Shock Synthesis of Gd$_2$Zr$_2$O$_7$

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Abstract. We dealt with shock compression on a composition of Gd$_2$Zr$_2$O$_7$ by explosive-driven flyer impact methods, because Gd$_2$Zr$_2$O$_7$ with r$_{Gd}$/r$_{Zr}$ ratio of 1.46 lies at the structural boundary between ordered pyrochlore and defect fluorite structures. The results indicate recovered products depend on shock conditions that we need to specify by further study.

Introduction

Shock compression process provides unique environments for materials synthesis due to not only the realized high pressure and high temperature but also the shock-enhanced kinetics and fast quenching [1]. The process is a time-limited reaction and favors martensitic phase transformation in general. There are many trials to use shock compression techniques for investigation of solid state reactions [2]. The most typical one has been known historically as diamond synthesis, and the process has been developed to optimize the yield of products. Here we report a progress of shock synthesis of oxide compounds using explosive-driven plate impacts.

Rare earth pyrochlore compounds of A$_2$B$_2$O$_7$, where A is a rare earth element and B is a tetravalent cation such as Zr$^{4+}$ and Ti$^{4+}$, exhibit several interesting properties for physical, chemical and industrial applications. The pyrochlore structure is known to form if the cation radii ratio (r$_A$/r$_B$) lies in the range 1.46–1.80. However, the fluorite structure is favored with r$_A$/r$_B$ below 1.46. The cation radii ratio r$_A$/r$_B$ has an important effect on the high pressure structural stability. Gd$_2$Zr$_2$O$_7$ with r$_A$/r$_B$ ratio of 1.46 lies at the structural boundary between ordered pyrochlore and defect fluorite. Hence it is expected to show interesting structural behavior as a function of temperature and pressure. We tried to understand the effect of shock compression on Gd$_2$Zr$_2$O$_7$. Among A$_2$B$_2$X$_7$ (X is anion such as O and F) compounds there are three discrete structures of pyrochlore, fluorite, and weberite. Their structural relations are based on the fluorite structure (AX$_2$) where each anion is at the center of the cation tetrahedral (A$_4$X) and the lattice is characterized by a lattice constant of $a = \sim$5 Å with Z=1. In pyrochlore structure, different A and B cations make A$_4$X, B$_4$X, and A$_2$B$_2$X, and the lattice is expanded double ($a = \sim$10 Å) and the number of Z=8. Weberite consists of A$_3$BX, AB$_3$X, and A$_2$B$_2$X, with lattice constants of $\sqrt{2}a$, 2$a$, and $\sqrt{2}a$ and with Z=4. Therefore, pyrochlore and weberite have their corresponding superlattices in addition to the fluorite structure.

Shock compression technique has never been applied to solid-solid reactions in complicate chemical systems to our knowledge. We explore such chemical systems using shock compression techniques.
Experimental methods

We dealt shock compression on two starting mixtures of a composition Gd$_2$Zr$_2$O$_7$ (powdered mixture of Gd$_2$O$_3$ + 2 ZrO$_2$ and the product heated in air at 900 °C for 2 hours), encapsulated in copper containers, by explosive-driven flyer impact methods [3]. A copper flyer with a diameter of 40 mm and a thickness of 2 mm is accelerated to a high velocity by the detonation of the main explosive charge of nitromethane (CH$_3$NO$_2$), initiated by a booster charge of 8701 explosive [3]. Peak shock pressure reflected within a sample is calculated by the impedance match method from the known impact velocity. The shock velocity (Us km/s)- particle velocity (Up km/s) relation of copper [4] with density of 8.924 g/cm$^3$) is used as $U_s = 3.91 + 1.51U_p$. The starting material preheated at 900 °C (sample I) was partially reacted to a fluorite structure with monoclinic ZrO$_2$ according to the powder x-ray diffraction (XRD) analysis (Fig. 1 A, B, and C). Another starting material (sample II) was a mixture of Gd$_2$O$_3$ and monoclinic ZrO$_2$ as the received powders.

