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Structural, Optical Absorption and Low-Temperature Magnetocaloric Characterization of Sol–Gel Synthesized $\text{NaHo}(\text{WO}_4)_2$ Ceramics

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Abstract

$\text{NaHo}(\text{WO}_4)_2$ (NHoW) ceramic powder was synthesised via the sol-gel route to investigate its magnetocaloric properties at low temperatures. Preliminary investigations such as powder XRD, FE-SEM analysis, FTIR, Raman and UV-Vis absorption studies have been performed over the synthesised ceramics powder to ascertain its existence in the desired phase and texture. Photoluminescence measurements were also performed on the title compound to elucidate its excitation and emission characteristics in the UV-Vis range only. Magnetization measurements revealed the sample's antiferromagnetic character well below 5K. A reasonable and maximum change in magnetic entropy (ΔS_M) at 9K could be noticed for an applied magnetic field of 100 kOe, and this observation suggests that the compound signifies magnetocaloric assistance for freon-free refrigeration applications.

Keywords: Sol–gel synthesis, XRD, Raman Spectroscopy, Magnetic properties, Cryogenics, Luminescence, Magnetocaloric effect

1. Introduction

Magnetocaloric (MC) cooling technology has attracted notable attention as an alternative to conventional gas-compression refrigeration, offering higher energy efficiency, reduced power consumption, and environmentally friendly operation [1-4]. The magnetocaloric effect (MCE) is a fundamental magneto-thermodynamic phenomenon that originates from the interaction between an externally applied magnetic field and the magnetic moments or spin sublattices present in a material. When the magnetic field is applied or removed, the system's magnetic entropy changes drastically, enabling reversible heating and cooling. With these distinct properties, magnetic refrigeration (MR) plays a vital role in next-generation cooling technology. In addition, MR applications span a wide temperature range, including ambient, high-temperature, and cryogenic refrigeration systems. In particular, cryogenic magnetic refrigeration for liquefying hydrogen, helium, and other technologically important gases contributes to the development of energy-efficient and sustainable cooling systems [5, 6].

In the last three decades, researchers have made steady efforts to develop and engineer efficient magnetocaloric materials [7]. Researchers have tested such systems on a wide range of compounds, including intermetallic alloys, amorphous systems, oxides, composites, and hybrid materials. Researchers have synthesised and systematically investigated them for their magnetic and magnetocaloric properties [8-12]. Among them, rare-earth-based oxides are of considerable interest because of their large magnetic moments, strong spin–lattice coupling, excellent thermal and chemical stability, and tunable magnetic exchange interactions. In particular, the alkaline rare-earth double tungstates with the general chemical formula $\text{ARE}(\text{WO}_4)_2$ (A = alkali metal ion and RE = Rare-earth ion) have appeared as an important class of multifunctional materials [13-19]. They exhibit high chemical stability and crystallise predominantly in the tetragonal scheelite-type structure, making them suitable for diverse applications such as laser host materials, luminescent phosphors, optical devices, solid-state lighting, catalysis, and magnetic refrigerants [20-22].

Significant focus has been given by researchers to the investigation of the cryogenic magnetic properties of double tungstates belonging to the $\text{LiRE}(\text{WO}_4)_2$, $\text{NaRE}(\text{WO}_4)_2$, $\text{KRE}(\text{WO}_4)_2$, $\text{RbRE}(\text{WO}_4)_2$ and $\text{CsRE}(\text{WO}_4)_2$ families, where RE represents Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Tm^{3+} , Er^{3+} and Yb^{3+} ions [22-25]. Although several studies have reported the structural and optical properties of these materials, few studies address their magnetocaloric performance in the

cryogenic temperature regime [26-29]. Recent studies have confirmed that rare-earth double tungstates can show considerable magnetic entropy changes under moderate magnetic fields (5-7T), making them among the contenders for low-temperature magnetic refrigeration applications. Related systems have shown large cryogenic magnetocaloric effects, with entropy change values of approximately 10.3 and 24.8 J kg⁻¹ K⁻¹ under applied magnetic fields up to 5 T [25].

Among rare-earth ions, Gd³⁺-based compounds frequently possess superior magnetocaloric performance because of the half-filled 4f electronic configuration of Gd³⁺ ions, which results in a large spin-only magnetic moment, negligible orbital contribution and minimal magnetic property anisotropy [30]. Ho³⁺ ions can be advantageous for cryogenic magnetocaloric applications because of their large magnetic moments and strong response to external magnetic fields [31, 32]. These considerations demonstrate the need for systematic investigations of structure–property relationships in rare-earth double tungstates, more specifically the connections between crystal structure, magnetic exchange interactions and magnetocaloric-type behaviour, to facilitate the development of efficient low-temperature magnetic refrigerants [33, 34]. Although the physical properties of double tungstates have attracted significant research interest, their magnetocaloric behaviour has received comparatively less attention. P. Sravandas *et al.* [35] reported on the magnetocaloric behaviour of KTm(WO₄)₂ single crystals measured along the magnetic easy axis, revealing the appreciable magnetic entropy changes in the low-temperature region. Despite these advances, systematic investigations linking the structural, vibrational, optical, magnetic and magnetocaloric characteristics of sodium-based rare-earth double tungstates remain unstudied.

Therefore, this work aims to study the structural, morphological, vibrational, optical, magnetic, and cryogenic magnetocaloric characteristics of NHoW ceramics synthesised via the sol–gel method. The prepared samples were systematically characterised using several experimental techniques, including structural, vibrational, morphological, optical, and magnetic analyses. We also studied the low-temperature magnetic behaviour and magnetocaloric performance of the synthesised compound.

2. Experimental Procedure

All chemicals were purchased from Sigma-Aldrich (3N). Sodium nitrate (NaNO_3), Holmium oxide (Ho_2O_3) and ammonium paratungstate ($(\text{NH}_4)_6\text{W}_7\text{O}_{24}\cdot 6\text{H}_2\text{O}$, APT) were used as the starting precursors for the synthesis of NHoW. Citric acid and ethylene glycol served as the fuel and polymerising/binding agent, respectively. NHoW ceramics were synthesised via the sol–gel combustion method [35, 36]. Initially, a stoichiometric amount of Ho_2O_3 was dissolved in hot dilute nitric acid to prepare the corresponding Holmium nitrate solution. Subsequently, a separately prepared sodium nitrate solution was added to the holmium nitrate solution under continuous stirring. Stoichiometric amounts of APT were accurately weighed and dissolved in deionised water. An appropriate amount of citric acid was then added to the mixed metal-ion solution to facilitate the formation of metal–citrate complexes. The precursor solutions were mixed gradually under continuous magnetic stirring, and the resulting solution was adjusted to pH 6.5 with aqueous ammonia. Subsequently, an appropriate amount of ethylene glycol was added as a polymerising agent. The mixture was then heated at 80 °C for 5 h under constant stirring to facilitate gelation and evaporate excess solvent. The prepared gel was dried at 120 °C for 2 h to remove residual moisture and form a rigid xerogel. Further thermal treatment at 250 °C for 30 minutes initiated an auto-combustion reaction, yielding a porous black powder. Finally, the obtained powder was calcined at 800 °C for 4 hours to achieve a well-crystallised NHoW ceramic powder.

Phase identification was performed using a PANalytical X'Pert PRO X-ray diffractometer (XRD). Fourier transform infrared (FT-IR) spectra were recorded with a Jasco 6300 spectrometer to identify characteristic functional groups and bonding features. Raman spectra were obtained using a Jobin Yvon HR800 spectrometer with an excitation wavelength of 630 nm to examine the lattice vibration scattering modes. We observed the surface morphology using a ZEISS SUPRA™ 40 field emission scanning electron microscope (FE-SEM). We analysed optical properties by diffuse reflectance UV–visible spectroscopy (Shimadzu UV-2101PC). At the same time, photoluminescence (PL) excitation and emission spectra were also recorded using a JASCO FP-6300 spectrofluorometer equipped with a 150 W xenon lamp. Magnetic measurements were carried out in the temperature range 2–300 K using a vibrating sample magnetometer (VSM).

