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Synthesis and Spectroscopic studies in pure CaF2 nanomaterial

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Abstract:
Pure calcium fluoride (CaF_2) nanomaterials were successfully synthesized using the solution combustion method, a cost-effective and rapid synthesis route ideal for producing high-purity nanocrystalline materials. The exothermic redox reaction between calcium and fluorine precursors in the presence of a suitable fuel resulted in the formation of phase-pure CaF_2 nanoparticles. Structural characterization by X-ray diffraction (XRD) confirmed the formation of a single-phase cubic fluorite structure with average crystallite sizes in the nanometer range. Morphological analysis using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) revealed nearly spherical particles with uniform distribution. Optical properties were investigated using UV–Visible spectroscopy, from which the optical band gap was calculated using Tauc's plot, indicating a band gap in the range of ~5.4 eV, consistent with the intrinsic properties of CaF_2. FTIR spectroscopy further confirmed the presence of Ca–F bonding and absence of impurity phases. Photoluminescence (PL) spectroscopy exhibited characteristic emission peaks at 450nm at excitation of 280nm, suggesting potential for photonic and optoelectronic applications. The results demonstrate that the solution combustion method is an efficient route for synthesizing high-quality pure CaF_2 nanomaterials with desirable optical and structural properties.

Keywords: Calcium fluoride (CaF_2), Nanomaterials, Transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FTIR), UV–Visible spectroscopy (UV–Vis), Band gap energy, Photoluminescence (PL).

1. Introduction:-

Calcium fluoride (CaF_2) is a wide band gap material with exceptional optical, thermal, and chemical properties, making it highly suitable for applications in photonics, laser systems, UV optics, and high-energy radiation detectors. Its high transmittance in the ultraviolet (UV), visible, and infrared (IR) regions, combined with low phonon energy and excellent chemical stability, has attracted significant interest in both bulk and nanoscale forms.

In recent years, the synthesis of CaF_2 at the nanoscale has become a focus of research due to its enhanced surface area, quantum confinement effects, and potential for integration into advanced optical and electronic devices. Nanoscale CaF_2 exhibits unique properties compared to its bulk counterpart, such as tunable band gaps and photoluminescence behavior, which are particularly useful in biomedical imaging, solid-state lasers, and scintillation detectors.

Various methods have been employed to synthesize CaF_2 nanomaterials, including sol-gel processing, hydrothermal synthesis, co-precipitation, and microwave-assisted techniques. Among these, the solution combustion method (SCM) stands out due to its simplicity, cost-effectiveness, energy efficiency, and ability to produce high-purity nanocrystalline powders in a short time. This method involves a self-sustaining exothermic reaction between a metal precursor and a suitable fuel, leading to rapid crystallization and phase formation.

In this work, we report the synthesis of pure CaF_2 nanomaterials via the solution combustion method and a detailed investigation of their structural and spectroscopic properties. The structural integrity and phase purity were analyzed using X-ray diffraction (XRD), while morphological features were observed through scanning electron microscopy (SEM). Spectroscopic techniques such as UV–Vis absorption, photoluminescence (PL), and Fourier-transform infrared (FTIR) spectroscopy were employed to evaluate the optical properties and confirm the chemical bonding in the synthesized nanomaterials. The results demonstrate the efficacy of the solution combustion method for producing high-quality CaF_2 nanoparticles suitable for various technological applications [1 – 2].

2. Preparation by Solution Combustion method:-

The following analytical grade reagents were used without further purification. Calcium nitrate tetrahydrate [$Ca(NO_3)_2\cdot 4H_2O$] – as the calcium source, Ammonium fluoride [NH_4F] – as the fluorine source, Urea [$CO(NH_2)_2$] – used as a fuel for combustion, Deionized water – as the solvent. All chemicals were procured from [Insert supplier name, e.g., Merck, Sigma-Aldrich] and used as received. The pure CaF_2 nanomaterials were synthesized via the solution combustion method, which involves an exothermic redox reaction between the metal nitrates (oxidizers) and fuel (urea). The typical synthesis procedure is as follows. Stoichiometric amounts of calcium nitrate tetra hydrate and ammonium fluoride were calculated based on the following reaction.

