

Synthesis, characterization and optical properties of LaAlO₃:Ho³⁺ phosphor

Vijay Singh^a, D.T. Naidu^b, R.P.S. Chakradhar^c, Y.C. Ratnakaram^d, Jun-Jie Zhu^{a,*}, Manish Soni^e

^a Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China

^b Department of Physics, Rao and Naidu Engineering College, Ongole 523001, AP, India

^c Glass Technology Laboratory, Central Glass and Ceramic Research Institute, Kolkata 700032, Council of Scientific & Industrial Research (CSIR), India

^d Department of Physics, S.V. University PG Centre, Kavali 524201, AP, India

^e Department of Physics, Sadhu Vaswani College, Bairagarh, Bhopal 462030, India

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ABSTRACT

Holmium-doped lanthanum aluminate (LaAlO₃) powder phosphors have been prepared at furnace temperatures as low as 500 °C by using the combustion route without further calcining treatment. Powder X-ray diffraction and Fourier-transform infrared spectrometry measurements were used to characterize the prepared combustion products, while the optical properties were studied using UV–vis–NIR and photoluminescence spectroscopy. The Judd–Ofelt (J–O) model was applied to obtain the oscillator strengths (f) and three phenomenological intensity parameters. Using J–O parameters (Ω_2 , Ω_4 and Ω_6) the radiative transition probabilities (A_{ab}), radiative lifetimes (τ_R) and branching ratios have been calculated for certain excited states of Ho³⁺. Using the Fuchtbauer–Ladenberg formula, the stimulated emission cross-sections (σ_{emi}) for some interesting transitions, such as ⁵S₂ → ⁵I₈ and ⁵F₅ → ⁵I₈ of Ho³⁺ in LaAlO₃, were determined and discussed.

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1. Introduction

Phosphors are important materials of modern technology because of their ability to convert incident electromagnetic radiation into light. Rare-earth (RE) ions have been widely known as activators in different host matrices because of their high-efficiency emission performance [1]. Therefore the development of RE-ion-doped novel luminescent phosphors is of interest due to their potential applications in different optical display systems [2–7]. As a part of our programme on aluminate phosphors [8–10], in the present study we report the optical properties of Ho³⁺-ion-doped lanthanum aluminate (LaAlO₃) phosphor. LaAlO₃ has been chosen as a host material since it has a reasonably larger band gap of over 5 eV, and a high thermal stability up to 2100 °C [11]. There are only a few reports on spectroscopic properties of LaAlO₃ doped with RE ions. A preliminary work on spectroscopic properties of LaAlO₃ with

Ho³⁺ has been published by Deren and Krupa [12]. Optical transitions of Ho³⁺ in YAG were studied by Malinowski et al. [13]. Green up-converted emission by infrared pump in Ho³⁺-doped YAlO₃ has been very well explained by Osiać [14]. Wang et al. [15] reported optical transitions in Ho³⁺-doped La₃Ga₅SiO₁₄ crystals. Recently, Deren et al. [16] studied Green up-conversion emission in LaAlO₃ crystal doped with holmium ions. There is a little work on optical properties of LaAlO₃ doped with Ho³⁺ ions. However, no detailed analysis of Judd–Ofelt (J–O) theory has been performed on Ho³⁺-doped LaAlO₃ powder phosphors.

This paper presents the results of optical properties of LaAlO₃:Ho³⁺ phosphors prepared by a low-temperature initiated, self-propagating and gas-producing solution combustion method. The combustion method involves rapidly heating a concentrated aqueous solution of corresponding metal nitrates (oxidizer) and urea (fuel) at 500 °C within 5 min. Important features of the combustion process are fast, economical and *simple in doping and scale up*. The nature and structural details of the synthesized phosphor have been investigated by X-ray diffraction (XRD) and Fourier-transform infrared spectrometry (FTIR) studies. The optical properties were studied using diffuse reflectance,

* Corresponding author. Tel./fax: +86 25 8359 4976.

E-mail address: jjzhu@mail.nju.edu.cn (J.-J. Zhu).

excitation and emission spectra. The experimental data obtained have been analyzed in the context of the J-O theory. Spectral intensities (I), intensity parameters (Ω_λ), radiative transition probabilities (A_{ab}), radiative lifetimes (τ_R), branching ratios (β) and emission cross-sections (σ_{emi}) have been evaluated and discussed.