3. Results and Discussion

3.1.1. Structural Analysis of NHoW Ceramics

Fig. 1 (a) presents the room-temperature X-ray diffraction (XRD) pattern of $\text{NaHo}(\text{WO}_4)_2$ (NHoW) ceramics. The diffraction profile shows sharp, intense reflections across the entire measured 2θ range, indicating high crystallinity and phase homogeneity in the synthesised sample. All diffraction peaks were successfully indexed to a tetragonal scheelite-type crystal structure with the space group $I4_1/a$ (JCPDS No. 25-829), confirming the successful formation of single-phase NHoW ceramics without any detectable impurities or secondary phases. The diffraction peaks shift slightly toward higher 2θ values relative to the standard reference pattern. This difference is due to the incorporation of smaller Ho^{3+} ions (ionic radius $\approx 0.901 \text{ \AA}$) into the crystal lattice. The relatively smaller ionic size of Ho^{3+} compared to Gd^{3+} ions ($\approx 0.938 \text{ \AA}$) induces lattice contraction, resulting in compressive strain within the scheelite framework [37], and this leads to the displacement of diffraction peaks toward higher angles, corresponding to a decrease in interplanar spacing as well as in lattice parameters. The inset of Fig. 1(a) clearly projects the systematic peak shift, showing the lattice contraction arising from the substitution effect of Ho^{3+} ions.

Powder X-ray diffraction (PXRD) pattern of the synthesised $\text{NaHo}(\text{WO}_4)_2$ (NHoW) ceramic was analysed using the MAUD refinement program to determine its crystallographic and structural characteristics[38, 39]. The refinement used the tetragonal scheelite structure with space group $I4_1/a$, which is commonly observed in rare-earth double tungstate materials (fitted image shown in Fig. S1). The experimental and calculated diffraction patterns matched closely across the entire 2θ range recorded in this study, demonstrating the suitability of the adopted structural model. The excellent fit from the Rietveld refinement confirms the formation of single-phase, well-crystallised NHoW ceramics and verifies the accuracy of the refined structural parameters summarised in Table 1.

Refinement also yielded low residual factors and satisfactory goodness-of-fit values ($R_{\text{wp}} = 6.305\%$, $R_p = 4.396\%$, $R_b = 3.22\%$ and $\chi^2 = 1.645$), showing a reliable structural fitting. The excellent agreement between the measured and calculated diffraction patterns additionally confirms that the proposed structural model accurately describes the crystal structure of NHoW[40]. The diffraction pattern showed no evidence of secondary crystalline phases or impurity-related reflections, suggesting that the synthesised sample is highly phase-homogeneous within the measurement sensitivity. The lattice parameters calculated from the refinement closely

match those reported for sodium rare-earth double tungstates [39], suggesting that the incorporation of Ho^{3+} ions does not induce any considerable structural distortion of the scheelite framework. The diffraction peaks are sharp, well resolved, and nearly symmetric, indicating high crystallinity and structural homogeneity in the synthesised material. The refined diffraction pattern showed no signs of peak splitting, anomalous peak shifts, or secondary phases. No evidence of structural distortion or phase segregation was detected, indicating that the tetragonal scheelite structure remains intact after synthesis. The results confirm the formation of a single-phase NHoW sample with good crystallinity.

3.1.2. Crystallite Size and Microstrain

Crystallite size and crystalline strain of the synthesised NHoW powders were determined from the broadening of the X-ray diffraction peaks using the Williamson–Hall (W–H) method. This procedure allows independent evaluation of the contributions of crystallite size and crystal strain to peak broadening. The W–H relation can be written as[41]:

$$\beta \cos \theta = \frac{K\lambda}{D} + 4\varepsilon \sin \theta$$

where ' D ' denotes the average crystallite size, ' ε ' represents the crystalline strain, λ is the wavelength of Cu $K\alpha$ radiation (1.5406 Å), ' β ' corresponds to the full width at half maximum (FWHM) of the diffraction peaks, and K is the shape factor taken as 0.89.

We used a linear fit to the plot of $\beta \cos \theta$ vs $4 \sin \theta$ to determine the microstructural parameters. Fig. 1(b) shows the linear fit plots of NHoW. The intercept of the fitted line was used to estimate the crystallite size, whereas the slope was used to estimate the crystal strain. The calculated crystallite size was found to lie between 50-60 nm, suggesting the formation of fine nanocrystalline particles. The contribution from size-induced broadening becomes relatively small and may be attributed to the instrumental broadening, possibly causing uncertainty in the calculated values.

The presence of crystal lattice strain indicates local distortions inside the crystalline lattice arising from defects, dislocations, and residual stresses generated during the combustion-assisted sol–gel synthesis process. Such microstructural imperfections can modify the local crystal-field environment and influence magnetic exchange interactions among the Ho^{3+} ions. Consequently,

these structural features are likely to play a major role in determining the low-temperature magnetic and magnetocaloric behaviours of NHoW, particularly under externally applied magnetic fields.

3.2. Morphological and Compositional Analysis of NHoW Ceramics

Morphology of the synthesised $\text{NaHo}(\text{WO}_4)_2$ (NHoW) powder was examined using field-emission scanning electron microscopy (FE-SEM), and the representative micrograph is shown in Fig. 2(a). The microstructure is composed of closely packed grains with irregular polyhedral shapes and slight agglomeration. Clear grain boundaries and relatively smooth grain surfaces are visible, indicating sufficient crystallisation and grain development during calcination. The particles are fairly distributed homogeneously across the observed region and are predominantly in the submicron size range. No obvious pores, secondary phases, or isolated regions were detected, indicating a homogeneous microstructure consistent with the phase-pure nature established by X-ray diffraction analysis. The agglomerated appearance of some particles may result from particle coalescence during high-temperature treatment, a phenomenon frequently observed in oxide materials prepared by the sol–gel route.

The particle size distribution was further evaluated from measurements of a large number of grains, and the resulting histogram is shown in Fig. 2(b). The distribution displays a near-normal profile with an average particle size of approximately 0.55–0.60 μm . The relatively narrow size variation indicates that grain growth proceeded in a controlled manner during synthesis. Moreover, the absence of multiple distribution peaks suggests homogeneous particle formation throughout the sample. Particle sizes determined from FE-SEM are considerably larger than the crystallite size obtained from Williamson–Hall analysis (90–200 nm), implying that each particle consists of several smaller crystallites. This difference confirms that the synthesised powder consists of polycrystalline aggregates rather than individual single-crystal grains [42].

We investigated the elemental composition of NHoW by energy-dispersive X-ray spectroscopy (EDS) and elemental mapping, as shown in Fig. S2. The results confirmed the presence of Na, Ho, W, and O as the compound's constituent elements. Elemental mapping demonstrates a uniform distribution of all elements across the analysed area, with no indication of compositional inhomogeneity or elemental segregation. In addition, the EDS spectrum showed no

extraneous impurity peaks, further supporting the high purity of the synthesised material and consistent with the XRD findings.