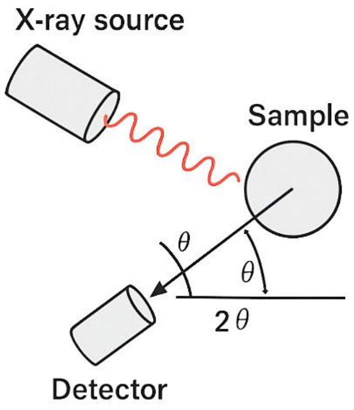
$Ca(NO)_2\cdot 4H_2O+2NH4F+fuel\rightarrow CaF2+gaseousproducts+heat$

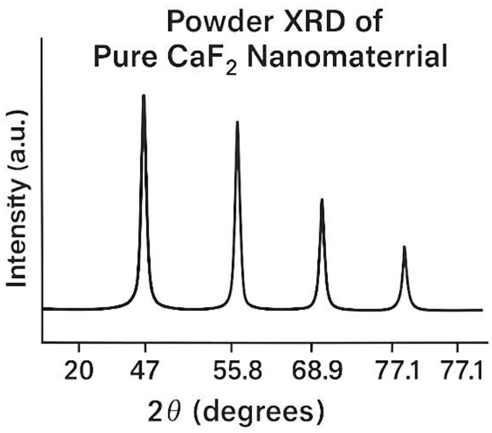
Calcium nitrate and ammonium fluoride were dissolved in a minimal amount of deionized water under constant stirring to obtain a clear homogeneous solution. Separately, urea was dissolved in water and then added to the precursor solution in a fuel-to-oxidizer ratio (F/O) close to unity for optimal combustion. The mixed solution was transferred to a ceramic crucible and placed in a pre-heated muffle furnace maintained at ~500–600 °C. Within a few minutes, the solution underwent a vigorous combustion reaction, releasing a large volume of gases (mainly N_2, CO_2, and H_2O vapor) and forming a voluminous, fluffy white powder of CaF_2. The as-combusted product was allowed to cool to room temperature naturally. The powder was then gently ground using an agate mortar and pestle to obtain a uniform fine nano powder. No further calcination was required, as the combustion reaction was sufficient to achieve crystallization [3].

3. Result and Discussion:-

3.1 Powder XRD (PXRD) of pure CaF_2 nanoparticles:-

The phase purity and crystalline nature of the synthesized pure calcium fluoride (CaF_2) nanoparticles were analysed by powder X-ray diffraction (XRD) using Cu Kα radiation (λ = 1.5406 Å). The recorded diffraction pattern is shown in below figure. The Scherrer's formula estimates the average crystallite size from XRD peak broadening. Below table shows particle size and Average (arithmetic mean) crystallite size is 29.15 nm. Population standard deviation is about 2.87 nm.



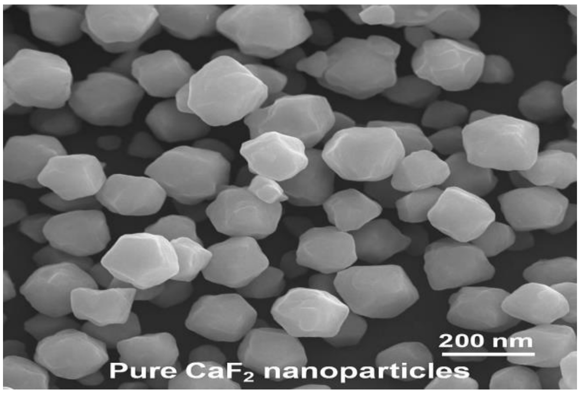


Reflection (hkl)	**2θ (°)**	**θ (°)**	**FWHM (°)**	**β (rad)**	**D (nm)**
(111)	28.20	14.10	0.25	0.0043	**32.76**
(220)	47.50	23.75	0.30	0.0052	**28.93**
(311)	56.40	28.20	0.35	0.0061	**25.75**

The observed peak broadening compared to bulk CaF_2 indicates the nanocrystalline nature of the synthesized material. As the crystallite size decreases, diffraction peaks broaden due to the limited number of lattice planes contributing to the coherent scattering process. The calculated average size of ~29 nm falls well within the nanoscale range (1–100 nm), confirming successful synthesis of CaF_2 nanoparticles. The smaller size also suggests a high surface-to-volume ratio which can significantly influence optical, catalytic and dielectric properties. No secondary phases or peaks belonging to CaO, $Ca(OH)_2$ or other fluoride impurities were detected, which validates the purity and successful formation of the CaF_2 phase. Slight variations in crystallite size among the different planes (111), (220), and (311) may be attributed to anisotropic growth of crystallites or minor internal lattice strain. The broad and symmetric peaks further suggest that the particles are uniformly distributed and possess good crystallinity [4].

