The transformation of andalusite to mullite and silica: Part I. Transformation mechanism in [001]A direction

ANGELIKA HÜLSMANS, MARTIN SCHMÜCKER, WERNER MADER, AND HARTMUT SCHNEIDER

1Institut für Anorganische Chemie der Universität Bonn, Römerstrasse 164, D-53117 Bonn, Germany
2Deutsches Zentrum für Luft- und Raumfahrt, Institut für Werkstoff-Forschung, D-51147 Köln, Germany

ABSTRACT

The high-temperature transformation of andalusite (Al2O3·SiO2 = A) single crystal to 3:2-mullite (3Al2O3·2SiO2 = M) and non-crystalline silica (SiO2) taking place between 1500 and 1600 °C was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Electron diffraction studies confirmed the topotactical orientation relationship ([100]A || [010]M, [010]A || [100]M, [001]A || [001]M) between the primary product (A) and the product phase (M), which was predicted by Pannhorst and Schneider (1978) on the basis of single-crystal X-ray diffraction studies. The transformation starts at the (001)A surface and proceeds rapidly along to the cA-axis. The overall reaction front is parallel to (001) of andalusite and mullite, though on the microscopic scale it exhibits a zigzag shape with facets parallel to {011}A and {201}M. The development of {011}A and {011}M microfacets is favorable, because both lattice planes exhibit a small misfit, which is close to zero at the transformation temperature. The undistorted and direct transition from andalusite to mullite and the high velocity of the reaction along [001]A suggests that the AlO6 octahedra which occur in both structures are being preserved during the transformation. Other structural units, however, have to be decomposed and restructured. The newly formed mullite crystallites display an acicular shape elongated to the c-axis with an average size of about 250 nm along their small dimension. Excess non-crystalline SiO2 is exsolved between the mullite crystallites in small channels running parallel to [001]M. The major amount of the exsolved silica liquid is transported to the (001) surface of the former andalusite crystal by means of capillary forces.

INTRODUCTION

Andalusite and mullite belong to the aluminosilicate phases which can be described using the formula Al23Si22O18-x (Cameron 1977). For x = 0 the polymorphs sillimanite, kyanite, and andalusite are formed (Al2SiO4 respectively, Al2O3·SiO2). Mullite is a compound which frequently has a composition range between x = 0.25 (3Al2O3·2SiO2: 3:2-mullite) and x = 0.40 (2Al2O3·SiO2: 2:1-mullite). Recent studies have shown that the values of x can be extended up to approximately 0.825 corresponding to an Al2O3 content of 89 mol% (Fischer et al. 1994).

The crystal structures of andalusite and mullite are well known (Taylor 1929; Burnham and Buerger 1961; Burnham 1963; Angel and Prewitt 1986). The structures of andalusite and mullite are orthorhombic with space groups Pnma (no. 58) and Pbam (no. 55) and lattice parameters aA = 779 pm, bA = 789 pm, cA = 555 pm, and aM = 754 pm, bM = 768 pm, cM = 288 pm [structure data from JCPDS cards no. 13-122 (A) and no. 15-776 (M)]. They are both built up of chains of edge-sharing AlO6 octahedra running parallel to the crystallographic c-axis (see Fig. 1). In andalusite the octahedral chains are crosslinked by double chains consisting of SiO4-tetrahedra and trigonal bipyramids, resulting in an unusual fivefold coordination of aluminum. In mullite the connection between the AlO6 octahedra chains is realized by Al-Si-tetrahedral double chains with a statistical cation occupation in the tetrahedra. According to the higher Al2O3-content in mullite, more tetrahedral sites are occupied by Al3+ than by Si4+. To compensate the excess of negative charge some bridging oxygen atoms (Oc) of the tetrahedral double chains are not occupied producing Oc-vacancies. Due to these Oc-vacancies the adjacent Al-atoms are shifted out of their ideal position toward new Al5+-positions, and new oxygen positions (Oc') are created which are surrounded by three AlO6-tetrahedra forming AlO6-triclusters (Fig. 1). In electron diffraction patterns of mullite diffuse streaks and satellite reflections can be observed in the [100] and [010] direction. These reflections become more intense with increasing Al-content (Cameron 1977). Their distribution can be interpreted in terms of an incommensurable superstructure with a complex ordering scheme (McConnell and Heine 1985).

In the andalusite to mullite reaction,

$$3 \text{Al}_2\text{Si}_3\text{O}_9 \rightarrow 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{SiO}_2$$

which takes place between approximately 1400 and 1600 °C, only the 3:2-mullite composition is produced. The phase transformation was investigated by Sanadaga et al. (1962), Pannhorst and Schneider (1978), and Schneider and Majdic (1979). According to single-crystal X-ray diffraction studies and light microscopic observations Pannhorst and Schneider (1978) supposed that the transformation proceeds in a topotactical reaction and mullite and andalusite should have the orientation relationship: aA || bA, bM || aA, and cM || cA.