p–T PHASE RELATIONS OF $CH_3NH_3PbX_3$
(X = Cl, Br, I) CRYSTALS†

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Abstract—Pressure–temperature phase relations of $CH_3NH_3PbX_3$ (X = Cl, Br, I) crystals were studied by using a high pressure DTA apparatus in the range between 0.1 Pa and 200 MPa. A triple point was found in each compound below 100 MPa. By pressurization, the low pressure phases disappeared at the triple point in the chloride and bromide while a new high-pressure phase appeared in the iodide. The pressures and temperatures of the triple points are 75.1 MPa, 175.7 K for $CH_3NH_3PbCl_3$, 43.2 MPa, 152.9 K for $CH_3NH_3PbBr_3$, and 84.8 MPa, 176.2 K for $CH_3NH_3PbI_3$. All the boundaries between the cubic and tetragonal phases are upward convex and that of the iodide has a maximum at about 120 MPa. Other phase boundaries are essentially straight lines in the measured pressure and temperature ranges. By the use of the Clausius–Clapeyron equation, the transition volumes were calculated from the slopes of the phase boundaries and the transition entropies obtained in a previously published calorimetric experiment (*J. Phys. Chem. Solids* **51**, 1383 (1990)).

1. INTRODUCTION

$CH_3NH_3PbX_3$ (X = Cl, Br, I) crystallizes in the cubic perovskite structure in the highest temperature phases [1] and undergoes two or three phase transitions [2–4]. Transition temperatures determined by the authors [5] and the structures determined by Poglitsch *et al.* [3] are summarized in Table 1. The bromide has two tetragonal phases. One of them corresponds to the tetragonal phase of the chloride and the other to that of the iodide. In a recent paper [5], we reported calorimetric and spectroscopic studies of the phase transitions of $MAPbX_3$ (X = Cl, Br, I), where MA represents the methylammonium ion, $CH_3NH_3^+$. All the phase transitions were of the first order. The large transition entropies indicated that the phase transitions are of the order–disorder type. The entropy values were interpreted with structural models in which each MA ion is disordered with respect to the orientations of the C–N axis itself and around the C–N axis.

In the present paper, we investigate the pressure dependence of the phase transitions of $MAPbX_3$ (X = Cl, Br, I) by using a high pressure DTA. Our purpose is to determine the *p–T* phase diagrams of the three halides and thereby to obtain

the basic data for discussing the mechanism of the solid state phase transitions. For ammonium halides [6, 7], a systematic relation between the transition pressure and the ionic size of the halogen has been established; the increase in pressure is equivalent to the decrease in ionic size of the halogen. It is another purpose of the present work to examine whether or not such a systematic relation exists in the present compounds.

2. EXPERIMENTAL

The sample preparation of $MAPbX_3$ is the same as described in the previous paper [5]. The DTA experiments were performed with a home-made apparatus described elsewhere [8]. It was essentially a metal block made of copper–beryllium alloy. Two wells were drilled symmetrically in the block, one being for the sample and the other for the reference material. The temperature difference between the two wells was measured by a copper–constantan thermocouple encapsulated in a stainless-steel sheath and was recorded on a strip chart as a function of temperature. The apparatus was designed for the temperature range between 90 and 400 K. Hydrostatic pressure was applied to the sample crystals using helium gas as the pressure-transmitting medium. The pressure range of the measurement was between 0.1 MPa (atmospheric pressure) and 200 MPa. The applied

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Table 1. Structures and transition temperatures of $CH_3NH_3PbX_3$ (X = Cl, Br, I)

$CH_3NH_3PbCl_3$	orthorhombic		tetragonal				cubic
	$P222_1$	171.5 K	$P4/mmm$		177.2 K		$Pm3m$
$CH_3NH_3PbBr_3$	orthorhombic		tetragonal		tetragonal		cubic
	$Pna2_1$	148.8 K	$P4/mmm$	154.0 K	$I4/mcm$	236.3 K	$Pm3m$
$CH_3NH_3PbI_3$	orthorhombic				tetragonal		cubic
	$Pna2_1$		161.4 K		$I4/mcm$	330.4 K	$Pm3m$

Structures are determined by Poglitsch et al. [3] and transition temperatures are determined by the authors [5].

pressure was not regulated but the pressure change experienced during the traverse of any phase transition was within 0.1 MPa. The effect of hydrostatic pressure on the calibration of the thermocouple is . small (~ 0.3 mK MPa^{-1} at 50°C). Therefore, the ambient pressure calibration was used without correction. The mass of the DTA sample was 0.4–0.7 g.