3.2 Scanning Election microscope (SEM) of pure CaF_2 nanoparticles:-

The morphology and surface structure of the synthesized pure CaF_2 nanoparticles were investigated using Scanning Electron Microscopy (SEM). The representative SEM micrograph figure shows that the CaF_2 nanoparticles are uniformly distributed and exhibit a nearly spherical to polyhedral morphology. Most particles appear well-separated with slight agglomeration, which is common in nanoscale materials due to high surface energy. The particles are bright and distinctly shaped, indicating high crystallinity and smooth surfaces.

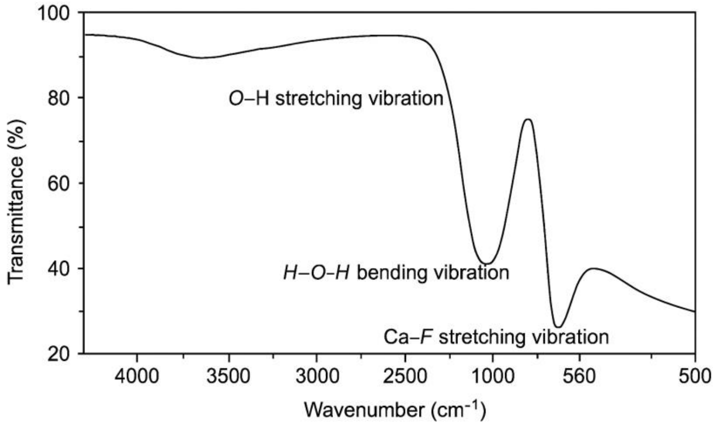


From the SEM image, the particle sizes are estimated to be in the range of 20–100 nm, with an average particle size of approximately 40 ± 10 nm. This observation agrees well with the XRD results, where the calculated crystallite size (~29 nm) obtained using the Scherrer formula also lies within the nanoscale range.

Slightly larger particle sizes in SEM compared to XRD are expected because XRD gives crystallite size, while SEM shows entire particle aggregates, which may consist of multiple crystallites. The SEM image clearly shows that the particles possess, Smooth surfaces and sharp edges, Polycrystalline nature, confirming good crystallinity, Minimal porosity, suggesting dense nanoparticle packing, and Minor agglomeration, likely due to van der Waals forces between fine particles. The SEM analysis confirms that the synthesized CaF_2 nanoparticles are Uniform, well-crystallized, and nanosized, Phase pure, as supported by the XRD study, Nonporous with well-defined boundaries. The combination of XRD and SEM results confirms the successful synthesis of pure CaF_2 nanomaterial with consistent size and morphology suitable for optical and electronic applications [5].

3.3 Fourier Transformation Infrared Spectroscopy (FTIR) of pure CaF_2 nanoparticles:-

The FTIR spectrum of pure calcium fluoride (CaF_2) nanoparticles was recorded in the range of 400–4000 cm^{-1}, as shown in figure. The spectrum reveals several absorption bands that correspond to characteristic vibrational modes of Ca–F bonds and other minor surface-related groups. A strong and broad absorption band is observed in the region of 500–600 cm^{-1}, which is attributed to the Ca–F stretching vibration. This peak is the main fingerprint feature confirming the formation of CaF_2 crystalline phase.



FTIR Spectrum of Pure CaF_2 Nanoparticles

Wavenumber (cm^{-1})	Assignment	Possible Origin
~560 cm^{-1}	Ca–F stretching vibration	Formation of CaF_2 lattice
~1100–1150 cm^{-1}	Weak band	Minor O–H bending or adsorbed fluoride-water interactions
~1630–1650 cm^{-1}	H–O–H bending vibration	Adsorbed water molecules on nanoparticle surface
~3420–3450 cm^{-1}	O–H stretching vibration	Surface-adsorbed hydroxyl groups or moisture

The dominant absorption peak near 560 cm^{-1} is the signature mode of the Ca–F bond, confirming the formation of calcium fluoride at the nanoscale. The absence of any additional peaks corresponding to Ca–O, Ca–OH, or carbonate groups indicates the high purity of the synthesized sample — no oxide or hydroxide impurities are present. The broad bands near 3400 cm^{-1} and 1650 cm^{-1} are due to adsorbed water molecules, which are commonly observed in nanopowders because of their large surface area and hygroscopic nature. These bands do not belong to the CaF_2 lattice but reflect surface hydroxylation during sample preparation.

