

## Research Article

# Simulation and Optical Absorption Analysis of Cr<sup>3+</sup> doped Single Crystals of Potassium Magnesium Sulfate Chloride (Kainite)

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**Abstract**— The zero field and crystal field splitting parameters for single crystals of Potassium Magnesium Sulphate Chloride (Kainite), KMgCST (KMgClSO<sub>4</sub>·3H<sub>2</sub>O) doped with Cr<sup>3+</sup> ions are ascertained utilizing superposition model. For computation, the proper positions of the Cr<sup>3+</sup> ions in the distorted KMgCST are considered. The zero field splitting parameters that are computed using local distortion closely match the values observed in experiments. The optical energy values for Cr<sup>3+</sup> in KMgCST are estimated using the Crystal Field Analysis Program and crystal field parameters. The results show that a Cr<sup>3+</sup> ion replaces one Mg<sup>2+</sup> ion in KMgCST single crystals.

**Keywords**— Cr<sup>3+</sup> ions in KMgCST; Crystal field; Optical spectroscopy; Superposition model; Zero-field splitting; EPR.

## 1. Introduction

The local symmetry of transition ions in crystals is investigated using the electron paramagnetic resonance (EPR) technique. The EPR of Cr<sup>3+</sup> ion intoxicated into different crystals yields rich information about the parameters for zero field splitting (ZFS) and crystal fields (CF) [1-5]. When monovalent ions are substituted with divalent or trivalent impurities, it is crucial to compensate for the charge imbalance. Positive ion vacancies provide the charge compensation in systems where monovalent ions are replaced by divalent or trivalent impurities [6, 7]. The crystal's optical characteristics are influenced by doped impurities that result in slight structural changes. Superposition Model (SPM) is primarily used to determine ZFS and CF parameters theoretically [8–10].

Kainite, a mineral, having chemical formula KMgClSO<sub>4</sub>·3H<sub>2</sub>O is widely used in fertilizer industry [11]. It also falls under the category of mineral salts, which include antigorite and zeolites [12, 13], and are employed as catalysts in a variety of chemical processes.

EPR investigation for Cr<sup>3+</sup> ions in KMgCST was carried out and spin Hamiltonian parameters estimated [14]. Mg<sup>2+</sup> ions have an ionic radius of 0.072 nm, marginally greater than Cr<sup>3+</sup> ions (0.0615 nm). As a result, as mentioned in [14], Cr<sup>3+</sup> ions take the place of Mg<sup>2+</sup> ions.

The altered crystallographic axes (a, b, and c\*) and the laboratory axes (x, y, and z) are selected in parallel. The symmetry adopted axes (magnetic axes) are represented by (X, Y, Z). The crystallographic a axis is found to correspond with the g and D tensors of Cr<sup>3+</sup> ions' principal Z axis. This investigation presents the CF and ZFS parameters for Cr<sup>3+</sup> ions in KMgCST single crystal as analyzed by the superposition model (SPM). The objective is to examine the ZFS parameters, CF parameters, and lattice distortion for the Cr<sup>3+</sup> ions in KMgCST at octahedral sites. The Crystal Field Analysis (CFA) computer program and CF parameters are used to estimate the optical energy values for Cr<sup>3+</sup> ions in KMgCST. In subsequent research, CF and ZFS parameters assessed could be helpful in locating crystals for a variety of academic and commercial uses.

The purpose of the study and its subject introduction were covered in this section. The following is the arrangement of the paper's remaining sections. The related work for the SPM analysis is given in Section 2. The techniques for determining the ZFS and CF parameters are explained in Section 3. The procedure is given in Section 4. Section 5 presents the results and discussion. The study's conclusion and future scope are covered in section 6.

## 2. Related Work

As mentioned in [1-10], the SPM analysis was performed for a number of ion-host systems. Z = 16 and space group C2/m,

kainite (KMgClSO<sub>4</sub>·3H<sub>2</sub>O, KMgCST) crystallizes in a monoclinic system. β = 94° 55', a = 19.72 Å, b = 16.23 Å, c = 9.53 Å are the cell parameters [15]. Four chains make up a lattice along the Mg (H<sub>2</sub>O)<sub>2</sub>–(SO<sub>4</sub>)<sub>2</sub>–(H<sub>2</sub>O)<sub>2</sub>–Mg (H<sub>2</sub>O)<sub>2</sub>–(SO<sub>4</sub>)<sub>2</sub>— b-axis, the mirror plane contains the SO<sub>4</sub> tetrahedra. The chains are dispersed throughout the cell's (0 1 0) cross-section. The chains are held vertically together by K<sup>+</sup> and Cl<sup>-</sup> ions. The asymmetric portion of the unit cell contains two magnesium atoms. Fig. 1 shows the KMgCST crystal structure and the symmetry adopted axis system (SAAS).