To determine the pressures and temperatures of the phase transitions precisely, the DTA measurements were carried out with rather slow heating rate (0.3–1.0 K min^{-1}) and the rate was kept as nearly constant as possible for the measurement of the same phase transition at different pressures. All the phase transitions observed in the present study were of the first order, and so the transition temperatures were determined as the intersections of the extrapolation of the rising part of the peaks and the base lines. In all cases, the transition temperatures determined at 0.1 MPa agreed within 0.1 K with those determined by the previous heat capacity measurement [5].

3. RESULTS AND DISCUSSION

Figure 1 shows the experimental DTA curves of MAPbCl$_3$ at several pressures up to 75.0 MPa. The heating rate was 0.3–0.4 K min^{-1}. At atmospheric pressure (0.1 MPa), two endothermic peaks corresponding to the $P222_1 - P4/mmm$ and $P4/mmm-Pm3m$ transitions were observed at 171.4 K and 177.2 K, respectively. With increasing pressure, the peak at 171.4 K shifted to higher temperatures and the one at 177.2 K to lower temperatures. The two peaks merged into one at 75.0 MPa, above which only a single peak was observed. This indicates the existence of a triple point at around 75 MPa in MAPbCl$_3$.

Figure 2 shows the experimental DTA curves of MAPbBr$_3$ in the low temperature range. The heating rate was 0.3–0.4 K min^{-1}. The triple point among the $Pna2_1$, $P4/mmm$, and $I4/mcm$ phase of the MAPbBr$_3$ crystal was located at round 43 MPa. Figure 3 shows the experimental DTA curves of MAPbI$_3$ in the
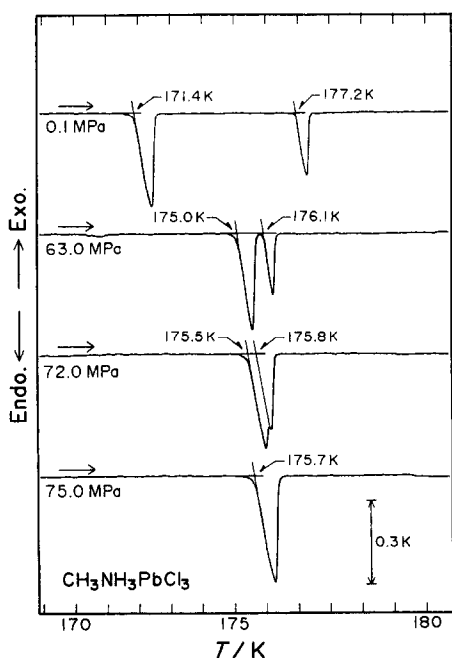

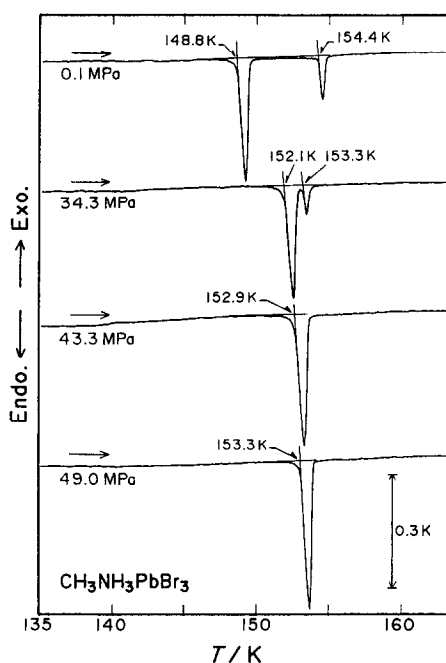Fig. 1. DTA curves of $CH_3NH_3PbCl_3$ under various pressures.