3.3. Vibrational and Structural Studies on NHoW Ceramics (FT-IR and Raman Analysis)

FT-IR spectrum of calcined $\text{NaHo}(\text{WO}_4)_2$ (NHoW) powder is shown in Fig. 3(a). Absorption bands appearing in the spectral range $400\text{--}1000\text{ cm}^{-1}$ are associated with the intrinsic vibrational modes of isolated $[\text{WO}_4]^{2-}$ tetrahedral groups exhibiting S_4 site symmetry in the tetragonal scheelite structure. Characteristic absorption peaks centred at 932, 847, 797, and 721 cm^{-1} originate from the stretching vibrations of the WO_4 tetrahedra. These bands are assigned to the asymmetric (ν_3) and symmetric (ν_1) stretching modes of the W–O bonds, demonstrating the presence of well-formed tungstate tetrahedral units within the crystalline lattice[35]. The band centred at 449 cm^{-1} is assigned to the bending vibration (ν_4 mode) of the tetrahedral unit. Absence of additional bands related to W–O–W bridging or secondary tungsten oxide phases confirms the presence of isolated WO_4 tetrahedra rather than distorted octahedral units. Vibrational features below 400 cm^{-1} are associated with the lattice modes, including the translational motions of Na^+ and Ho^{3+} cations within the structural framework[35, 36].

Raman spectrum of the NHoW sample, as shown in Fig. 3(b), exhibits eight well-defined vibrational bands in the range $100\text{--}1000\text{ cm}^{-1}$, consistent with the factor-group analysis of scheelite-type compounds crystallising in the space group $I4_1/a$. Raman spectrum of $\text{NaHo}(\text{WO}_4)_2$ is characterised by several well-defined vibrational bands arising from the WO_4 tetrahedral groups. The strong peaks observed at 918, 803 and 771 cm^{-1} are assigned to the symmetric (ν_1) and asymmetric (ν_3) stretching vibrations of the W–O bonds within the tetrahedra. Bands appearing at 403, 331 and 280 cm^{-1} are related to the bending vibrations (ν_2 and ν_4) of the WO_4 units. In the lower frequency region, the modes centred at 207, 146 and 112 cm^{-1} are attributed to the lattice vibrations involving the translational motion of Na^+ , Ho^{3+} and $(\text{WO}_4)^{2-}$ species [43]. The observation of these external modes, which are governed by the masses of the constituent ions and the crystal lattice motions, is consistent with the formation of a well-ordered scheelite-type structure[35].

3.4. Optical absorption/Emission Properties of NHoW Ceramics

UV–Vis diffuse reflectance spectrum of NaHo(WO₄)₂ (NHoW) is presented in Fig. 4(a). A strong absorption band is observed in the ultraviolet region between 230 and 300 nm. This absorption is ascribed to a charge-transfer transition within the (WO₄)²⁻ groups, in which electrons are excited from O 2p orbitals to the vacant W 5d states [39]. Similar absorption bands have been reported for other scheelite-type tungstates and are characteristic of the tungstate framework. The broad and intense nature of this band suggests the presence of well-formed (WO₄)²⁻ tetrahedral units in the crystal structure.

In addition to the host-lattice absorption, several weak absorption bands are observed at wavelengths above 320 nm. These bands are attributed to the 4f–4f transitions of Ho³⁺ ions. The transitions are forbidden in free ions but become weakly allowed in solids because of the crystal-field interaction. In NaHo(WO₄)₂, Ho³⁺ ions occupy S₄ symmetry sites in the tetragonal scheelite structure (space group I4₁/a). The absence of inversion symmetry at these sites perturbs the electronic energy levels of Ho³⁺ and increases the intensity of electric-dipole transitions. As a result, weak Ho³⁺ absorption bands can be detected in the diffuse reflectance spectrum.

Fig. 4(b) shows the excitation profile monitored at 546 nm emission. A broad band centred at approximately 290 nm is assigned to the charge-transfer absorption of the (WO₄)²⁻ groups. This band reflects the host lattice's ability to absorb UV radiation and subsequently transfer excitation energy to Ho³⁺ ions. Several sharp excitation lines are also observed between 310 and 700 nm, corresponding to the intra-configurational 4f–4f transitions of Ho³⁺. These peaks are assigned to transitions from the Ho³⁺ ground state (⁵I₈) to the excited levels ⁵G₄, ⁵G₅, ³K₈ + ⁵G₆, ⁵F₃ and ⁵F₄[44, 45]. The narrow linewidths of these electronic transitions are characteristic of rare-earth ions and arise from the shielding of the 4f electrons by the filled 5s² and 5p⁶ outer shells, which minimises their interaction with the surrounding crystal lattice. Although the crystal field has only a limited influence on the positions of the 4f levels, it splits the degenerate multiple states. In the tetragonal scheelite structure, this crystal-field interaction leads to Stark splitting of the Ho³⁺ energy levels.

The emission spectrum displays (Fig. 4(b)) distinct bands at 489, 546 and 671 nm corresponding to the ⁵F₃ → ⁵I₈, (⁵F₄, ⁵S₂) → ⁵I₈ and ⁵F₅ → ⁵I₈ transitions, respectively[44, 45]. The clear resolution of these emission signals reflects the influence of the local S₄ symmetry surrounding the Ho³⁺ ions. Among the observed emissions, the green band at 546 nm is the most prominent, showing efficient radiative relaxation from the thermally coupled ⁵F₄ and ⁵S₂ excited

states. The strong luminescence response can be associated with the favourable crystal-field environment of the scheelite host, which limits non-radiative de-excitation pathways. In addition, the rigid WO_4 tetrahedral framework and its relatively low phonon energy help reduce phonon-assisted energy losses. Therefore, it supports efficient radiative emission from the Ho^{3+} centres.

3.5. Magnetic and Magnetocaloric Analysis on NHoW Ceramics

Fig. 5 presents the temperature dependence of magnetic susceptibility ($\chi(T)$) measured under zero-field-cooled (ZFC) and field-cooled (FC) conditions over 2–300 K. The synthesised NHoW ceramics exhibit paramagnetic behaviour across the entire temperature range studied. Magnetic susceptibility decreases progressively with increasing temperature, indicating the characteristic thermally activated disordering of localised magnetic moments due to association with Ho^{3+} ions. In rare-earth-based tungstate systems, the magnetic behaviour is likely governed mainly by the partially filled 4f electronic configuration of Ho^{3+} ions, whose localised nature gives rise to strong spin–orbit coupling and crystal-field effects. As temperature increases, thermal fluctuations overcome the exchange interactions between neighbouring magnetic ions, leading to the observed monotonic decrease in magnetic susceptibility.

A closer examination of the low-temperature magnetic susceptibility revealed a noticeable separation between the zero-field-cooled (ZFC) and field-cooled (FC) curves. Below the irreversibility point, FC susceptibility remains slightly higher than the corresponding ZFC values [41]. This behaviour indicates magnetic anisotropy and weak competing magnetic interactions in the system. The observed irreversibility may originate from spin canting, anisotropic exchange interactions, or the development of short-range antiferromagnetic correlations. In rare-earth-based compounds, the strong influence of crystal-field splitting on the localised 4f moments can modify both the orientation and relaxation dynamics of the magnetic moments, giving rise to the divergence between the ZFC and FC susceptibilities at low temperature. The observed separation between the ZFC and FC curves is relatively weak and does not exhibit the abrupt increase generally associated with ferromagnetic ordering. Instead, it suggests weak antiferromagnetic interactions accompanied by magnetic frustration or anisotropic spin dynamics at low temperatures.

Importantly, the ZFC susceptibility curve does not exhibit any sharp cusp, frequency-dependent anomaly or pronounced freezing feature that is typically associated with canonical spin-

glass systems. Therefore, the possibility of spin-glass freezing can be excluded in the present compound. The absence of long-range magnetic ordering down to 2 K further indicates that the magnetic exchange interactions are relatively weak compared with the thermal energy in the investigated temperature range. Such behaviour is often observed in rare-earth double tungstates, where the magnetic ions remain largely paramagnetic due to large interionic separations and weak superexchange pathways mediated by oxygen and tungstate groups.

