CHEMICAL EFFECTS OF SHOCK WAVES IN SOLIDS

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Summary. Structural and chemical changes induced by intense shock waves are summarized for the case of inorganic solids. Special attention has been paid for the material synthesis via high-pressure phase transformation. Shock-induced phases are not always high-pressure phase itself, but frequently obtained as metastable phases from unquenchable high-pressure phases during the decompression stage. Typical example is demonstrated in the case of TiO₂, which has been explained as a result of a sequential rutile-fluorite-α-PbO₂ transition. It is pointed out that shock waves induce highly disordered phases such as diaplectic glass in tectosilicate minerals, and also in two-dimensionally disordered phase of X-Nb₂O₅. Importance of decomposition reaction induced by shock loading is discussed. Marked contrast is noted between diffusion-controlled decomposition in solid state, and rapid decomposition accompanied by degassing as typically shown in shock reduction of transition metal oxides.

1. Introduction

Shock waves exhibit diverse physical and chemical phenomena in solids, corresponding to the magnitude of the shock pressures and the virgin state of the shocked materials. These phenomena can be conveniently understood in terms of pressure, temperature and mechanochemical effects. Pressure effects are generally believed to be comparable to static high pressure experiments, and are applied to equation-of-state studies at extreme compressions. Among the phenomena due to the pressure effects of shock waves, shock-induced phase transformations are the most important and have been discussed in detail (Duvall and Graham, 1977;
Syono, 1984; 1987; 1988). In some cases, the uniaxial character of shock loading plays an important role in shock-induced phase transformation and provides a unique aspect. Pressure effects are particularly featured in single crystals and bulk solid materials without porosity, where the temperature effects can be treated as subsidiary ones.

Intense shock loading is inevitably accompanied by high temperatures, which also demonstrates very remarkable phenomena such as melting. These temperature effects are enhanced in porous or powder materials, and sometimes counteract the pressure effect. Shock temperature effects have found remarkable applications, such as the shock compaction of powder materials; the shock compaction of amorphous alloy powders is especially promising for industrial applications (Cline and Hopper, 1977; Morris, 1983; Kasiraj et al., 1984; Schwarz et al., 1984; Toda et al., 1985).

However, shock effects are not limited to simple pressure or temperature effects alone to be compared to static high pressure conditions. Shock loading is known to introduce a large number of defects and dislocations in solids, due to extensive plastic deformations, and to enhance the reactivity of shocked materials. Sometimes the diffusion rate is enhanced to unusually high levels in the shock process (Alekseevskii et al., 1979a; Kleiman et al., 1986), leading to rapid chemical reactions (Horiguchi and Nomura, 1966; Batsanov et al., 1982; Graham et al., 1986; Kleiman et al., 1985). These mechanochemical aspects of shock waves have been advocated by the Batsanov group in the USSR (1982) and Graham and his coworkers, and various kinds of experimental studies are now being carried out (Morosin and Graham, 1982; Graham et al., 1986). They are particularly enhanced in powder and porous materials, and are now utilized for material synthesis and processing on an industrial scale (Graham and Sawaoka, 1987).

It is noteworthy that remarkably inhomogeneous textures can be introduced by shock loading, even in solid materials such as single crystals. For example, intergrowth textures consisting of dialectric glass and crystals of submicrometer scale have been observed in shocked quartz (Anan'In et al., 1974) and feldspar (Kitamura et al., 1977). These textures are particularly well developed in brittle materials with low thermal conductivity, and can be interpreted as the results of inhomogeneous temperature distribution due to the heterogeneous yielding model first proposed by Grady (1977), as thermal equilibrium cannot be attained during the short duration of shock process.

For the purpose of material synthesis and modification by shock waves, the investigation of residual effects in solids is of primary importance. In this article, structural or chemical changes introduced in solids by intense shock waves will be reviewed, mostly on the basis of investigations carried out by the author's group in the last decade. Particular emphasis will be put on shock-induced changes in solids via high pressure phase transformations and the
decomposition reactions induced by shock waves, which are to be discussed from the microscopic viewpoint.

