Unconventional multicenter bonds in gold halide perovskites at room and high pressure

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Abstract

Cesium gold halides are prominent lead-free distorted double perovskites with potential as photovoltaic, photocatalytic, and photosensitive materials. They exhibit $Cs_2Au_2X_6$ (X= Cl, Br, I) stoichiometry and crystallize in a tetragonal structure at room pressure due to the presence of mixed-valence gold states (Au^I and Au^{III}). At moderate pressures, they tend to undergo a phase transition to the cubic perovskite with $CsAuX_3$ stoichiometry, characterized by single-valence Au^{II} [1]. Despite the great effort in understanding the phase transitions and properties of these compounds, the chemical bonding present in the different phases of the cesium gold halides —and its relation to their properties— is far from being understood [2,3]. A systematic theoretical bonding analysis of $Cs_2Au_2Cl_6$ reveals that the pressure-induced tetragonal-to-cubic phase transition in the whole $Cs_2Au_2X_6$ family is governed by a fundamental change in the chemical bonding. In $Cs_2Au_2X_6$, bonding is dominated by 1D and 2D X–Au–X electron-rich multicenter bonds (ERMBs). In contrast, $CsAuX_3$ features 3D electron-deficient multicenter bonds (EDMBs) occurring as infinite linear –X–Au–X–Au–X– chains in the three directions (Figure 1). This transformation reflects the gradual pressure-induced polymerization of the $[Au^ICl_2]^-$ and $[Au^{III}Cl_4]^-$ anions into a three dimensional network. The bonding change follows the stages recently proposed by the unified theory of multicenter bonding (UTMB), which explains the origin and mechanism of formation of ERMBs and EDMBs in compounds involving electron-rich elements with valence s- and p-type electrons [4-6]. Importantly, this study reveals that low-symmetry perovskites can feature ERMBs and that cubic perovskites, even those including elements with valence d-type electrons, such as gold, can exhibit EDMBs. These findings provide a bonding-based framework for understanding the unconventional properties of distorted and ideal perovskites that cannot be adequately described within the traditional classification of ionic, covalent, and metallic bonds.

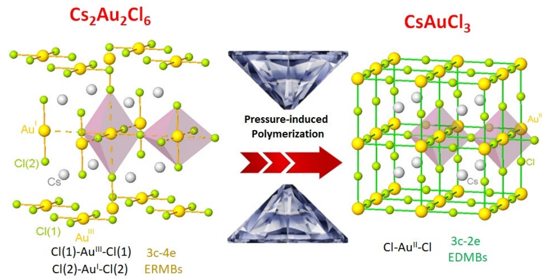

Figure 1. Tetragonal-to-cubic pressure-induced phase transition in the distorted tetragonal perovskite $Cs_2Au_2Cl_6$ leads to a pressure-induced polymerization of Au^ICl_2 and $Au^{III}Cl_4$ units (with 1D and 2D ERMBs, respectively) that result in $Au^{II}Cl_6$ units in cubic perovskite $CsAuCl_3$ (with 3D EDMBs).

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