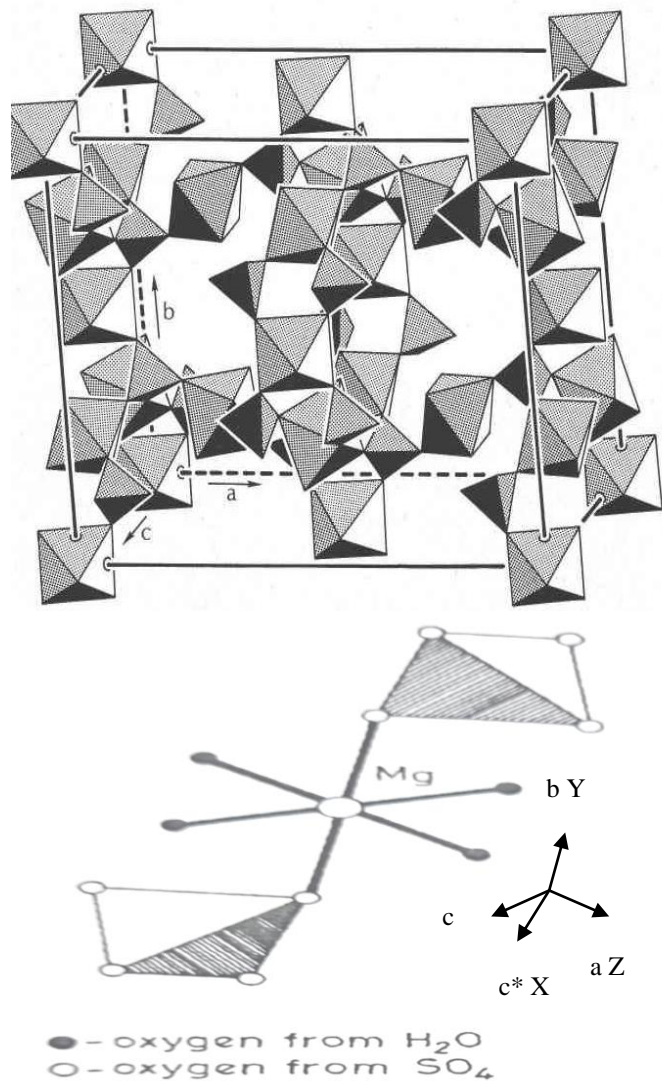


Fig.1. Symmetry adopted axis system (SAAS) and crystal structure of KMgCST.

The symmetry adopted axes (SAA) or local site symmetry axes are the directions of mutually perpendicular metal-ligand bonds. The Z axis of SAAS is the metal-ligand bond Mg-O (crystal a-axis), and for center I, the other two axes (X, Y) are perpendicular to it (Fig. 1). This suggests that in the KMgCST crystal, Cr<sup>3+</sup> takes the place of Mg<sup>2+</sup> with symmetry roughly orthorhombic. The ionic radius of Mg<sup>2+</sup> ions is 0.072 nm, while that of Cr<sup>3+</sup> ions is 0.0615 nm, suggesting that Mg<sup>2+</sup> ions' positions can be slightly distorted by Cr<sup>3+</sup> ions.

### 3. Theory/Calculation

In crystals, the energy states of Cr<sup>3+</sup> ions are determined utilizing the spin Hamiltonian [16, 17, 18]:

$$\mathcal{H}_{ZFS} = \mu_B B \cdot g \cdot S + \sum B_k^q O_k^q = \mu_B B \cdot g \cdot S + \sum f_k b_k^q O_k^q, \quad (1)$$

