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Shock-Wave Study of the Metallization of Alkali Halides up to 400 GPa

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Abstract. Alkali halide materials under high pressure are of fundamental interest, due to the number of phase transformations they exhibit under compression. For example, the phase transition from wide band gap insulator into electrical conductor, observed in many insulators under shock and static compression, has been poorly explored for many alkali halides. Results of early shock experiments pose a number of unresolved questions such as the possibility of non-equilibrium behavior at high shock pressures. In this study we investigate the optical properties of alkali halides NaCl, KBr, CsBr and CsI, under shock loading up to 400 GPa, by measuring shock wave speed and reflectivity using line VISAR in decaying-shock experiments. Significant increases in the optical reflectivity with shock pressure in all four cases indicate conditions of metallization at high pressures. The results are analyzed with respect to previous shock and static measurements on the alkali halides.

INTRODUCTION

Alkali halides are widely used in high-pressure research as pressure media under static compression and transparent optical windows under dynamic compression [1]. However, the study of some alkali halides' response to shock compression has given rise to inconclusive results, leading to an incomplete picture of their high pressure behavior. Early work under shock compression [2-3] showed evidence for substantially reduced brightness temperatures compared to expected alkali halide Hugoniot temperature. Suggested explanations range from a highly reflective shock front to the existence of non-equilibrium radiation that is present as a result of shock wave structure, which are addressed in this work. Additionally, the insulating character of the alkali halides is expected to break down under compression – following the trend set by other insulating materials [4-5]. An attempt to give clear identification of the optical behavior of shocked single crystal alkali halides is discussed in this study.

METHOD

Laser-driven, decaying shock-wave experiments on four alkali halides – CsI, CsBr, KBr and NaCl – were completed using the Janus optical laser at Lawrence Livermore National Laboratory's Jupiter Laser Facility, with observations of shock conditions and optical properties recorded by dual-channel line VISAR operating at 532 nm. The laser drive, at 527nm, used 1 or 2 of Janus' arms with phase plates providing a focal spot of 600 μm circular diameter or 1000 μm square; pulses of 2 ns duration were used. The shock targets consisted of a single-crystal alkali halide sample a few millimeters thick, adjacent to a metallic pusher base several tens of microns in thickness of Al, Cu or Au on which was placed a hydrocarbon ablator. A piece of anti-reflection coated window material was attached to the top surface of the samples with optical adhesive to reduce spurious back-reflections (Fig. 1). In general, samples were dried in a vacuum oven for 24 hours or more to eliminate adsorbed water. Reflectivity measurements of the shock front are measured relative to the known reflectivity of the pusher surface prior to shock breakout [6-8]. Conversion from measured shock velocities to pressures are completed through the Hugoniot relationships and the known equations of state [9]. The results from all the shots are tabulated below in Table I and plotted in Fig. 2.

Literature values for the refractive index dependence on density for each alkali halide at low pressure are used to predict the expected reflectivity trends for each alkali halide in the insulating compressed phases, based on the assumption that there is a linear relationship between the changes in refractive index and density [2,10-11]. Reflectivities are calculated by using Fresnel's equation of reflectivity at the shock interface between the shocked and un-shocked regions in the sample; associated pressures are calculated by using the known Hugoniots. The sharp deviation from these trends in the data is then used to establish the breakdown of insulating conditions and onset of metallization [12]. The pressure point at which this occurs is denoted the metallization onset pressure (MOP) and describes the