2. Material Synthesis by Shock Process

Shock compression technique has long been applied to material synthesis, and is currently recognized as a promising means of obtaining unique materials otherwise unavailable. Processes leading to shock synthesis can be divided into two categories: one is to obtain a shock-induced high-pressure phase or its derivative by making use of phase transformations induced by shock waves, and the other is to synthesize materials of the ambiently stable phase with the aid of the ultrafast reactivity at high temperatures induced by shock loading. Both processes have been utilized for material synthesis; the former case is typically represented by the formation of diamond (Bergmann and Barley, 1987) and wurtzite-type BN (Akashi and Sawaoka, 1987), which are now applied on an industrial scale. Shock formation of stishovite (Kleeman and Ahrens, 1973) and coesite (Deribas et al., 1966), high pressure phases of SiO₂, is also possible, although the yield is extremely low. On the other hand, the shock synthesis of intermetallic compounds or complex oxides from constituent elements or oxides belongs to the latter case, and such a technique has been extensively studied for materials processing.

2.1 Shock Synthesis via High Pressure Phase Transformation
i) Formation of high pressure phase by shock compression

One of the most successful cases of retaining a high pressure phase by shock compression experiments is exemplified by the zircon-scheelite transition in ZrSiO₄. Shock loading of zircon single crystals above 53 GPa results in complete conversion to the scheelite type (Kusaba et al., 1985). The volume change accompanying the phase transition amounts to about 10% in spite of a lack of change in the primary coordination number of cations. A simple shearing mechanism for the zircon-scheelite transition has been proposed to explain why the transition can be completed within the short duration of shock loading (Kusaba et al., 1986). Reverse transition in the decompression stage seems to be hindered by some blocking mechanism, which may be related to the considerable residual strain observed in the shock-synthesized scheelite type ZrSiO₄. This is also consistent with the fact that this transition is not realized at room temperature under static conditions, suggesting the involvement of a thermal activation process.

A similar displacive mechanism leading to shock synthesis is proposed for the intermetallic compound Nb₃Si. Shock synthesis of this new superconducting material with Tc = 18 K has been reported by several authors (Pan et al., 1975; DewHughes, 1979; Olinger and Newkirk, 1981; Ohshima et al., 1983). Olinger et al. (1982) explained the transition from the Ti₃P-type
ambient phase to the A15-type superconducting phase by assuming rotation of
an atom block. Very recently, Neumeier et al. (1988) succeeded in improving
the yield of the A15 phase by precooking the specimen to liquid nitrogen
temperature before the shot to minimize the annealing effect by residual
temperature. The A15-type structure has been proven to be a high pressure
phase, denser by 3% than Ti$_3$P-type phase, by synthesis experiments at static
high pressure above 20 GPa (Iwasaki et al., 1982). A superconducting phase of
Ta$_3$Si with Tc = 8.6 K has also been obtained by shock synthesis (Pan et al.,
1977).

Complete conversion was also observed in an H-type to T-type phase
transition in Nb$_2$O$_5$ above about 20 GPa (Adadurov et al., 1971; Kikuchi et al.,
1985a). Since T-Nb$_2$O$_5$ is a metastable low-temperature phase, the transition is
considered to be primarily induced by high pressure rather than high temperature,
although the transition mechanism is not yet disclosed. A similar shock-induced
high pressure phase of CaF$_2$ and BaF$_2$ with a PbCl$_2$-type structure was reported
by German et al. (1975). Phase transition from C-type to B-type rare earth
oxides by shock loading (German et al. 1982) was also interpreted as due to a
pressure-induced mechanism rather than a residual temperature effect, since the
estimated shock temperature is much lower than the transition temperature at
normal pressure. Shock-synthesis of an orthorhombic α-PbO$_2$ type SiO$_2$
claimed by German et al. (1973) was criticized (Kikuchi et al., 1988) but a new
Fe$_2$N type SiO$_2$ was reported very recently (Sekine et al., 1987).

