

Compressibility of RbBr at Elevated Pressures

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Compressibility data of RbBr measured by an *in situ* X-ray energy-dispersive diamond-anvil pressure cell are reported. Measurements of molar volumes were made at room temperature to greater than 15 GPa. The results obtained with a pressure transmitting medium were in agreement with those of previous workers (Bridgman (1) and Vaidya and Kennedy (2)) using the piston-displacement technique at lower pressures. The results obtained without a pressure transmitting medium, but were probably hydrosopic, were systematically more compressible than those of previous workers. Measurements from this work, combined with Bridgman's (1) and Vaidya and Kennedy's (2) piston-displacement measurements to 40,000 kg/cm² and 45 kbar, respectively, yielded values of $K_T^\circ = 13.84 \pm 1.03$ GPa and $K_T^{\circ'} = 5.24 \pm 0.29$. © 1991 Academic Press, Inc.

Introduction

The compressibility of RbBr was measured previously by Bridgman (1) to 100,000 kg/cm² and by Vaidya and Kennedy (2) to 45 kbar by the piston-displacement technique. Molar volumes at higher pressures are needed to obtain bulk moduli and their derivatives from a wider pressure range, and to detect potential phase transition other than $Fm3m = Pm3m$ at pressures greater than those previously attained. This work, carried out by using a diamond-anvil pressure cell, also offers a comparison with that carried out by piston displacement.

Experimental Method

RbBr (99.9%, Ventron Alfa Products, Lot No. 88686-050274) and NaF (Spectrum Chemical, Lot No. 59115K14) were used as starting materials. Samples were heated in vacuum at 120°C for 24 hr to drive away

possible moisture contamination. After drying they were placed in a desiccator and evacuated. Two milligrams of each of the starting materials was examined with a Philips powder X-ray diffractometer and with Cu radiation from 70° to 5° 2θ at a 1°/min scan rate. No peaks other than those compatible with those listed in ASTM files are present.

A standard Bassett type diamond-anvil pressure cell with two opposed ¼ carat Type II diamonds was used for the experiment. Alignment of the diamonds was carried out by aligning the two opposed carbide rockers. The starting material was loaded into a predrilled sample chamber 250 μm in diameter and approximately 100–115 μm in thickness at approximately the center of a stainless steel or alloy gasket that was placed in between the diamond anvils, with the lower side of the gasket slightly glued to prevent it from slipping. A collimated X-ray beam with a 125-μm beam diameter was centered