2. Experimental

2.1. Synthesis

Lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were used as oxidizers, urea ($\text{CH}_4\text{N}_2\text{O}$) was used as fuel and Ho_2O_3 as a dopant. The oxidizer:fuel ratio was calculated based on oxidizing (O) and fuel (F) valencies of the reactants, keeping $\text{O/F} = 1$, as reported earlier [17].

The above materials were mixed according to the chemical formula $\text{La}_{0.96}\text{Ho}_{0.04}\text{AlO}_3$. The starting materials were crushed and ground in China dish with minimum quantity of de-ionized water to form a solution. The dish was then transferred into a furnace maintained at 500°C . Initially, the paste melted and underwent dehydration followed by decomposition with the evolution of large amounts of gases (oxides of nitrogen and ammonia). The mixture then frothed and swell, forming foam, which ruptured with a flame and glowed to incandescence. During incandescence the foam further swell to the capacity of the container. The entire combustion process was over in less than 5 min. The formed powders were free from any carbon residue. The flowchart for the combustion process is summarized in Fig. 1.

2.2. Instruments

Powder XRD study was performed on a Philips X pert X-ray diffractometer with graphite monochromatized CuK_α radiation

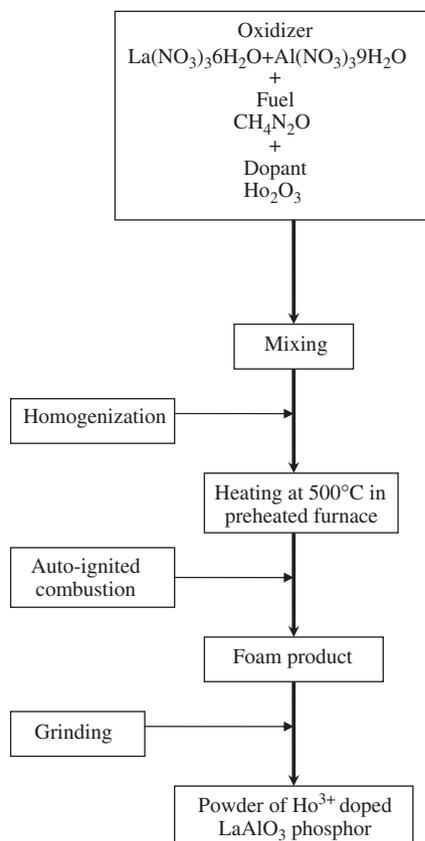


Fig. 1. Flowchart for the preparation of (a) $\text{LaAlO}_3:\text{Ho}^{3+}$ powder phosphor.

($\lambda = 0.15418 \text{ nm}$) and nickel filter at a scanning step of 0.03° , continue time 10 s, in the 2θ range $10\text{--}80^\circ$. FTIR spectrum was taken using a Perkin-Elmer Rx1 instrument. Diffuse reflectance spectra (DR-UV-vis-NIR) were recorded using a Varian CARY apparatus in the range $250\text{--}2500 \text{ nm}$ at room temperature. Photoluminescence measurements were performed using a Hitachi F-4000 spectrofluorometer at room temperature.

3. Results and discussion

3.1. X-ray diffraction

Fig. 2a shows the XRD reflections for $\text{La}_{0.96}\text{Ho}_{0.04}\text{AlO}_3$ powder phosphor. The phase analysis demonstrates that $\text{La}_{0.96}\text{Ho}_{0.04}\text{AlO}_3$ is hexagonal with unit cell dimensions $a = 5.369 \text{ \AA}$ and $c = 13.13 \text{ \AA}$. This is in good agreement with the standard JCPDS files (82-0478; Fig. 2b). The peaks and intensities of the prepared powder and that of the standard were the same. This indicates that the pure-phase formation was complete during the reaction process at the furnace temperature (500°C), and a further calcination step is not necessary.