Another plausible mechanism for shock synthesis without extensive
atomic diffusion is demonstrated by the shock crystallization of amorphous
materials. Fcc-type Nb-Si alloy was successfully synthesized from rapidly
quenched amorphous alloy by shock loading to 60 GPa (Wang et al., 1981).
The process apparently has an optimum shock loading condition—the shock
temperature should be higher than the crystallization temperature. Actually,
shock loading below 50 GPa showed no appreciable change. On the other hand,
shock loading to 77 GPa resulted in the formation of the ambient phase of Ti$_3$P
type Nb$_3$Si, probably due to an annealing effect at high residual temperatures. In
general, shock crystallization tends to suppress multi-phase crystallization,
because the time is not sufficient for the nucleation growth process
accompanying atomic diffusion.

ii) Metastable phase formation during the decompression stage

Shock-induced high pressure phases being retained after the passage of
shock waves is rather rare, and most shock-induced high pressure phases with
electronic or displacive origins revert to the ambient phase. Such examples are
found in semiconductor to metal transitions in Si, Ge, GaAs, GaP, etc. (Syono
et al., 1977; Goto et al., 1982; Goto and Syono, 1982), spin-pairing transition
in Fe$_2$O$_3$ (Goto et al., 1981) and probably Fe$_3$O$_4$ (Syono et al., 1977), and
transition due to a change in bond nature, such as LiNbO$_3$ and LiTaO$_3$ (Goto
and Syono, 1985; Syono, 1988). However, in some cases, metastable phases different from the starting materials were obtained in the decompression stage, although the high pressure phase is ultimately unstable upon the release of shock pressure.

The most typical case was found in the formation of $\alpha$-PbO$_2$-type TiO$_2$ through the shock process. Although high pressure phases with very high density have been detected in shock compression measurements (McQueen et al., 1967; Al'tshuler et al., 1973; Syono et al., 1987), the recovered phase was always $\alpha$-PbO$_2$ type with a density only 3% higher than rutile (McQueen et al., 1967; Linde and DeCarli, 1969; Kusaba et al., 1988). Therefore, the $\alpha$-PbO$_2$ phase has been suggested to be formed metastabily in the decompression stage of the shock process. A comprehensive model which explains both the shock compression behavior and residual effects was presented by Kusaba et al. (1988), based on the scenario suggested by Hyde et al. (1972). The model consists of a displacive-type phase transition from rutile to fluorite under shock loading, and spontaneous collapse of the shock-induced fluorite phase to the $\alpha$-PbO$_2$-type phase during the shock release. The anisotropy observed in the phase transition pressures and the yield of the $\alpha$-PbO$_2$ type phase was completely explained by this model. The most decisive evidence was obtained from TEM observation of the relative orientation of coexisting rutile and $\alpha$-PbO$_2$ lamellae with respect to the shock loading direction (Fig. 1).

Direct evidence that the $\alpha$-PbO$_2$ phase was metastabily formed in the decompression stage from the fluorite-related phase induced by shock loading was obtained in MnF$_2$ (German and Podurets, 1982), which is proved to have no stability field of the $\alpha$-PbO$_2$ phase in pressure-temperature diagrams (Lityagina et al., 1972). It is noteworthy that the yield of $\alpha$-PbO$_2$ phase was remarkably improved by precooling the specimen to liquid nitrogen temperature, since the reverse transformation to the ambient phase by prolonged annealing at high residual temperatures is suppressed.

The shock-recovered phase and starting material also show remarkable similarity both in structure and energy in BaZnGeO$_4$ (Takei et al., 1983; Kikuchi et al., 1985b). The shock-induced phase showed a small orthorhombic distortion from the original stuffed trydImite structure with hexagonal symmetry, and is supposed to be metastabily formed from an unquenchable high pressure phase during the release of shock pressure.

