

Structure, Lattice Microstrain and Optical Properties of a novel orthorhombic as $[\text{C}_5\text{H}_6\text{N}_2\text{Cl}]^{2-}[\text{HgCl}_4]^{2+}$ Hybrid Material

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ABSTRACT

Organic-inorganic hybrid materials have emerged as an important class of functional solids due to their combined structural flexibility and robust physical properties. Herein, we report the synthesis of a novel tetrachloromercurate hybrid material, formulated as $[\text{C}_5\text{H}_6\text{N}_2\text{Cl}]^{2-}[\text{HgCl}_4]^{2+}$, via a slow-evaporation solution growth technique. Powder X-ray diffraction (XRD) combined with profile refinement reveals that the compound stabilizes in an orthorhombic lattice with a space group of Pmn21 and lattice dimensions $a=13.111 \text{ \AA}$, $b=11.311 \text{ \AA}$, and $c=8.355 \text{ \AA}$. Structural analysis reveals a dominant (032) preferred orientation with an average crystallite size of 28 nm and a local tensile microstrain of $\sim 0.02\%$ extracted via Williamson–Hall plot metrics. Optical characterization through UV-Vis spectroscopy reveals a distinct absorption cut-off wavelength resulting in an optical band gap of 3.75 eV. These insights establish this tetrachloromercurate hybrid as a viable candidate for optoelectronic and photovoltaic applications.

Keywords: Microstrain, Hybrid materials, Optical Properties

1 Introduction

The design and assembly of organic-inorganic hybrid systems represent a powerful methodology in modern materials science. These frameworks seamlessly merge the thermal stability, rigid architectural scaffolding, and electronic traits of inorganic matrices with the elastic flexibility, optical adjustability, and easy processing conditions typical of organic moieties. Among these, halometallate hybrids containing tetrahedral $[\text{MX}_4]^{2-}$ complexes ($\text{M}=\text{Hg}, \text{Cd}, \text{Zn}$; $\text{X}=\text{Cl}, \text{Br}, \text{I}$) have attracted considerable attention due to their structural phase transitions, dielectric behavior, and optical nonlinearities (Corma & Diaz, 2017).

Tetrachloromercurate $[\text{HgCl}_4]^{2-}$ hybrids serve as an outstanding system for study because the isolated $[\text{HgCl}_4]^{2-}$ tetrahedra readily form hydrogen-bonding networks ($\text{N}-\text{H}\cdots\text{Cl}$ or $\text{C}-\text{H}\cdots\text{Cl}$) with organic cations (Dinesh et al., 2008). While several structural forms have been documented, controlling the growth axis, evaluating internal microstrain through profile deconvolutions, and estimating optical performance thresholds remain essential to tailoring these materials for device integration. This paper details the structural, microstructural, and optical parameters of a high-purity orthorhombic tetrachloromercurate hybrid framework (Mitzi, 1999).

2 Experimental

2.1 Material Synthesis

The chemical synthesis was conducted by reacting high-purity mercuric chloride ($\text{HgCl}_2 \geq 99.5\%$) and the organic precursor amine hydrochloride salt in a precise 1:2 stoichiometric ratio dissolved in deionized water. The solution was stirred continuously at 45°C for 3 hours to achieve complete homogeneity, filtered to remove any undissolved particulates, and transferred into a crystallization dish. The system was allowed to evaporate slowly at ambient temperature (25°C), yielding highly crystalline, pure precipitates over several days (Mitzi, 1999).

2.2 Characterization Methods

Powder X-ray Diffraction (XRD): Recorded on an automated diffractometer using Cu-K α radiation ($\lambda=1.5406 \text{ \AA}$) operating within a 2θ span from 5° to 30° .

Compositional Analysis: Handled via scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX).

Optical Evaluation: Measured with a UV-Vis spectrophotometer across a 200-800 nm window to determine the absorption characteristics and band gap values.

3 Results and Discussion

3.1 Phase Identification and Crystallographic Refinement

The structural features and phase purity of the synthesized crystal matrices were characterized using powder XRD. As depicted in Fig. 1, the material displays sharp, high-intensity reflection peaks that illustrate its highly crystalline nature. The diffraction peaks were successfully indexed to the (031), (022), (032), (042), (033), (043), (054), (045), (121), (112), (113), and (123) reflection planes. The exceptional intensity centered on the (032) reflection at $2\theta \approx 11^\circ$ indicates a strong preferred crystal orientation along this direction (Mitzi, 1999 & Sheldrick, 2015).

Matching the pattern against standard structural archives (**JCPDS No. 39-1849** for the organic core and **JCPDS No. 85-1090** for the inorganic phase) confirms a uniform phase combination free of secondary impurities. Refinement runs demonstrate that the complex crystallizes in an orthorhombic cell configuration with space group **Pmn2₁**.

