Peculiarities of $CsPbBr_3$ perovskites melting in quasi-equilibrium conditions

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ABSTRACT

The melting behavior of $CsPbBr_3$ perovskite was studied by differential thermal analysis (DTA). It was found that melting of $CsPbBr_3$ occurs non-isothermally in the temperature range of 561-570 °C. From the temperature dependence of the solid-phase melting rate, it was established that at 567±1 °C the change in the mechanism of the solid-phase melting goes from fragmentation to dissolution at the surface. The obtained values of the activation energy of the melting of the solid phase in $CsPbBr_3$ show that the activation energy of the dissolution of the solid-phase fragments is 4 times greater than the energy of the fragmentation of the solid phase.

Keywords*:* metal halide perovskite, $CsPbBr_3$, differential thermal analysis, melting, quasi-equilibrium conditions.

1. INTRODUCTION

Perovskites are a class of materials with a special crystal structure that allows for highly efficient photovoltaic cells. They were discovered more than a hundred years ago, but their potentials in solar energy have only become clear in recent decades. Perovskite solar cells are an emerging area of research among next-generation photovoltaic technologies due to their high conversion efficiency [1]. They can be produced at room temperature more economically than silicon, making them cheaper and more sustainable for manufacturing.

Metal halide perovskite single crystal has also attracted a great deal of attention in the field of photoelectric detection. All-inorganic perovskite single crystals are much more stable than the hybrid counterparts, but their rapid fabrication is less successful. The halide perovskite $CsPbBr_3$ exhibits extraordinary performance as an ionizing radiation detector operating at room temperature in light of its excellent photoelectric properties [2]. While the structural degradation of all inorganic $CsPbBr_3$ nanoparticles in the presence of moisture is considered as one of its major limitations for use as an active component in various light-harvesting and light-emitting devices [3], the pseudo-cubic $CsPbBr_3$ microcrystals exhibit remarkable stability, and their optical properties remain largely unchanged after long-term exposure to air. The authors [4] reported an electrical characterization of $CsPbBr_3$ single crystals operating up to the time scale of hours.

The material's UV-to-visible broadband light harvesting ability is critical for photo-detectors, and the all-inorganic perovskite $CsPbBr_3$ is regarded as a promising candidate [5]. The authors in [6] presented a strategy for the rapid growth of high-quality $CsPbBr_3$ single crystal. They also demonstrated that the temperature at which the $CsPbBr_3$ single crystal grows is a crucial factor concerning the quality of the crystal. The aim of this work is to study the irregularities in melting of $CsPbBr_3$ by the differential thermal analysis (DTA) method.

2. EXPERIMENTS

The sample of $CsPbBr_3$ was synthesized by melting of an equimolar amount of CsBr and $PbBr_2$ (purity at least 99%) directly in the DTA ampoule in total amount of 500 mg. The ampoule was evacuated using a vacuum pump up to $4.6 \cdot 10^{-2}$ Pa and sealed under the vacuum. The sealing was done in order to avoid sublimation of the sample during heating and cooling. The DTA was used to study the phase equilibria in the vicinity of the melting point of $CsPbBr_3$. For investigating the melting peculiarities, the DTA experiment program includes heating the ampoules with the $CsPbBr_3$ sample at a given rate (5, 2 and 0.8 °C/min) to a certain temperature and dwelling it at the same temperature for 30 minutes with the aim of bringing the alloy to equilibrium state, followed by additional heating up to 640 °C after dwell and cooling at the same rate. The method of preparing ampoules and DTA processing of the thermograms were similar to the method described in detail in our previous work [7, 8].

