

Article

Temperature-Dependent Magnetic Properties of Pr₆O₁₁ Oxides Refined with the Wet Ball-Milling Method

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Abstract

In this work, gradient-sized Pr₆O₁₁ powders were fabricated via a wet ball-milling method with variable milling durations. The microstructural evolution and temperature-dependent magnetic properties of different Pr₆O₁₁ powders were systematically investigated. The results reveal that wet ball-milling effectively refines powder particle size and introduces controllable lattice defects without altering the intrinsic crystal structure. Magnetic measurements over a temperature range of 3–300 K demonstrate that the unmilled powder exhibits typical paramagnetic behavior. However, milling-induced particle refinement significantly enhances the low-temperature magnetic moments of Pr₆O₁₁, accompanied by characteristic superparamagnetic hysteresis at 3 K. Furthermore, the fitted paramagnetic Curie temperature θ_p and Curie constant C confirm that the magnetic regulation is milling-affected and dependent on milling time. Prolonged milling above 1 day cannot continuously increase low-temperature magnetic moments. The above temperature-dependent magnetic properties of milled Pr₆O₁₁ can possibly be attributed to milling-induced grain refinement and lattice distortion, as supported by the microstructure analysis. This work provides valuable physical insights into the low-temperature magnetic properties of Pr₆O₁₁ and offers guidance for its magnetic functional applications.

Keywords: Pr₆O₁₁ oxide; magnetic properties; temperature dependent; ball-milling

1. Introduction

Mixed-valence rare earth oxides have emerged as a pivotal class of functional materials owing to their unique 4f electronic configurations, reversible valence transition behavior, and defect-dependent physical and chemical performances [1–4]. They exhibit broad application prospects in magnetic functional devices and catalytic fields. As a typical non-stoichiometric praseodymium oxide, Pr₆O₁₁ features a stable fluorite-derived cubic structure with intrinsically coexisting Pr³⁺ and Pr⁴⁺ ions, accompanied by abundant lattice oxygen vacancies. This endows it with distinct temperature-sensitive catalytic and electronic characteristics that are absent in single-valence lanthanide oxides [4,5]. Different from conventional magnetic rare earth oxides, pure Pr₆O₁₁ bulk materials present para-magnetism, while nano-sized Pr₆O₁₁ powders display anomalous physical responses and temperature-dependent spin evolution behaviors. This makes them a research

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hotspot in the field of condensed matter magnetism in recent years [5–8]. The microstructural morphology, grain size distribution and defect concentration of Pr_6O_{11} powders are the core factors determining their variable-temperature physical properties [9,10]. Precise structural modulation is the key to unlocking their excellent magnetic functional performance. A series of temperature-dependent physical and chemical phenomena of Pr_6O_{11} , including spin glass-like anomalies near 5 K and improved catalytic behavior, have been gradually revealed [11–13].

At present, research on Pr_6O_{11} mainly focuses on pristine powders prepared by sol-gel, high-temperature calcination and self-propagating methods [14,15]. Wet ball-milling, as an important post-treatment refinement method, can introduce unique structural modulation effects different from in situ synthesis: high-energy mechanical force induces grain refinement and lattice distortion, while the liquid-phase medium regulates the surface defect uniformity of powders. Relevant mechanical modification studies on rare earth magnetic materials have proven that wet milling can effectively adjust the critical temperature of magnetic phase transition, optimize magnetic entropy change, and improve the stability of magnetic response of powders [10,16–18]. Benefiting from the liquid-phase dispersion environment, wet ball-milling can uniformly refine Pr_6O_{11} coarse particles into finer powders and further modulate the valence state ratio and surface spin disorder state.