In order to further understand the nature of magnetic interactions, the inverse magnetic susceptibility ($1/\chi$) as a function of temperature was analysed, as shown in the inset of Fig. 5. In the high-temperature region, the inverse susceptibility follows a linear Curie–Weiss dependence, indicating that the system obeys conventional paramagnetic behaviour above the magnetic correlation regime. The data were fitted using the Curie–Weiss relation[38]:

$$\frac{1}{\chi} = \frac{T - \theta}{C}$$

where C is the Curie constant and θ is the Weiss temperature. From the fitting, values of $C = 13.204 \text{ emu kOe}^{-1} \text{ K mol}^{-1}$ and $\theta = -33.10 \text{ K}$ were obtained. The negative Weiss temperature from Curie–Weiss fitting indicates the predominance of antiferromagnetic interactions in the NHoW ceramics. The relatively small magnitude of θ suggests that these interactions are weak, consistent with the absence of long-range magnetic ordering over the temperature range investigated. This behaviour is characteristic of rare-earth-based compounds, where localised 4f moments are influenced by weak exchange coupling and crystal-field effects, resulting in short-range magnetic correlations rather than a magnetically ordered ground state.

The effective magnetic moment was evaluated from the Curie constant according to:

$$\mu_{eff} = \sqrt{8C}$$

Using this relation, the Curie–Weiss fitting yielded an effective magnetic moment of **10.27 μB per Ho^{3+} ion**. This value is close to the theoretical free-ion moment of **10.61 μB** expected for Ho^{3+} . The slight difference between the experimental and theoretical values (only a 3% deviation from the original value) may be due to crystal-field effects and weak interactions between neighbouring (antiferromagnetic) Ho^{3+} ions [46]. The good agreement between these values indicates that the magnetic response of $\text{NaHo}(\text{WO}_4)_2$ mainly originates from the localised

4f electrons of Ho^{3+} [47, 48]. Similar deviations from the free-ion value have been reported for numerous rare-earth-based materials, in which crystal-field effects and spin–orbit interactions strongly influence the magnetic properties and anisotropic behaviour of the systems.

The field dependence of magnetization for NHoW ceramic was investigated at 300 K and 2 K under applied magnetic fields up to 100 kOe, and the resulting $M(H)$ curves are shown in Fig. 6. The measurements were performed to examine the magnetic response of the material and the evolution of Ho^{3+} magnetic moments under an external field. At 300 K, magnetization increases steadily with increasing magnetic field and remains unsaturated over the entire field range. This response is characteristic of paramagnetic materials, where thermal agitation hinders complete alignment of magnetic moments. No measurable hysteresis is observed, and both the coercive field and remanent magnetization are essentially absent, indicating that the sample does not exhibit ferromagnetic ordering at room temperature. These results agree with the magnetic susceptibility and Curie–Weiss analyses, which showed a predominantly paramagnetic state with weak antiferromagnetic interactions between Ho^{3+} ions. The observed magnetization arises mainly from the localised 4f electrons of Ho^{3+} , which dominate the compound's magnetic behaviour at elevated temperature.

The magnetic response of NHoW originates from the Ho^{3+} ions, whose 4f electrons remain highly localised within the crystal lattice. Since the outer electronic shells shield the 4f orbitals, magnetic interactions between neighbouring Ho^{3+} ions are relatively weak. The large orbital contribution of Ho^{3+} together with strong spin–orbit coupling also introduces considerable magnetic anisotropy, making it difficult for the magnetic moments to align completely even under strong applied fields. The magnetization behaviour changes noticeably at 2 K. While the room-temperature $M(H)$ curve is nearly linear, the low-temperature curve shows a clear nonlinear field dependence. Magnetization rises rapidly at low fields and then increases more gradually as the field is further increased, indicating enhanced alignment of the Ho^{3+} moments. A closer inspection of the low-field region reveals a narrow hysteresis loop with small but finite coercivity and remanence. The appearance of this weak hysteresis indicates that a minor ferromagnetic component coexists with the dominant antiferromagnetic interactions. One possible explanation is canting of magnetic moments due to anisotropic exchange interactions and crystal-field effects. In rare-earth tungstates, the crystal electric field can modify the orientation of the Ho^{3+} moments and

favour non-collinear magnetic arrangements. As a result, the antiparallel moments may (Antiferromagnetic ordering) not fully compensate each other, producing a small net magnetization. This interpretation is consistent with both the weak hysteresis observed at low temperatures and the negative Weiss temperature obtained from the Curie–Weiss analysis.

The narrow hysteresis loop observed in NHoW indicates magnetic anisotropy. The Ho^{3+} ion, with a large total angular momentum ($J = 8$), is strongly influenced by the crystal field, resulting in a preferred orientation of the magnetic moments within the lattice. This anisotropy contributes to the finite coercive field observed at 2 K. The magnetisation increases continuously with the applied field, remains unsaturated up to 100 kOe, and reaches approximately 49 emu g^{-1} . The absence of magnetic saturation suggests that complete alignment of the Ho^{3+} moments is not achieved even under high magnetic fields. This behaviour can be attributed to crystal-field effects and magnetic anisotropy, which restrict the free rotation of the moments. Weak magnetic correlations at low temperatures may also contribute to the incomplete spin alignment. Similar non-saturating magnetization has been reported for several rare-earth double tungstates and related compounds, where the magnetic response is governed by the interplay among crystal-field splitting, spin–orbit coupling, and weak exchange interactions.

Fig. 7 shows the isothermal magnetization curves of NHoW measured between 6 and 40 K in magnetic fields up to 100 kOe. At all temperatures, the magnetization increases continuously with increasing field, reflecting the progressive alignment of the Ho^{3+} magnetic moments. The highest magnetization is obtained at 6 K, reaching approximately 58 emu g^{-1} at 100 kOe. As the temperature increases, the magnetization decreases, and the field dependence becomes more linear because thermal fluctuations reduce the degree of moment alignment. No anomalies or discontinuities are observed in the $M(H)$ curves over the entire field range, indicating the absence of a field-induced magnetic phase transition. The magnetization curves also exhibit negligible hysteresis, suggesting a reversible magnetic response. Such magnetic reversibility is advantageous for magnetocaloric applications, as it minimises energy losses during repeated magnetization and demagnetisation cycles. The pronounced increase in magnetization with applied field at low temperatures is associated with the large magnetic moment of the Ho^{3+} ions. This magnetic response is advantageous for magnetocaloric applications, since a strong variation in

magnetization with field generally leads to a larger magnetic entropy change during magnetization and demagnetisation.

Fig. 8 displays the Arrott plots (M^2 versus H/M) derived from isothermal magnetisation measurements recorded between 6 and 40 K in 2 K intervals. Arrott plots [29] were used to examine the magnetic behaviour of NHoW and to identify the nature of the magnetic transition in the investigated temperature range. All isotherms exhibit positive slopes throughout the investigated temperature and field ranges. According to the Banerjee criterion[49], this behaviour is indicative of a second-order magnetic phase transition. The absence of negative-slope regions rules out a first-order transition and suggests that the magnetic state evolves smoothly under the applied magnetic field. In addition, the Arrott curves show no discontinuities or anomalous features, reflecting a gradual development of magnetization with decreasing temperature and increasing magnetic field [50]. This observation is consistent with the negligible hysteresis observed in the magnetization measurements and demonstrates the highly reversible nature of the magnetic response. The characteristics of the present Arrott plots are consistent with those reported for several rare-earth double tungstates and molybdates, where second-order magnetic transitions and field-induced spin alignment dominate the low-temperature magnetic response. Similar magnetic features have been reported in other rare-earth scheelite compounds, where reversible changes in magnetic entropy and low magnetic losses accompany the magnetocaloric effect. The positive curvature and absence of magnetic instability further support the suitability of the present compound for cryogenic magnetocaloric applications.