Hard X-Ray, Gamma-Ray, and Neutron Detector Physics XXVI, edited by Nerine J. Cherepy, Michael Fiederle, Ralph B. James, Proc. of SPIE Vol. 13151, 131510N
 · 0277-786X · doi: 10.1117/12.3027496

3. RESULTS AND DISCUSSIONS

The dependence of the volume fraction of the solid phase in the $CsPbBr_3$ alloy on the dwell temperature is presented in Fig. 1. It shows that the range of dwell temperatures can be divided into four regions. In the region I (T_{dwell} is less than 554°C), the sample contains only the solid phase, and practically no structural changes occur in it ($\varphi_{sol.phase}$ ~ 100 %). In the region II (T_{dwell} = 554-561°C), a slight decrease of the solid phase fraction is observed. However, upon further cooling from this temperature, crystallization was not observed. This means that some structural rearrangements of the solid phase occur in this interval, which is not related to the formation of the melt. This effect can be called the pre-melting effect [9, 10]. It is obvious that defects in the crystal lattice are intensively formed in this temperature interval. The region III (T_{dwell} = 561-570°C) is characterized by a sharp decrease of the solid phase fraction, i.e. it is in this interval the equilibrium between the liquid and solid phases is established. As can be seen, the temperature of 567 °C, which is most used in the literature as the $CsPbBr_3$ melting temperature [11], is within this interval. Finally, at dwell temperatures higher than 570 °C, the $CsPbBr_3$ is a homogeneous liquid melt (region IV). This graph also illustrates that changing the heating rate from 5 to 0.8 K/min does not affect the change in the thermodynamic parameters of the $CsPbBr_3$ melting process.

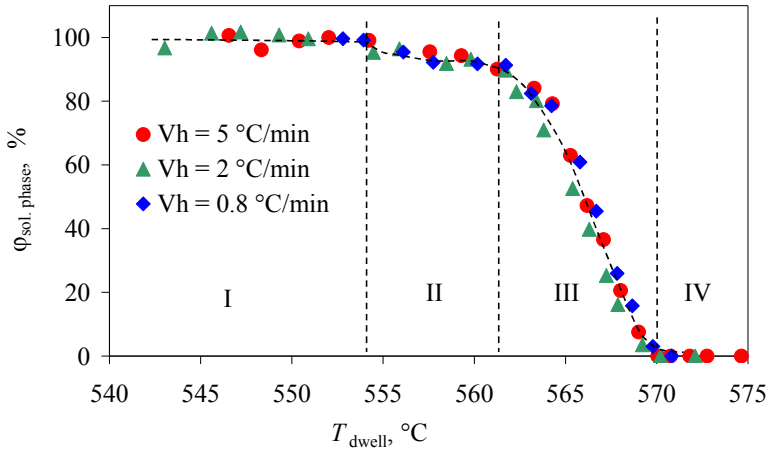


Figure 1. Dependence of the volume fraction of the solid phase in the $CsPbBr_3$ alloy on the dwell temperature.

These assumptions are also confirmed in Fig. 2, which illustrates the dependence of the melting temperature of the solid phase in the $CsPbBr_3$ alloy on the dwell temperature. Similar to Fig. 1, in region I (Fig. 2), the melting temperature of the solid phase practically does not change with increasing dwell temperature, which indicates the stability of the structure of the solid phase. In region II (Fig. 2), a slight increase in the melting temperature of the solid phase is observed, which indicates an increase in the defect density of this solid phase. In region III, there is a more significant

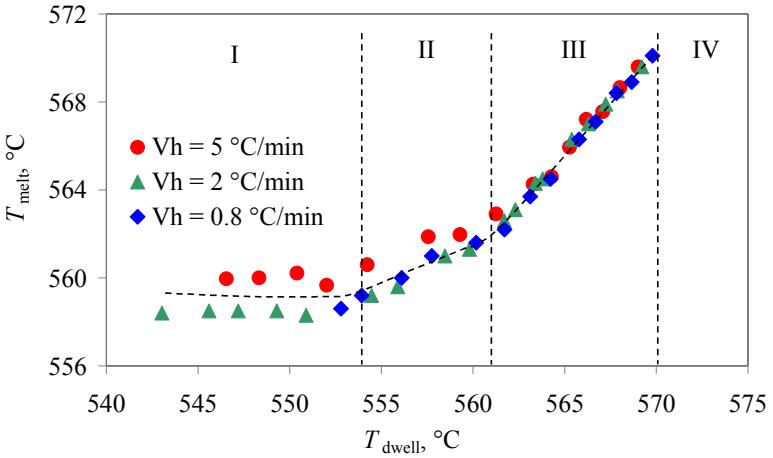


Figure 2. Dependence of the melting temperature of the solid phase in the $CsPbBr_3$ alloy on the dwell temperature.

