

Dehydration of potassium alum induced by shock loading

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Abstract. Potassium alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) powder filled into a copper container were shock loaded up to 6.3 GPa by flyer plate impact. Recovered samples were characterized by X-ray diffraction (XRD) analysis, Raman spectroscopy, and scanning electron microscopy (SEM). XRD and Raman results of samples shocked at 4.4 GPa and below indicated that there was no sign of phase transition. In contrast, the XRD pattern of the sample shocked at 6.3 GPa was clearly different from the initial sample. Unlike previous results obtained from hydrostatic pressure experiments, an irreversible phase transition to an amorphous phase occurred under shock compression at 6.3 GPa. The morphology of the sample surface indicated the ejection of water vapor caused by shock loading. The amorphization may be attributed to the vaporization of water molecules caused by shock pressure and shock-induced heat.

1. Introduction

Potassium aluminum sulfate dodecahydrate ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$), often called potash alum, belongs to the group of double salts. Potash alum has been used as a food additive and as a material for cosmetic formulations, such as in antiperspirants, cleansing products, and skin care products. The dehydration reactions of potash alum have been investigated by thermal analysis, microscopic observation during dehydration, and photoacoustic spectroscopy in the ultraviolet-visible (UV-vis) region [1–4]. The dehydration reaction begins at around 60 °C [4]. Approximately 10 or 11 water molecules are eliminated from potash alum heated at 180 °C and above, and a fraction of potash alum transforms to a higher-temperature phase, $\text{KAl}(\text{SO}_4)_2$. Most of the crystallization water molecules are eliminated up to 250 °C and the heated sample becomes crystalline $\text{KAl}(\text{SO}_4)_2$ [4, 5].

Shock wave data are crucial in models of impact cratering and accretionary interactions in the solar system [6, 7]. The impact-induced dehydration of minerals is of interest because the ejection of dust and volatile gases due to high-velocity collisions between the Earth and meteorites has been considered to be a possible mechanism for the formation of the hydrosphere and oceans [8, 9]. The shock-induced dehydration of minerals including antigorite serpentine [10], Muscovite [11], and Mg- and Ca-sulfates and their hydrates [12] has been studied. A projectile impact on potash alum will result in dehydration by the ejection of water molecules. Sakuntala *et al.* observed a reversible phase transition of potash alum to an amorphous phase with a higher orientational disorder (OD) under high pressure [13, 14]. Significant changes observed in the Raman spectra and XRD patterns indicated that a phase transition occurs above 6.0 GPa. However, the behavior of potash alum under shock loading has not yet been investigated.



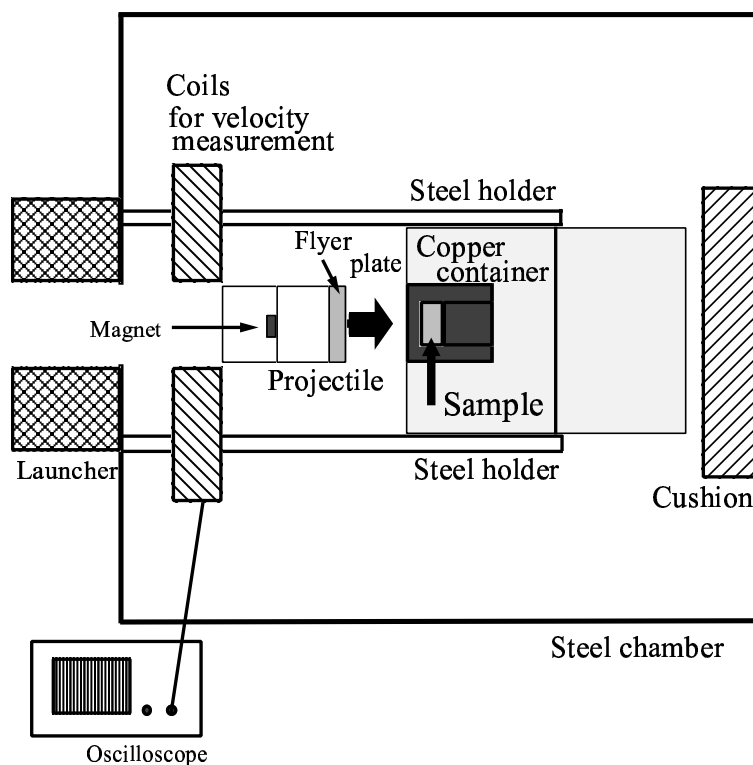


Figure 1. Loading configuration with gas-gun shock-compression fixture.