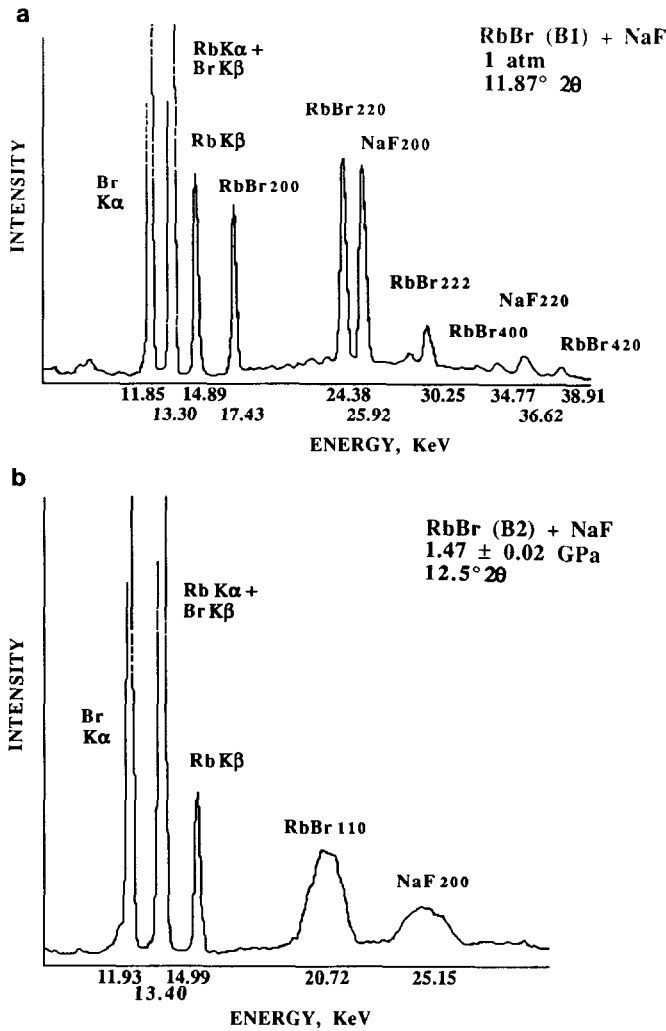


FIG. 1. Energy-dispersive spectra of RbBr (B1) + NaF at room pressure and $11.87^\circ 2\theta$ (a) and of RbBr (B2) + NaF at 1.47 GPa and $12.5^\circ 2\theta$ (b).

at the sample chamber by placing a film between the diamond anvils and adjusting the alignment repeatedly until the exposure of film appeared centered and the image of the beam was circular in shape. Pressure in the 250- μm sample chamber in between the diamond anvils was generated by hydraulic force applied to a piston 2.54 cm in diameter, by a 5 : 1 lever.

The sample assembly was placed on a translation stage and the assembly was cen-

tered with the X-ray beam by manipulating the precise position of the sample assembly with the translations after an initial optical alignment.

A polychromatic X-ray beam from a Rigaku RU200 rotating anode generator was used. Operating conditions were 50 kV and 15 mA. A vertical slit collimates the diffracted beam. A Kevex solid state 3040 Si(Li) detector collected energy-dispersive spectra, which were then processed by a

Tracor-Northern (TN-1710) multichannel analyzer. Routine energy calibration with AgBa and with three additional fluorescence peaks of RbBr at known diffraction angles at room pressure suggested peak centroids are accurate to within ± 5 eV, and better for peaks of superior qualities or peaks collected over an extended period of time (Fig. 1). The Bragg equation

$$d = (hc/E)/2 \sin \theta$$

was used to obtain the d -spacings, where h is the Planck's constant, c is the speed of light, E is the energy of the peak centroid, and θ is half of the diffraction angle 2θ , which is limited to between 8° and 16° (2θ) by geometrical configuration of the experimental setup. The d -spacings were then used to calculate the lattice parameters and molar volumes of the sample at various pressures. Sample pressures were determined by placing an internal standard in each run, and the molar volume of the standard used to calculate pressure was determined by using a Murnaghan equation of state of the standard. Calibration of the diffraction angle was carried out by measuring standards with known d 's and E 's. Various potential pressure standards were attempted in an initial stage and two halides, LiF and NaF, were most suitable because their peak positions did not interfere with that of RbBr and there is no phase transition over the pressure range of this work. Further experiments suggested NaF to be more workable than LiF because LiF is too light a diffractor and requires a large amount of material to produce a good spectrum. In using a large LiF to RbBr ratio the peak intensity of RbBr was reduced. Various ratios of RbBr to NaF in the starting material mixture were experimented with: 1:1, 1.5:1, 2:1, and 1:1.5 by volume. All were successful. The results reported here were obtained with a 1:1 ratio. RbBr and NaF were weighed to make a 1000-mg batch of mixture, transferred to an agate mortar, and ground for an extended

period of time. Minor recrystallization of RbBr can sometimes be observed under an optical microscope during grinding. For later batches of starting materials, an oil (Liquid Petroleum Light U. S. P.) was admixed with the mixture (discussed below). In run 401 about $1 \mu\text{l}$ of oil was introduced by a hypodermic syringe to 100 mg of RbBr + NaF mixture. In later experiments (runs 501 to 522) a reduced amount of oil, about $0.5 \mu\text{l}$, was introduced to 100 mg of mixture. The sample and oil were ground to a sticky homogeneous mixture, and as much as possible was packed into the sample chamber by a dental pick, compressed slightly with the flat edge of the tool, and packed again until the surface of the sample chamber was flat.