increase in the melting temperature of the solid phase with a change in the dwell temperature. This indicates a more intensive destruction of the solid phase and appearance of a larger fraction of the melt. This leads to a change in the composition of this solid phase as a result of establishing equilibrium between the solid and liquid phases. The last portions of the solid phase melt at temperatures of 570 °C or above. At higher temperatures, the effects of melting of the solid phase after an intermediate dwell are not fixed, so the temperature 570 °C is sufficient to bring the $CsPbBr_3$ into a liquid state. Fig. 2 (region III) also shows that the melting temperature of the solid phase in the $CsPbBr_3$ alloy practically does not depend on the heating rate, which characterizes the reaching of equilibrium between the melt and the solid phase of a certain composition. However, it has some influence on the defect formation processes in the solid phase (regions I and II). If the heating rate practically does not affect the thermodynamic melting parameters of the solid phase in the $CsPbBr_3$ alloy, then the kinetic parameters of the melting process should depend on it. As illustrated Fig. 3, a decrease in the heating rate from 5 to 0.8 °C/min leads to a decrease in the solid phase melting rate from 0.3 to 0.05 min^{-1} in the initial stages. It is obvious that the faster heating of the sample promotes faster bond breaking. At the heating rates used here, a slight but monotonic increase in the solid phase melting rate is observed with an increase in the melting temperature of the solid phase. However, upon reaching a certain temperature, the increase in the melting rate accelerates. This may indicate changes in the melting mechanism of the solid phase.

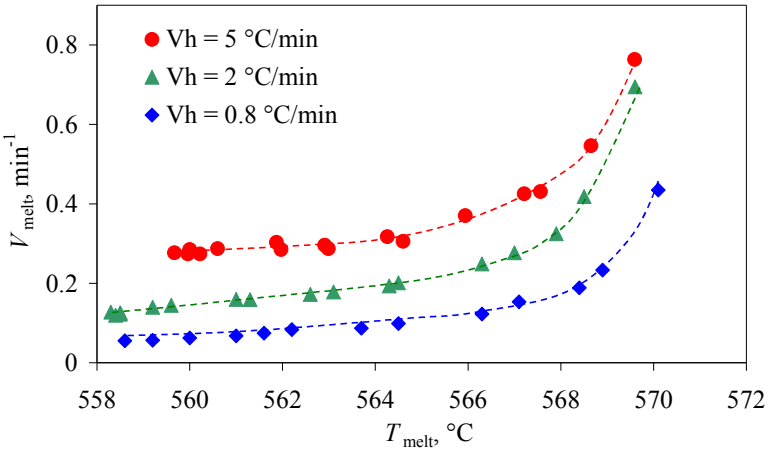


Figure 3. Dependence of the melting rate of the solid phase on its melting temperature in the $CsPbBr_3$ alloy.

Analysis of the data presented in Fig. 3 in semi-logarithmic coordinates shows that for each heating rate the experimental points can be approximated by two straight lines intersecting at certain temperatures. A decrease in the heating rate leads to a slight shift of the intersection points (critical temperature - $T_{critical}$) towards higher temperatures. These critical points, obviously, indicate a change in the mechanism from the fragmentation of the solid phase (lines 1, 3, 5, Fig. 4, Table 1) to the dissolution of solid phase fragments from the surface (lines 2, 4, 6). The activation energy