where spectroscopic splitting factor, Bohr magneton and steady magnetic field are represented by g, μ<sub>B</sub> and B, respectively. O<sub>k</sub><sup>q</sup>(S<sub>x</sub>, S<sub>y</sub>, S<sub>z</sub>) represent the extended Stevens operators (ESO) and S stands for the effective spin operator [19, 20]; the ZFS parameters, f<sub>k</sub> = 1/3 and 1/60 the scaling factors for k = 2 and 4, respectively are given by B<sub>k</sub><sup>q</sup> and b<sub>k</sub><sup>q</sup>. For orthorhombic symmetry of the Cr<sup>3+</sup> ion (S = 3/2), the estimated ZFS terms in (1) are as given below [21, 22]:

$$\begin{aligned} \mathcal{H}_{ZFS} &= B_2^0 O_2^0 + B_2^2 O_2^2 = \frac{1}{3} b_2^0 O_2^0 + \frac{1}{3} b_2^2 O_2^2 \\ &= D(S_z^2 - \frac{1}{3} S(S+1)) + E(S_x^2 - S_y^2), \end{aligned} \quad (2)$$

B<sub>k</sub><sup>q</sup>, b<sub>k</sub><sup>q</sup> and the traditional ZFS parameters D, E have relations as:

$$b_2^0 = D = 3 B_2^0, \quad b_2^2 = 3E = 3 B_2^2. \quad (3)$$

Using SPM [21-22], in ESO notation, the ZFS parameters in any symmetry are found as:

$$b_k^q = \sum_i \bar{b}_k(R_0) \left( \frac{R_0}{R_i} \right)^{t_k} K_k^q(\theta_i, \varphi_i), \quad (4)$$

where the spherical polar coordinates of i-th ligand are represented by (R<sub>i</sub>, θ<sub>i</sub>, φ<sub>i</sub>). The k-th rank ZFS contribution from a ligand at the distance R<sub>i</sub> is given by the intrinsic parameters  $\bar{b}_k$  and the geometrical information is provided by the coordination factors K<sub>k</sub><sup>q</sup>. In ESO notation [23] K<sub>k</sub><sup>q</sup> r k = 1 to 6 are presented in [24] (Appendix A1).

Eq. (4) yields traditional ZFS parameters, D and E, in terms of the intrinsic parameters  $\bar{b}_k$ , the power-law exponents t<sub>k</sub> and the reference distance R<sub>0</sub>, as given below [24, 25-27]:

$$b_2^0 = D = \frac{\bar{b}_2(R_0)}{2} \left[ \left( \frac{R_0}{R_i} \right)^{t_2} \sum_i (3 \cos^2 \theta_i - 1) \right] \quad (5)$$

$$b_2^2 = 3E$$

$$= \frac{b_2^2}{3} = \frac{\bar{b}_2(R_0)}{2} \left[ \left( \frac{R_0}{R_i} \right)^{t_2} \sum_i \sin^2 \theta_i \cos 2\phi_i \right]$$

### 4. Experimental Method/Procedure/Design

Table 1 presents the Cr<sup>3+</sup> ion position and ligands' spherical polar coordinates for center I in KMgCST [15]. These specifics are employed for Cr<sup>3+</sup> ions in KMgCST ZFS and CF computations.

Table 1. The Cr<sup>3+</sup> ion's fractional coordinates and ligands' (center I) spherical polar co-ordinates (R, θ, φ) in a single KMgCST crystal.

| Cr <sup>3+</sup> Position                                 | Ligands | Spherical polar co-ordinates of ligands |       |        |
|---|---------|---|-------|--------|
|   |         | RÅ                                      | θ°    | φ°     |
| ND: Substitutional<br>(0.0000, 0.0000, 0.0000)            | O1      | 9.4911                                  | 23.23 | 20.40  |
|   | O2      | 5.9749                                  | 48.65 | 72.31  |
|   | Ow1     | 2.1728                                  | 15.50 | 1.18   |
|   | Ow2     | 10.6079                                 | 49.75 | 87.31  |
|   | Ow3     | 7.7182                                  | 9.74  | 33.67  |
| WD: substitutional Centre I<br>(0.2185, 0.1264, -0.00182) | O1      | 9.5972                                  | 24.41 | -30.43 |
|   | O2      | 5.6194                                  | 45.13 | -38.53 |
|   | Ow1     | 4.7197                                  | 63.43 | 30.02  |
|   | Ow2     | 10.1996                                 | 47.64 | -57.06 |
|   | Ow3     | 6.2761                                  | 7.57  | -82.22 |
|   | Ow4     | 5.6195                                  | 75.40 | -44.80 |

WD = With distortion, ND = No distortion.