The container after shot was cut open to remove the sample. The successfully recovered samples as well as the starting materials were investigated by powder x-ray diffraction methods to identify phases present in products. We carried out a series of recovery experiments as a function of impact velocity and porosity.

![Fig. 1. XRD patterns using Cu Kα radiation for sample I.](image1)

(A) Gd$_2$O$_3$ after heated at 1000°C for 4 hours,
(B) ZrO$_2$ after heated at 800°C for 4 hours,
(C) Product from a mixture of (A) and 2 (B) after heated at 900°C for 2 hours,
(D) Recovered sample I with porosity of 48% at 43.5 GPa,
(E) Recovered sample I with porosity of 40% at 60.0 GPa, and
(F) Recovered sample I with porosity of 54% at 84.9 GPa.

![Fig. 2. XRD patterns using Cu Kα radiation for sample II.](image2)

(A) Gd2O3 as received, (B) ZrO2 as received,
(C) Recovered sample II with porosity of 50% at 60.0 GPa,
(D) and (E) Recovered sample II with porosity of 30% at 84.9 GPa. Peak with Cu indicates the highest peak for Cu.
Results and discussion
We have started a series of shock recovery experiments on various pyrochlore compounds that has not known yet, and explore novel compounds using shock compression. We report and discuss the results on two bulk compositions of Gd₂Zr₂O₇. Impact velocities of 1.85 km/s, 2/36 km/s, and 3.06 km/s of Cu flyers correspond to peak shock pressures of 43.5 GPa, 60.0 GPa, and 84.9 GPa, respectively.

The XRD patterns of recovered samples indicate completely transformed to the fluorite structure with no additional peaks (Fig. 1 F) from sample I. The peaks sharpen with increasing shock pressure (Figs. 1 D and E). The starting sample (Fig. 1 C) indicates peaks corresponding to a fluoride structure and Gd₂O₃ with no ZrO₂. Although this result suggests that the fluorite is non-stoichiometric, the initial monoclinic ZrO₂ may be transformed to cubic or tetragonal structure at shock-induced high temperatures. The maximum peaks for fluorite and tetragonal (or cubic) ZrO₂ are close around 30 degree each other, and the difference between tetragonal and cubic ZrO₂ is indistinguishable by XRD [5].

The products from the raw powder mixture (sample II), however, display two types of XRD patterns (Fig. 2). One consists of relatively broad peaks corresponding to a pyrochlore structure (Figs. 2 C and E) and the other indicate relatively sharp peaks of pyrochlore structure (Fig. D), although both contain significant amounts of copper powders from container and may contain small amount of tetragonal (or cubic) ZrO₂. The copper contamination that we did not observed in sample I may suggest higher shock temperatures in sample II than sample I because the starting Gd₂O₃ powder was poorly crystalline (Fig. 2 A).

Then, the presence of a large amount of copper in the recovered sample II can be explained by high temperatures, although the porosity difference may affect the shock temperature. The formation of fluorite Gd₂Zr₂O₇ suggests relatively high temperatures (>1530°C) in hot press sintering [6]. If this is the case, our shock temperatures could be close to this. The effects of porosity of the initial powders pressed in the recovery container are not well controlled in the present study, and we need further study. However, high temperatures generated in powdered samples are found to promote solid reaction significantly. It is difficult to understand the shock pressure effect on the solid reaction due to a small difference between fluorite and pyrochlore structures at high pressures. Based on a detailed study of the lattice parameter of Gd₂Zr₂O₇ with fluorite and pyrochlore structures at ambient condition [7], the pyrochlore has slightly larger volume than the fluorite and can be the low pressure. Therefore, we need to know shock conditions to understand the solid reactions. And also it is interesting to compare the static compression results on Gd₂Zr₂O₇ at room temperature [8, 9]. The results indicate back transformation from pyrochlore to defect-fluorite formed above 15 GPa [8] and amorphization above ~35 GPa due to distortion of cation [9].

Summary
Shock compressions of powders with a composition of Gd₂Zr₂O₇ produced both defect fluorite and ordered pyrochlore structures detected by x-ray diffraction methods. The results need to be specified to understand the solid reactions.

References