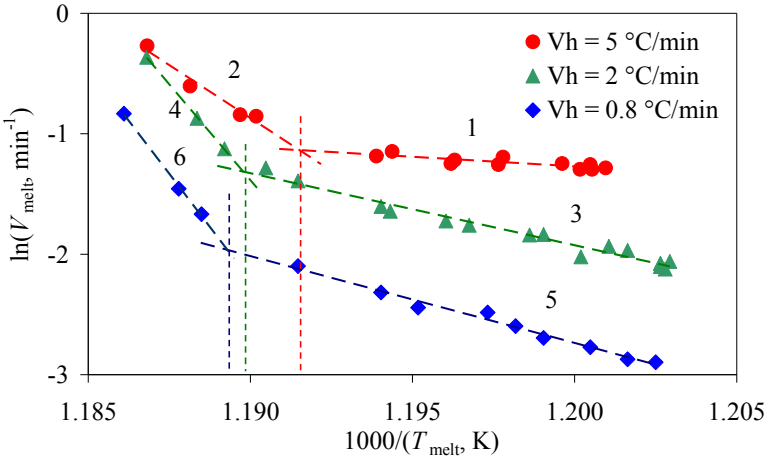


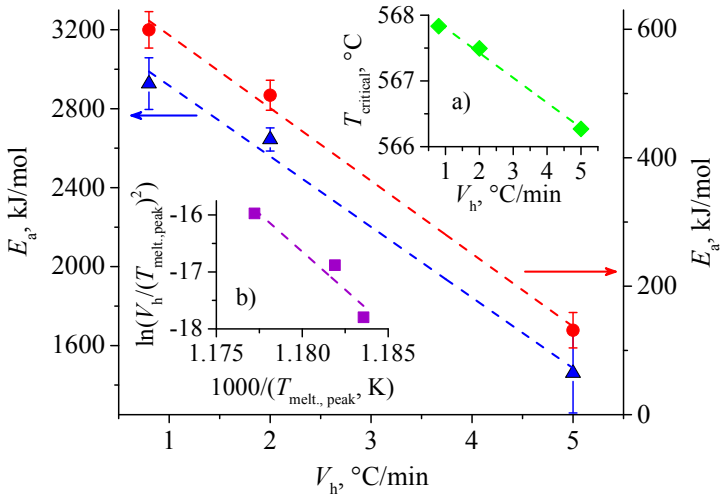
Figure 4. Melting-rate logarithm versus reciprocal melting temperatures of the solid phase in the $CsPbBr_3$ alloy.

Table 1. Linear dependencies and activation energy values extracted from the lines on Fig. 4.

V_h, °C/min	$T_{critical}$, °C	Line number	Temperature range	Equation	E_a, kJ/mol
5	566.3	1	$T < T_{critical}$	$\ln V_{melt} = (-16\pm3)\cdot10^3\cdot T_{melt}^{-1} + (18\pm4)$, $R^2 = 0.72$	131±28
		2	$T > T_{critical}$	$\ln V_{melt} = (-176\pm24)\cdot10^3\cdot T_{melt}^{-1} + (208\pm29)$, $R^2 = 0.96$	1461±202
2	567.5	3	$T < T_{critical}$	$\ln V_{melt} = (-60\pm3)\cdot10^3\cdot T_{melt}^{-1} + (70\pm3)$, $R^2 = 0.97$	497±23
		4	$T > T_{critical}$	$\ln V_{melt} = (-318\pm7)\cdot10^3\cdot T_{melt}^{-1} + (377\pm8)$, $R^2 = 0.99$	2644±59
0.8	567.8	5	$T < T_{critical}$	$\ln V_{melt} = (-72\pm3)\cdot10^3\cdot T_{melt}^{-1} + (84\pm4)$, $R^2 = 0.98$	599±28
		6	$T > T_{critical}$	$\ln V_{melt} = (-352\pm16)\cdot10^3\cdot T_{melt}^{-1} + (417\pm19)$, $R^2 = 0.99$	2927±131

values obtained from the linear dependences (Table 1) show that fragmentation requires several times smaller activation energy than the dissolution of solid phase fragments (clusters) from the surface. For example, at heating rate of 2 °C/min, the E_a value of the fragmentation process is 497±23 kJ/mol, while the process of dissolving clusters from the surface requires a larger value of E_a = 2644±59 kJ/mol. In addition, a decrease in the heating rate leads to an increase in the activation energy of both the fragmentation process of the solid phase and the dissolution of clusters from the surface. It is obvious that the equilibrium treatment (at a lower rate) contributes to the formation of more homogeneous and chemically stable fragments during the heating process.