Moreover, the second-order transition inferred from the Arrott analysis is in good agreement with the broad magnetic entropy change peaks observed in the -DSM analysis. Such continuous magnetic transitions are advantageous for magnetic refrigeration because they minimise hysteresis losses and improve thermodynamic reversibility during repeated magnetization–demagnetisation cycles. The strong-field dependence of magnetisation observed at 2 K has important implications for the magnetocaloric performance of the NHoW ceramic. According to Maxwell thermodynamics, the magnetic entropy change (ΔS) can be expressed as[50, 51]:

Fig. 9 illustrates the temperature dependence of the calculated magnetic entropy change under applied magnetic fields ranging from 10 to 100 kOe. The resulting profiles show broad maxima around 8–10 K, corresponding to the compound's magnetic ordering region. The broad, nearly symmetric peaks indicate a typical second-order magnetic phase transition, which is generally associated with continuous spin alignment and negligible thermal and magnetic hysteresis losses. Negligible hysteresis and reversible magnetic response are advantageous for magnetocaloric applications, ensuring efficient operation during repeated magnetic-field cycling.

The magnitude of $-\Delta S_M$ increases progressively with increasing magnetic field strength, demonstrating strong field sensitivity of the magnetic moments. Under a field variation of 100 kOe, the maximum entropy change reaches approximately 109 J kg⁻¹ K⁻¹ near 9 K. The increase in entropy change at higher magnetic fields arises from the effective suppression of spin disorder and the increased alignment of magnetic moments under the external field. Above the peak, the entropy change gradually decreases as thermal fluctuations dominate, weakening exchange interactions and reducing field-induced spin ordering.

The observed magnetocaloric behaviour is comparable to that reported for several rare-earth-based tungstates and molybdates, where large low-temperature entropy changes are attributed to the substantial magnetic moments of rare-earth ions and weak magnetic anisotropy. In particular, rare-earth double tungstates, Ln(WO₄)₂, and molybdate analogues have been reported to exhibit broad entropy peaks and reversible magnetocaloric responses in the cryogenic temperature regime [22, 52, 53]. The present material exhibits a comparable or even higher $-\Delta S_M$ magnitude than many scheelite-type rare-earth oxides, suggesting efficient magnetic-moment participation during the field-induced ordering process [54, 55].

Furthermore, the broad operating temperature range observed in the present system is advantageous compared with materials exhibiting sharp entropy peaks, as it can provide improved refrigerant capacity and broader cooling applicability. The coexistence of a large entropy change, reversible magnetic behaviour and a broad temperature response indicates that the investigated compound is a promising candidate for cryogenic magnetic refrigeration and low-temperature, energy-efficient cooling technologies.

This relation demonstrates that a large variation in magnetisation with the applied magnetic field directly enhances the magnetic entropy change. Therefore, the rapid increase in

magnetization at low temperatures under high magnetic fields is highly favourable for achieving a significant magnetocaloric response. Furthermore, the relatively small hysteresis losses observed in the present system are advantageous for magnetic refrigeration applications, as they minimise dissipative energy during cyclic magnetisation and demagnetisation. Another important feature of the NHoW ceramic is the coexistence of weak antiferromagnetic interactions and strong magnetic anisotropy, which may broaden the temperature dependence of the magnetic entropy change. Broad entropy peaks are particularly beneficial for active magnetic refrigeration because they improve the relative cooling power (RCP) and enhance cooling efficiency over a wider operating temperature interval. The absence of strong ferromagnetic hysteresis, combined with a large field-induced variation in magnetisation, suggests that the synthesised NHoW ceramic is a promising candidate for low-temperature cryogenic magnetocaloric applications.

Fig. 10 shows the variation of the RCP of NHoW with applied magnetic field. RCP increases from $\sim 80 \text{ J kg}^{-1}$ at 10 kOe to nearly 2330 J kg^{-1} at 100 kOe. This increase reflects the stronger magnetic response of the Ho^{3+} moments under higher applied fields. The RCP growth is more pronounced at lower and intermediate fields and becomes less steep as the field increases. However, the RCP does not saturate up to 100 kOe. Such behaviour is consistent with the non-saturating magnetisation observed in the $M(H)$ curves, indicating that complete alignment of the Ho^{3+} moments is not achieved within the investigated field range. High RCP values observed at high magnetic fields demonstrate NHoW's ability to transfer substantial heat during a magnetic refrigeration cycle. Table 2 summarises the maximum magnetic entropy change values of the present compound, along with those reported for several previously studied cryogenic magnetocaloric materials, for comparison. Together with magnetic hysteresis and reversible magnetic response, these results suggest that NHoW is a promising material for low-temperature magnetic cooling applications.

4. Conclusion

- Successful synthesis of $\text{NaHo}(\text{WO}_4)_2$ (NHoW) ceramic powder was achieved from the sol-gel route at a calcination temperature of 800°C , and powder X-ray diffraction ascertained the tetragonal crystalline phase of the obtained powder with a space group $I4_1/a$.

- Microstructure and texture analyses performed on the title ceramic revealed the existence of well-defined crystalline grains with uniform morphology.
- Both FT-IR and Raman spectral signatures of NHoW ceramic powder elucidate its vibrational structure and, more specifically, characteristic tetragonal WO₄²⁻ modes of vibration are observed in Raman, indeed confirming the structural integration of the space lattice of double tungstate.
- Optical emission study revealed the strong emission around 540 nm arising out of ⁵F₄/³S₂ to ⁵I₈ transitions of Ho³⁺ ions. This optical transition could demonstrate the crystal field-assisted luminescence property of the titled compound
- even though the NHoW is a well-studied paramagnetic species at ambient temperature, antiferromagnetic order (AFM) could be noticed below 5K due to localised interaction of Ho³⁺ ions with their neighbouring magnetic moments.
- A narrow hysteresis loop observed from the M–H studies, together with the absence of magnetic saturation even under a high applied magnetic field, provides clear evidence that the magnetization mechanism is influenced by crystal-field effects and magnetic anisotropy in the crystalline solid.
- Strong performance in the cryogenic temperature regime provides a favorable magnetocaloric response of the titled compound and a maximum magnetic entropy change of 33.6 J/kg K could be detected at 5K under a magnetic field of 70 kO.
- A conjured observation of favourable properties of NHoW, such as its crystalline stabilities, reasonable performance on the magnetocaloric behaviour and possessing a higher value of reversible magnetization, together with its photoluminescence characteristics, would make the chosen double tungstate, one among the prospective candidates, available for deployment in cryogenic cooling and optoelectronic device applications.

Author Contributions

1. **A. Durairajan- Methodology, Investigation Writing – original draft**
2. **G. Ramesh Kumar- Writing – original draft, Writing – review & editing,**

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Data availability

All data generated and analyzed during this study are included in this manuscript or can be available from the corresponding author on reasonable request.

Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

Table Captions

Table 1. Refinement (The Maud) results and lattice parameters of the NaHo(WO₄)₂ compounds.

(R_{wp}, R_p and R_b represent the weighted-profile value, the Bragg-intensity value and the statistically expected value, respectively.)

Table 2. The maximum values of ΔS_m for NaHo(WO₄)₂ compounds and some other cryogenic MCE materials.

Figure captions

Fig. 1. (a) XRD patterns of the synthesised gel and different thermally treated NHoW samples (Inset shows the higher intensity peak shift compared to the NGdW sample), (b) Williamson-Hall plots for different thermal-treated NHoW samples

Fig. 2. (a) FE-SEM micrographs of calcined NHoW sample, (b) The particle size distribution of NHoW

Fig. 3. FT-IR(a) & Raman (b) spectra NHoW sample

Fig. 4. UV-Visible(a), Excitation(b) and Emission(c) Spectra of NHoW sample

Fig. 5. Temperature dependence of magnetization of NHoW in ZFC & FC sequences. Inset:

Cuire-Weiss fit

Fig. 6. Magnetic hysteresis loop of NHoW at 300 K and 2 K, measured at $H = 1$ kOe. Inset: M-H loop at 2 K near the origin.