3.2. FTIR studies

The FTIR spectrum of $\text{La}_{0.96}\text{Ho}_{0.04}\text{AlO}_3$ powder phosphor is shown in Fig. 3. The broad band at 3434 cm^{-1} is attributed to absorbed water. The weak band at 1622 cm^{-1} corresponds to the deformation vibration of water (δ_{OH}) molecules. The bands between 1330 and 1550 cm^{-1} are due to the asymmetric stretching vibration and the symmetric stretching vibration of the NO_3^- group, which are expected to form from the starting material. The sharp bands observed in the range $700\text{--}400 \text{ cm}^{-1}$ can be assigned to the metal-oxygen stretching frequencies. Quite similar to the XRD results the FTIR also showed sharp metal-oxygen bonds, indicating a crystalline nature and therefore avoiding the post-processing requirements. Adak and Pramanik [18] reported the formation of LaAlO_3 by the evaporation of polyvinyl alcohol added to a mixed metal nitrate solution and obtained broad Al-O bands in the as-formed condition and sharp Al-O bands (439 and 667 cm^{-1}) only after thermal treatment at 700°C for 2 h. It is significant that combustion process produce sharp Al-O bands even at furnace temperatures as low as 500°C within a few minutes.

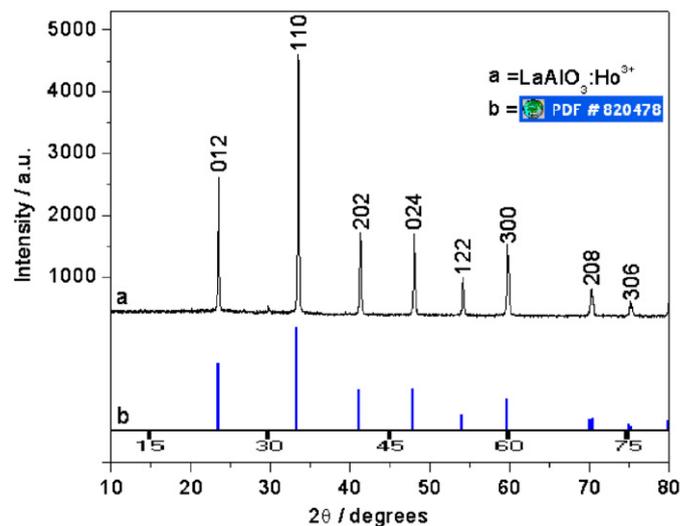


Fig. 2. Powder XRD pattern of (a) $\text{LaAlO}_3:\text{Ho}^{3+}$ and (b) LaAlO_3 (JCPDS, No. 82-0478).

3.3. Optical properties

3.3.1. UV–vis–NIR studies

Fig. 4 shows the UV–vis–NIR spectrum of Ho³⁺-doped LaAlO₃ powder phosphor at room temperature. From the spectra, eleven absorption peaks are observed. The observed band positions are assigned by comparing the band positions in the absorption spectrum with an energy level scheme of Ho³⁺, published by Carnall et al. [19]. The spectral intensities for the observed bands, which are often expressed in terms of the oscillator strength f_{exp} , were determined by measuring the areas under the absorption curve using the relation

$$f_{\text{exp}} = \frac{4\epsilon_0 mc^2}{Ne^2 \lambda^2} \int_{\text{band}} \alpha(\lambda) d\lambda \quad (1)$$

In this expression ϵ_0 is the dielectric constant, λ the mean wavelength associated with the absorption band, $\alpha(\lambda)$ the absorption coefficient and N the number of holmium ions per cm³. The theoretical oscillator strengths (f_{cal}) of the transitions between a and b states are calculated using the standard J-O

theory [20,21], which is defined as

$$f_{\text{cal}}(a \rightarrow b) = \frac{8\pi mc^2}{3h(2J+1)\lambda} \frac{1}{9n} \sum_{\lambda=2,4,6} \Omega_{\lambda} | \langle a || U^{\lambda} || b \rangle |^2 \quad (2)$$