Fig. 2. DTA curves of $CH_3NH_3PbBr_3$ under various pressures in the low temperature range.

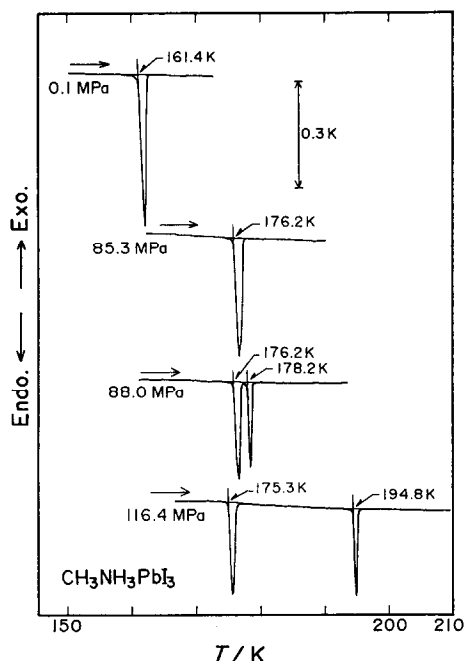Fig. 3. DTA curves of $CH_3NH_3PbI_3$ under various pressures in the low temperature range.

Fig. 4. DTA curves of $CH_3NH_3PbBr_3$ under various pressures in the high temperature range.

low temperature region. The heating rate was 0.6–0.9 K min^{-1}. The $Pna2_1 - I4/mcm$ transition of the crystal occurred at higher temperatures with increasing pressure. On further pressurization, the peak split into two at around 85 MPa. The two peaks separated further at higher pressures. This indicates that the triple point exists at about 85 MPa, above which a new phase appears. Thus, the triple points were found in all of the three $MAPbX_3$ (X = Cl, Br, I) crystals below 100 MPa.

The experimental DTA curves of $MAPbBr_3$ and $MAPbI_3$ in the high temperature region are shown in Figs 4 and 5, respectively. The heating rates were 0.7–1.0 and 0.7–0.8 K min^{-1} for $MAPbBr_3$ and $MAPbI_3$, respectively. An endothermic peak due to the $I4/mcm - Pm3m$ transition was observed in both samples. As indicated by the scales (and by the increased noise level in the base line of the curves) in Figs 4 and 5, the peak heights of these transitions are much smaller than those of the other transitions shown before. This is because the $I4/mcm - Pm3m$ transitions of both crystals are of a gradual type and the first-order component of the transition entropy is only 4–6% of the total [5]. The peak temperature decreased monotonically and the peak shape became broader with increasing pressure for $MAPbBr_3$. For $MAPbI_3$, however, the transition line had a maximum around 110 MPa, below which the slope dT_{trs}/dp was positive and above which negative. The peak shape and area did not change significantly in the whole pressure range.
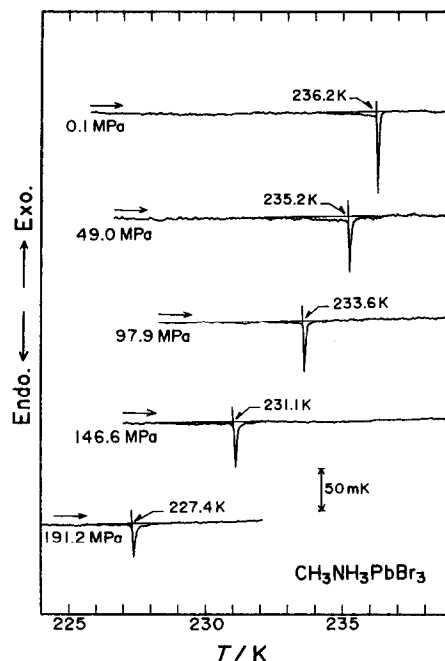
Table 2 summarizes the transition temperature T_{trs}, its pressure dependence dT_{trs}/dp, the transition entropy $\Delta_{trs}S$, and the transition volume $\Delta_{trs}V$. Here, $\Delta_{trs}S$ is the value determined from calorimetry at atmospheric pressure [5]. The quantity includes the contribution from the gradual part of the transition. The volume change associated with the transition
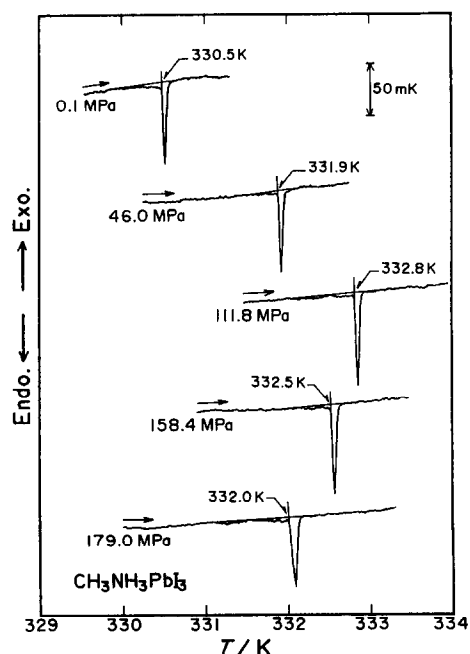