Although previous studies have demonstrated that mechanical milling or nanostructuring can significantly influence the electrical conductivity [19], photocatalytic degradation performance [20], and nonlinear varistor properties [21] of Pr_6O_{11} -based materials, none of these works have systematically addressed the quantitative correlation between wet ball-milling parameters and the intrinsic temperature-dependent magnetic behavior of Pr_6O_{11} powders. Nevertheless, most current studies focus on the modification effect of Pr_6O_{11} on composite materials and its catalytic properties, while systematic investigations on the intrinsic temperature-dependent magnetic properties of refined Pr_6O_{11} powders are still insufficient. Furthermore, a quantitative correlation between wet ball-milling parameters (milling time et al.) and the variable-temperature magnetic properties of Pr_6O_{11} remains unclear. Aiming at existing research gaps, including the unclear structure–magnetism relationship and unsystematic variable-temperature magnetic evolution of wet ball-milled Pr_6O_{11} powders, this paper systematically investigates the temperature-dependent magnetic behaviors of Pr_6O_{11} oxides refined via wet ball-milling.

2. Experimental Methods

Different Pr_6O_{11} oxide powders were successfully prepared via a facile wet ball-milling strategy. Firstly, for each sample, 20 g of pristine Pr_6O_{11} powder (purity: 99.99%) was blended with agate milling balls at a powder-to-ball mass ratio of 1:10. The agate milling balls used are 0.5 mm and 3 mm with a number ratio of about 1:1. Then, 50 mL anhydrous ethanol was added into the 0.4 L milling jar with mixed powder and balls, and the jar was tightly sealed for wet ball-milling. Subsequently, the sealed milling tank was mounted on a planetary ball-mill, and the milling speed was set as 250 rpm. Variable milling durations (1 day, 4 days, and 7 days) were implemented to achieve gradient particle size refinement of Pr_6O_{11} powders. After reaching the preset milling time, the agate balls were manually separated from the mixed suspension. The residual powder–ethanol mixture was then transferred to a drying oven and heated at 140 °C for complete solvent evaporation. Finally, a series of high-purity Pr_6O_{11} powders with different milling days were obtained for subsequent microstructural characterization and temperature-dependent magnetic performance testing.

The texture of the Pr_6O_{11} powders was evaluated by X-ray diffraction (XRD, D8 Advance, Bruker, Karlsruhe, Germany). The morphology and particle size of Pr_6O_{11} powders were characterized by scanning electron microscopy (SEM, S-4800, Hitachi, Tokyo, Japan).

The magnetic properties of Pr_6O_{11} powders were measured using a vibrating sample magnetometer (VSM, Quantum Design, San Diego, CA, USA).

3. Results and Discussions

Figure 1 exhibits the crystal structure and X-ray diffraction (XRD) characterization results of wet ball-milled Pr_6O_{11} powders with different milling times. Figure 1a presents a schematic diagram of cubic fluorite-type Pr_6O_{11} . Figure 1b displays the full-range XRD patterns of samples milled for 0, 1, 4, and 7 days. All diffraction peaks of four groups of powders perfectly match the standard PDF cards of Pr_6O_{11} , and no miscellaneous diffraction signals are detected, which confirms that wet ball-milling only induces microstructural modulation without introducing impurity phases or altering the intrinsic cubic fluorite crystal structure of Pr_6O_{11} [4,10].

