into 3/2-mullite and SiO_2 . In nature the transformation of andalusite into mullite probably occurs only under very special circumstances, and it is metastable with regard to the andalusite-sillimanite transition. However, since andalusite is a rather common raw material in ceramic and refractory products, the topology of the transformation to mullite has a substantial bearing on the application of aluminium silicate ceramics. Our investigation is intended to provide new data for the discussion of this problem.

Experimental. Gem-quality andalusites from Minas Gerais (Brazil) and crystals from the pegmatite of Dolni Bori (ČSSR) were used for our experiments. According to the X-ray analysis, the gem-quality samples were mineralogically pure, whereas those from Dolni Bori contained an insignificant amount of quartz (< 2%). Heating experiments were performed within the hot zone of a voltage-stabilized rhodium furnace with andalusite powder (grain diameter < 45 microns) and with single crystal samples. The temperatures were

measured by means of a Pt-Rh₁₀Pt₉₀ thermocouple with an accuracy of $\pm 10^\circ\text{C}$.

Experiments on andalusite powder were performed with different experimental conditions, varying the temperature (between 1310 and 1530 °C) and the annealing time (15 to 120 min.). The samples were brought to the high temperatures directly and were quenched to room temperature at the end of the experiments. X-ray powder diffraction patterns were obtained on a Philips powder goniometer. From these patterns cell parameters of the phases andalusite and mullite were calculated using a least-squares programme.¹

Single-crystal heating experiments, all lasting two hours, were performed at 1460, 1480, 1500, 1520, 1540, and 1600 °C. The crystals were heated from room temperature up to the required temperature with a heating rate of approximately 200 °C/hour and were quenched to room temperature at the end of the experiments. Then the crystals were subjected to an X-ray investigation, and oscillation, Weissenberg, and precession photographs were made using Ni-filtered Cu-K_α radiation.

Infrared spectra of powder samples annealed at various temperatures for one hour were taken with a Beckman IR-10 spectrometer (wave number range: 2000–350 cm^{-1}) and with a Beckman Fourier spectrometer FS 720 (wave number range: 400–40 cm^{-1}).

Results. X-ray powder investigations yielded a thermal transformation of andalusite within a temperature range from ~ 1300 to $\sim 1530^\circ\text{C}$. The lattice constants of the high-temperature phase agree well for all experimental conditions with those of 3/2-mullite but never with those of 2/1-mullite or sillimanite (Table I). This is in accordance with the observations by other investigators (see e.g. Harders and Kienow, 1960).

The single-crystal investigations of the heat-

¹ All computations were carried out on the Univac 1108 computer at the University of Karlsruhe Computer Center.

treated samples yielded simultaneous X-ray reflections of andalusite and 3/2-mullite (fig. 2) in a wide temperature range. While the andalusite reflections are still sharp after the heat treatment the new 3/2-mullite reflections are smeared out. They have a typical shape, which is observed on all photographs: 3/2-mullite reflections, except the $0k0$ reflections, show two intensity maxima which are connected by streaks of lower intensity; the $0k0$ reflections have only one intensity maximum in the centre of the reflections, which are only slightly streaked. This indicates that the maxima of the smeared-out 3/2-mullite reflections are due to the superposition of two different 3/2-mullite lattices which have the b^* -axis in common. The orientational relationships between the two 3/2-mullite lattices and the parent andalusite lattice are determined as:

1. $(011)_a // (20\bar{1})_m$ and $(100)_a // (010)_m$
2. $(0\bar{1}\bar{1})_a // (201)_m$ and $(100)_a // (010)_m$

As the formation of 3/2-mullite on $\{100\}$ of andalusite will give rise to only one orientation of the 3/2-mullite crystallites it follows that the formation of 3/2-mullite takes place on $\{011\}$ of andalusite. The orientational relationship between the two 3/2-mullite lattices can be deduced from fig. 2. There are

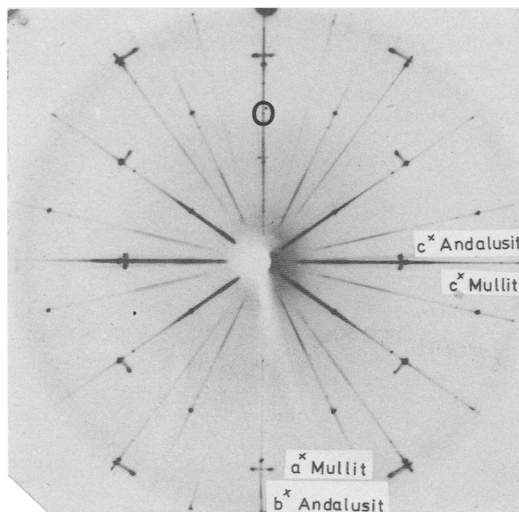


FIG. 2. Precession photograph of an andalusite single crystal after heat treatment at 1520 °C. Good reflections belong to the $(0kl)$ -plane of andalusite; several weak reflections that are forbidden in $Pnmm$ are visible, one being enclosed by a circle. The forbidden reflections may be explained by simultaneous diffraction (Umweganregung) and are not due to a new high-temperature phase as we concluded in a preliminary report (Schneider and Pannhorst, 1976); smeared out reflections belong to (hol) -planes of 3/2-mullite; for further explanation see text.

two mirror planes parallel to (010) and (001) of andalusite and two twofold axes parallel to $[010]$ and $[001]$ of andalusite. With respect to the 3/2-mullite lattices the symmetry elements have no rational (or very high) indices. The orientational relationship between the two 3/2-mullite lattices therefore is not that of a twin law, since a twin is understood as a rational, symmetrical intergrowth of two individual crystals of the same kind of species (Buerger, 1945).