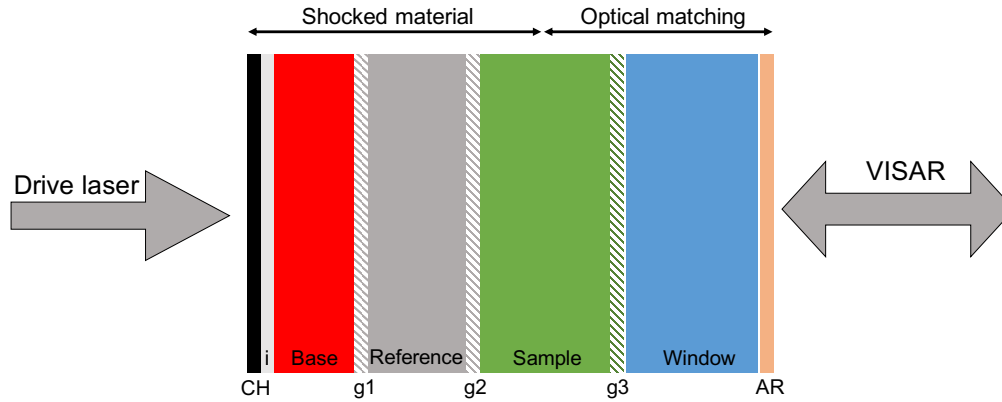


FIGURE 1. Schematic of shock target layers (Not to scale). Left to right: CH is the ablator, i is the intermediate layer, Base is the metallic pusher, g1 is a glue layer, Reference is an optical reference layer, g2 is a glue layer, Sample is the alkali halide single crystal, g3 is a glue layer, Window is the optical matching layer and AR is the anti-reflection coating on the window. Optional layers of sample stack are indicated in grey. Adjacent layers in the shock target are either directly deposited or attached by adhesive glue (DOUBLE/BUBBLE epoxy green or Norland Optical Adhesive 63). The CH ablator layer is 5-12 μm thick. The adhesive glue layers g1 and g2 are approximately 1 μm or less in thickness, when present. The right side of the target is for optical matching using an anti-reflection (AR) coated window (Glass, LiF), optically glued to target (g3, adhesive thickness is arbitrary). Intermediate (i) layer only in NC1 (see table I); g1/Reference layers only in NC1 and KB2 (see table I); g2 not present when layers are direct deposited (CNC1, CNC2, GKB1, GCB1).

pressures required to induce the continuous crossover from the purely insulating phase towards a new phase at high pressures which is conducting.

RESULTS AND DISCUSSION

It is shown that in the case of CsI there is good agreement between all four shots that were taken. In direct comparison with the expected reflectivity of a compressed insulator, the measured reflectivity from VISAR shows that there is a deviation away from the insulator-like behavior at ~ 50 GPa and towards a phase which has a much higher reflectance. The reflectivity deviation occurs in the liquid phase, given that the data are all above the shock melting pressure [13] of CsI. Further comparison with a statically compressed sample [14] shows that the MOP of CsI is dependent on the type of compression; as such the static MOP is higher (~ 100 GPa) than under shock compression (40 GPa). This can be explained by the significantly higher temperature attained on adiabatic shock compression, in comparison to isothermal compression, which results in both melting, which can decrease the pressure at which metallization occurs [4,12], as well as increased electronic excitation into the conduction band [5,15].

Results from CsBr show a similar trend to CsI, with additional features. The presence of a reflectivity plateau at low pressures just above and parallel to the line for the expected insulator phase could indicate a liquid insulator refractive index slightly larger than estimated from the literature, but otherwise following the typical linear refractive index-density trend of an insulator. CsBr exhibits a higher MOP than its Iodide counterpart at ~ 80 GPa. In comparison with Kormer et al. [3] there is a discrepancy between the reflectivity measurements around ~ 100 GPa; Kormer reports a reflectivity of $\sim 5\%$ at 112 GPa in agreement with insulator reflectivity and the present data suggesting a reflectivity closer to $\sim 15\%$. Notably, reflectivity is only detectable above melting, consistent with a large jump in refractive index when entering the melt [11], and similarly metallization occurs in the liquid.

In KBr, even more detail is visible: by examination of the low-pressure data (Fig. 2c inset) we observe shock melting over the pressure range 20 - 40 GPa by the changes in reflectivity, shifting between that of liquid and solid insulating KBr [11]. Complete melting is determined to occur at ~ 33 GPa, in close agreement with independent measurements of the shock melting pressure in KBr [16]. The MOP here is observed at ~ 50 GPa – agreeing well with that in CsI, and again metallization occurs in the liquid.