Fig. 5. DTA curves of $CH_3NH_3PbI_3$ under various pressures in the high temperature range.

Table 2. Thermal quantities related to the phase transitions of $CH_3NH_3PbX_3$ (X = Cl, Br, I)

Compound	Transition	$\dfrac{dT_{trs}/dP}{10^{-2}\,K\,MPa^{-1}}$	$\dfrac{T_{trs}}{K}$	$\dfrac{\Delta_{trs}S}{J\,K^{-1}\,mol^{-1}}$ †	$\dfrac{\Delta_{trs}V}{cm^3\,mol^{-1}}$ ‡
$CH_3NH_3PbCl_3$	tet II – cubic	−0.61*	177.2(177.2)	14.6	−0.09
	ortho I – cubic	3.2	—	—	—
	ortho I – tet II	5.7	171.4(171.5)	10.0	0.57
$CH_3NH_3PbBr_3$	tet I – cubic	−0.57*	236.2(236.3)	8.2	−0.05
	tet II – tet I	−3.2	154.4(154.0)	4.1	−0.13
	ortho II – tet II	9.6	148.8(148.8)	11.2	1.08
	ortho II – tet I	7.1	—	—	—
$CH_3NH_3PbI_3$	tet I – cubic	3.5*	330.5(330.4)	9.7	0.34
	ortho II – tet I	17.5	161.4(161.4)	19.0	3.3
	? – tet I	58.1	—	—	—
	ortho II – ?	−3.6	—	—	—

Cubic: $Pm3m$; tet I: tetragonal $I4/mcm$; tet II: tetragonal $P4/mmm$; ortho I: orthorhombic $P222_1$; ortho II: orthorhombic $Pna2_1$.
?: a new high pressure phase.
*: gradient at 0.1 MPa (atmospheric pressure).
( ): value determined by the heat capacity measurement [5].
†: from Ref. 5.
‡: calculated by the Clausius–Clapeyron equation.

$\Delta_{trs}V$ was derived from the dT_{trs}/dp and $\Delta_{trs}S$ values combined with the Clausius–Clapeyron equation,

$$\frac{dT_{trs}}{dP} = \frac{\Delta_{trs}V}{\Delta_{trs}S}.$$

All the values of the transition volume are quite small; less than 2% of the molar volume of $MAPbX_3$ (Cl: $110\,cm^3\,mol^{-1}$, Br: $124\,cm^3\,mol^{-1}$, I: $153\,cm^3\,mol^{-1}$). This indicates that the structural disorder discussed previously in relation to the transition entropies [5] is such that the methylammonium ions are packed as efficiently in the disordered phases as in the ordered phases.

Figure 6 depicts the pressure–temperature phase diagram of the three $MAPbX_3$ (X = Cl, Br, I) crys-

tals. The space groups of the structures determined by Poglitsch *et al.* [3] are shown in the figure. The triple points are found in all of these compounds at rather low pressures compared with those of other ammonium and methylammonium compounds [6, 7, 9]. The precise locations of the triple point were determined as the intersections of the extrapolated transition lines. They are as follows:

$MAPbCl_3$: 75.1 MPa, 175.7 K,
$MAPbBr_3$: 43.2 MPa, 152.9 K,
$MAPbI_3$: 84.8 MPa, 176.2 K.