Cr<sup>3+</sup> ion in KMgCST is expected to be substituted at both the interstitial site and the Mg<sup>2+</sup> ion site having comparable ligands environment. The Cr<sup>3+</sup> ion has orthorhombic local symmetry. Using t<sub>2</sub> = -0.12,  $\bar{b}_2(R_0) = 2.34 \text{ cm}^{-1}$  [28] and Cr<sup>3+</sup> ion octahedral coordination with Cr<sup>3+</sup>-O<sup>2-</sup> bond in LiNbO<sub>3</sub>, b<sub>2</sub><sup>0</sup> and b<sub>2</sub><sup>2</sup> were determined. The current study uses t<sub>2</sub> = -0.96 and  $\bar{b}_2(R_0) = 2.34 \text{ cm}^{-1}$  for center I to estimate the b<sub>K</sub><sup>q</sup> because with oxygen acting as a ligand, the Cr<sup>3+</sup> ion in KMgCST exhibits distorted octahedral coordination (Fig. 1). Equation (5) is used to obtain the ZFS parameters.

### 5. Results and Discussion

Equation (5) yields the traditional parameters of ZFS, D and E for the Cr<sup>3+</sup> ion in KMgCST single crystal. The reference distance R<sub>0</sub> = 0.200 nm is used [29] to get the parameters of ZFS, |D| = 930.9 × 10<sup>-4</sup> cm<sup>-1</sup> and |E| = 797.3 × 10<sup>-4</sup> cm<sup>-1</sup> for center I. For symmetry that is orthorhombic, b<sub>2</sub><sup>2</sup> / b<sub>2</sub><sup>0</sup> should be in the range 0 and 1 [30]. In the current computation, |b<sub>2</sub><sup>2</sup> / b<sub>2</sub><sup>0</sup>| = 2.569 and |E| / |D| = 0.856 for center I. It is found that the computed values of |D| and |E| do

not agree with the experimental ones and |b<sub>2</sub><sup>2</sup> / b<sub>2</sub><sup>0</sup>| also does not fall in the given range [30]. Therefore, with above t<sub>2</sub> and reference distance R<sub>0</sub>, the ZFS parameters |D| and |E| are computed for Cr<sup>3+</sup> at the Mg<sup>2+</sup> site with distortion having position Mg<sup>2+</sup> (0.2185, 0.1264, -0.00182) for center I. The local surrounding about Cr<sup>3+</sup> ion is shown in Fig. 2. The traditional ZFS parameters established now are |D| = 975.5 × 10<sup>-4</sup> cm<sup>-1</sup>, |E| = 57.2 × 10<sup>-4</sup> cm<sup>-1</sup> for center I, which match fairly well with the values of the experiment. The ratio |b<sub>2</sub><sup>2</sup> / b<sub>2</sub><sup>0</sup>| = 0.176 and |E| / |D| = 0.058 for center I lie in the specified range [31]. Further, with above t<sub>2</sub> and reference distance R<sub>0</sub>, the ZFS parameters |D| and |E| are computed for Cr<sup>3+</sup> ion at the interstitial site but the values established differ much from the experimental ones. Due to this reason, these results are not presented here.

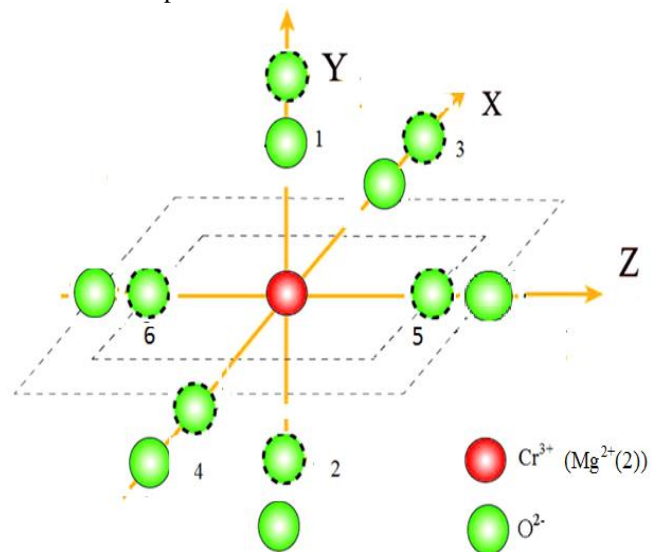


Fig. 2. Graphical depiction of local surrounding of Cr<sup>3+</sup> ion (after distortion positions shown by dotted circles).