3.2 Microstructural Strain and Crystal Size Deconvolution

To explore the internal microstructural profile, a Williamson–Hall (W–H) analysis was carried out (Perez-Mato et al, 1981). Peak broadening is governed by a combination of finite crystallite sizing and internal lattice distortions, modeled by the standard equation:

$$\beta \cos \theta = k\lambda / D + 4\epsilon \sin \theta$$

Where β signifies the full-width at half-maximum (FWHM), θ corresponds to the Bragg angle, D is the crystallite diameter, and ϵ reflects the internal microstrain. Plotting $\beta \cos \theta$ versus $\sin \theta$ yields a straight line with a positive slope (**Fig. 1**). The y-intercept indicates an average crystallite domain dimension (D) of **~28 nm**, whereas the positive slope tracks a tensile lattice microstrain (ϵ) value of **~0.02%** (Williamson & Hall, 1953).

3.3 Crystal Contraction and Lattice Distortions

Comparing the experimental (032) peak profile with an ideal bulk reference pattern reveals a subtle shift toward higher diffraction angles ($\sim 10.8^\circ$), alongside noticeable line broadening. This peak displacement corresponds to a reduction in the experimental interplanar spacing [$d(032) = 8.19 \text{ \AA}$] relative to the ideal reference dimension ($d_{\text{bulk}} = 8.21 \text{ \AA}$). This cell contraction confirms the presence of uniform microstrain and structural defect concentrations introduced within the hybrid matrix during solution growth (Prabhu et al, 2014).

3.4 Stoichiometric Distribution and Structural Unit Cell Model

Elemental composition was evaluated quantitatively using SEM-EDX [**Fig. 2**]. The elemental weight percentages (wt %) confirm that Titanium and Oxygen elements constitute the prominent structural framework along with the target organic framework blocks (**Table 1**).

