

Photoluminescence in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ -Based Perovskites:

Structural Disorder, Donor Doping and Implications for Visible Light-Emitting Applications

Review Article

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Abstract

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) perovskite oxides have been extensively studied due to their unusual dielectric, electrical and optical properties. In recent years, increasing attention has been directed toward their photoluminescent behavior, particularly in the visible region, motivated by potential applications in light-emitting devices. This review summarizes and critically discusses the current state of knowledge on photoluminescence in CCTO-based materials, with emphasis on the role of structural order–disorder phenomena, defect chemistry and donor doping, especially with niobium (Nb^{5+}). The relationships between synthesis methods, thermal treatment, local coordination environments and electronic structure are examined. Special attention is given to the formation of localized electronic states associated with mixed $\text{TiO}_6/\text{TiO}_5$ coordination and oxygen vacancies, which are key factors governing visible light emission. The review highlights how controlled structural disorder and donor doping can be used as effective strategies to enhance photoluminescence at relatively low processing temperatures, reinforcing the technological relevance of CCTO-based perovskites for visible light-emitting applications.

Keywords: $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$; photoluminescence; perovskite oxides; structural disorder; donor doping; light-emitting materials.

1. Introduction

Perovskite-type oxides with general formula ABO_3 represent one of the most versatile classes of functional materials in solid-state chemistry and condensed matter physics. Their structural flexibility allows a wide variety of cation substitutions, leading to remarkable physical properties such as ferroelectricity, high dielectric permittivity, magnetoresistance and photoluminescence [1–5]. Among

these materials, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) has emerged as a particularly intriguing compound due to its complex crystal structure and multifunctional behavior.

Originally investigated for its giant dielectric constant, CCTO has since been explored in different contexts, including optical and photophysical applications [6–9]. More recently, the photoluminescence (PL) properties of CCTO and related titanate systems have attracted growing interest, especially regarding visible light emission under ultraviolet excitation. These studies have revealed that PL in CCTO is not an intrinsic property of a perfectly ordered lattice, but rather a phenomenon strongly dependent on structural disorder, defects and local coordination environments.

This review aims to provide a comprehensive overview of photoluminescence in CCTO-based materials, focusing on the interplay between crystal structure, disorder, donor doping and optical emission. Particular emphasis is placed on niobium-doped CCTO, which serves as a model system to understand how electron donor species influence defect chemistry and radiative recombination mechanisms.

2. Crystal Structure and Order–Disorder Phenomena in CCTO

CCTO crystallizes in a complex perovskite-related structure derived from the ABO_3 framework, where Ca^{2+} and Cu^{2+} ions occupy distinct crystallographic sites and Ti^{4+} ions are coordinated by oxygen in octahedral environments. The ideal structure consists of TiO_6 octahedra forming a three-dimensional network, with Ca and Cu ions occupying interstitial positions [10–12].

However, experimental studies have shown that the actual structure of CCTO is highly sensitive to synthesis route and thermal treatment. At lower processing temperatures, incomplete crystallization often results in a partially disordered structure characterized by mixed coordination environments, including TiO_5 units and oxygen vacancies [13–15]. As temperature increases, these defects are progressively eliminated, leading to a more ordered TiO_6 network.

Structural disorder in CCTO is not merely a crystallographic imperfection, but a key factor influencing its physical properties. Several studies have demonstrated that local distortions, vacancy-related defects and mixed coordination clusters play a crucial role in determining the electronic structure and optical response of the material [16–18].

3. Origin of Photoluminescence in Titanate-Based Perovskites

Photoluminescence in titanate perovskites has been widely attributed to electronic transitions involving localized states within the band gap. These states are typically associated with structural defects, such as oxygen vacancies, undercoordinated Ti centers and distorted Ti–O bonds [19–21].

In fully ordered titanate structures, where Ti is exclusively coordinated by six oxygen atoms, non-radiative recombination pathways dominate, resulting in weak or absent PL emission. In contrast, partially disordered structures containing TiO_5 units and oxygen vacancies introduce localized electronic levels that favor radiative recombination, giving rise to visible light emission [22–24].

The coexistence of TiO_6 and TiO_5 clusters has been identified as a particularly favorable configuration for PL. Electronic transitions involving oxygen 2p orbitals and titanium 3d or 4d states are strongly influenced by local symmetry breaking, which enhances emission efficiency in the visible range [25–27].

4. Donor Doping Effects: The Role of Niobium

Donor doping represents an effective approach to tailoring the electronic and optical properties of perovskite oxides. Niobium (Nb^{5+}), when substituted for Ti^{4+} in the CCTO lattice, introduces extra electrons that must be compensated by changes in local structure or defect concentration [28–30].

Several studies have shown that Nb doping promotes the formation of localized electronic states within the band gap, leading to a reduction of the optical band gap and modification of PL emission characteristics. These effects are often accompanied by subtle structural distortions and increased defect density, particularly at moderate doping levels [31–33].

Importantly, excessive doping or high-temperature processing tends to restore structural order, reducing defect-related emission centers and suppressing photoluminescence. This observation reinforces the idea that an optimal balance between order and disorder is required to maximize PL intensity in Nb-doped CCTO systems.

5. Influence of Synthesis Route and Thermal Treatment

The synthesis method plays a decisive role in determining the degree of structural disorder and, consequently, the photoluminescence properties of CCTO-based materials. Soft chemical routes, such as polymeric precursor and sol–gel methods, offer superior chemical homogeneity and enable lower crystallization temperatures compared to conventional solid-state reactions [34–36].

Thermal treatment is equally critical. Studies consistently report that intermediate calcination temperatures, typically around 450–550 °C, favor the coexistence of ordered and disordered domains, resulting in enhanced visible PL emission. At higher temperatures, complete crystallization leads to defect annihilation and PL quenching [37–39].

These findings suggest that low- to moderate-temperature processing is not only sufficient, but actually desirable for optimizing the optical performance of CCTO-based phosphors.

6. Implications for Visible Light-Emitting Applications

The strong visible photoluminescence observed in partially disordered and donor-doped CCTO materials highlights their potential for application in light-emitting devices. Compared to conventional ceramic phosphors, CCTO-based materials offer the advantage of lower processing temperatures, reduced energy consumption and tunable emission through defect engineering.

Niobium-doped CCTO, in particular, has demonstrated emission in the blue-green region of the visible spectrum, which is of considerable interest for solid-state lighting and optoelectronic devices. The ability to tailor emission properties through controlled disorder rather than complex compositional changes represents a significant advantage from a technological perspective [40–42].

7. Conclusions and Perspectives

This review highlights the central role of structural disorder and donor doping in governing the photoluminescence behavior of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ -based perovskites. The literature clearly demonstrates that visible PL emission in CCTO is not an intrinsic property of a perfectly ordered lattice, but rather arises from localized electronic states associated with mixed coordination environments and defects.

Niobium donor doping emerges as an effective strategy to enhance and tune photoluminescence, particularly when combined with moderate thermal treatment that preserves partial structural disorder. These insights provide valuable guidelines for the rational design of CCTO-based materials for visible light-emitting applications.

Future research should focus on quantitative correlations between defect concentration and emission efficiency, as well as on extending these concepts to thin films and device architectures.

6. Bibliographical References

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