Table 2 displays the Cr<sup>3+</sup> ion's ZFS parameters in KMgCST, both calculated and experimental. It is noted that the ZFS parameters |D| and |E| are in good agreement with the values obtained from the experiment [14] when the distortion is incorporated into calculation.

Table 2. ZFS parameters of Cr<sup>3+</sup> in a single crystal of KMgCST for center I, along with reference distance, calculated and experimental.

| ZFS (10 <sup>-4</sup> cm <sup>-1</sup> ) | Calculated parameters of ZFS (cm <sup>-1</sup> ) |   |                             | Traditional parameters of |
|--|--|---|-----------------------------|---------------------------|
|  | R <sub>0</sub> <sup>Å</sup>                      | b <sub>2</sub> <sup>0</sup>                               | b <sub>2</sub> <sup>2</sup> |                           |
| Site                                     |  |   |                             | D                         |
|  |  | b <sub>2</sub> <sup>2</sup> / b <sub>2</sub> <sup>0</sup> |                             | E                         |
| ND                                       | 2.00   | 0.09309   | 0.23919                     | 930.9                     |
|  | 797.3  | 0.856   |                             |                           |
| Center I                                 |  |   |                             |                           |
| WD                                       | 2.00   | 0.09755   | 0.01717                     | 975.5                     |
|  | 57.2   | 0.058   |                             |                           |
|  |  | 975.5°  | 57.1°                       | 0.058                     |

WD = With distortion, ND = No distortion, ° = experimental.

The transition metal ion CF energy states in crystals [31–34] may be found using Wybourne operators as given below [16, 35, 36]:

$$\mathcal{H}_{CF} = \sum_{kq} B_{kq} C_q^{(k)} \quad (6)$$

where CF Hamiltonian is given by  $\mathcal{H}_{CF}$ . SPM can be used to find the CF parameters in (6) for a metal-ligand complex [21–22] as:

$$B_{kq} = \sum_i \bar{A}_k \left( \frac{R_0}{R_i} \right)^{t_k} K_{kq}(\theta_i, \varphi_i). \quad (7)$$

$R_0$  gives the reference distance,  $R_i$ ,  $\theta_i$ ,  $\varphi_i$  denote the  $i^{\text{th}}$  ligand spherical polar coordinates and  $K_{kq}$  are the coordination factors [31].  $B_{kq}$  ( $k = 2, 4; q = 0, 2, 4$ ) [31] are obtained by

using the values of  $A_2 = 40, 400 \text{ cm}^{-1}$ ,  $t_2 = 1.3$ ,  $t_4 = 3.4$  and

$A_4 = 11, 700 \text{ cm}^{-1}$ . Table 3 lists the calculated  $B_{kq}$  parameters. For center I, the ratio  $|B_{22}|/|B_{20}| = 0.880$  suggests that the  $B_{kq}$  parameters that were evaluated are standardized [30]. The total Hamiltonian is diagonalized to determine the  $\text{Cr}^{3+}$  ion's CF energy levels in KMgCST single crystals using the  $B_{kq}$  parameters found in Table 3 and the CFA computer program [32, 33]. The calculated energy values are shown in Table 4. The calculated and experimental energy values for  $\text{Cr}^{3+}$ : KZnCST with oxygen ligands are contrasted [11] as no optical absorption study of  $\text{Cr}^{3+}$ : KMgCST is reported. The theoretical and experimental energy values appear in reasonable agreement based on Table 4. Therefore, theoretical examination of  $\text{Cr}^{3+}$  ions at  $\text{Mg}^{2+}$  sites in KMgCST validates the findings of the experiment [11, 14].