where m is the electron mass, h the Planck constant, n the refractive index, λ the transition wavelength, c the light velocity in a vacuum, Ω_{λ} are the J-O intensity parameters and $||U^{\lambda}||$ the double reduced matrix elements of the unit tensor operator of rank $\lambda = 2, 4$ and 6 , which were taken from literature [22]. The refractive index of LaAlO₃ is high ($n = 2.08$, $\lambda = 580$ nm). The Sellmeier equation [17] was used to calculate the n value appropriate to the observed transition. The experimental and calculated oscillator strengths are shown in Table 1. The RMS deviation between the experimental and calculated spectral intensities, which are also presented in Table 1, is very small, confirming the validity of approximations made in J-O theory. From the least-square fit of measured and calculated oscillator strengths the three intensity parameters Ω_{λ} ($\lambda = 2, 4$ and 6) were calculated. In the above least-square fit method the spectral intensities of the bands ³H₆+³D₂ and ³K₆+³F₄ are not included due to uncertainty in the measurement of spectral intensities. The resulting set of J-O parameters was found to be $\Omega_2 = 5.524 \times 10^{-20}$ cm², $\Omega_4 = 4.592 \times 10^{-20}$ cm² and $\Omega_6 = 2.875 \times 10^{-20}$ cm².

In general, the Ω_{λ} value strongly depends on covalent bonding and its structure. Ω_2 parameter indicates covalency of the metal

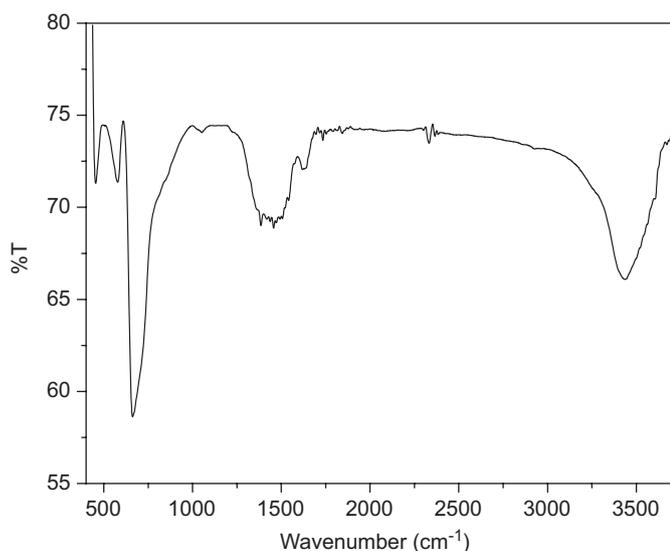


Fig. 3. FT-IR spectrum of LaAlO₃:Ho³⁺ phosphor.

Table 1

Experimental ($f_{\text{exp}} \times 10^6$) and calculated ($f_{\text{cal}} \times 10^6$) spectral intensities of Ho³⁺-doped LaAlO₃ powder phosphors

Energy level	f_{exp}	f_{cal}
⁵ I ₇	3.44	3.37
⁵ I ₆	2.08	2.40
⁵ F ₅	8.66	7.12
⁵ F ₄ , ⁵ S ₂	9.18	8.86
⁵ F ₃	1.88	2.61
⁵ F ₂ , ³ K ₈	0.37	0.345
⁵ G ₆	34.93	34.82
⁵ G ₅	5.34	7.34
⁵ G ₄ , ³ K ₇	1.57	1.34
³ H ₆ , ³ D ₂	9.69	10.42
³ K ₆ , ³ F ₄	2.31	2.29