In the case of NaCl there are datasets with significantly different behaviour (Fig. 2d). In one dataset, considered to be on an ideal sample, the recorded signal from the VISAR agrees well with that of the insulating solid-state reflectivity up to much higher pressures than expected for a material with a published shock melting pressure of 60 ± 5

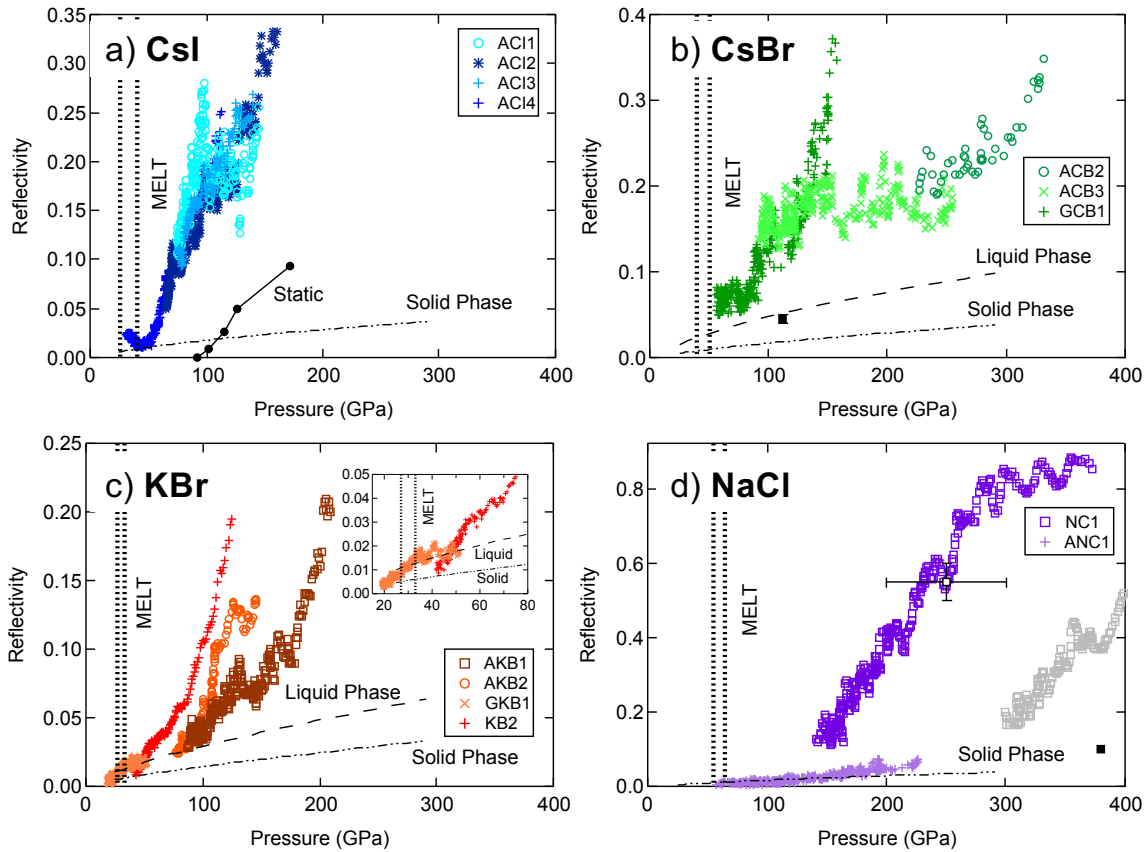


FIGURE 2. Pressure-reflectivity response of four alkali halides up to 400 GPa. a) CsI b) CsBr c) KBr d) NaCl. Each plot shows the measurements from multiple shots; each individual shot is indicated by a different marker. The expected reflectivity of insulating states as a function of pressure, calculated from the change in refractive index with density [10-11], is shown for the solid (double dot-dashed line) and liquid phases (dashed line). Prior shock reflectivity measurements (filled black squares) and predictions based on a measured reduced brightness temperature (open black square) [3] are shown for comparison. Filled black circles show prior pressure-reflectivity measurements under static compression in CsI [14]. Inset on c) shows a magnified plot of the low pressure region of c). Known shock melting pressure ranges are also shown as vertical dotted lines [13,16-17]. Grey curve in (d) indicates a possible, but less likely, pressure range for the high reflectivity dataset, with poorer agreement between VISAR channels.

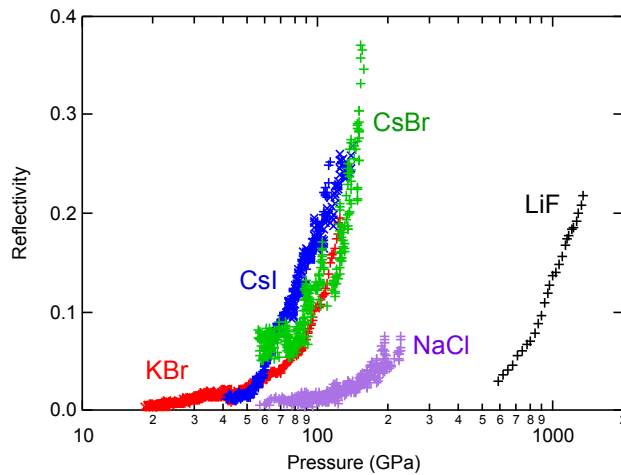


FIGURE 3. Comparison of the trends in the reflectivity dependence near metallization onset pressure (MOP) for five Alkali Halides under shock compression. LiF reflectivity – pressure-relationship is taken from Ref.[15].