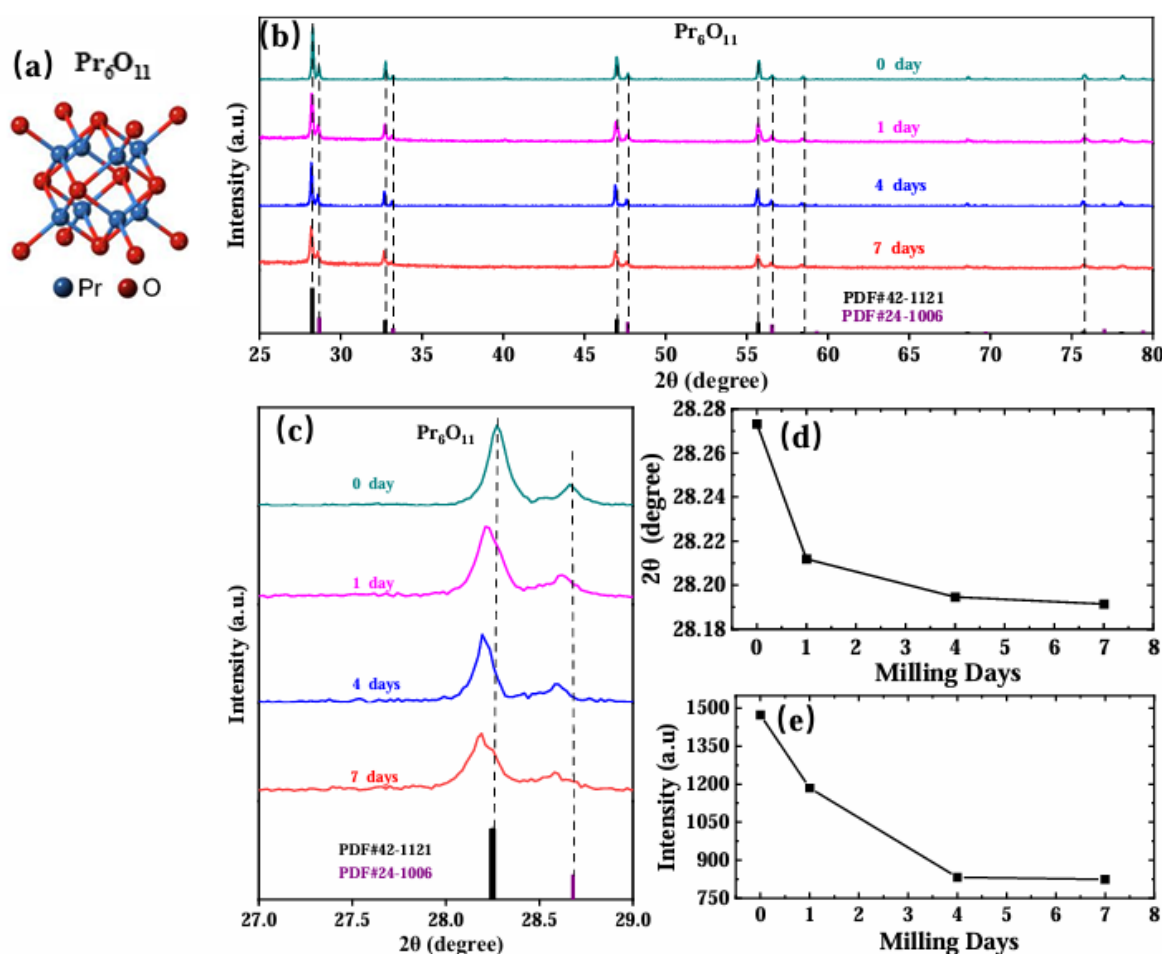


Figure 1. (a) Schematic picture of cubic fluorite structure Pr_6O_{11} . (b) XRD full patterns of Pr_6O_{11} powders with milling durations of 0-day, 1 day, 4 days, and 7 days. (c) Magnified XRD patterns at low angles (from 27 to 29 degrees) with the milling time-dependent (d) peak position and (e) peak intensity around 28.2° .

Figure 1c is the enlarged local diffraction pattern at from $27\text{--}29^\circ$, intuitively reflecting the regular shift and attenuation of the characteristic diffraction peak with prolonged milling. The corresponding quantitative evolution curves are summarized in Figure 1d and Figure 1e. With the extension of ball-milling time, the 2-theta value of the main diffraction peak around 28.2° gradually shifts to a lower angle, and the peak intensity decreases monotonically. The peak position and intensity both reach a stable saturated state after 4 days of milling. This phenomenon may originate from the combined effect of grain refinement

and milling-induced lattice microstrain. Mechanical collision and friction break large particles into fine grains, while lattice distortion and defects may be generated inside the crystal lattice, resulting in lattice expansion. This accounts for the left shift of diffraction peaks. Meanwhile, grain refinement reduces the crystallinity of powders, leading to continuous attenuation of diffraction peak intensity [6,14].

Figure 2 presents the fitting results of XRD patterns and Williamson-Hall (W-H) strain analysis for powders milled for 0, 1, and 7 days. Figure 2a–c compares the original experimental XRD curves (black lines) and full-profile fitting profiles (red lines). The peaks were fitted with a Gaussian function. The high fitting coefficient R^2 values (0.98636, 0.97252, and 0.95801) indicate good agreement between the experimental data and the fitted model.