In this study, potash alum heated at various temperatures was characterized using Raman spectroscopy and X-ray diffraction analysis to determine the structural phase transformation associated with the elimination of water molecules.

2. Experiment

Transparent octahedral grains of potash alum (Wako Chemicals, 99%) were used. The starting potash alum powder was prepared by pulverizing potash alum crystals using an agate motor. Samples were pressed into copper containers with an inner diameter of 20 mm at 75 and 78% of the theoretical maximum density (TMD) of the powder. All handling processes were conducted in air. An approximately 1.5 mm thick Cu plate was mounted on a 30 mm diameter projectile and accelerated using a single-stage powder-propellant gun. The flyer velocity was measured by the magnet flyer method, which involves embedding a magnet in the flyer. The flyer velocity was varied between 0.8 and 1.3 km/s. Details of the shock-compression procedure have been reported elsewhere [15]. Table 1 shows a summary of the shock-loading conditions and figure 1 shows a schematic diagram of the experimental arrangement.

The peak pressures shown in table 1 were calculated according to the impedance matching method using the Hugoniot relation for potash alum with the porosity incorporated using McQueen's approach [16]. The calculated Hugoniot relation for potash alum was estimated using thermodynamic and elastic constants [13].

The crystal structures of recovered samples were analyzed using XRD (Rigaku RINT-2200) with Cu $K\alpha$ radiation. Raman spectra were measured in a backscattering geometry with a micro-Raman spectrometer (Seishin-Shoji RA-07F) equipped with a monochromator (Horiba

Table 1. Experimental conditions for shock compression of potash alum.

Shot	Flyer velocity (km/s)	Packing density (%)	Calculated pressure (GPa)
1	0.82	75	2.7
2	0.96	75	3.6
3	1.32	78	6.3
4	1.07	75	4.4

Jobin Yvon 500M) and a charge-coupled-device (CCD) detector (Horiba Jobin Yvon Symphony). Radiation with a wavelength of 532 nm from a neodymium-doped yttrium aluminum garnet laser was used for excitation of the Raman spectra. The laser power used to excite the target was <50 mW and the size of the focus spot on the sample was approximately 20 μm in diameter. The spectral resolution was estimated to be approximately 5 cm^{-1} . The microstructure of the samples was characterized using scanning electron microscopy (SEM; Hitachi, S-4500). All measurements were performed at room temperature.

3. Results and discussion

Shots 1, 2 and 4, where the potash alum powder samples were shocked at 4.4 GPa and below, were well consolidated. The container used for shot 3 was broken, so that only a limited amount of the sample could be recovered. The results indicate that some materials inside the container vaporize, which results in water vapor ejection and/or the decomposition of potash alum [17].

Figure 2 shows typical XRD patterns of shock-recovered potash alum. Figure 2 shows the XRD pattern of potash alum heated at 180 °C for 2 h and that of a $\text{KAl}(\text{SO}_4)_2$ crystal. The $\text{KAl}(\text{SO}_4)_2$ crystal was obtained by heating $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ powder at 500 °C for 2 h. The XRD pattern of the potash alum crystals heated at 180 °C for 2 h suggests a phase transition to an amorphous phase; the heat-induced amorphization of alum has been previously revealed by XRD analysis [18]. The XRD patterns of the samples recovered from shot 2 and 4 are similar to that of shot 1 shown in figure 2. These XRD patterns are consistent with the powder XRD pattern corresponding to $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. A broad peak at around 20 ° and some sharp peaks are observed in the XRD pattern of the shot 3 sample (6.3 GPa), which indicates the sample consists of an amorphous material, partly dehydrated potash alum, and $\text{KAl}(\text{SO}_4)_2$ crystal.