Various stainless steel and alloy gaskets were used in the experiments: T-301, Inconel-718, Rene-41, and Udimet. Since steel transforms from a bcc to an hcp structure at about 11 GPa, which is within the pressure range of this work, only preliminary runs at low pressure used steel gaskets. Udimet appeared more brittle than others. Inconel appeared to be successful and was used for most runs. The duration of the spectrum collection varies. Fluorescence peaks for energy calibration were acquired rapidly, in minutes for Rb and Br K peaks. Most runs required about 6 to 8 hr at stages where sample thickness was not greatly reduced and 12 hr and longer where samples became thinner at later stages.

Results

Experimental results are listed in Tables I and II and plotted in Fig. 2. Only selected energy and angle calibrations using RbK α , BrK α , RbBr B_1 , RbBr (200), RbBr (220), RbBr (222), RbBr (400), NaF (220), and RbBr (420) are listed in runs 200, 201, and 301 for illustrative purpose. Calibrations were individually made for each run and detailed calibration for individual runs is

TABLE I
 ENERGY, *d*-SPACING, VOLUME, AND PRESSURE OF RUNS OF RbBr + NaF

No.	Energy (keV)	<i>d</i> (Å)	<i>V</i> (Å ³)	<i>V_p</i> / <i>V_{p=0}</i>	<i>P</i> - <i>P</i> ₀ (GPa)	Note
200	16.539 ± 0.001					RbBr B1
	16.534 ± 0.001					RbBr B1
	13.345 ± 0.001					RbKα
	11.870 ± 0.003					BrKα
	11.871 ± 0.002					BrKα
201	22.402 ± 0.001	2.577	48.405	0.592		BrBr B2 110
	22.408 ± 0.001	2.577	48.405	0.592		BrBr B2 110
	26.484 ± 0.002	2.180	82.915	0.831	13.163	NaF200
	26.482 ± 0.002	2.180	82.915	0.831	13.163	NaF200
	13.351 ± 0.001					RbKα
202	13.351 ± 0.001					RbKα
	22.386 ± 0.001					RbBr 110
	22.451 ± 0.001	2.572	48.124	0.589		RbBr 110
	22.460 ± 0.001	2.571	48.068	0.588		RbBr 110
	22.457 ± 0.001	2.571	48.073	0.588		RbBr 110
	26.694 ± 0.002	2.163	80.957	0.812	15.841	NaF 200
	26.682 ± 0.002	2.164	81.070	0.813	15.681	NaF 200
206	22.000 ± 0.001	2.625	51.129	0.626		RbBr 110
	21.996 ± 0.001	2.625	51.157	0.626		RbBr 110
	26.057 ± 0.002	2.216	87.038	0.872	8.557	NaF 200
	26.093 ± 0.002	2.213	86.678	0.869	8.911	NaF 200
207	21.374 ± 0.001	2.701	55.756	0.682		RbBr 110
	21.383 ± 0.001	2.700	55.684	0.681		RbBr 110
	25.517 ± 0.002	2.263	92.687	0.929	3.942	NaF 200
	25.514 ± 0.002	2.263	92.711	0.929	3.924	NaF 200
124	20.726 ± 0.001	2.786	61.150	0.748		RbBr 110
	20.714 ± 0.001	2.787	61.255	0.750		RbBr 110
	25.162 ± 0.001	2.295	96.652	0.969	1.535	NaF 200
	25.213 ± 0.001	2.290	96.072	0.963	1.852	NaF 200
	125	21.257 ± 0.001	2.716	56.680	0.694	
21.256 ± 0.001		2.716	56.693	0.694		RbBr 110
21.253 ± 0.001		2.717	56.718	0.694		RbBr 110
25.444 ± 0.002		2.269	93.490	0.937	3.406	NaF 200
25.446 ± 0.002		2.269	93.453	0.937	3.430	NaF 200
126	21.592 ± 0.001	2.674	54.084	0.662		RbBr 110
	21.588 ± 0.001	2.675	54.116	0.662		RbBr 110
	25.789 ± 0.003	2.240	89.867	0.901	6.037	NaF 200
	25.781 ± 0.003	2.240	89.867	0.901	6.037	NaF 200
	127	22.001 ± 0.001	2.625	51.131	0.626	
21.982 ± 0.001		2.627	51.254	0.627		RbBr 110
25.835 ± 0.001		2.235	89.303	0.895	6.507	NaF 200
25.829 ± 0.001		2.236	89.375	0.896	6.446	NaF 200
204		22.412 ± 0.001	2.576	48.365	0.592	
	22.383 ± 0.001	2.580	48.546	0.594		RbBr 110
	26.509 ± 0.003	2.178	82.665	0.829	13.488	NaF 200
	26.500 ± 0.003	2.179	82.745	0.829	13.385	NaF 200
208	21.522 ± 0.002	2.683	54.609	0.668		RbBr 110
	21.538 ± 0.002	2.681	54.493	0.667		RbBr 110

