

Temperature-Controlled Polymorphism in Organic and Semi-Organic Nonlinear Optical Crystals: A Critical Review of Thermal, Structural, Dielectric, and Mechanical Properties

Vibha S Sikchi ^{a b c}, Mohd Anis ^d, B.B.Raje Shaikh ^e, M.I.Baig ^{b*}

^a Department of Physics, Vidyabharati junior college, karanja lad, district Washim Maharashtra, India 444105

^b Prof. Ram Meghe College of Engineering and Management. Badnera Amravati Maharashtra, India 444701

^c Sant Gadge Baba Amravati University, Amravati Maharashtra, India 444602

^d Department of Physics and Electronics, , Maulana Azad College of Arts, Science and Commerce, Chatrapati Sambhaji Nagar Maharashtra, India 431004

^e Department of Physics, Government College of Arts and Science, Chatrapati Sambhaji Nagar Maharashtra, India 431004

Abstract

Polymorphism — the ability of a chemical compound to crystallize into more than one distinct crystal structure — is a central lever for tuning the structural, optical, thermal, and nonlinear optical (NLO) behaviour of organic and semi-organic crystals. Because different polymorphs of the same compound differ in molecular packing, hydrogen-bonding networks, and crystal symmetry, they can display markedly different second-harmonic generation (SHG) efficiency, optical transparency, dielectric response, and thermal stability [1,2]. Crystallization temperature is among the most influential external parameters governing which polymorph forms, since it shapes nucleation kinetics, growth rate, and the intermolecular interactions that lock in a particular packing arrangement. This review synthesizes the existing literature on organic, inorganic, and semi-organic NLO crystals, the mechanisms of temperature-dependent (enantiotropic and monotropic) polymorphism, and the structural factors that connect crystal symmetry to SHG activity. It shows that although individual polymorphic NLO crystals have been extensively characterized using X-ray diffraction, FTIR, UV–Visible spectroscopy, thermal analysis, and SHG measurement, systematic comparative studies that track a single compound across multiple crystallization temperatures — and link the resulting structural changes directly to NLO performance — remain scarce. This gap constrains the rational, predictive design of next-generation photonic materials and motivates a temperature-controlled comparative research programme using the slow evaporation solution growth technique [3].

1. Introduction

Nonlinear optical (NLO) materials underpin a large share of modern photonics because they respond to intense light fields in a non-proportional way, enabling second-harmonic generation (SHG) [4,25], sum- and difference-frequency generation, optical rectification, electro-optic modulation, and optical switching. These effects are exploited in laser frequency conversion, optical communication, quantum optics, biomedical imaging, holography, and integrated photonic circuits [5]. The continued growth of photonic technology has driven demand for NLO crystals that combine high SHG efficiency with a broad transparency window, thermal and mechanical robustness, a high laser-damage threshold, and ease of growth — a combination rarely found in any single material class.

The literature groups NLO crystals into three broad classes. Organic crystals, built from π -conjugated donor–acceptor molecules, offer very large nonlinear coefficients and fast optical response but are typically limited by weak thermal and mechanical stability and moisture sensitivity; urea, benzotriazole derivatives, 4H-1,2,4-triazole-3,5-diamine polymorphs,

and DAST are frequently cited examples [12,13]. Inorganic crystals such as KDP, KTP, lithium niobate, BBO, and LBO provide excellent thermal stability, mechanical strength, and laser-damage resistance, but their nonlinear coefficients are comparatively modest and their growth is often slow and costly. Semi-organic crystals — organic molecular cations or anions combined with inorganic counter-ions, such as L-histidinium phosphite, piperazinium tetrachlorozincate monohydrate, rubidium hydrogen succinate hydrate, and dilithium fumarate tetrahydrate — sit between these extremes, retaining much of the organic nonlinear response while gaining inorganic-like thermal and mechanical stability [14].

Across all three classes, the slow evaporation solution growth technique remains the most widely used laboratory method for producing single crystals, owing to its simplicity, low cost, and compatibility with careful control of solvent, pH, supersaturation, evaporation rate, and temperature [3,39]. Because these growth parameters govern nucleation and crystal-packing pathways, they also govern which polymorph — and therefore which set of optical, thermal, and dielectric properties — ultimately forms.

2. Classification and Comparative Properties of NLO Crystals

The three classes of NLO materials trade off nonlinear response against stability in largely complementary ways, as summarized below.