GPa [17]; this would seem to suggest that NaCl stays in the solid insulator phase up to much higher pressures than previously recorded or that there is little change in refractive index between liquid and solid NaCl. The MOP in this case is suggested as ~ 150 GPa. In the second, based on an early experiment performed on a sample of unknown quality, there is an extremely rapid rise in reflectivity from 150 GPa to 380 GPa reaching a maximum reflectivity of $\sim 80\%$; the extremely high value of reflectivity is confirmed in this experiment by use of a thin layer ($\sim 30 \mu\text{m}$) of a second reference material (α -Quartz [5], which also becomes reflecting during the experiment) placed between the metal base and sample (Fig. 1). In the scale of typical maximum values for shock reflectivity measured historically, 80% reflectivity is unusually high, but is inconsistent with values measured in NaCl in the subsequent better controlled experiment, though the MOP suggested by the trend in the data – at around 125 GPa – is roughly the same. Historical direct measurement [3] of reflectivity (10% reflectivity at 380 GPa) in generally good agreement with extrapolation of the better controlled dataset; however, a reflectivity as high as 50-60% at 200-300 GPa was expected from the separate measurements of the reduction in brightness temperature [3], in direct agreement with the earlier dataset (NC1, Fig.2). This gives some weight to the validity of the earlier shot despite its high magnitude. This would suggest that the reflectivity can at least partly account for the low brightness temperatures measured, as suggested by Kormer et al. [3], but the collected results also suggest a shock reflectivity sensitive to the specific experimental conditions. It is possible that the earlier sample of NaCl in the present results, which was not as carefully prepared and dried, could have been contaminated by water. Indeed, the results suggest that the adsorption of water adsorption may play a particularly strong role in the optical properties of the shocked alkali halides.

The variation in the response of each alkali halide under compression is shown in Fig. 3. Measurements of the reflectivity of LiF are taken from a prior study [15] and compared to our results. The behavior of the lighter alkali halides (LiF and NaCl) shows deviation from insulator-like reflectivity at very high pressures; whilst the behavior of the heavier samples (KBr, CsBr, CsI) show the deviations at much lower pressures. KBr, CsBr, and NaCl show an unusual irreproducibility in reflectivity in the metallization regime but generally good agreement with expected insulator reflectivities at lower pressures; this suggests the variability in reflectivity in the metallization regime is not due simply to measurement error. No systematic difference in reflectivity depending on base material was identified.

The trend of MOP as a function of the atomic weight and electronic band gap is shown in Fig. 4. There is clearly a link between the composition of each alkali halide and its shock response. A nearly linear trend in the MOP with initial band gap is suggested across these alkali halides; this would suggest that materials with smaller band gaps would have a lower MOP therefore would be easier to metallize. The presence of d-shell electrons in the heavier alkali halides could also provide an additional reasoning for the apparent trend, as all show relatively similar MOP despite a wide range in atomic weight. These observations show that there are clear systematics which dictate the

TABLE I. Record of shots taken at Janus, the target base, beam intensity, and pressure range reached in each shot. Thicknesses of layers present are in parenthesis.