TABLE I—Continued

No.	Energy (keV)	d (Å)	V (Å ³)	$V_p/V_{P=0}$	$P - P_0$ (GPa)	Note
205	25.733 ± 0.003	2.244	90.362	0.906	5.645	NaF 200
	25.696 ± 0.004	2.247	90.761	0.910	5.334	NaF 200
	22.441 ± 0.001	2.573	48.174	0.590		RbBr 110
	22.428 ± 0.001	2.574	48.258	0.590		RbBr 110
	26.318 ± 0.001	2.194	84.477	0.847	11.269	NaF 200
203	26.249 ± 0.003	2.200	85.138	0.853	10.525	NaF 200
	22.335 ± 0.001	2.585	48.863	0.598		RbBr 110
	22.320 ± 0.001	2.587	48.959	0.599		RbBr 110
	26.502 ± 0.003	2.179	82.734	0.829	13.394	NaF 200
121	26.478 ± 0.003	2.181	82.950	0.831	13.121	NaF 200
	20.717 ± 0.001	2.787	61.235	0.749		RbBr 110
	20.720 ± 0.001	2.787	61.203	0.749		RbBr 110
122	25.155 ± 0.001	2.295	96.741	0.970	1.487	NaF 200
	25.149 ± 0.001	2.296	96.804	0.970	1.453	NaF 200
	20.706 ± 0.001	2.789	61.328	0.750		RbBr 110
	20.702 ± 0.001	2.789	61.367	0.751		RbBr 110
	25.159 ± 0.001	2.295	96.703	0.969	1.507	NaF 200
123	25.158 ± 0.001	2.295	96.703	0.969	1.507	NaF 200
	20.734 ± 0.001	2.785	61.077	0.747		RbBr 110
	20.728 ± 0.001	2.786	61.130	0.748		RbBr 110
	25.130 ± 0.001	2.298	97.032	0.973	1.333	NaF 200
301	25.157 ± 0.001	2.295	96.720	0.970	1.498	NaF 200
	17.433 ± 0.001					RbBr 200
	24.624 ± 0.001					RbBr 220
	25.924 ± 0.002					NaF 200
	30.253 ± 0.001					RbBr 222
	34.772 ± 0.001					RbBr 400
	36.622 ± 0.001					NaF 220
	38.911 ± 0.001					RbBr 420
	11.842 ± 0.001					BrK α
	13.289 ± 0.002					RbK α
	22.172 ± 0.002	2.719	56.860	0.696		RbBr 110
	26.804 ± 0.001	2.249	91.040	0.913	5.122	NaF 200
	22.169 ± 0.001	2.719	56.860	0.696		RbBr 110
303	26.818 ± 0.001	2.248	90.839	0.911	5.274	NaF 200
	22.182 ± 0.003	2.718	56.787	0.695		RbBr 110
304	26.843 ± 0.001	2.246	90.637	0.909	5.430	NaF 200
	22.221 ± 0.001	2.713	56.480	0.691		RbBr 110
305	26.872 ± 0.001	2.244	90.398	0.906	5.616	NaF 200

Note. The 2θ settings are 12.5° for runs 200 to 123 and 11.9° for runs 301 to 305.

available upon request to the author. Only (110) of RbBr and (200) of NaF are listed in Tables I and II. Parameters of other peaks are available upon request to the author. Runs in Table I were carried out with starting materials consisting of RbBr and NaF alone. As presented in a V/V_0 vs P diagram (Fig. 2), it was obvious that they were sys-

tematically more compressible than those reported by Bridgman (1) and Vaidya and Kennedy (2) using the piston-displacement technique. Table II lists later experiments using a starting material consisting of RbBr + NaF + oil. These are in agreement with those of previous workers (1, 2). The apparent nonhydrostatic effect is discussed later.