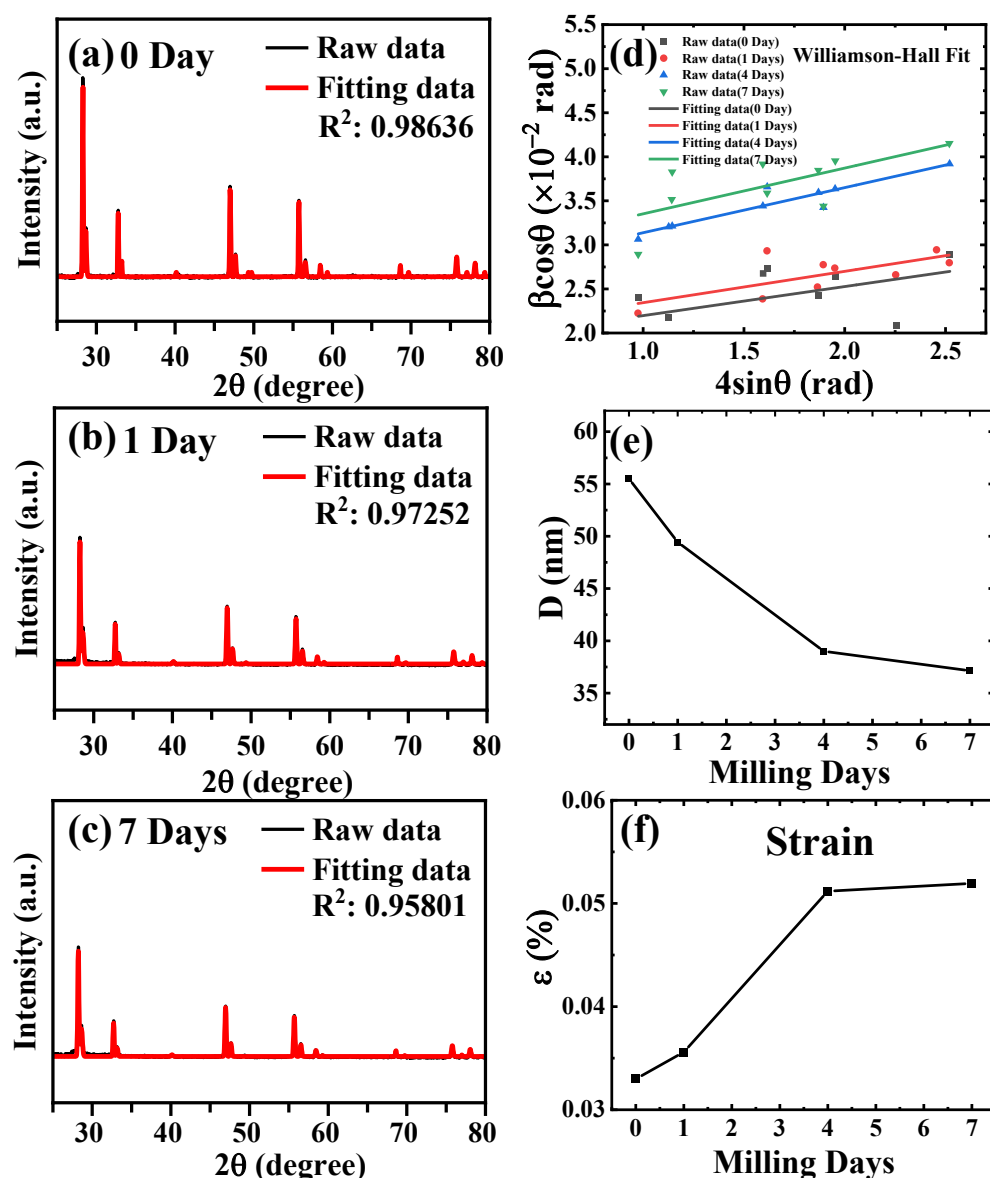


Figure 2. (a–c) Fitted XRD full patterns of Pr_6O_{11} powders with different milling durations (0, 1 and 7 days); the fitting error R^2 is included. (d) Williamson-Hall (W-H) plot of fitting results among which β and θ are the fitted FWHM and peak angle of the XRD pattern; linear fitting to the results is indicated. (e) Fitted average grain size and (f) fitted lattice strain from the W-H plot as a function of milling days.

