JIRRS
Journal International Review of Research Studies

Received: 13/01/2026 - **Accepted:** 06/02/2026
Vol: 01.01
Pages: 1-9

Structural Order–Disorder Effects and Photoluminescence Behavior in Aluminum-Doped $CaCu_3Ti_4O_{12}$: A Comprehensive Review

Everson Ferreira Junior[1]
[1]Universidade Federal de Itajubá, MG, Brazil

Corresponding author: eversonjunior@gmail.com

Abstract

Calcium copper titanate ($CaCu_3Ti_4O_{12}$ – CCTO) has attracted significant attention due to its remarkable dielectric, optical, and photoluminescent properties. In particular, structural disorder at short and medium range has been strongly correlated with visible photoluminescence (PL) emission at room temperature. This review discusses the structural, vibrational, optical, and electronic modifications induced by aluminum doping in CCTO, emphasizing the role of order–disorder transitions, cluster formation ($[TiO_6]$, $[TiO_5]$, and $[AlO_6]$), oxygen vacancies, and band gap modulation. Special attention is given to thermal evolution between 300 °C and 800 °C, where coexistence between amorphous and crystalline domains leads to maximum PL intensity. Spectroscopic evidence from XRD, FT-IR, Raman, UV–Vis, and photoluminescence analyses is critically interpreted to establish correlations between local structural rearrangements and electronic transitions. The review consolidates experimental findings and theoretical interpretations, highlighting aluminum as an electron acceptor dopant capable of modifying defect density and tuning optical gap energies.

---

1. Introduction

Perovskite-type oxides (ABO_3) represent one of the most versatile classes of functional materials due to their tunable structural and electronic properties. Among them, $CaCu_3Ti_4O_{12}$ (CCTO) stands out because of its colossal dielectric constant and visible photoluminescence at room temperature

ALUMÍNIO FINAL - Inglês

.

Unlike conventional semiconductors, where luminescence is typically associated with band-to-band recombination, CCTO exhibits broad PL emission bands strongly influenced by structural disorder and defect states within the band gap. The coexistence of octahedral $[TiO_6]$ and pentacoordinated $[TiO_5]$ units creates localized states responsible for charge transfer processes.

The incorporation of dopants such as aluminum modifies the Ti–O framework, influences oxygen vacancy concentration, and promotes structural reorganization. Aluminum acts as an electron acceptor species, potentially reducing defect-related recombination centers and altering optical transitions.

This review critically examines:

- Structural evolution during thermal treatment
- Cluster formation and defect chemistry
- Optical band gap modulation
- Correlation between order–disorder degree and PL emission
- Role of aluminum as structural organizer

---

2. Crystal Structure of CCTO and Defect Chemistry

CCTO crystallizes in a body-centered cubic structure (space group $Im\bar{3}$), derived from the perovskite framework. In its ideal configuration:

- Ca occupies the A-site
- Cu partially occupies square-planar coordinated positions
- Ti occupies octahedral B-sites

However, real materials synthesized via soft chemical routes exhibit deviations from perfect periodicity. The presence of:

- Oxygen vacancies ($V_0^{\cdot}$ or $V_0^{\cdot\cdot}$)
- Distorted TiO_6 octahedra
- TiO_5 units
- Short-range disorder

creates localized electronic states within the forbidden band gap

ALUMÍNIO FINAL - Inglês

.

The defect reactions may be simplified as:

[TiO6]x+[TiO5VOx]→[TiO6]′+[TiO5VO·][TiO_6]^x + [TiO_5V_O^x] \rightarrow [TiO_6]' + [TiO_5V_O^{\bullet}][TiO6]x+[TiO5VOx]→[TiO6]′+[TiO5VO·]

These structural distortions are fundamental to understanding luminescent behavior.

Received: 13/01/2026 - **Accepted:** 06/02/2026
Vol: 01.01
Pages: 1-9

3. Influence of Thermal Treatment on Structural Ordering

Thermal processing plays a decisive role in phase formation and defect evolution.

3.1 Low Temperatures (300–400 °C)

At this stage:

- Polymer precursor decomposition occurs
- Organic residues are removed
- Initial nucleation of CCTO begins
- Material exhibits high structural disorder

Thermogravimetric analysis reveals significant mass loss associated with organic decomposition

ALUMÍNIO FINAL - Inglês

.

3.2 Intermediate Temperature (500 °C)

This region is critical.

- Coexistence of amorphous and crystalline domains
- Presence of TiO_6 and TiO_5 clusters
- Maximum structural disorder/order balance
- Highest photoluminescence intensity

The intermediate structural arrangement favors electronic transitions involving defect states.