The metastable phase realized during the decompression stage of the shock process is not always crystalline, but tends to show some kinds of disordering because of the extremely fast process. Remarkable disordering introduced by incomplete quenching of the shock-induced high pressure phase was noticed in a two-dimensionally disordered structure of so-called X-Nb$_5$O$_5$, which is made up of a block structure similar to the original H-Nb$_5$O$_5$, as shown in a high resolution TEM photograph (Fig. 2) (Kikuchi et al., 1985a). This phase was only observed above 40 GPa when the shock loading direction was perpendicular
to the block axis consisting of NbO$_6$ octahedra array. Higher pressure was required than the transition pressure to T-Nb$_2$O$_5$, which has a higher density than H-Nb$_2$O$_5$ and hence its derivative, X-Nb$_2$O$_5$. This clearly indicates that the X-Nb$_2$O$_5$ was formed during decompression from an unquenchable high pressure phase.

![Image of electron micrograph](image)

**Fig. 1.** Electron micrograph of a rutile (TiO$_2$) single crystal shocked along (100) to about 30 GPa. The incident electron beam is also parallel to (100) of rutile. Lamellae consisting of rutile and $\alpha$-PbO$_2$ phases have specific crystallographic orientations with each other, as shown in the electron diffraction, indicating that the $\alpha$-PbO$_2$ phase was presumably formed from a shock-induced fluorite-like phase during the decompression (Kusaba *et al.*, 1988).

Probably the diaplectic glass obtained by shock loading of some silicate minerals such as quartz and feldspar (Stoffler, 1974; Arndt, 1984) could also be understood as a three-dimensionally disordered metastable phase realized during the decompression stage of the shock process, without excursion to melting. Infrared and Raman studies of shocked anorthite glass revealed that the diaplectic glass was more likely crystalline, rather than ordinary fused glass (Velde *et al.*, 1987). Recent X-ray structure analysis of shocked anorthite glass (Okuno *et al.*, 1985) lends support to the more closely packed geometry formed by a pivoting
motion of (Si, Al)O₄ tetrahedra (Arndt, 1984; Stolper and Ahrens, 1987) compared with thermally obtained fused glass of the same composition, since the most remarkable environment change in shocked glass was found around the Ca modifier ions, with no essential alteration in Si and Al network tetrahedra.

Fig. 2. High resolution electron micrograph of X-Nb₂O₅, a two-dimensionally disordered phase of H-Nb₂O₅, which is obtained by shock loading of H-Nb₂O₅ along the b-axis (block axis) above 40 GPa and is thought to be formed during shock release. The incident beam is along the block axis, which corresponds to the b-axis of H-Nb₂O₅. White dots indicate vacant space surrounded by corner-shared NbO₆. Note two shear bands, crossing at approximately right angles, supposedly formed by shock loading (Kikuchi et al., 1985a).
2.2 Material Synthesis via Rapid Reaction Rate in Shock Compression

Shock synthesis of various complex compounds has been recognized to be a rapid and efficient means for obtaining a large quantity of materials on an industrial scale. Examples of complex oxide formation from constituent oxides are ZnFe$_2$O$_4$ (Morosin et al., 1986), PbZrO$_3$ (Martynova et al., 1975), Ln$_2$TiO$_5$ (Ln = Lanthanoid) (Shcherbakova et al., 1979), etc. Very recently this method was successfully applied to synthesizing a remarkably large disc of high temperature superconducting oxides (Graham et al., 1987; Murr et al., 1987).

Various kinds of intermetallic compounds such as Nb$_3$Sn (Otto et al., 1973), Ni$_3$Al (Simonsen et al., 1986), Ti$_x$Al$_y$ etc. have also been prepared by shock loading of mixtures of constituent elements. Considerable improvement in the solubility limit of Cu–Ga alloy was attained by shock synthesis (Alekseevskii et al., 1979b).

3. Decomposition Reaction in Shock Process

Decomposition reactions also lead to permanent changes of material state in the shock process, although they have been noticed only very recently and are not investigated in detail. The nature of shock-induced decomposition reactions varies greatly, whether they take place in the solid state or are instantly induced by rapid degassing. In this section, some examples of decomposition reactions are discussed.

3.1 Solid State Decomposition by Shock Loading

Because of the short duration of shock pressures, reactions which require extensive atomic diffusion are generally inhibited in the shock process, as in the case of reconstructive phase transformation. Decomposition reactions which occur in the solid state are also restricted, and reaction products show very peculiar textures.