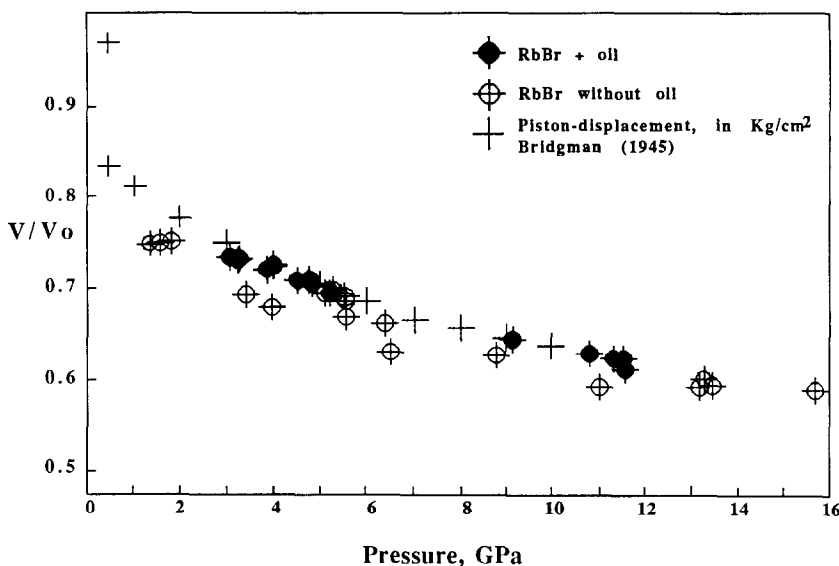


FIG. 2. $V_p/V_{p=0}$ versus pressure of runs.

The $Fm\bar{3}m = Pm\bar{3}m$ ($B1$ [NaCl] = $B2$ [CsCl]) transition occurred shortly after the experiment began. As soon as pressure was applied, the sample immediately transformed into the $B2$ structure. Repeated attempts were made to measure the lower pressure region of Fig. 2 by raising the pressure in as small amount an increment as possible by hand-cranking the hydraulic pump with minimal increments. The lowest pressure achieved was around 1.5 GPa. It appears that the instrument was not sensitive in this pressure range and it was necessary to rely on piston displacement data for low P measurements and for the $Fm\bar{3}m = Pm\bar{3}m$ transition.

Experiments with oil as a pressure transmitting medium are expected to demonstrate more compressibility than those carried out without a pressure transmitting medium. The result obtained was opposite to this expectation. Efforts were made to examine this effect. All calibrations and data reductions were reexamined and no inconsistency or systematic error was found.

It appeared possible that this effect was

related to the nature of the sample. A batch of the sample in the runs without oil was analyzed with a Materials Analysis Co. wavelength-dispersive X-ray electron microprobe for Rb, Br, Na, and F. The total concentration obtained for these elements was 95.1 wt%. Repeated analyses detected no other element present in the sample. Therefore the near 5% unaccounted for is most likely due to an element or elements lighter than F, not detectable by an electron microprobe. The most likely impurity phase is H_2O . This is consistent with the hydroscopic nature of alkali halides. Although dried and stored in a desiccator until immediately prior to the experiments, the sample could still have interacted with (air) moisture during some stage(s) of the experiments. Therefore the apparent "dry" runs without a pressure transmitting oil were likely to be wet runs containing nearly 5% of a pressure transmitting medium other than oil, such as water, and became more compressible than those with oil. This was verified by comparison with a run with a sample consisting of 95 wt% of RbBr + NaF