Fig. 7. Isothermal magnetization at various temperatures for NHoW

Fig. 8. Arrott plot at different temperatures for NHoW

Fig. 9. Temperature dependence of entropy change (ΔS_M) for NHoW

Fig. 10. Magnetic field dependence of the RCP of the NHoW sample

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Table 1 Refinement (The Maud) results and lattice parameters of the NaHo(WO₄)₂ compounds. (R_{wp}, R_p and R_b represent the weighted-profile value, the Bragg-intensity value and the statistically expected value, respectively.)

	NaHo(WO ₄) ₂	NaGd(WO ₄) ₂ [38, 39]
Crystal structure	Tetragonal	Tetragonal
Space group	<i>I4₁/a</i>	<i>I4₁/a</i>
$\alpha(^{\circ})$	90	90
$\beta(^{\circ})$	90	90
$\gamma(^{\circ})$	90	90
a(Å)	5.210(2)	5.240(3)
b(Å)	5.210(2)	5.240(3)
c(Å)	11.275(5)	11.366(4)
V(Å ³)	306.049	312.207
Z	2	2
R _{wp} (%)	6.305	8.06
R _p (%)	4.396	5.96
R _b (%)	3.22	00
χ^2	1.645	1.977

Table 2 The maximum values of $\Delta S_M^{\max}$ for NaHo(WO₄)₂ compounds and some other cryogenic MCE materials.

	$\Delta S_M^{\max}$ (J/kg K)	$\mu_0 H$	θ	RCP(J/kg)	Reference
NaHo(WO ₄) ₂	92.34	0-70 kOe	-33K	1750	Present work
NaGd(MoO ₄) ₂	32.6	0-5T	2.6K	--	[26]
CsGd(MoO ₄) ₂	26.8	0-7T	--	215	[54]
LiGd(MoO ₄) ₂	30.5	0-5T	6.2K	--	[26]
KGd(MoO ₄) ₂	29.1	0-5T	7.4K	--	[26]
HoCrWO ₆	4.1	0-5T	19.8K	120	[55]
TbGd(MoO ₄) ₃	13.64	0-70kOe	-0.76K	--	[22]