3.3 High Temperatures (700–800 °C)

- Long-range crystalline order established
- Reduction of defect density
- Narrowing of Urbach tail
- Decrease in PL intensity

XRD confirms well-defined cubic structure at 800 °C

Received: 13/01/2026 - **Accepted:** 06/02/2026
Vol: 01.01
Pages: 1-9

ALUMÍNIO FINAL - Inglês

.

---

4. Spectroscopic Evidence of Structural Rearrangement

4.1 X-Ray Diffraction (XRD)

XRD patterns show progressive crystallization with increasing temperature. Aluminum doping introduces additional reflections related to α-Al_2O_3 phases, indicating partial segregation or cluster formation

ALUMÍNIO FINAL - Inglês

.

4.2 FT-IR Spectroscopy

Bands between 430–650 cm^{-1} correspond to metal–oxygen (M–O) vibrations.
The 780 cm^{-1} band becomes sharper with increasing crystallinity, suggesting TiO_6 octahedral stabilization.

The presence of bands near 386 cm^{-1} indicates α-alumina coordinated with six oxygen atoms

ALUMÍNIO FINAL - Inglês

.

4.3 Raman Spectroscopy

Characteristic vibrational modes at:

- ~290 cm^{-1}
- ~450 cm^{-1}
- ~510 cm^{-1}

are associated with TiO_6 rotational modes.

Aluminum incorporation causes subtle shifts, reflecting lattice distortion and modified symmetry.

---

5. Optical Band Gap Modulation

UV–Vis spectroscopy reveals that:

- Pure CCTO exhibits narrower optical gap
- Al-doped samples show increased band gap

Using Kubelka–Munk formalism:

(αhv)2∝(hv−Eg)(\alpha h\nu)^2 \propto (h\nu - E_g)(αhv)2∝(hv−Eg)

Reported values:

- Pure CCTO: ~1.74–2.0 eV
- Al-doped: ~2.54 eV

  ALUMÍNIO FINAL - Inglês

Aluminum reduces localized defect states, increasing structural organization and widening the optical gap.

6. Photoluminescence Mechanism

The PL emission originates from charge transfer processes involving:

- Oxygen 2p orbitals
- Titanium 3d orbitals

In structurally disordered systems, electron–hole recombination occurs via defect levels inside the band gap.

6.1 Pure CCTO

Maximum emission ~490 nm (orange region).

6.2 Al-Doped CCTO

Shift to ~425 nm (violet region)

ALUMÍNIO FINAL - Inglês

.

The substitution of TiO_5 units by AlO_6 reduces oxygen vacancy concentration and modifies recombination pathways.

Increasing aluminum content:

- Decreases PL intensity
- Increases structural order

Received: 13/01/2026 - **Accepted:** 06/02/2026
Vol: 01.01
Pages: 1-9

- Reduces defect density

Thus, maximum emission occurs at intermediate disorder.

---

7. Order–Disorder Model

The photoluminescence intensity can be understood through a structural competition model:

- Completely amorphous → low emission
- Fully crystalline → low emission
- Intermediate disorder → maximum emission

Clusters involved:

- [TiO_6–TiO_6]
- [TiO_6–TiO_5]
- [TiO_6–AlO_6]

Aluminum stabilizes octahedral coordination, suppressing TiO_5-related defect states.

---

8. Role of Aluminum as Electron Acceptor

Al^{3+} substitution modifies charge balance:

- Acts as acceptor species
- Alters oxygen vacancy equilibrium
- Promotes octahedral symmetry
- Reduces mid-gap states

This leads to:

- Band gap widening
- PL quenching at higher doping
- Improved structural organization

---

9. Applications and Perspectives

Understanding PL behavior in CCTO systems opens perspectives for:

- Visible light emitters
- Optical sensors
- Defect-engineered ceramics
- Tunable band gap materials
- Dielectric–optical multifunctional devices

Future research should focus on:

- Controlled defect engineering
- In situ structural studies
- DFT modeling of Ti–O–Al interactions
- Correlation between dielectric and optical responses

---

10. Conclusion

This review consolidates experimental and theoretical insights into aluminum-doped CCTO systems. The photoluminescent behavior is strongly governed by structural order–disorder transitions and cluster chemistry involving TiO_6, TiO_5, and AlO_6 units.

Maximum PL intensity occurs at intermediate thermal treatment (~500 °C), where structural heterogeneity promotes defect-mediated electronic transitions. Aluminum acts as a structural organizer and electron acceptor dopant, reducing oxygen vacancy concentration and modulating band gap energy.

The interplay between crystallinity, defect density, and local coordination environment defines the optical performance of CCTO-based materials.