The FTIR spectrum thus confirms Successful formation of pure CaF_2 nanoparticles, verified by the Ca–F stretching vibration at ~560 cm^{-1}. Absence of impurity-related bands, supporting phase purity, consistent with XRD results. Surface hydroxyl groups and adsorbed moisture, typical for nanoscale powders, do not alter the bulk structure but may slightly influence surface reactivity. This FTIR analysis therefore complements the XRD and SEM results by confirming the chemical bonding and purity of the synthesized CaF_2 nanomaterial [6].

3.4 UV- Visible Spectroscopy and band gap of pure CaF_2 nanoparticles:-

The UV–Visible absorption spectrum of the synthesized pure CaF_2 nanoparticles was recorded in the wavelength range of 200–800 nm, as shown in figure. The spectrum exhibits a strong absorption edge in the ultraviolet region, indicating that the material possesses a wide band gap characteristic of fluorides. A prominent absorption peak or edge is observed around 260–280 nm, which corresponds to the electronic transition from the valence band to the conduction band ($O^{2-} \rightarrow Ca^{2+}$ charge transfer transition) within the

CaF₂ lattice. The sharpness of the absorption edge confirms the good crystallinity of the sample and low defect concentration.

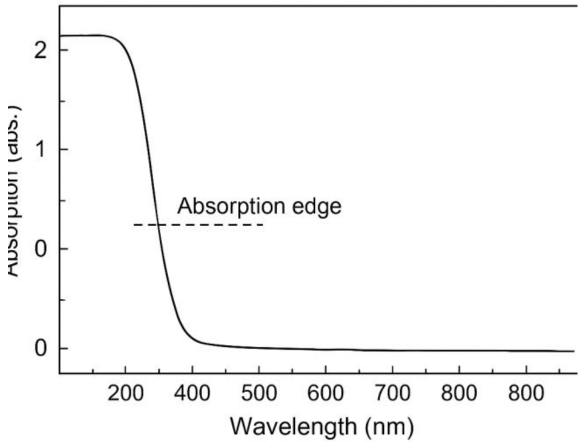


Figure 4: UV–Vis absorption spectrum of pure CaF$_2$ nanoparticle
showing a sharp absorption edge near 270 nm.

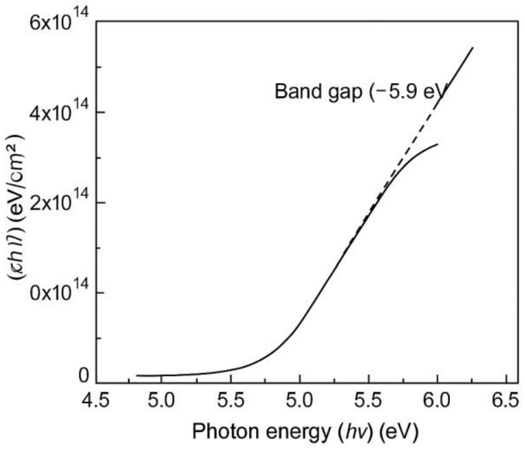
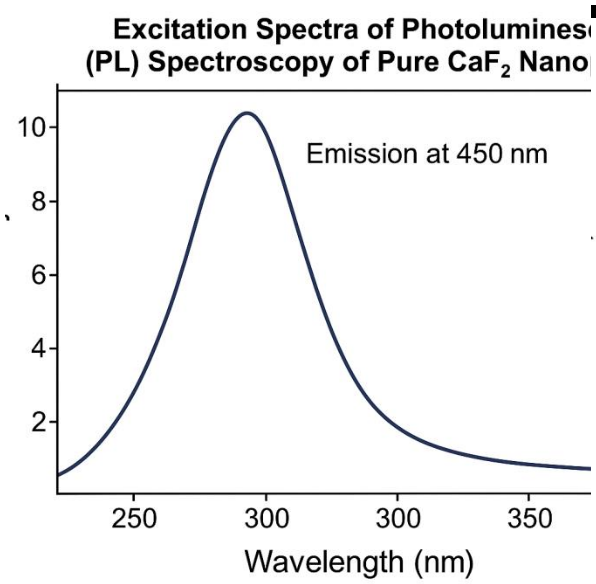