RMS deviation: ±0.724

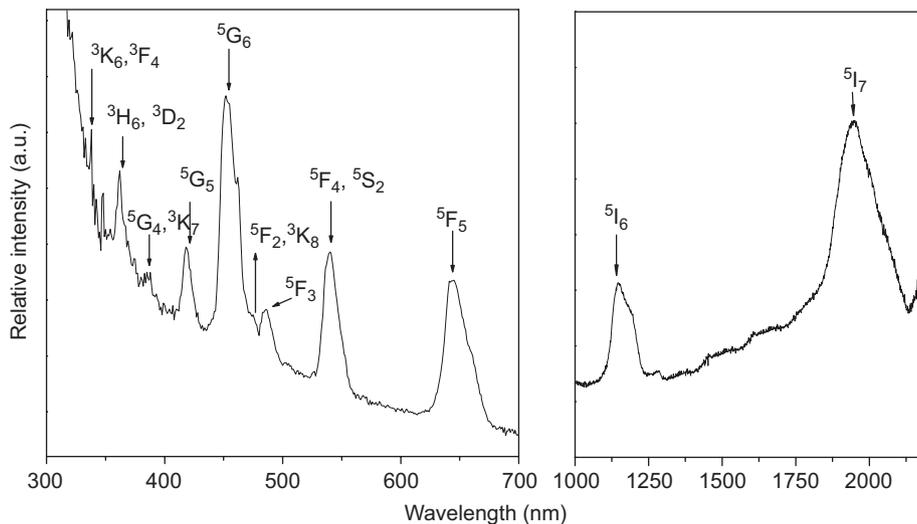


Fig. 4. UV–vis–NIR spectrum of LaAlO₃:Ho³⁺ phosphor.

ligand bond, and Ω_4 , Ω_6 are related to the rigidity of the host matrix. The values of the J-O parameters are also useful to calculate the spectroscopic quality factor $X = \Omega_4/\Omega_6$, which is critically important in predicting the stimulated emission for the laser-active medium. In the present work, Ω_2 parameter is high, which indicates the strong covalency characteristic of this material.

Using the calculated set of J-O intensity parameters (Ω_j), the radiative transition probabilities (A_{ab}) for emission between J manifold of Ho^{3+} were calculated using the relation

$$A_{ab} = \frac{64\pi^4 c^2}{3h(2J+1)\lambda^3} \frac{1}{4\pi\epsilon_0} f_{\text{cal}}(a \rightarrow b) \quad (3)$$

and thus it was feasible to determine the total radiative transition probabilities ($A_T = \sum_b A_{ab}$), the radiation lifetimes $\tau_R = (\sum_b A_{ab})^{-1}$ and luminescent branching ratio $\beta_{ab} = (A_{ab}/\sum_b A_{ab})$ from the excited levels. Total radiative transition probabilities (A_T) and life times (τ_R) of certain excited state of Ho^{3+} ions in LaAlO_3 phosphor are shown in Table 2. The branching ratios (β_{ab}) of certain transitions, ${}^3\text{H}_6 \rightarrow {}^5\text{I}_7$, ${}^3\text{K}_8 \rightarrow {}^5\text{I}_8$, ${}^5\text{F}_2 \rightarrow {}^5\text{I}_8$, ${}^5\text{F}_3 \rightarrow {}^5\text{I}_8$, ${}^5\text{F}_3 \rightarrow {}^5\text{I}_7$, ${}^5\text{S}_2 \rightarrow {}^5\text{I}_8$, ${}^5\text{F}_4 \rightarrow {}^5\text{I}_8$, ${}^5\text{F}_5 \rightarrow {}^5\text{I}_8$, of Ho^{3+} ions in LaAlO_3 phosphor have been measured and are found to be 0.598, 0.671, 0.516, 0.453, 0.343, 0.801, 0.719, 0.771, respectively. It is observed that among the different transitions, the transition ${}^5\text{S}_2 \rightarrow {}^5\text{I}_8$ (0.801) has higher branching ratio; it can be concluded that this transition is useful for laser excitation.

3.3.2. Photoluminescence studies

The emission cross-section is a very important parameter for measuring laser materials. Good laser transitions are characterized by large cross-section for stimulated emission. The J-O theory can successfully account for the induced emission cross-section that is observed. The emission cross-section can be obtained from the spectroscopic data by two commonly applied methods, i.e., by the reciprocity method and by Fuchtbauer-Ladenberg (FL) formula. Using the FL formula, the emission cross-section can be expressed in the following form:

$$\sigma_{\text{emi}} = \frac{\lambda_0^4 A}{8\pi c n^2} \frac{I(\lambda_0)}{\int I(\lambda) d\lambda} \quad (4)$$

where A is the spontaneous radiation emission probability, λ_0 the peak wavelength and n the refractive index of the host material.

