Recently, perovskite-type CH$_3$NH$_3$PbI$_3$ solar cells is attracting attention as high performance solar cells because of high conversion efficiencies. However, in order to put perovskite solar cells to practical use, it is necessary to enhance long-term durability. One of the reasons of this problem would be instability of the structure of the CH$_3$NH$_3$PbI$_3$ crystal at room temperature. As shown in Fig. 1, phase transition takes place at 330 K from tetragonal to cubic structure.\(^1\)

The purpose of the present research is to improve the structural stabilities of the perovskite crystals from calculation. The stability of perovskite structures can be estimated by a tolerance factor (\(t\)-factor),\(^2\) which is expressed in the following equation: \(t = (R_A + R_X)/\sqrt{2(R_B + R_X)}\). In the case of the CH$_3$NH$_3$PbI$_3$ crystal, (CH$_3$NH$_3$)$^+$, Pb$^{2+}$, and I$^-$ ions are located in A, B, and X sites, respectively. When the value of "\(t\)" is in the range from 0.81 and 1.11, the crystal structures would be perovskite structures. If the value of "\(t\)" is equal to 1, the perovskite crystals has ideal cubic structures.

In the case of the CH$_3$NH$_3$PbI$_3$ crystal, the \(t\)-factor is 0.912. This fact means that the CH$_3$NH$_3$PbI$_3$ crystal is slightly unstable. When the ions with larger ionic radii than that of (CH$_3$NH$_3$)$^+$ ions are introduced to A sites, \(t\)-factor increases. On the other hand, when the ions of smaller ionic radii are introduced to A sites, \(t\)-factor decreases. If the ions of smaller ionic radii than that of Pb$^{2+}$ ions are introduced to B sites, or ions smaller than I$^-$ ions introduced to X sites, \(t\)-factor increases in both cases.

Perovskite structures can be stabilized by introducing suitable ions. Structural stabilities of the perovskite structures can be controlled by changing ionic radii of doping or replacing ions.

**Fig. 1.** Perovskite crystals of (a) tetragonal and (b) cubic structures.

**References**