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The crystalline-to-amorphous transition in shock-loaded mullite $Al_2^{VI}(Al_{2+2x}Si_{2-2x})^{IV}O_{10-x}$ in the light of shear modulus anisotropy

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Abstract

We present experimental evidence for shock-wave induced amorphization in polycrystalline and single crystal mullite, $Al_2^{VI}(Al_{2+2x}Si_{2-2x})^{IV}O_{10-x}$, at peak pressures above 35 GPa. The transition proceeds along with a network of very thin glass lamellae (planar deformation features (PDFs)) of mullite-normative composition extending parallel to low-index crystallographic planes including {1 2 0}, {2 3 0} and {1 1 0}. Cumulative microstructural evidence from the PDFs derived via analytical transmission electron microscopy suggests a shear-induced formation mechanism. Experimental PDFs match the relative minima of the calculated representation surfaces of the shear modulus suggesting that suitable PDF orientations can be derived from the elastic anisotropy of mullite. PDFs in mullite are in good agreement with those reported for naturally shocked sillimanite.

Unlike the formation of shear-induced PDF-type glass lamellae in shocked mullite, the thermal decomposition of mullite following high post-shock temperatures results in a fine-grained phase assemblage consisting of corundum plus amorphous silica, and represents the most abundant transformation mechanism in the shock regime investigated (20–40 GPa). No stishovite was observed. At shock levels beyond 35 GPa thermal decomposition of mullite may occur along with PDFs within the same specimen.

Keywords: Shock deformation; Electron microscopy; Plasticity; Mullite; Structural applications

1. Introduction

Dynamic compression of solid matter is a traditional domain of the geological science community where primary interest is directed towards the effects of shock metamorphism upon terrestrial crustal rocks and extraterrestrial impactites.[1–5] Notably the high strain rates released during shock loading bear a high potential for materials processing. Shock-assisted compaction has been employed successfully for the compaction of covalently bonded ceramic systems (e.g. SiC, BN, AlN, graphite, diamond) of high purity which are difficult to densify otherwise. During shock loading, different sources of energy dissipation such as friction, fracture and partial melting are released upon acceleration of the powder particles by the shock wave creating high dislocation densities and point defect concentrations.[6–11]

In response to shock-induced compression either in the laboratory or during a natural impact, crystalline constituents develop a variety of structural defects which are distinctively different from those introduced during static deformation[12–14]. With increasing pressure these characteristic defects include planar fracture, mechanical twinning, kink bands, mosaicism, and the so-called planar deformation features (PDFs) introduced via shock-induced amorphization.

PDFs define the most intriguing class of shock indicators. They consist of straight, narrow glass lamellae exhibiting the same chemical composition as the host crystal and have been described for a number of shock-loaded rock-forming minerals,[12,15–17] but as discussed in the present study, they may form in ceramic compounds as well. PDFs reflect elastic instabilities on specific closely packed crystallographic planes following the breakdown of the general Born stability criterion as defined by a positive definite matrix of the stiffness tensor c_{ij}, once a critical shock level has been exceeded.[18,19] While destabilization of some crystal lattices upon shock compaction

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may be accomplished without a shear component,[20] it is generally accepted that the very thin (of the order of ×10 nm) PDFs are formed by a shear process during dynamic compression.[21,22] These findings are in line with the general conception that even in uniaxial compression state shear is always effective on selected crystallographic planes. The PDF fine structure may be affected by post-shock annealing effects and in some systems frictional melting seems to be associated with PDFs.[23] The orientation of PDFs shows no pressure dependence. With increasing pressure, thickening of PDFs may yield extended areas of so-called diaplectic glasses.[22,24] It has been emphasized that accommodation of the compressed volume behind the shock front can only be achieved via regularly spaced lamellae of dense amorphous material.[20,22] Therefore PDFs must not be confused with amorphization of crystalline matter upon static compression.[25–27]

Although the shock response of Al_2O_3[28–30] and the Al_2SiO_5 polymorphs, particularly sillimanite, is well documented in the literature,[31,32] dynamic compression of ceramic compounds such as the alumosilicate mullite has only attracted attention in recent years.

The natural occurrence of mullite is rare. It was first reported in the early 1920s from a high-level intrusion of an Al-rich clay shale by a basaltic magma at the Isle of Mull in the Western Scottish Highlands.[33] Not surprisingly, naturally shocked mullite is presently unknown. However, the crystal structures of mullite and sillimanite are very similar suggesting that an in-depth comparison of the shock behavior of mullite derived in the laboratory with naturally shocked sillimanites will provide a more detailed assessment of the shock performance of this family of compounds.