The formation of ultrafine particles is one such characteristic feature inherent to the shock process, as typically demonstrated in some shocked silicate minerals. A TEM photograph of zircon, ZrSiO$_4$, shocked to 53 GPa (Fig. 3) shows that ultrafine ZrO$_2$ particles are dispersed in the amorphous SiO$_2$ matrix (Kusaba et al., 1985). A metastable phase of tetragonal ZrO$_2$ is retained due to a few ten nm size particles. Growth of the decomposed ZrO$_2$ particles is restricted by limited diffusion during the short duration of shock pulses.

Similar decomposition was also observed in Mg$_2$SiO$_4$ shocked above 75 GPa, where a dissociation reaction to MgO + MgSiO$_3$ took place (Syono et al., 1981a). TEM and AEM observation of the shocked products revealed that 10 nm size MgO particles are dispersed in the amorphous MgSiO$_3$ matrix. Because at ambient pressure Mg$_2$SiO$_4$ (olivine) shows neither decomposition nor incongruent melting, the observed dissociation reaction cannot be ascribed to the high temperature effect in the shock released state, but is related to the shock
pressure effect. The dissociation showed good correspondence with the observed anomaly in the shock compression curve of Mg$_2$SiO$_4$ above about 50 GPa (Syono et al., 1981b).

![Electron micrograph of the decomposition product of shocked ZrSiO$_4$, revealing that fine particles of metastable t-ZrO$_2$ are embedded in the amorphous SiO$_2$ matrix (Kusaba et al., 1985).](image)

Disproportionation of Al$_2$SiO$_5$ under shock compression apparently depends on the structure type and porosity of the specimen (Schneider and Hornemann, 1977; Schneider et al., 1980; Schneider and Hornemann, 1981). Sillimanite and andalusite powders were found to break down to Al$_2$O$_3$ + SiO$_2$ (+ mullite in the case of andalusite) for the pressure range of 28-62 GPa, while no remarkable change was detected in shocked kyanite powders. Even a single crystal of andalusite showed gradual decomposition at shock pressures of 36-58 GPa, suggesting that the decomposition cannot be ascribed solely to temperature effects.

3.2 Rapid Decomposition Accompanied by Degassing
(i) Shock reduction of oxides of Vb group elements (V, Nb and Ta)
Some transition metal oxides are known to be reduced instantly upon shock loading by releasing oxygen gas. The most typical cases of such shock reduction have been demonstrated in the oxides of Vb group elements, V, Nb and Ta. These phenomena were first noticed by several Russian investigators (Adadurov et al., 1972; Breusov et al., 1973; Anan’in et al., 1975). We have thoroughly reinvestigated all these oxides by means of X-ray and thermal analyses (Syono et al., 1983; Kikuchi et al., 1986; 1988). Experimental results are summarized in Fig. 4.

![Diagram of shock reduction of M₂O₅ (M = V, Nb and Ta) (Syono et al., 1983; Kikuchi et al., 1986). The spinel phase (Fe, V)₃O₄ is a reduction product around the interface boundary of V₂O₅ and the stainless steel used for container material.](image)

The reduction scheme shows considerable discrepancy between these oxides. The formation pressures of rutile-type oxides by shock reduction to tetravalent states increase in the order of V, Nb and Ta. V₂O₅ was found to be reduced to VO₂ at pressures as low as 30 GPa, while rutile type NbO₂ and TaO₂ were formed above about 40 and 50 GPa, respectively. Furthermore, the yield of rutile type oxides is much higher in Nb- than in Ta-oxides, while the stoichiometry to the dioxide is closer in Ta than in Nb oxides. An intermediate phase of Nb₁₂O₂₉ was observed to occur before the appearance of rutile-type NbO₂.