The Raman spectrum of the shot 4 sample is consistent with that of the unshocked sample (figure 3). No Raman peaks were observed for the shot 3 sample because of strong fluorescence. The shot 4 sample had no additional peaks corresponding to other phases or amorphous phases, and no deviation or broadening of each peak depending on shock pressure was observed. The Raman spectrum of the samples recovered from shot 1 and 2 are similar to that of shot 4 shown in figure 3. Consequently, the XRD and Raman results of samples shocked at 4.4 GPa and below indicate that there is no phase transition.

The morphology of the sample shocked at 6.3 GPa is clearly different from that of unshocked crystal and the sample heated at 200 °C for 2 h (figure 4). The SEM image of the sample shocked at 6.3 GPa (figure 4(b)) has cavities and string-like structures with diameters of several tens of micrometers. Although holes are also evident on the surface of the heated sample (figure 4(c)), only blocky crystalline structures are observed. As mentioned above, the container used for shot 3 was broken. Combined with the breakage, both figures 4(b) and (c) suggest that the ejection of water vapor and/or gas due to dissociation of $\text{KAl}(\text{SO}_4)_2$ from inside of the sample. The dissociation of $\text{KAl}(\text{SO}_4)_2$ occurs at around 930 °C [4]; therefore, the ejecta could only be water vapor. In addition to shock-induced heat, a powder sample undergoes severe deformation and

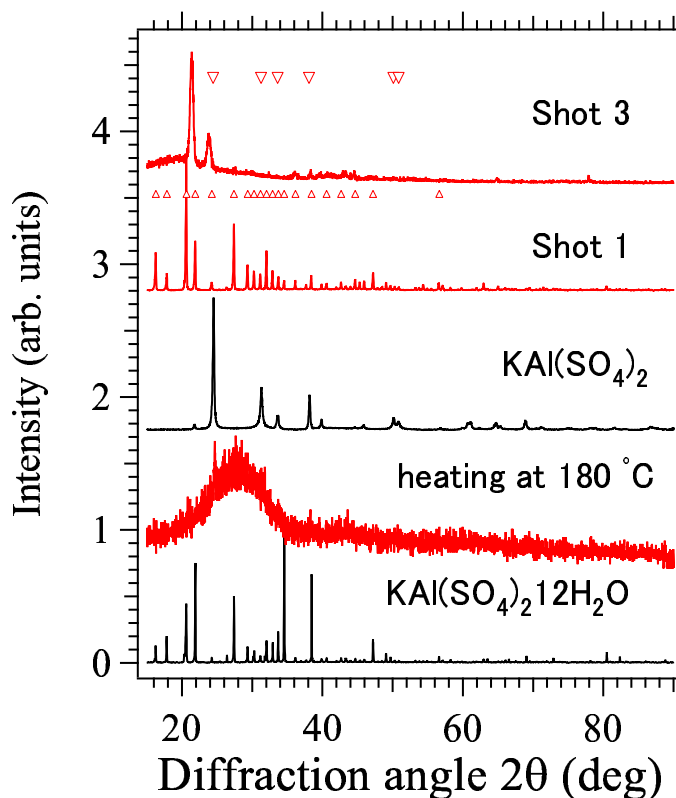


Figure 2. XRD patterns of potash alum after shock compression and after heating. The triangles (Δ) and inverted triangles (∇) denote $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{KAl}(\text{SO}_4)_2$, respectively.

friction during shock loading [19], which may be the reason for the difference in the morphology of the heated sample and the sample shocked at 6.3 GPa.

The pressure-induced reversible phase transition of potash alum occurs at around 6 GPa, although it is dependent on the OD of the potash alum [13]. This phase transition is transformation from crystalline to an amorphous phase and this change has been observed by the XRD and Raman spectra. The observed changes in the XRD patterns and the morphology of the sample shocked at 6.3 GPa suggest the occurrence of a shock-induced irreversible phase transition to the amorphous phase. The critical pressure for the phase transition corresponds well, but the stability of the amorphous phase caused by static pressure and shock loading appear to be different. The shock-induced amorphization of potash alum is attributed to the elimination of water molecules. The amorphous potash alum does not return to crystalline potash alum unless the amorphous absorbs water molecules. On the other hand, Sakuntala *et al.* suggested that the OD is the driving mechanism of the pressure-induced amorphization [13]. The amorphous phase of potash alum is equilibrium state under hydrostatic pressure. In addition to the effect of shock pressure, the effect of shock-induced heat and localized heat due to severe deformation and friction during shock loading is not negligible. It is speculated that the elimination of water molecules is caused by not only the effect of shock pressure but also these thermal effects. This may imply that the shock-induced amorphization of potash alum is similar to dehydration of potash alum caused by heating. Therefore, the difference in mechanism of amorphization results in the difference in the stability of the amorphous phase. On the other hand, reactions initiated