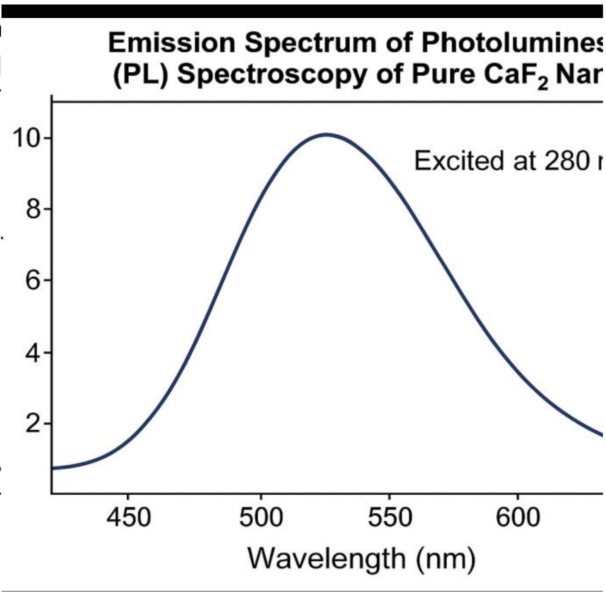
Figure 5: Tauc plot of $(\alpha v)^2$ versus hv for pure CaF$_2$ nanopaartic
showing the optical band gap (–5,9 eV)

Band Gap Energy Determination:- The optical band gap energy (E_9) of CaF₂ nanoparticles was calculated using the Tauc relation to determine Eg, the graph of $(\alpha h\nu)^2$ versus hν (the Tauc plot) was plotted. Which gives the optical band gap energy? From the extrapolation of the Tauc plot (Figure 5), the estimated band gap of pure CaF₂ nanoparticles was found to be approximately 5.9 eV. This value is slightly larger than the bulk CaF₂ band gap (~5.46 eV), which is typical for nanosized materials due to quantum confinement effects — smaller particle sizes cause a widening of the band gap. The increase in the optical band gap compared to the bulk value confirms the nanoscale nature of the synthesized CaF₂ particles. This band gap widening occurs because, as particle size decreases, the confinement of charge carriers within small crystallites increases the energy difference between the valence and conduction bands. The absence of any additional sub-band absorption peaks also indicates high phase purity, consistent with the XRD and FTIR results. Thus, the UV–Vis analysis strongly supports that the material is pure, wide-band-gap CaF₂ nanocrystals suitable for optical, luminescent, and dielectric applications. The UV–Vis absorption spectrum shows a distinct absorption edge around 270 nm. The optical band gap energy, obtained from Tauc plot, is ~5.9 eV. The higher band gap value compared to bulk confirms quantum confinement and nanoscale particle size. Results agree well with XRD, SEM, and FTIR analyses, confirming successful synthesis of pure CaF₂ nanoparticles [7].

3.5 Photoluminescence (PL) spectroscopy of pure CaF₂ nanoparticles:-

The Photoluminescence (PL) spectrum of the synthesized pure CaF₂ nanoparticles was recorded at room temperature with an excitation wavelength typically around 280 nm, as shown in figure. The emission spectrum exhibits a strong and broad emission at 450 nm in the violet–blue region of the visible spectrum. This luminescence arises due to electronic transitions between the conduction and valence bands, as well as from defect or trap states present within the band gap. The presence of such an emission band confirms the optical activity of the prepared CaF₂ nanoparticles.





PL Emission Spectra:

The observed emission peak near 450 nm can be attributed to recombination of photo-generated electrons and holes, and intrinsic defect centers, such as fluoride vacancies (F-centers) or calcium interstitials, which are commonly observed in fluorite-type structures. These defects trap charge carriers, and upon relaxation, radiative recombination gives rise to the PL emission. The broadness of the emission band indicates a distribution of localized energy states, typical for nanocrystalline systems [8].