Both the excitation and emission spectra of the Ho^{3+} powder phosphor were recorded using a Hitachi F-4000 spectrofluorometer at room temperature (shown in Figs. 5a and b, respectively). With the line of excitation as shown in Fig. 5a, the emission spectrum of the powder phosphors were recorded in the wavelength range 500–700 nm ($\lambda_{\text{exc}} = 453$ nm). The typical profile of emission spectrum of $\text{LaAlO}_3:\text{Ho}^{3+}$ has been shown in Fig. 5b. In the emission spectrum, two emission bands are identified nearly at 543 nm (green) and 644 nm (red). These bands are assigned to the transitions as ${}^5\text{S}_2 \rightarrow {}^5\text{I}_8$ and ${}^5\text{F}_5 \rightarrow {}^5\text{I}_8$,

Table 2

Total radiative transition probabilities A_T (s^{-1}) and radiative lifetime τ_R (μs) of certain excited states of Ho^{3+} in LaAlO_3 phosphors

Energy level	A_T (s^{-1})	τ_R (μs)
${}^3\text{H}_6$	49,799	20.84
${}^5\text{G}_6$	68,825	14.53
${}^3\text{K}_8$	2371	421.76
${}^5\text{F}_2$	12,410	80.57
${}^5\text{F}_3$	15,816	63.23
${}^5\text{S}_2$	16,172	61.84
${}^5\text{F}_4$	16,572	60.34
${}^5\text{F}_5$	9146	109.34

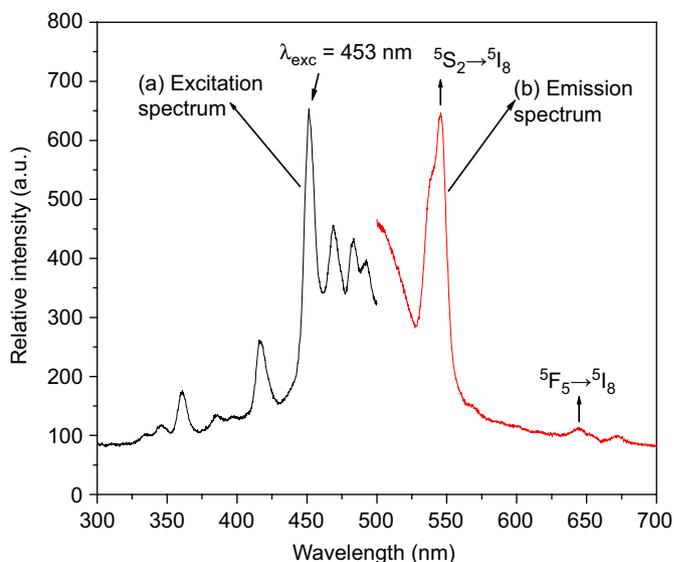


Fig. 5. (a) Excitation spectrum of $\text{LaAlO}_3:\text{Ho}^{3+}$ phosphor ($\lambda_{\text{emi}} = 543$ nm). (b) Emission spectrum of $\text{LaAlO}_3:\text{Ho}^{3+}$ phosphor ($\lambda_{\text{exc}} = 453$ nm).

respectively [15,23], where the ground state of Ho^{3+} is ${}^5\text{I}_8$. Using Eq. (4), the emission cross-section for both the emission transitions, ${}^5\text{S}_2 \rightarrow {}^5\text{I}_8$ and ${}^5\text{F}_5 \rightarrow {}^5\text{I}_8$, was calculated. The resulting values of emission cross-section are 4.093×10^{-20} and $3.493 \times 10^{-20} \text{ cm}^2$, respectively. It is observed that between the two transitions, the transition ${}^5\text{S}_2 \rightarrow {}^5\text{I}_8$ has high emission cross-section. On the basis of these studies it is concluded that the transition ${}^5\text{S}_2 \rightarrow {}^5\text{I}_8$ is more efficient for laser action.

4. Conclusions

Our work shows that the combustion synthesis technique is reliable and can be successfully used to produce Ho^{3+} -doped LaAlO_3 fine powder. The combustion process involves a self-propagating ignition route, low temperature, which is safe, fast and simple for the production of phosphor materials. Using J-O theory, spectral intensities of various observed peaks are calculated. J-O intensity parameters are estimated and from these, radiative transitions probabilities, radiative lifetimes and branching ratios of Ho^{3+} are calculated. From emission spectrum, peak stimulated emission cross-sections are reported for the two transitions ${}^5\text{S}_2 \rightarrow {}^5\text{I}_8$ and ${}^5\text{F}_5 \rightarrow {}^5\text{I}_8$.

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