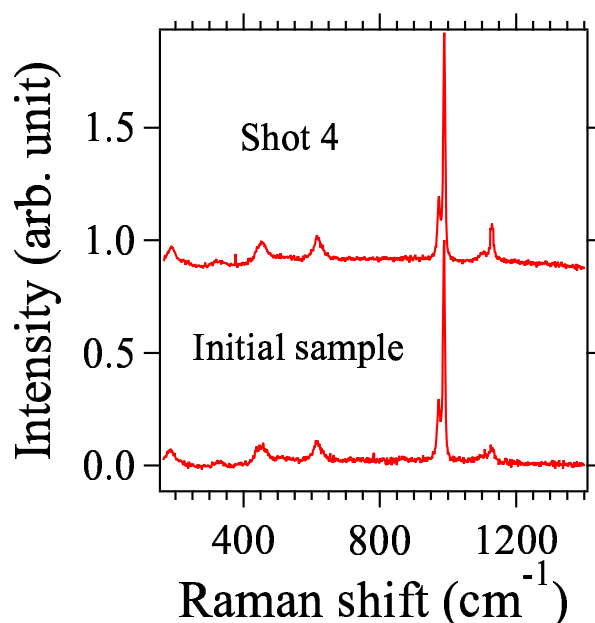


Figure 3. Raman spectra of potash alum before and after shock loading.

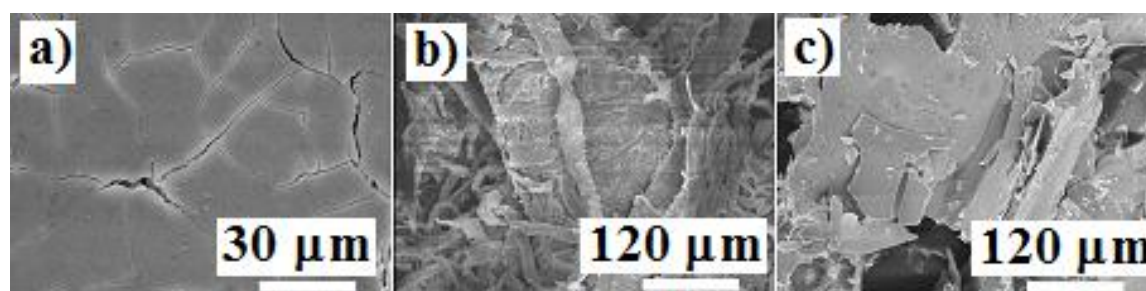


Figure 4. SEM images of sample surfaces (a) before and (b) after shock loading at 6.3 GPa, and (c) after heating at 200 °C for 2 h.

by shock waves have been classified as either shock-induced or shock-assisted reactions [20, 21]. The shock-assisted chemical reactions can also occur following unloading from the peak pressure, but due to bulk shock temperature increases in time scales of thermal equilibration. In contrast to shock-assisted reactions, shock-induced chemical reactions occur on a submicrosecond time scale during mechanical or pressure equilibration. In general, thermal dehydration of potash alum takes long [5]. It is speculated that shock-assisted dehydration reaction during shock loading results in amorphization of potash alum.

4. Conclusion

Shock-loaded potash alum powders were characterized and evidence of shock-induced dehydration and phase transition to an amorphous phase were obtained. The sample shocked at 6.3 GPa consisted of an amorphous material, partly dehydrated potash alum, and $\text{KAl}(\text{SO}_4)_2$ crystal. The morphology of the shock recovered sample was slightly different to that of the heated sample. Although the critical pressure for shock-induced amorphization was consistent

with that for hydrostatic pressure, the irreversibility of the shock-induced amorphous phase does not correspond with the reversibility of the amorphous phase caused by hydrostatic pressure. Thus, the irreversible amorphization may be attributed to vaporization due to the elimination of water molecules caused by shock pressure and shock-induced heat.

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