Property	Organic	Inorganic	Semi-Organic
NLO coefficient	Very high	Moderate	High
Thermal stability	Low	Excellent	High
Mechanical strength	Low	Excellent	High
Optical transparency	Good	Excellent	Excellent
Crystal growth	Easy	Difficult	Moderate
Photonic applications	Excellent	Excellent	Excellent

This complementarity is the central motivation for semi-organic crystal engineering: by pairing an organic component that supplies strong hyperpolarizability with an inorganic component that reinforces the lattice, researchers aim to approach the nonlinear response of purely organic crystals without sacrificing the durability associated with inorganic ones. NLO crystals more broadly find application in laser frequency doubling, optical parametric oscillators, electro-optic modulators, optical switches, optical communication systems, quantum computing hardware, biomedical imaging, holography, optical data storage, and terahertz generation [10,18].

3. Polymorphism as a Crystal-Engineering Strategy

Polymorphism allows a single chemical composition to yield multiple crystal structures, each with its own symmetry, band gap, dielectric constant, SHG efficiency, thermal stability, laser-damage threshold, and mechanical hardness. Because second-order NLO activity requires a non-centrosymmetric crystal structure, the specific polymorph obtained during growth can determine whether a material is SHG-active at all, and if so, how efficiently. This makes control over polymorph selection — rather than only chemical synthesis — a distinct and powerful axis of crystal engineering for photonic materials [2,9].

4. Temperature-Dependent Polymorphism

Crystallization temperature is repeatedly identified in the literature as one of the most influential external variables controlling polymorph selection. Temperature affects molecular mobility, nucleation kinetics, growth rate, hydrogen-bonding interactions, and lattice energy, and even modest changes during growth can steer a compound toward a different stable packing arrangement [6].

4.1 Enantiotropic versus Monotropic Behaviour

Temperature-dependent polymorphism is typically classified as enantiotropic, where two or more polymorphs interconvert reversibly across a defined temperature range and each is thermodynamically stable within its own interval, or monotropic, where transformation from a metastable to a more stable form is irreversible. This distinction matters for device design:

enantiotropic systems raise the possibility of tunable or switchable optical devices, whereas monotropic transitions pose a risk to the long-term stability of a fabricated device [1,8].

4.2 Thermodynamic Origins

The preference for one polymorph over another reflects competition between crystal structures with different Gibbs free energies. Lower growth temperatures tend to favour packing arrangements that minimize lattice energy, while higher temperatures introduce larger entropic contributions that can stabilize alternative arrangements. Small temperature shifts during growth can therefore alter hydrogen bonding, van der Waals contacts, π - π stacking, or coordination geometry enough to produce a structurally distinct polymorph [8].

4.3 Consequences for Symmetry and SHG

Because SHG requires a non-centrosymmetric lattice, a temperature-induced phase transition can either preserve or destroy this symmetry. Some reported inorganic systems undergo a transition from a non-centrosymmetric to a centrosymmetric phase that eliminates SHG activity outright, while transitions between two different non-centrosymmetric phases have instead been reported to enhance SHG through improved dipole alignment and crystal anisotropy. Compounds such as BiB_3O_6 , $\text{Ba}_3\text{Mg}_3(\text{BO}_3)_3\text{F}_3$, and $\text{BaTeMo}_2\text{O}_9$ illustrate how temperature-driven structural rearrangement can shift SHG efficiency and phase-matching behaviour even without any change in chemical composition [4,15].

4.4 Nucleation, Growth Kinetics, and Practical Sensitivity

Low crystallization temperatures generally build up supersaturation slowly, favouring thermodynamically stable polymorphs and better crystal quality, whereas higher temperatures can accelerate nucleation and favour metastable or more defect-prone forms. In solution-grown organic and semi-organic crystals — particularly amino-acid-based and donor-acceptor systems — even small shifts in evaporation temperature have been reported to alter hydrogen-bond networks enough to yield an entirely different polymorph, underscoring how sensitive these systems can be to growth conditions [15,39].