Fig. 1

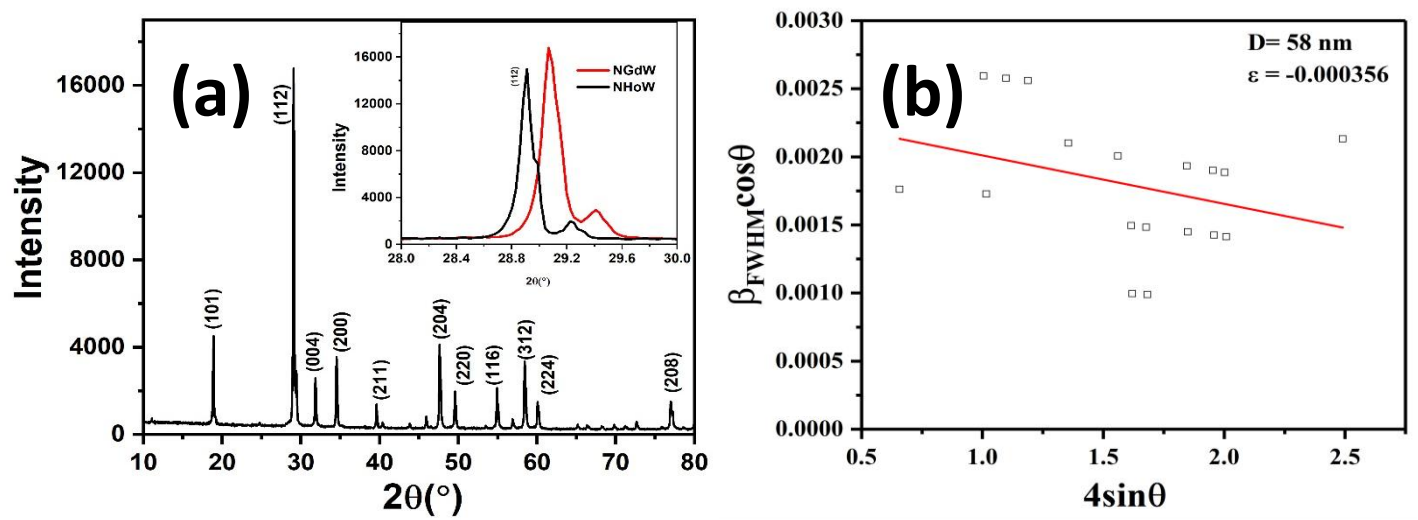


Fig. 2

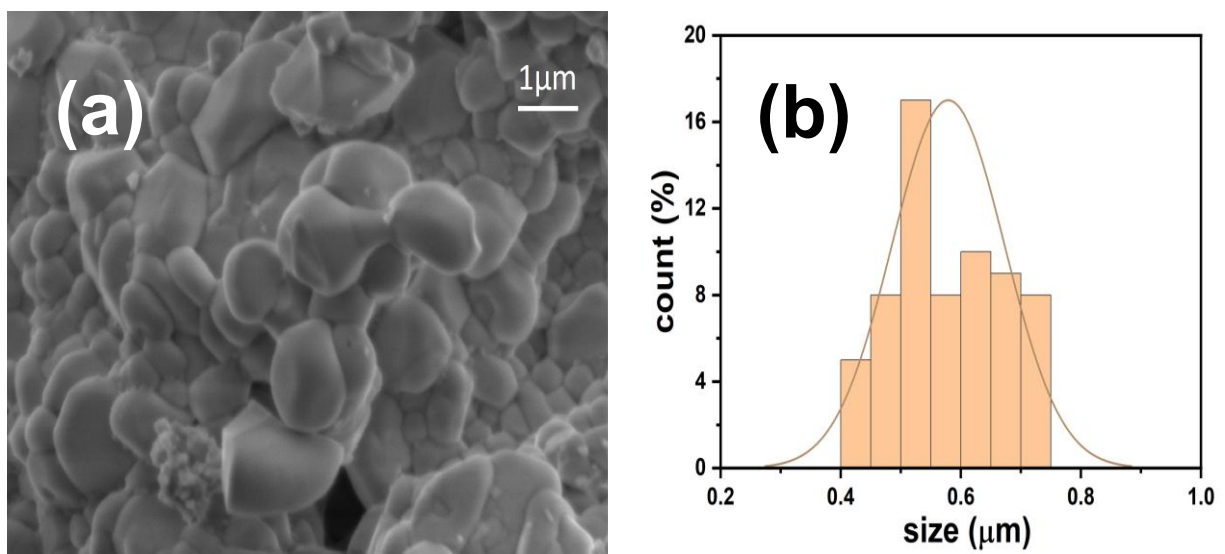


Fig. 4

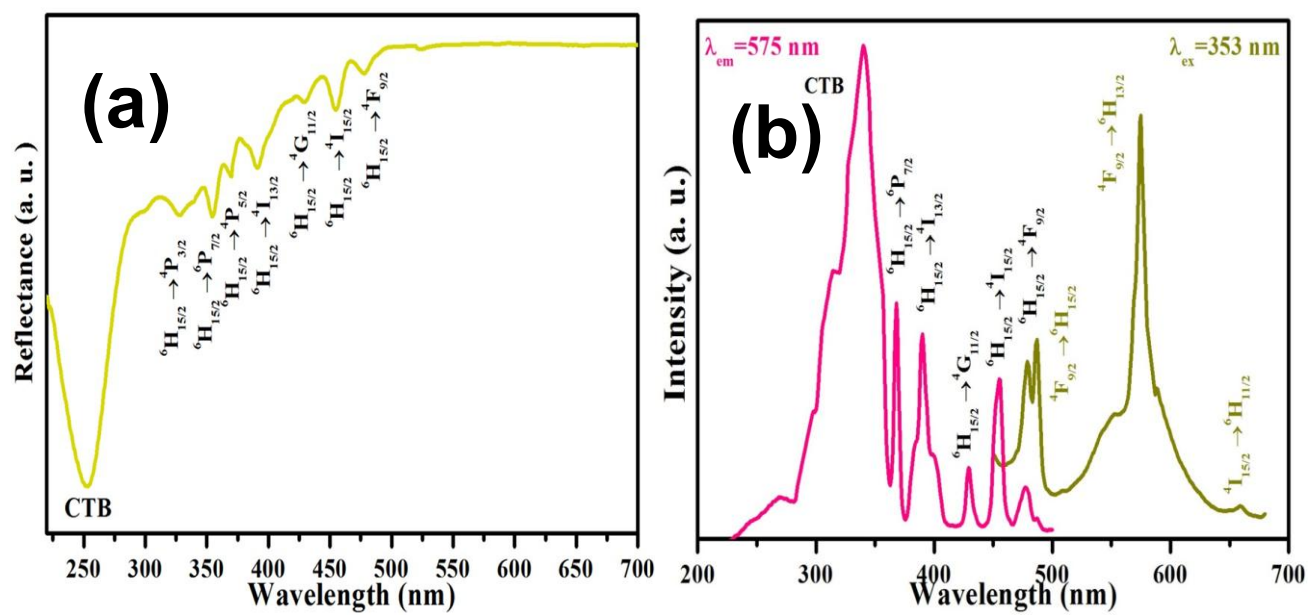


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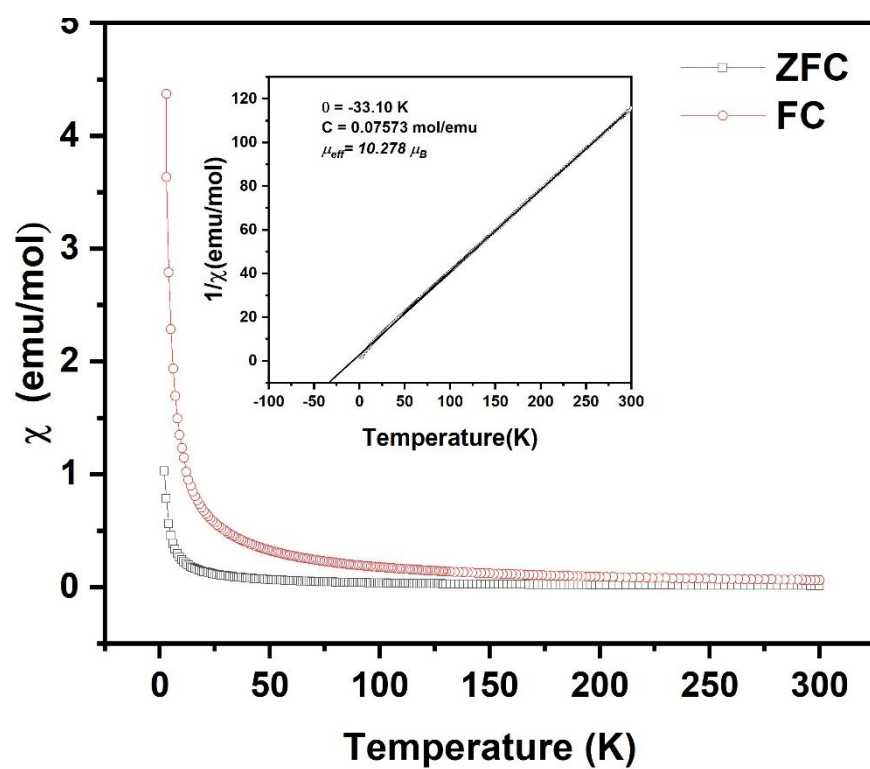