Similar decomposition reactions accompanied by the release of gas components in the shock process have also been found in other compounds, such as nitrides and hydrides. In the course of shock loading experiments of MoN intended to form B1 type compound, we observed that hexagonal δ-MoN gradually decomposed to form cubic γ-Mo₂N with a defective rock salt structure,
thereby losing part of its nitrogen (Kagawa et al., 1985). The yield of \( \gamma \)-Mo\(_2\)N increases with increasing shock pressure, and complete conversion was attained above about 50 GPa. The yield of \( \gamma \)-Mo\(_2\)N was found to be independent of the porosity of the starting materials, indicating that the decomposition may not be ascribed simply to the thermal effect in the shock released state. Probably the decomposition is instantly induced upon shock loading in a similar way to transition metal oxides.

Fig. 5. Schematic illustration of an inclined mirror experiment for Hugoniot measurements and streak photograph of \( V_2D \) shocked to 130.6 GPa. Two-step extinction of the inclined mirror trace labelled by arrows 1 and 2 indicates the successive arrival of two kinds of particles with different velocities, suggesting decomposition of \( V_2H(D) \) during the decompression (Syono et al., 1984).

More direct evidence for instant decomposition in the shock process was obtained in the Hugoniot measurements of \( V_2H \) and \( V_2D \) (Syono et al., 1984). Although the compression showed quite a normal behavior up to 135 GPa, a striking anomaly was observed in the decompression process above about 110 GPa; an inclined mirror trace of the streak photograph clearly demonstrated a two-step extinction, as shown in Fig. 5, implying that two kinds of particles with different free surface velocities arrived successively at the inclined mirror.
Although the slower component shows a normal free surface velocity of twice the particle velocity obtained from the impedance match solution, the faster component gives an abnormally high free surface velocity by a factor of 2.7. The simplest interpretation of this unusual phenomenon is given by the instantaneous decomposition of V_2H or V_2D to vanadium metal and hydrogen (or deuterium) in the shock decompression process, corresponding to the slower (normal) and faster (abnormal) components, respectively. Dehydration or devolatilization reactions in hydrous silicates and Mg(OH)_2 or CaCO_3 induced by shock compression might also be due to a similar rapid mechanism accompanying degassing (Lange and Ahrens, 1982; Boslough et al., 1982).

(ii) Redox reactions in the shock process

Besides the decomposition reaction, simultaneous oxidation and reduction in the shock process have come to be noticed frequently; i.e. Ta or Al + SiO_2, Fe (Cr, Ni) + GeO_2 or V_2O_5. Most of the reactions apparently take place along the interface between the oxide specimen and metallic container. Most thoroughly studied is the redox reaction in the Ta + SiO_2 system, in which Ta was ultimately oxidized to Ta_2O_5, and SiO_2 was reduced to silicon (Kikuchi et al., 1987). Figure 6 shows a TEM photograph of such an interface, where oxidized tantalum and reduced silicon particles are distributed in the shock-vitrified SiO_2 glass, to a certain distance from the interface boundary accompanied by decrease in their sizes. Formation of β-Ta_2O_5 and silicon was confirmed by X-ray diffraction analysis and high resolution electron microscopy.

A similar redox reaction had already been reported in impact experiments on quartz sands by a hypervelocity aluminum projectile, in which the aluminum was oxidized to Al_2O_3 and SiO_2 was reduced to silicon (Jammes et al., 1983). An important difference lies in that the redox reaction in this case is thermodynamically allowed, while the redox reaction of Ta + SiO_2 is not expected from thermodynamical equilibrium under ordinary conditions.

Reaction of oxide specimens with their stainless steel containers was also found recently. Shock loading experiments of a GeO_2 specimen above about 50 GPa resulted in the formation of a spinel phase with a unit cell dimension of 8.40 Å, close to that of Fe_2GeO_4, 8.411 Å (Kikuchi et al., 1988).

A similar reaction with the stainless steel container under shock loading was also found in V_2O_5. When the shock pressure exceeds about 45 GPa, and V_2O_5 is reduced to V_2O_3, a spinel phase with unit cell dimension of 8.444 Å simultaneously appears. The amount of spinel phase increased with increasing loading pressure. Chemical analysis of the spinel phase by AEM showed an Fe/V ratio of 1.4/1.6, indicating the formation of (V, Fe)_3O_4 spinel, although small amounts of Cr and Ni were also confirmed. Observed Mössbauer spectra also showed a striking resemblance to that of Fe_3O_4-FeV_2O_4 spinel solid solution.
Fig. 6. Fine particles dispersed in a shock-vitrified SiO₂ matrix, which were formed by a shock-induced redox reaction of the Ta-SiO₂ system at the interface boundary. The complete oxidation of tantalum to Ta₂O₅ and the reduction of SiO₂ to silicon was confirmed by means of analytical electron microscopy. The arrow shows a shock propagation direction perpendicular to the interface (Kikuchi et al., 1987).