4.5 Predictive and Operational Considerations

Recent work has moved from purely empirical polymorph discovery toward more predictive approaches, combining in-situ temperature monitoring, computational crystal-structure prediction, and thermodynamic modelling to anticipate phase stability ahead of synthesis [7]. Temperature control also matters after growth: during high-power laser operation, localized heating can shift phase-matching conditions, reduce conversion efficiency, or even trigger a polymorphic transformation in service, and monitoring intrinsic crystal properties rather than relying solely on external sensors has been reported to improve SHG stability in practical systems.

5. Comparative Summary: Low- versus High-Temperature Growth

Aspect	Low Temperature	High Temperature
Crystal stability	Thermodynamically stable polymorphs	Metastable or alternative polymorphs may form
Molecular packing	Dense and ordered	Greater molecular mobility and structural rearrangement
Crystal defects	Generally fewer	Increased probability of defects
SHG efficiency	Often higher if non-centrosymmetric	May increase or decrease depending on symmetry
Thermal stability	Usually higher	Phase transitions may occur
Photonic applications	Long-term stable devices	Useful for tunable or switchable optical devices

6. Critical Analysis and Research Gaps

Taken together, the literature shows steady progress in synthesizing and characterizing individual polymorphic NLO crystals using single-crystal and powder X-ray diffraction, FTIR, Raman spectroscopy, and thermal analysis [3,15], yet several recurring limitations restrict the field's ability to design NLO materials predictively:

- Most studies characterize one or two stable polymorphs of a compound rather than systematically mapping how polymorph formation changes across a temperature series, so the gradual influence of temperature on structure and performance is rarely captured.
- Papers typically report a single optimum growth temperature rather than a comparative study across conditions, leaving the mechanism linking temperature to structural transformation and NLO performance only partly understood.
- Temperature-dependent polymorphism has been studied more thoroughly in inorganic NLO materials than in organic or semi-organic systems, and few studies directly compare organic and semi-organic crystals grown under identical conditions.
- SHG efficiency is frequently measured, but is less often related quantitatively to specific structural parameters such as molecular orientation, dipole alignment, hydrogen-bonding geometry, packing density, or lattice distortion; dielectric constant, refractive index, birefringence, and damage threshold are usually studied in isolation rather than through an integrated structure–property framework.
- Reproducibility is limited by variation in solvent purity, evaporation conditions, concentration, supersaturation, and temperature-control accuracy across laboratories, and the absence of standardized growth protocols makes cross-study comparison difficult.
- Most characterization remains laboratory-scale; fewer studies evaluate whether a temperature-optimized polymorph retains its advantages under long-term operation, laser-induced stress, or environmental exposure in an actual photonic device.

These gaps point to a common conclusion: the field would benefit from systematic, temperature-controlled comparative studies — ideally spanning both organic and semi-organic crystal classes — that pair structural, thermal, dielectric, and SHG characterization within a single, consistent growth protocol.

7. Future Scope

- Predictive crystal-engineering strategies that regulate crystallization temperature, solvent composition, supersaturation, and evaporation rate together, to make polymorph selection reproducible rather than incidental.
- Broader comparative studies spanning multiple organic and semi-organic polymorphic systems, aimed at generalizable relationships between temperature, structure, and NLO performance rather than single-compound findings.
- Integration of computational crystal-structure prediction, molecular modelling, density functional theory, and machine learning with experimental growth to shorten the search for high-performance polymorphs.
- Extension of characterization to ultrafast optical response, electro-optic coefficients, birefringence, laser-induced damage threshold, optical limiting, and photostability, which matter increasingly for high-power laser and integrated photonic applications.
- Device-level evaluation — incorporating optimized polymorphs into frequency doublers, electro-optic modulators, optical switches, waveguides, and integrated photonic or quantum components.
- Development of greener, more scalable growth methods to support eventual industrial-scale production of polymorphic NLO crystals.

8. Conclusion

The literature confirms that crystallization temperature is a critical, controllable parameter for selecting among polymorphic forms of organic and semi-organic NLO crystals, and that the resulting structural differences can substantially alter SHG efficiency, optical transparency, dielectric behaviour, and thermal stability. At the same time, the existing body of work is dominated by single-polymorph characterization rather than systematic, temperature-controlled comparison, and organic–semi-organic comparisons under matched growth conditions remain particularly sparse. Closing this gap — through slow evaporation solution growth under carefully controlled temperature conditions, paired with integrated structural, thermal, dielectric, and SHG characterization — offers a promising route toward predictive, rather than empirical, design of next-generation photonic materials [2,6].

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