TABLE II
ENERGY, d -SPACING, VOLUME, AND PRESSURE OF
RUNS OF RbBr + NaF + OIL

No.	Energy (keV)	d (Å)	V (Å ³)	$V_P/V_{P=0}$	$P - P_0$	Note
401	17.633 ± 0.001					RbBr 200
	24.903 ± 0.002					RbBr 220
	26.182 ± 0.002					NaF 200
402	22.284 ± 0.001	2.736	57.953	0.709		RbBr 110
	27.072 ± 0.001	2.253	91.492	0.917	4.786	NaF 200
501	17.389 ± 0.001					RbBr 200
	24.561 ± 0.002					RbBr 220
	25.843 ± 0.003					NaF 200
	29.262 ± 0.001					RbBr 222
503	21.764 ± 0.001	2.764	59.728	0.731		RbBr 110
	26.483 ± 0.001	2.271	93.744	0.940	3.242	NaF 200
504	21.743 ± 0.001	2.767	59.893	0.733		RbBr 110
	26.482 ± 0.002	2.271	93.744	0.940	3.242	NaF 200
506	21.722 ± 0.002	2.769	60.058	0.735		RbBr 110
	26.441 ± 0.002	2.274	94.117	0.943	3.006	NaF 200
507	21.844 ± 0.001	2.754	59.074	0.723		RbBr 110
	26.592 ± 0.001	2.262	92.585	0.928	4.010	NaF 200
511	21.868 ± 0.001	2.750	58.831	0.720		RbBr 110
	26.562 ± 0.001	2.264	92.847	0.931	3.832	NaF 200
512	21.994 ± 0.001	2.736	57.913	0.709		RbBr 110
	26.664 ± 0.002	2.256	91.858	0.921	4.520	NaF 200
514	22.021 ± 0.001	2.731	57.637	0.705		RbBr 110
	26.703 ± 0.002	2.253	91.446	0.917	4.820	NaF 200
515	22.122 ± 0.002	2.719	56.859	0.696		RbBr 110
	26.748 ± 0.002	2.248	90.934	0.912	5.202	NaF 200
518	22.681 ± 0.001	2.652	52.751	0.645		RbBr 110
	27.202 ± 0.003	2.211	86.495	0.867	9.094	NaF 200
520	22.862 ± 0.001	2.631	51.514	0.630		RbBr 110
	27.369 ± 0.002	2.198	84.893	0.851	10.797	NaF 200
521	22.918 ± 0.001	2.624	51.110	0.625		RbBr 110
	27.424 ± 0.003	2.194	84.430	0.846	11.324	NaF 200
522	22.943 ± 0.001	2.622	50.978	0.624		RbBr 110
	27.442 ± 0.002	2.192	84.247	0.844	11.537	NaF 200
524	23.081 ± 0.002	2.606	50.057	0.612		RbBr 110
	27.448 ± 0.002	2.191	84.162	0.844	11.636	NaF 200

Note. The 2θ settings are 11.7° for runs 401 and 402, and 11.9° for other runs.

mixture and 5% of distilled deionized water. At 4.102 GPa, the (110) peak of RbBr was 21.414 keV, in good agreement with measurements of runs with nearly 5% unknown impurity.

The lack of sensitivity of the diamond-anvil pressure cell technique at the low pressure range required using previous workers' low pressure measurements in deriving the bulk modulus and its derivative. A least-squares fit of the data from runs with oil from this work alone gives values of K_T^0 and $K_T^{0'}$ of 25.30 ± 4.74 GPa and 3.75 ± 0.72 , respectively. The data from runs with oil from this work, combined with Bridgman's (1) and Vaidya and Kennedy's (2) measurements using the piston-displacement technique to 40,000 kg/cm² and 45 kbar, respectively, yielded values of $K_T^0 = 13.84 \pm 1.03$ GPa and $K_T^{0'} = 5.24 \pm 0.29$ by a least-squares fit. Adding Bridgman's measurements to 100,000 kg/cm² did not change these parameters significantly.

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