Sample	Material	Base Material	Conditions	Intensity ($\cdot 10^{13} \text{ W/cm}^2$)	Pressure (GPa)	
					Max.	Min.
CNC1	NaCl (2mm)	Cu ($50\mu\text{m}$)	Transparent	1.9		
ANC1	NaCl (2mm)	Al ($48\mu\text{m}$)	Reflecting	2.0	225	60
NC1 ^a	NaCl (1mm)	Al ($50\mu\text{m}$) ^b	Reflecting	7.8	380	140
NC2	NaCl (2mm)	Cu ($50\mu\text{m}$)	Transparent	1.0		
AKB1	KBr (2mm)	Al ($48\mu\text{m}$)	Reflecting	2.2	210	90
AKB2	KBr (2mm)	Al ($48\mu\text{m}$)	Reflecting	1.3	145	80
GKB1	KBr (2mm)	Au ($21.6\mu\text{m}$)	Reflecting	0.9	50	20
KB2 ^a	KBr (1mm)	Al ($50\mu\text{m}$)	Reflecting	1.0	125	40
ACB2	CsBr (2mm)	Al ($48\mu\text{m}$)	Reflecting	2.2	330	225
ACB3	CsBr (2mm)	Al ($48\mu\text{m}$)	Reflecting	2.0	250	95
GCB1	CsBr (2mm)	Au ($25.4\mu\text{m}$)	Reflecting	1.9	155	60
ACI1	CsI (2mm)	Al ($48\mu\text{m}$)	Reflecting	1.8	145	75
ACI2	CsI (2mm)	Al ($48\mu\text{m}$)	Reflecting	1.2	160	65
ACI3	CsI (2mm)	Al ($48\mu\text{m}$)	Reflecting	1.0	140	80
ACI4	CsI (2mm)	Al ($48\mu\text{m}$)	Reflecting	0.6	110	35

^a 32 μm Quartz reference layer between base and crystal (Fig. 1)

^b Intermediate layer of 2 μm Gold (Fig. 1)

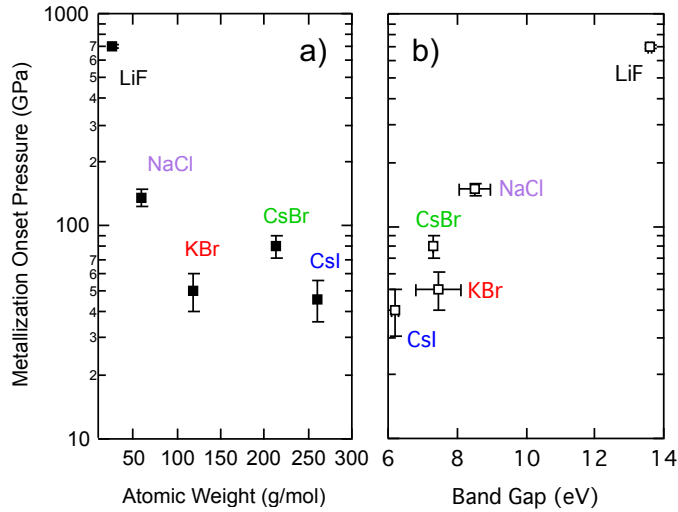


FIGURE 4. The onset of high reflectivity as a function of atomic weight (a) and electronic band gap [18] at ambient pressure (b) (LiF from [15]).

behavior of alkali halides under shock compression.

Where direct reflectivity measurements were previously available for these materials, it was interpreted that the reflectivities measured were anomalously low [3]. It was thought that shock fronts in these alkali halides exhibited non-equilibrium behavior associated with optical screening of the equilibrium Hugoniot state by an intermediate opaque, but not fully metallic state (see Fig. 43 of Ref. [2]). This interpretation that reflection depends on shock structure, when electrons are being excited into conducting states, is broadly consistent with our observations: we observe generally higher reflectivities than recorded in the historic, longer duration experiments, and we observe an unusual amount of inconsistency in the reflectivities in the metallic regimes in our own experiments but remarkably good agreement in the limit of lower reflectivity, with the data tending to approach that of an ideal insulator-insulator shock discontinuity. This confirms the data are likely accurate, but may measure some aspects of the internal shock-front structure which may strongly depend on loading conditions, timescale, and other factors.

CONCLUSION

In summary, we observe strong enhancements in the optical reflectivity of alkali halides NaCl, KBr, CsBr, and CsI with increasing pressure under dynamic compression. The trend in the onset pressure of elevated, metal-like reflectivities across the alkali halides, including LiF, shows a clear correlation with material properties, in particular initial electronic band gaps. Below the metallization onset the reflectivity tends to follow expected trends for shocked, insulating material, with low reflectivity attributed to real index of refraction differences across the shock front. In the metallization domain, reflectivities of alkali halides exhibit an abnormal degree of irreproducibility in different experiments, similar to prior observations. These irregularities may be related to a proposed intrinsic dependence of alkali halides reflectivity on shock front structure, though an influence of impurities, in particular water, cannot be ruled out.

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