4. Concluding Remarks

A materials response to shock waves strongly depends on the nature of the chemical bond, such as metallic, covalent or ionic. Shock-induced phase changes and chemical reactions also show diversity in accordance with the mechanism, which is rigorously controlled by the short duration of the shock process. Therefore, material development making use of shock compression techniques requires detailed knowledge of the mechanisms leading to such structure changes or chemical reactions. For this purpose, a microscopic approach, as represented by electron microscopy, is extremely useful for getting precise information on the inhomogeneous textures realized by non-equilibrium short-time shock processes, not only for basic research but also for application science.

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REFERENCES


*Note added in proof*

Since the manuscript was written in 1988, considerable amount of works has been accumulated with respect to this subject. However, because of limited time and space for rewriting, only works which have been carried out in the author's laboratory for 1989–1991 are summarized here, together with supplemented bibliography.

Investigations on the shock-induced phase transitions for various rutile type compounds of SnO$_2$, PbO$_2$ and FeTaO$_4$ were continued (Kusaba *et al.*, 1991). Comparative study with static high pressure experiments was also made for MnF$_2$ (Kusaba *et al.*, 1991). Concerning the mechanism of rutile-fluorite phase transformation under shock loading, molecular dynamical calculation for rutile under uniaxial compression was made and found to reproduce well the fast and anisotropic phase transition observed experimentally. Various kinds of sesquioxides were also shocked to 50 GPa (Atou *et al.*, 1990). Phase transformations in Y$_2$O$_3$ and Gd$_2$O$_3$ from the C-type to B-type rare earth oxide structure under shock loading were inferred to proceed via a virtual high pressure
phase of the A-type rare earth oxide, similar to the rutile-fluorite-\textit{PbO}_2 sequential transition found in TiO\textsubscript{2} (Kusaba et al., 1988). High pressure corundum phase of In\textsubscript{2}O\textsubscript{3} was recovered in the pressure range of 15–25 GPa, although the yield was very small (Atou et al., 1990).

Raman microprobe measurements of diaplectic feldspar glass obtained by shock loading showed that the glass transformation pressures as well as structure of Raman spectra were different with plagioclase composition reflecting structural type difference (Veldre et al., 1989). Microscopic textures of shocked quartz have also been studied in detail (Tattevin et al., 1990).

Shock loading effects on the high temperature superconducting oxides have been investigated extensively. Observation by electron microscopy of the shocked high Tc oxides revealed that the deformation textures induced by shock loading strongly depended on the structure. Very remarkable mica-like kink patterns observed in the shocked Bi system were ascribed to the well developed cleavage due to weak bonding between Bi-Bi layers (Syono et al., 1990; Kikuchi et al., 1990). Decomposition reactions induced by shock loading also affected the superconducting properties of the shocked high Tc oxides (Takeya et al., 1990) and rapid degassing in Tl\textsubscript{2}Ba\textsubscript{2}CuO\textsubscript{6} resulted in the appearance of superconductivity due to release of over-doping in the unshocked non-superconducting material (Kikuchi et al., 1990).

REFERENCES


Takeya, H., H. Takei, W. J. Jang, Y. Syono, M. Kikuchi and K. Kusaba, Shock-induced changes in La\textsubscript{2}CuO\textsubscript{4}, La\textsubscript{2}NiO\textsubscript{4}, La\textsubscript{2-x}Sr\textsubscript{x} CuO\textsubscript{4} and La\textsubscript{2-x}Sr\textsubscript{x} single crystal, \textit{Jpn. J. Appl. Phys.}, \textbf{29}, 1252–1256, 1990.