Discussion. The close structural relationship between andalusite and 3/2-mullite, particularly the existence of the same kind of octahedral chains, suggests a topotactic transformation in which the octahedral chains are preserved while the other structural units decompose and rearrange. From the single-crystal X-ray investigations the following orientational relationship between the andalusite and the 3/2-mullite lattices is obtained. The (011) plane of andalusite transforms into a $(20\bar{1})$ plane of 3/2-mullite; in these planes the a -axis of andalusite is parallel to the b -axis of 3/2-mullite ($[100]_a // [010]_m$) and the $[011]$ direction of andalusite becomes the $[102]$ direction in 3/2-mullite ($[011]_a // [102]_m$). Calculation of the lengths of the parallel vectors in real space shows that their differences are less than 2%. As both planes fit very well they are particularly suitable for a topotactic reaction.

Topotaxy requires, besides a definite orientational relationship between the lattices of the host (andalusite) and the product (3/2-mullite), a three-dimensional correspondence between the structures of the product and the host (Glasser *et al.* 1962). In fig. 3 a projection of andalusite along $[100]$ and 3/2-mullite along $[010]$ is given that demonstrates such a three-dimensional correspondence between the two structures. Within the boundary where the atoms belong to andalusite as well as to 3/2-mullite the differences between the atomic positions of the two structures are very small. Thus, when the boundary migrates through the crystal atoms that form the octahedral chains, the Al-atoms and oxygen atoms O_a, O_b, O_d (for notation see fig. 1), maintain their positions or undergo only minor shifts. On the other hand the O_c -atoms, the Al-atoms of the bipyramids, and Si-atoms of the tetrahedra of andalusite have to make larger movements during the phase transformation. Some of the movements that are necessary can be deduced from fig. 1. The tetrahedral chains of 3/2-mullite are almost inherent in the andalusite structure. Only one of the two O_c -atoms which form the shared edge of the bipyramids in andalusite has to move either out of the crystal to form a vacancy or by $1/2 c$ to complete the formation of the tetrahedral chain. The newly formed

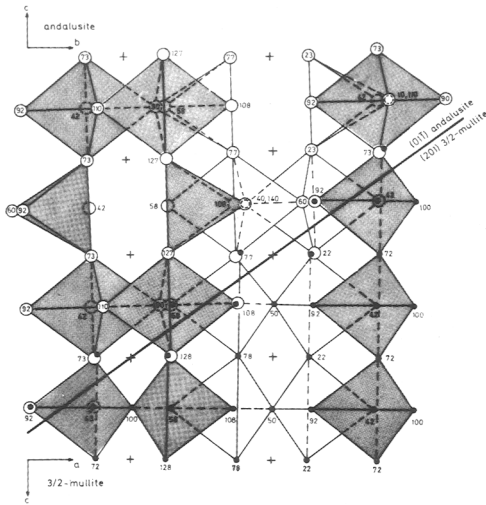


FIG. 3. Structural explanation for the topotactic transformation of andalusite into 3/2-mullite. Circles represent oxygen atoms of andalusite in a projection along $[100]$ (upper left); dots represent oxygen atoms of 3/2-mullite in a projection along $[010]$ (lower right); crosses represent aluminium atoms with octahedral coordination.

tetrahedral sites will be occupied by diffusion of Al and Si atoms into these sites.

The diffusion processes of the Al and Si atoms will be rather complicated because after the formation of 3/2-mullite there will be an excess of Al and a deficiency of Si and O with respect to andalusite. One unit cell of andalusite contains 8 Al, 4 Si, and 20 O atoms whereas the corresponding volume of 3/2-mullite contains 9 Al, 3 Si, and 19.5 O-atoms. Thus, 3/2-mullite contains one Al atom more than andalusite. This means that part of the andalusite crystal decomposes completely (at least 1 unit cell out of 9) to produce the Al atoms needed in the other parts.

The misfit between the atomic positions of andalusite and 3/2-mullite within the boundary (fig. 3) is very small at the beginning of the 3/2-mullite

formation on $\{011\}$ of andalusite. However, when the boundary migrates through the crystal this misfit between the atomic positions becomes larger with increasing distance from the nucleating point, since the two coordinate systems are not exactly parallel. This will induce considerable strain within the reaction zone. When the induced strain surmounts the elastic limits of the 3/2-mullite structure, gliding or tilting processes will be activated to reduce the strain. Perhaps such processes are responsible for the streaks that connect the reflections of the two different 3/2-mullite lattices.

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Note added in proof: Our conclusions are in accordance with the results obtained by infrared spectroscopy (MacKenzie, 1972; Walker, 1976).

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