To distinguish the individual contributions of crystallite size and microstrain to the X-ray diffraction (XRD) peak broadening, the Williamson-Hall (W-H) method was employed. The W-H equation is expressed as follows [21–24]:

$$\beta \cos \theta = K\lambda/D + 4\epsilon \sin \theta \quad (1)$$

where β is the full width at half maximum (FWHM), θ is the Bragg angle, K is the shape factor, λ is the X-ray wavelength, D is the average crystallite size, and ϵ represents the microstrain. By plotting $\beta \cos \theta$ against $4 \sin \theta$, the average crystallite size can be determined from the y -intercept, while the micro-strain is derived from the slope of the linear fit.

The Williamson-Hall linear fitting plots for all samples are displayed in Figure 2d, where the slope of each fitted straight line corresponds to the average lattice microstrain, and the intercept correlates with the average crystallite size. With the extension of wet ball-milling duration, the fitted straight line shifts upward evidently, revealing a possible increase in internal lattice distortion inside grains. Figure 2e quantitatively summarizes the evolution of average grain size D extracted from W-H fitting. The pristine unmilled powder possesses the largest average crystallite size of 58 nm. After 1 day of milling, the grain size drops sharply to 53 nm, followed by a continuous gradual reduction to 40 nm for the 7-day milled sample. The persistent grain refinement originates from repeated collision and shear force of agate balls, which fractures large crystallites into smaller nanoscale grains. The quantitative evolution of lattice strain ϵ is summarized in Figure 2f. The pristine 0-day sample possesses the minimum strain value of 0.02%. After 1 day of mechanical milling, the strain rises sharply to 0.033%, followed by a slow continuous growth up to 0.051% for the 7-day milled powder. This trend originates from severe plastic deformation induced by high-speed ball collision, which may introduce massive lattice defects and atomic displacement inside grains.

The dislocation density (ρ) of the synthesized samples was estimated using the Williamson-Smallman equation, which relates the microstructural parameters derived from XRD peak broadening. The relationship is expressed as follows:

$$\rho = \sqrt{3k\epsilon}/bD \quad (2)$$

where ϵ and D represent the average strain and crystallite size obtained from the Williamson-Hall plot, and $\sqrt{3k}/b$ is a crystal structure-related constant taken as the same for all milling conditions.

Based on the Williamson-Smallman equation, dislocation density ρ is further calculated and plotted in Figure 3. Dislocation density shows a similar increasing tendency to lattice strain: the raw sample exhibits the lowest dislocation density, while an obvious increase occurs after 1-day milling, and the value grows moderately with prolonged milling time after 4 days. Combined with the XRD peak shift results in Figure 1, the W-H analysis quantitatively confirms that wet ball-milling effectively introduces controllable lattice strain and dislocation defects in without changing its intrinsic crystal phase.

Figure 4 presents the SEM micrographs of Pr_6O_{11} powders with different wet ball-milling durations (0 day, 1 day, 4 days, and 7 days). For the pristine Pr_6O_{11} powder without ball-milling (Figure 4a,e), the particles exhibit irregular blocky morphology with large overall particle size and obvious particle agglomeration. The original powder shows a wide particle size distribution, and a large number of coarse particles with uneven sizes dominate the microstructure, which is caused by the high surface energy and spontaneous agglomeration tendency of rare earth oxide nanoparticles during preparation and storage. The average particle size (0.91 μm) of the raw powder is much larger than the XRD fitting results in Figure 2e, and the particle boundary is rough. This can be attributed to the agglomeration of nano-sized grains that cannot be well differentiated in the SEM images.