The high pressure phase of $MAPbI_3$ was found for the first time in the present work. By analogy with the phase relations of $MAPbBr_3$ and $MAPbCl_3$, this
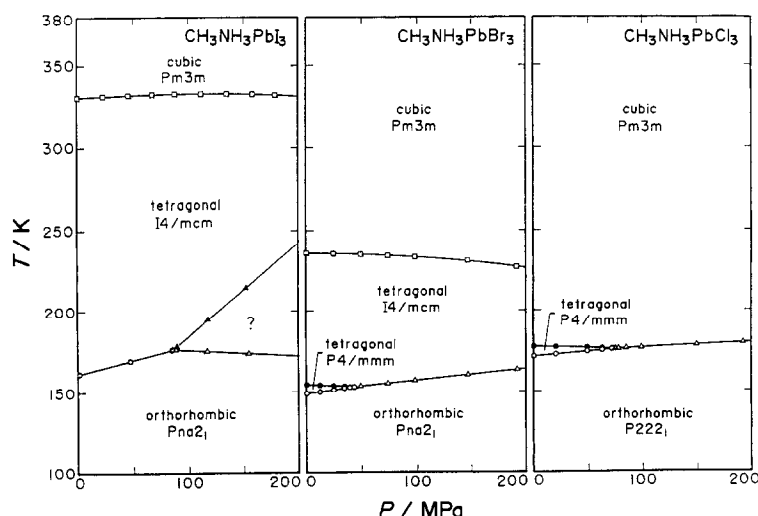

Fig. 6. $p–T$ phase diagrams of $CH_3NH_3PbX_3$ (X = Cl, Br, I) crystals.

phase may have the same structure as the tetragonal *P*4/*mmm* phase of $MAPbBr_3$ and $MAPbCl_3$. Structural study of this new phase under pressure is highly desirable.

All the boundaries between the cubic and tetragonal phases are upward convex while the other phase boundaries are essentially straight lines in the pressure and temperature ranges studied here. It is noteworthy that the transition line from the tetragonal to cubic phase in the iodide has a maximum around 120 MPa. This means that the transition volume $\Delta_{trs} V$ changes its sign from positive to negative according to the Clausius–Clapeyron equation. The transition entropy $\Delta_{trs} S$ should be positive for the thermodynamic stability condition. In fact, this quantity (or its isothermal part) is practically constant in the whole pressure region studied as revealed by the shape and area of the DTA peaks (Fig. 5).

An elegant systematic relation between the pressure and the ionic size of the halogen ion is known to hold in ammonium halides [7]: Ammonium chloride under atmospheric pressure corresponds to ammonium iodide under a high pressure while ammonium bromide corresponds to a situation in between with respect to the relative stability of the three crystalline phases differing from each other in the relative orientations of the ammonium ions. No such simple relation has been found so far for the present substances. This is probably due to the complexity of the interionic interaction and the manner in which the orientational disorder takes place in the present compounds in comparison with ammonium halides. However, we can make a general statement from the phase diagram given in Fig. 6: the stability domain of the tetragonal phase narrows at higher pressure both from below and above. Thus the

molar volume of the tetragonal phase is larger than those of the cubic and orthorhombic phases (in the iodide, for $p > 120$ MPa). It is unexpected that the molar volume decreases as the crystal undergoes the phase transition from the partially ordered tetragonal phase to the fully disordered cubic phase, even though the change in the molar volume is rather small as noted above. It is more common to find an increase of the molar volume accompanying a phase transition from an ordered to a disordered phase. However, molar volume reduction has also been found in methylammonium iodide as it undergoes a phase transition from a partially ordered tetragonal phase to the fully disordered cubic phase [9]. Significance at the molecular level of these uncommon properties, shared by the crystals containing methylammonium ions, is still to be investigated. In particular, numerical calculation of the interionic interactions among three ions (MA^+, Pb^{2+}, X^-) taking various types of orientational disorder into account is a subject for a future study.

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