Table 3. The parameters  $B_{kq}$  of  $\text{Cr}^{3+}$  for center I with distortion in a single crystal of KMgCST.

| Site     | $R_0^A$ | $B_{kq} (\text{cm}^{-1})$ Parameters Computed |          |          |          |          |                     |
|----------|---------|---|----------|----------|----------|----------|---------------------|
|          |         | $B_{20}$                                      | $B_{22}$ | $B_{40}$ | $B_{42}$ | $B_{44}$ | $ B_{22} / B_{20} $ |
| Center I | WD 2.00 | 5724.185                                      | 5041.045 | 780.666  | 155.454  | -1104.54 | 0.880               |

WD = With distortion

The configurational-coordinate (CC) model, along with Franck-Condon analysis, now provides an explanation for the phosphors activated by  $\text{Cr}^{3+}$  and their optical absorption spectra [37]. In  $\text{Cr}^{3+}$ , the different transitions between excited states and ground states are a consequence of the lattice vibrations' strong coupling (CC model) [37]. The CC model is not being used here and so there is difference between excited-state peak energies found here and energies of the zero-phonon line (ZPL) discussed in [37, 38]. Two groups of oxide-phosphors doped with  $\text{Cr}^{3+}$  are taken up: (i) O-Cr-A type, (ii) O-Cr-B type. The luminescence properties of type (i) phosphors are found from the luminescence transitions linked with  ${}^2E_g$  as the strength of their crystal fields falls in the region of  $Dq/B > 2.1$  while type (ii) phosphors have a crystal-field strength lying within the range of  $Dq/B < 2.1$ , as a result, the optical transitions related with  ${}^4T_{2g}$  are utilized to

obtain their luminescence properties. KMgCST:  $\text{Cr}^{3+}$  falls under (i) type phosphors ( $Dq/B = 2.38$  which is  $> 2.1$ ) [38].

## 6. Conclusion and Future Scope

For  $\text{Cr}^{3+}$  ions in KMgCST single crystals, to calculate the zero-field splitting (ZFS) and crystal field (CF) parameters, the superposition model (SPM) is utilized. Calculations are performed using  $\text{Cr}^{3+}$  ions at interstitial site,  $\text{Mg}^{2+}$  ion sites, and distortion models in KMgCST crystal. When distortion is taken into account in the calculation, the experimental values and the calculated traditional ZFS values for the  $\text{Cr}^{3+}$  ion at  $\text{Mg}^{2+}$  sites in the KMgCST single crystal are reasonably in agreement. In the KMgCST lattice, it is established that the  $\text{Cr}^{3+}$  ions will replace  $\text{Mg}^{2+}$  ion sites. The CF energy values for  $\text{Cr}^{3+}$  ions at  $\text{Mg}^{2+}$  sites calculated with the CFA package and CF parameters show a good degree of agreement with the experimental values. Therefore, the experimental analysis is validated by the theoretical results.

Table 4. Energy values obtained by computation and experimentation (center I) of  $\text{Cr}^{3+}$  in KMgCST single crystal.

| Transition from ${}^4A_{2g}(F)$ state | Observed band ( $\text{cm}^{-1}$ ) | Calculated band ( $\text{cm}^{-1}$ )     |
|---------------------------------------|------------------------------------|--|
|                                       |                                    | Center I                                 |
| ${}^2E_g(G)$                          | 11975                              | 11672, 11844                             |
| ${}^2T_{1g}(G)$                       |                                    | 12083, 12397, 13083                      |
| ${}^4T_{2g}(F)$                       | 17235                              | 15922, 16301, 16760, 16817, 17636, 18017 |
| ${}^4T_{1g}(F)$                       | 24385                              | 18085, 18778, 18832, 20976, 21182, 26544 |
| ${}^4T_{1g}(P)$                       |                                    | 26771, 26875, 27051, 27067, 28460, 28683 |
| ${}^2T_{1g}(aD)$                      |                                    | 37346, 39238, 40066                      |
| ${}^2E_g(bD)$                         |                                    | 44453, 44812                             |

(The values of Racah parameters A, B, and C, the spin-orbit coupling constant, and the Trees correction are 0, 724, 2484, 276 and  $70 \text{ cm}^{-1}$ , respectively)

Correlating optical and EPR data of many more ion-host systems in the future to obtain crystals for various scientific and industrial applications may be made easier with the modeling strategy taken into account in this investigation.

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## Declarations:

### Ethical Approval:

This study did not take place on any private or protected land, nor did it involve any research involving human or animal subjects. Corresponding locations did not require any special permissions.

**Competing interests:**

The authors affirm that no known conflicting financial interests or personal relationships could have influenced any of the work described in this paper.

**Authors' contributions:**

Vikram Singh and Maroj Bharati - completed the figure preparation, wrote the manuscript, and did calculations.  
Ram Kripal- concept and oversight.  
The manuscript has been reviewed by all authors.

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The data will be provided upon request.

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