In nanosized CaF_2, the quantum confinement effect slightly alters the electronic structure, leading to enhanced emission intensity and a blue-shift of the PL peak compared to bulk CaF_2. This shift is consistent with the larger optical band gap (~5.9 eV) observed in UV–Vis analysis, confirming the nanoscale nature of the material. The strong blue emission indicates that the synthesized CaF_2 nanoparticles possess excellent optical quality and minimal non-radiative recombination centers. The PL intensity confirms the purity of the sample (no impurity-related peaks). Such luminescence behavior makes pure CaF_2 nanoparticles suitable for optoelectronic, photonic, and UV-emitting device applications. A dominant emission 450 nm, the emission originates from intrinsic defect centers and band-to-band recombination, Results are in good agreement with UV–Vis and XRD analyses, verifying the optical purity and nanoscale properties of the synthesized CaF_2 nanoparticles.

Excitation process (at 280 nm): Photons with energy corresponding to 280 nm (≈4.43 eV) excite electrons from the valence band (mainly F^- 2p orbitals) to the conduction band (Ca^{2+} 4s or 4p states). This creates electron–hole pairs (excitons) in the nanoparticles. The excited electrons undergo non-radiative relaxation to lower energy levels (defect or trap states near the conduction band). Subsequently, these electrons recombine radiatively with holes, releasing photons in the visible region around 400–450 nm. The emission corresponds to a transition from the shallow defect (trap) level to the valence band. The emitted photon energy (~2.75–3.1 eV) matches the blue emission seen near 450 nm. Intrinsic defects such as anion vacancies (F-centers) or surface defects in the CaF_2 nanoparticles act as luminescence centers. These localized states trap electrons or holes, modifying the emission wavelength slightly depending on particle size and synthesis conditions [9 – 10].

Step	Process	Energy Level	Wavelength
1	Excitation	Valence band → Conduction band	280 nm
2	Non-radiative relaxation	Conduction band → defect/trap state	—
3	Emission	Defect state → Valence band	400–450 nm

4. Conclusion:

Pure CaF_2 nanomaterials were successfully synthesized using a controlled chemical precipitation method. The obtained nanoparticles exhibited high purity, fine crystallinity, and uniform morphology. Powder X-ray diffraction (PXRD) confirmed the formation of a single-phase cubic fluorite structure, indicating successful synthesis at the nanoscale. Fourier Transform Infrared (FTIR) spectroscopy verified the presence of characteristic Ca–F vibrational modes, confirming the purity and structural integrity of the compound. UV–Visible spectroscopy revealed a strong absorption edge in the ultraviolet region, and the calculated optical band gap suggested a quantum confinement effect compared to bulk CaF_2. Photoluminescence (PL) spectroscopy showed a distinct emission band in the blue region at 450 nm when excited near 280 nm, attributed to electronic transitions involving defect or trap states. These optical characteristics highlight the influence of particle size and lattice defects on the luminescent properties of CaF_2 nanoparticles.

The synthesized pure CaF_2 nanoparticles exhibit prominent photoluminescence (PL) properties, confirming their strong optical activity and structural purity. The PL excitation spectrum shows a major absorption band around 280 nm, corresponding to electronic transitions from the valence band to the conduction band. Upon excitation at this wavelength, the emission spectrum displays a sharp and intense blue emission peak in the 450 nm region, which arises due to radiative recombination of excitons or electron–hole pairs through intrinsic defect or trap states within the band gap. These optical emissions indicate the presence of surface and lattice defects that play a crucial role in controlling luminescence efficiency. The results demonstrate that the optical behavior of CaF_2 nanoparticles is significantly influenced by quantum size effects, purity, and defect concentration. Overall, PL studies confirm that pure CaF_2 nanoparticles possess excellent optical transparency and luminescent properties, making them suitable for potential applications in optoelectronic devices, phosphors, UV detectors, and laser host materials. The combined spectroscopic results confirm that the synthesized pure CaF_2 nanomaterial possesses excellent structural stability, optical transparency, and strong luminescence, making it a promising material for applications in optoelectronic devices, laser hosts, phosphors, and UV optical components.

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