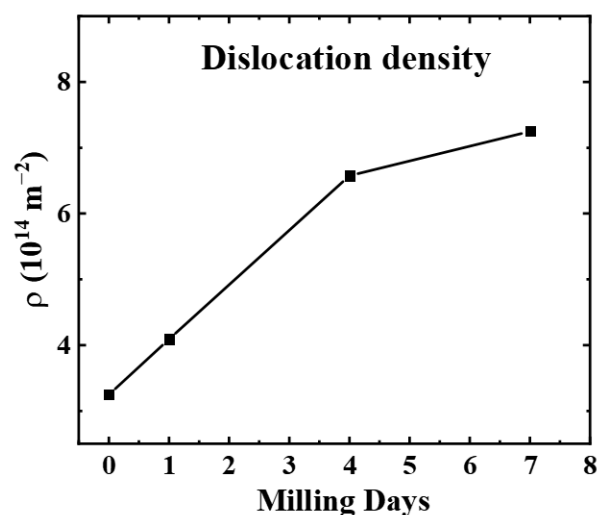


Figure 3. The dislocation density (ρ) of the samples estimated using the Williamson-Smallman equation.

After 1 day of wet ball-milling (Figure 4b,f), the high-energy mechanical collision and shear action effectively break the large agglomerated clusters and coarse particles of Pr_6O_{11} . The overall particle size of the powder is reduced ($0.40 \mu\text{m}$), the particle agglomeration phenomenon is partially alleviated, and the particle size distribution becomes more concentrated compared with the pristine sample. With the milling time extended to 4 days (Figure 4c,g), the refinement effect is further improved ($0.37 \mu\text{m}$). The coarse particles in the powder are basically eliminated, and the particle morphology tends to be uniform and regular. The particle size distribution range is further narrowed. The liquid-phase environment of wet ball-milling effectively inhibits the secondary agglomeration of newly generated fine particles, enabling the Pr_6O_{11} powder to obtain a homogeneous microscopic morphology and stable particle size distribution. When the wet ball-milling duration reaches 7 days (Figure 4d,h), the particle size of Pr_6O_{11} powder is further refined ($0.35 \mu\text{m}$). However, compared with the 4-day milled sample, the refinement amplitude of particle size decreases significantly and tends to be stable. After long-term milling, the particle crushing rate and cold welding rate of Pr_6O_{11} reach dynamic equilibrium, and the particle size no longer decreases sharply.

Figure 5 illustrates the temperature-dependent magnetic hysteresis (M-H) loops of Pr_6O_{11} powders at measuring temperatures ranging from 3 K to 300 K. For all four groups of powders, a consistent thermally induced magnetic attenuation trend is observed upon heating from 3 K to 300 K. The continuous increase in thermal excitation energy during heating fundamentally changes the spin arrangement and exchange coupling state of Pr ions, forming typical thermally induced magnetic attenuation behavior.

At the initial ultra-low temperature of 3 K, all Pr_6O_{11} samples exhibit the strongest magnetic hysteresis performance. With the continuous heating process from 3 K to room temperature, the thermal excitation energy acting on Pr electrons increases gradually, which induces systematic attenuation of magnetic properties and gradual degeneration of hysteresis loops for all Pr_6O_{11} samples. When the temperature rises to 300 K, the thermal disturbance completely dominates the magnetic behavior of Pr_6O_{11} powders, and all samples achieve consistent paramagnetic characteristics. At this stage, the structural advantages brought about by ball-milling refinement, including large specific surface area and lattice defects, cannot offset the destructive effect of high-temperature thermal fluctuation on spin alignment. It can be confirmed that the magnetic behavior of Pr_6O_{11} is also strongly dependent on the ball-milling time. The unmilled 0-day sample with coarse powder always maintains paramagnetic signals during the whole heating stage. In contrast,

the refined 1-day milling sample exhibits a strong magnetic regulation ability with strong low-temperature magnetic moments. The excessively refined 7-day milling sample does not show further enhanced thermal magnetic performance, presenting a saturated magnetic attenuation trend during heating, which is consistent with the structural saturation phenomenon of long-term wet ball-milling.