To estimate the activation energy of the described processes and the critical temperature in quasi-equilibrium conditions (when the heating rate approaches 0), we approximated the dependences of these parameters on the heating rate (Fig. 5) by linear functions. It can be seen that the E_a of the process of fragmentation of the solid phase (red circles) in quasi-equilibrium conditions will be 704 ± 26 kJ/mol, and the energy of the process of dissolving clusters from the surface (blue triangles) will reach 3275 ± 111 kJ/mol. The critical temperature, at which the mechanism of the heating process changes under equilibrium conditions (green diamonds, insert a, Fig. 5), will approach 568.2 °C.



▲ $E_a = (-358 \pm 35)\cdot V_h + (3275 \pm 111)$, $R^2 = 0.98$

● $E_a = (-113 \pm 8)\cdot V_h + (704 \pm 26)$, $R^2 = 0.98$

◆ $T_{critical} = (-0.38 \pm 0.03)\cdot V_h + (568.2 \pm 0.1)$, $R^2 = 0.99$

■ $\ln(V_h / T_{melt.,peak}^2) = (267 \pm 74)\cdot10^3\cdot T_{melt.,peak}^{-1} + (299 \pm 87)$, $R^2 = 0.93$

Figure 5. Linear dependence of the activation energy on the heating rate for both fragmentation (red circles) and dissolution from the surface (blue triangles) for $CsPbBr_3$ solid phase melting. Insert ***a*** shows the dependence of the critical temperature on the heating rate (green diamonds). Insert ***b*** shows the dependence of parameters according to Kissinger equation (violet squares)

A sufficiently large value of E_a of the process of dissolution of clusters from the surface indicates the high stability of such clusters, and therefore their possible presence in the melt even at higher temperatures. These clusters can cause supercooling during the crystallization. It should be noted that all three dependencies can be approximated by straight lines (R^2 = 0.98). For comparison, we also obtained the E_a value of the liquid phase formation process using the Kissinger equation, as it was applied in [12, 13]. The experimentally obtained points are not described by a linear dependence (Fig. 5, insert b), and the obtained value E_a= 2200±600 kJ/mol is characterized by a rather significant scatter. However, it correlates with the value obtained in [12]. The value obtained in such a way for E_a corresponds to the middle of the energy range of the process of cluster dissolution from the surface.

4. CONCLUSION

Peculiarities of the melting processes of $CsPbBr_3$ perovskite were investigated by the DTA method using different heating rates. We found that $CsPbBr_3$ melts non-isothermally with pre-melting. We observed that in the dwell-temperature interval of 561-570 °C an equilibrium between the liquid and solid phases is established. At dwell temperatures higher than 570 °C, the $CsPbBr_3$ became a homogeneous liquid melt. It was established that at 567±1 °C the change in the mechanism of solid phase melting occurs from the fragmentation to the dissolution from the surface. Additionally, it was found that changing the heating rate from 5 to 0.8 °C/min does not affect the change in the thermodynamic parameters of the $CsPbBr_3$ melting process. As for kinetic parameters of the melting processes, we found that the activation energy of the dissolution of solid-phase fragments is more than 4 times greater than the activation energy of fragmentation of the solid phase.

ACKNOWLEDGEMENTS

This study has received funding through the EURIZON project, which is funded by the European Union under grant agreement No.871072 (P. Fochuk and V. Kopach). Also, this work was partially supported by a grant from the Simons Foundation (Award Number: 1030286, authors P. Fochuk, O. Kopach and V. Kopach). The work of A. E. Bolotnikov and R. B. James was supported in part by the U.S. Department of Energy, Office of Defense Nuclear Nonproliferation Research and Development, and the work by R. B. James was partially supported by the DOE NNSA Minority Serving Institution Partnership Program (MSIPP).

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