Fig. 6

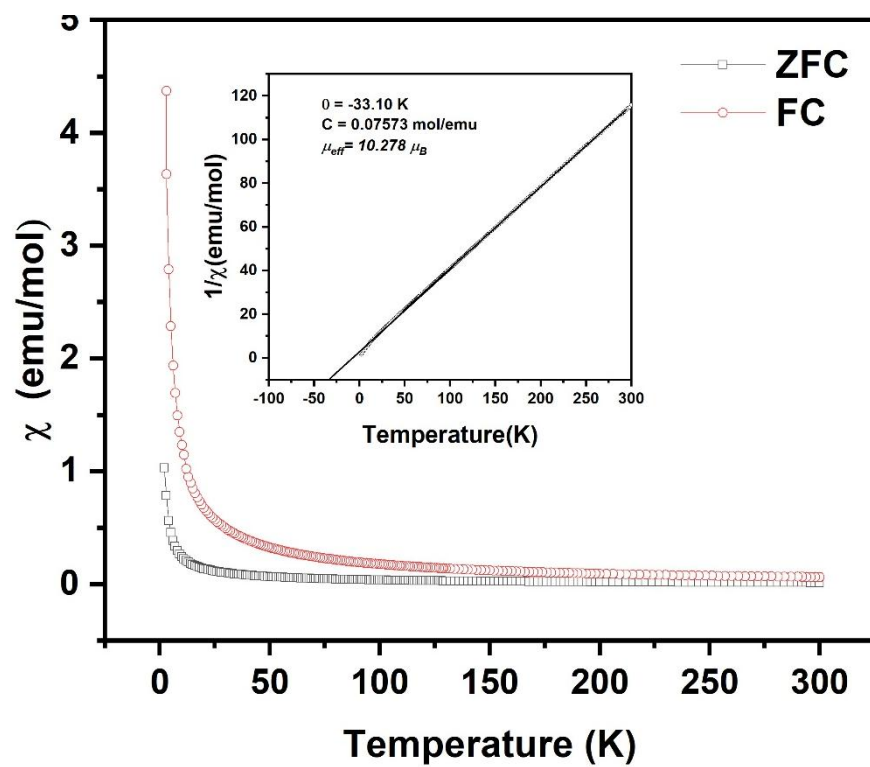


Fig. 7

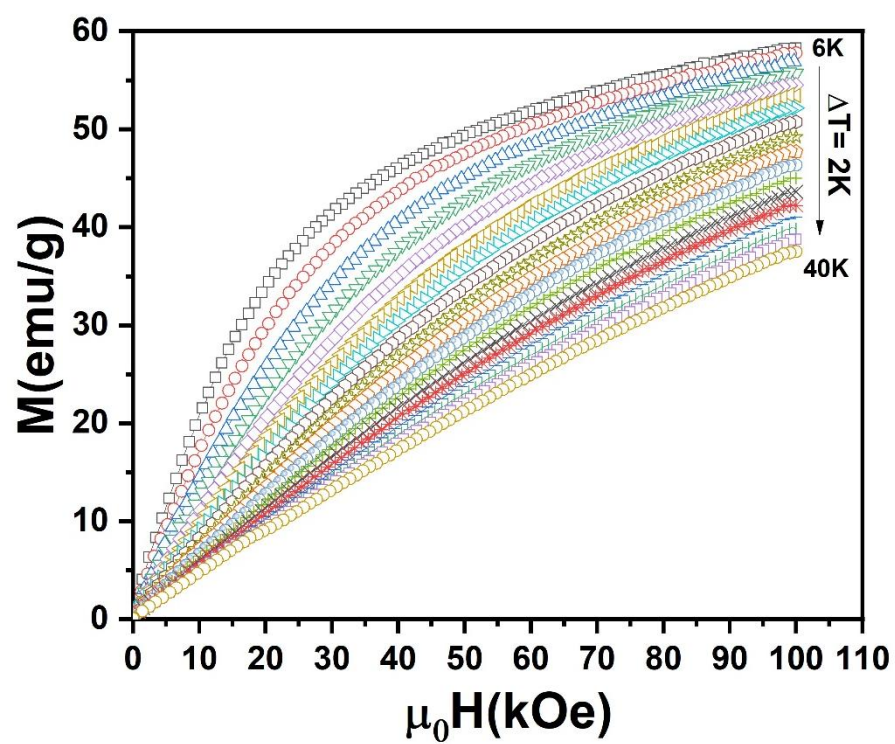


Fig. 8

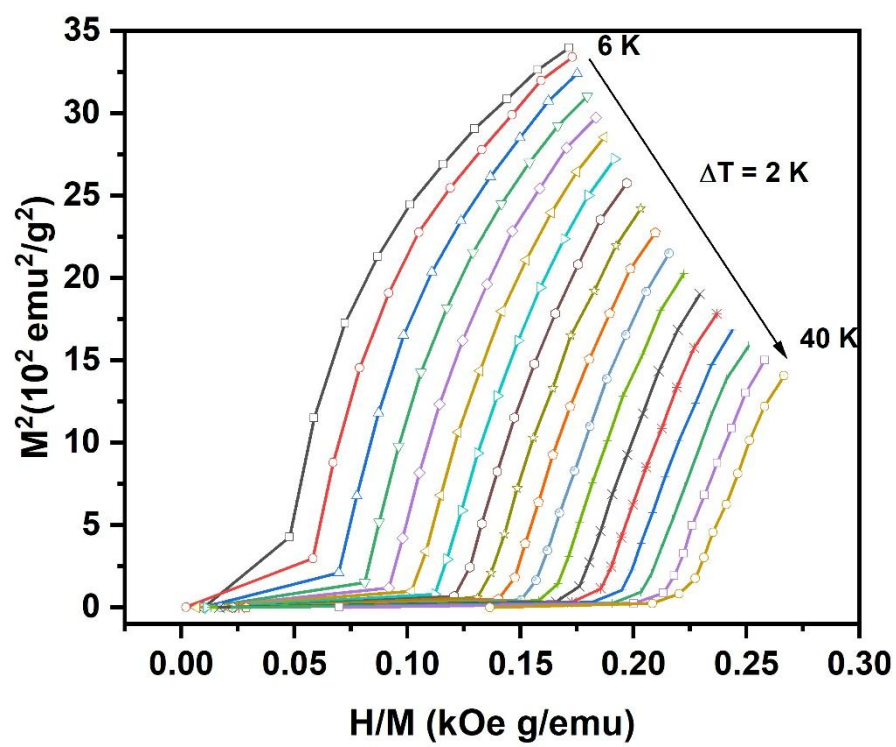


Fig. 9

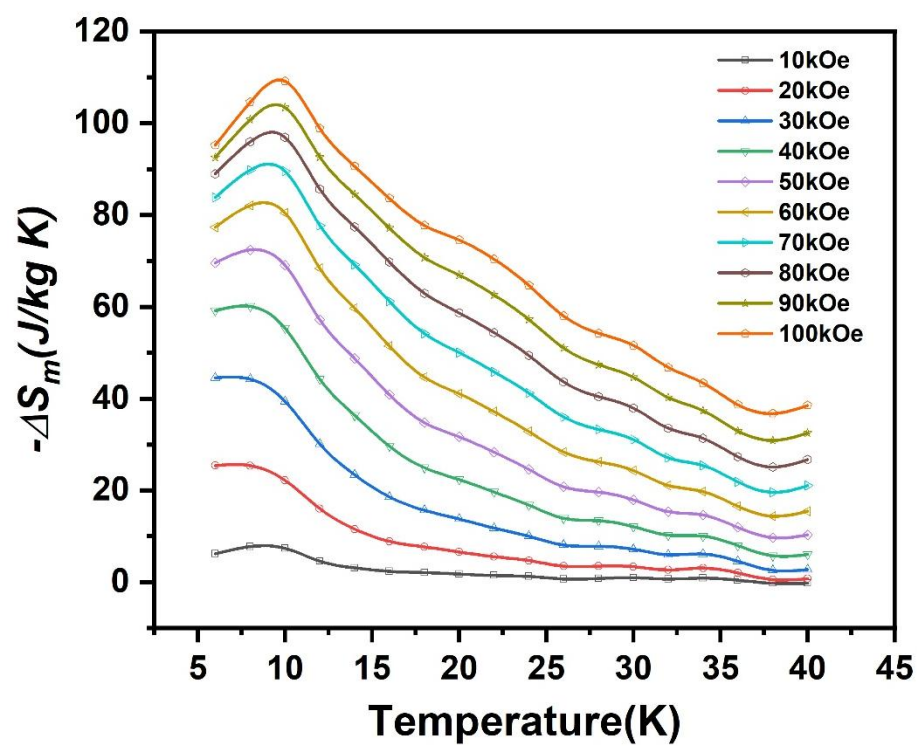
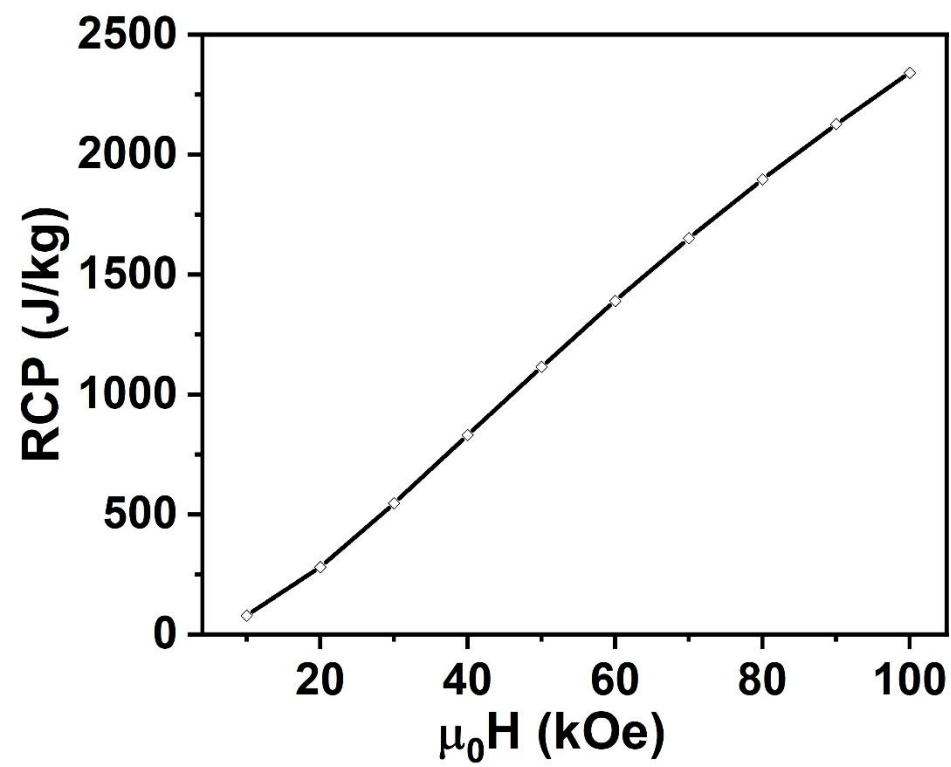


Fig. 10



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