6. Bibliographical References

[1] A. Tikhonovsky, K. Kim, S.K. Lee et al., *Jnp. J. Appl. Phys.* 45, 8014, **(2006).**

[2] G.Y. Yang, E.C. Dickey, C.A. Randall et al., J. Appl. Phys. 96, 7492, **(2004).**

[3] T.B.Adams,D.C.Sinclair,A.R.West, *Advanced Materials. 14,* 1321–1323 **(2002).**

[4] T. Mitsui and W.B. Westphal, *Physical Review* 124, 1354, **(1961).**

[5] Y.H. Han, J.B. Appleby and D.M. Smyth, *J. Am. Ceram. Soc.* **70**, 96, (1987).

Received: 13/01/2026 - **Accepted:** 06/02/2026
Vol: 01.01
Pages: 1-9

[6]N.Kolev, R.P.Bontchev, A.J.Jacobson, et al, *Physical Review*, B66, (132), 102–132106, **(2002).**

[7]P.Lunkenheimer,V.Bobnar,A.V.Pronin, et el, *Physical Review*, B66, (052), 105–052109, **(2002).**

[8]D.C.Sinclair,T.B.Adams,F.D.Morrison,A.R.West, *Appl. Phys.* 80(2002)2153–2156.

[9] L.Chen,C.L.Chen,Y.Lin,Y.B.Chen,X.H.Chen,R.P.Bontchev, C.Y. Park,A.Jacobson, *Appl. Phys.* 82, 2317–2320, **(2003).**

[10] W.J. Lee, Y.M. Kim, H.G. Kim, *Thin Solid Films,* 269, 75–79, **(1995).**

[11] M. Kakihana, M. Yoshimura, *Bull.Chem.Soc.Jpn*, **72** 1427, **(1999).**

[12] A. Z. Simões, A. Ries, F. M. Filho, J. A. Varela, E. Longo, *Appl. Phys.* 85, 5962–5965, **(2004).**

[13] L. Ramajo, L. Parra, R. Reboredo, M. Zaghete, M. Castro, *Mater.Chem. Phys.* 107 110–114, **(2008).**

[14] C .Masingboon,S. Maensiri,T. et al., *Appl. Phys,* A91, 87–95, **(2008).**

[15] L.Marchin,S.Guillemet-Fritsch,B.Durand. *Progressin Solid State Chemistry,* 36, 151–155, **(2007).**

[16] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th edition, Wiley, New York, pp. 386–388, **(1986).**

[17] L.C.Kretly,A.F.L.Almeida, et al, *Microwaveand Optical TechnologyLetters*, 39, 145–150, **(2003).**

[18] L.He,J.B.Neaton,M.H.Cohen,D.Vanderbilt, *Physical Review*, B65, 214112–214123, **(2002).**

[19] J.-G. Li, T. Ishigaki, X. Sun, *Journal of Physical Chemistry,* C 111, 4969–4976, **(2007).**

[20] F. MOURA, A.Z. SIM, R.C.DEUS, M.R. SILVA, J.A.VARELA, E.LONGO. *Ceramics International*, 39, 3499–3506, **(2013).**

[21] D. Valim, A.G. Souza Filho, et al, *Physical Review*, B 70, 132103, **(2004).**

[22] C.Masingboon,S.Maensiri, et al, *Appl. Phys,* A91, 87–95, **(2008).**

[23] L.Marchin, S.Guillemet-Fritsch, B.Durand, *Progress in Solid State Chemistry*, 36, 151–155, **(2007).**

[24] D.L. Wood, J. Tauc, Weak absorption tails in amorphous semi- conductors, *Physical Review,* B 5, 3144–3151, **(1972).**

[25] P.Kubelka,F.Munk, Technische Physik, 12, 593–601, **(1931).**

Received: 13/01/2026 - **Accepted:** 06/02/2026
Vol: 01.01
Pages: 1-9

[26] Ch.Kant,T.Rudolf, et al, *Physical Review*, B77, 045131–045134, **(2008).**

[27] B. Bouma, G. Blasse, *J. Phys. Chem*. Solids, 56 (2): 261, **(1995).**

[28] A.P.A.Marques,D.M.A.Melo, *Journal of Solid State Chemistry*, 179, 671–678, **(2006).**

[29] D.A. Spassky, S.N. Ivanov, *Radiation Measurements*, 38, 607–610, **(2004).**

[30] F.M.Pontes,C.D.Pinheiro,E.Longo, *JournalofLuminescence,* 104, 175–185, **(2003).**

[31] C. Ariadne, T. *J. Ceramint,December* , Pages 15981–15984, **(2014).**