Mullite, $Al_2{}^{VI}(Al_{2+2x}\,Si_{2-2x})^{IV}O_{10-x}$, $(0.17 < x < 0.50)$ has an oxygen-deficient orthorhombic structure with straight chains of edge-sharing $[AlO_6]$ octahedra extending parallel to the *c*-axis which are cross-linked by chains of doublets of $[(Si/Al)O_4]$ tetrahedra[34,35] (see also Section 4, Fig. 9 for a presentation of the mullite average structure). With the bulk composition ranging from nominally $3Al_2O_3 \cdot 2SiO_2$ $(x = 0.25)$ to $2Al_2O_3 \cdot 1SiO_2$ $(x = 0.40)$, mullite is the only stable phase in the binary system Al_2O_3–SiO_2 under normal conditions.

Apart from the fact that sillimanite features no oxygen vacancies, the structural differences between sillimanite and mullite are basically related to the site occupation factor of the aluminum and silicon atoms in the tetrahedral double chains. In sillimanite these are fully occupied in an ordered manner. In mullite they are only partially occupied (sites occupation factor $\sim$0.8) in a random manner which gives rise to bisection of the *c*-parameter. Moreover, sillimanite lacks the partially occupied tetrahedral chains extending parallel to the *c*-axis which involve the T^* sites with site occupation factors $\sim$0.2.

First results on shock-induced phase transitions of polycrystalline mullite including (i) the formation of planar deformation features as well as (ii) the thermal decomposition of mullite were reported in 1995.[36] Recently, the Hugoniot elastic limit of polycrystalline mullite was determined experimentally to be 16.1 GPa[37] which compares well to the Hugoniot elastic limit of sapphire (12–20 GPa[28]) for different crystallographic orientations. A phase transition in mullite occurring at 30.4 GPa was reported[38] while at 40 and 49 GPa, mullite nanocrystals were found to be embedded in a non-crystalline phase. Exposure to still higher shock pressures above 65 GPa resulted in complete decomposition of mullite to form a very fine-grained mixture of γ-alumina and amorphous silica.

The previous shock data for mullite still leave a variety of open issues and inconsistencies within the literature which are addressed in the present paper. The main focus of this study is directed towards the assessment and interpretation of planar deformation features observed in polycrystalline and single crystal mullite materials as compared to mullite's close structural relative sillimanite. The concept of a shear-induced formation process for PDFs proven successfully for a number of shock-loaded rock-forming minerals[21] is extended to the mullite system employing sillimanite for benchmarking. It will be shown that the formation of PDFs in mullite planes can indeed be rationalized via the elastic anisotropy of mullite and match with the ensemble of PDFs reported from naturally shocked sillimanite.[31] The thermal decomposition of mullite introduced by the high post-shock temperatures represents the second transformation mechanism of shocked mullite and is discussed complementary to shock-induced amorphization.

2. Experimental procedure and materials

2.1. Shock recovery experiments

The shock experiments were performed at the Ernst Mach Institute, Freiburg, Germany by planar impact techniques[2,13] in the 20–40 GPa pressure range. The experimental setup is depicted in Fig. 1a. The specimen was loaded in a cylindrical ARMCO (American Rolling Mill Company)-type iron sample container surrounded by intercalated steel plates which serve as momentum traps. Dynamic compression was achieved through a steel flyer plate accelerated by an explosive device. The flyer plate was resting on a spacer ring. Upon impact of the flyer plate on the upper sample container surface a plane shock wave was transmitted into the specimen. The specimens consisted of thin polished mullite sections, typically 0.5 mm thick and 10 mm in diameter, which were embedded in NaBr in order to suppress rarefaction waves from the lateral and bottom surfaces of the sample container (Fig. 1b).

Peak pressures transmitted into the samples could be varied by using different types of explosives and/or by modifying the thickness of the flyer plate, respectively. Peak pressures were determined by separate calibration tests using the pin contactor technique via measuring the free surface velocity at the upper container/sample interface as discussed elsewhere.[13] The pressure in the mullite sample was determined by impedance matching in a multiple reflection mode using the Hugoniot data of ARMCO-iron. Upon shock-loading the sample container is usually slightly deformed at the impact surface. At pressures above 30 GPa recovery of specimens for TEM preparation becomes progressively difficult due to complete fragmentation of the mullite materials and/or strong adhesion to the container material.