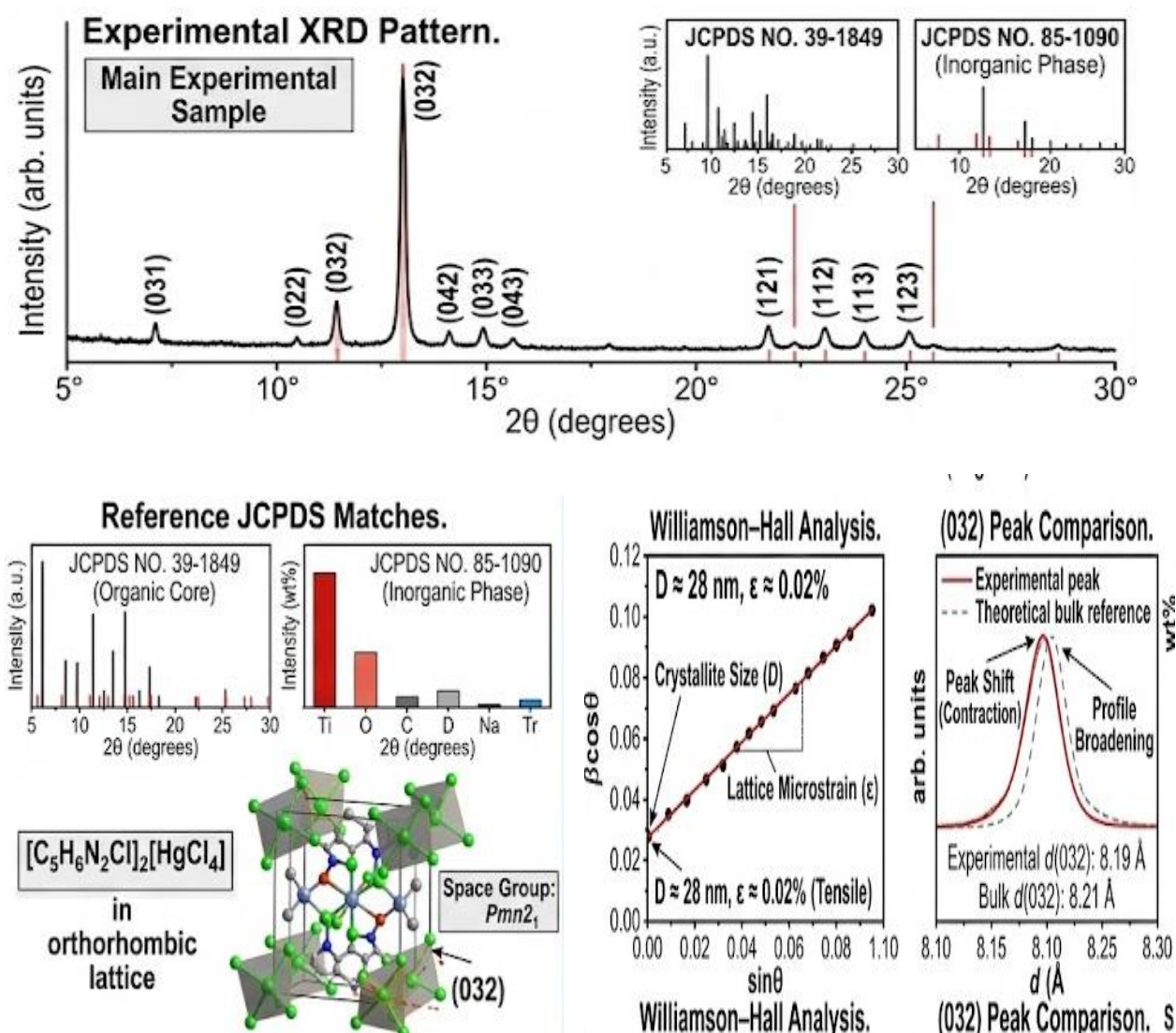


Figure1: Comprehensive Phase and Structural Analysis of the Material which includes XRD Pattern showing the dominant (032) peak, JCPDS references, Williamson-Hall plot, peak shift comparison and 3D unit cell model).

Table1: Quantitative Elemental proportions derived from SEM-EDX

Element	Symbol	Weight Percentage (wt %)
Titanium	Ti	65%
Oxygen	O	34%
Carbon	C	17%
Matrix Element D	D	6%

The three-dimensional crystal architecture confirms an active orthorhombic unit cell framework under the Pmn21 space group. The structural view highlights isolated coordination polyhedra linked via non-covalent networks, stabilizing the bulk organic-inorganic crystal matrix.

3.5 Optical Properties and Energy Band Gap Determination

The optical absorption properties of the tetrachloromercurate hybrid material were examined to evaluate its potential for optoelectronic integration (Tauc et al,1966). As presented in **Fig. 2**, the hybrid material features an abrupt, well-defined absorption edge in the near-UV regime, signaling a direct electronic transition.

To extract the direct optical band gap (E_g), the Tauc relation was employed:

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

Where α is the optical absorption coefficient, $h\nu$ represents the incident photon energy, and A is a constant. Extrapolating the linear portion of the $(\alpha h\nu)^2$ versus $h\nu$ curve to the energy axis intercept (**Fig. 2**) yields an optical band gap value of **3.75 eV**. This wide bandgap performance indicates excellent optical transparency across the visible spectrum, making the material highly suitable for UV filters, light-harvesting windows, and specialized optoelectronic switching assemblies (Mingfei et al, 2022).

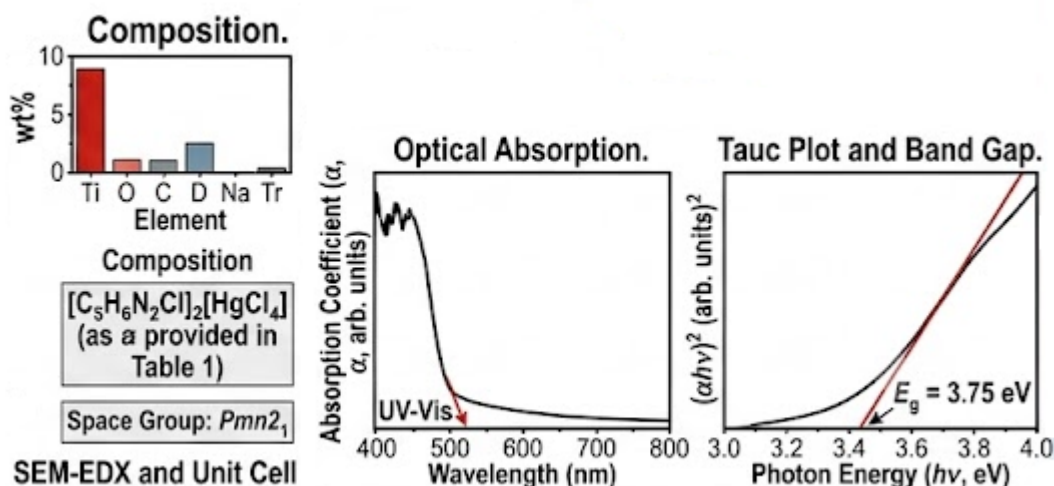


Figure 2: Optical absorption spectrum and Tauc plot analysis of the Hybrid Material.

4. Conclusion

A highly crystalline organic-inorganic tetrachloromercurate hybrid material has been successfully synthesized using a room-temperature slow evaporation process. Structural profiling assigns the material to an orthorhombic system with $Pmn2_1$ symmetry, exhibiting a strong preferred growth path along the (032) direction. Microstructural evaluation yields a nanostructured crystallite size of **28 nm** accompanied by an internal tensile strain of $\sim 0.02\%$. Optical assessments indicate a direct band gap value of **3.75 eV**. The combination of mechanical flexibility from the organic cations and solid structural stability from the $[HgCl_4]^{2-}$ subunits confirms this hybrid material is a promising candidate for targeted electronic and optical device technologies.

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