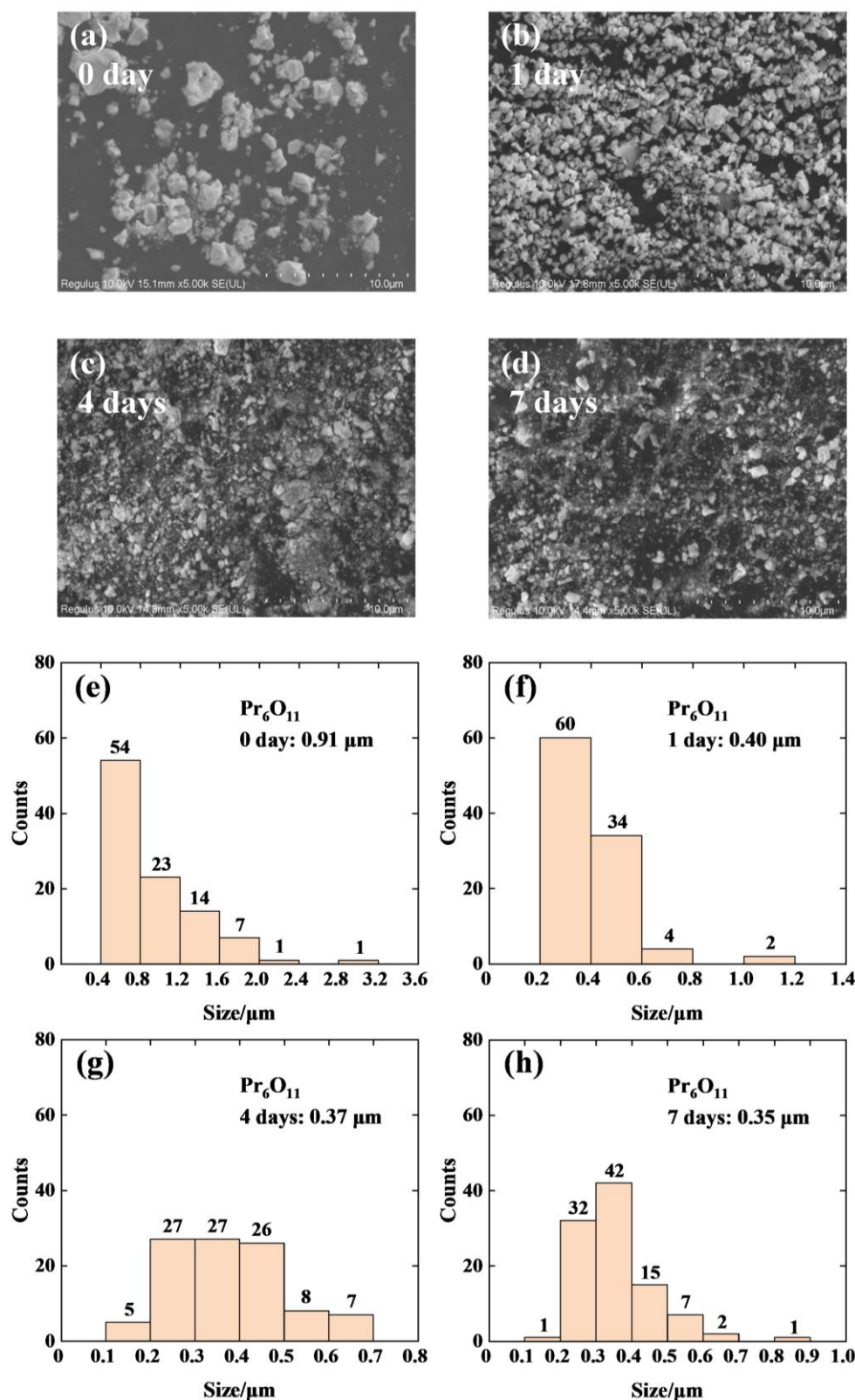


Figure 4. (a–d) SEM micrographs of Pr_6O_{11} powders with different wet ball-milling durations (0 days, 1 day, 4 days, and 7 days); (e–h) respective particle size distribution histograms and average particle sizes.

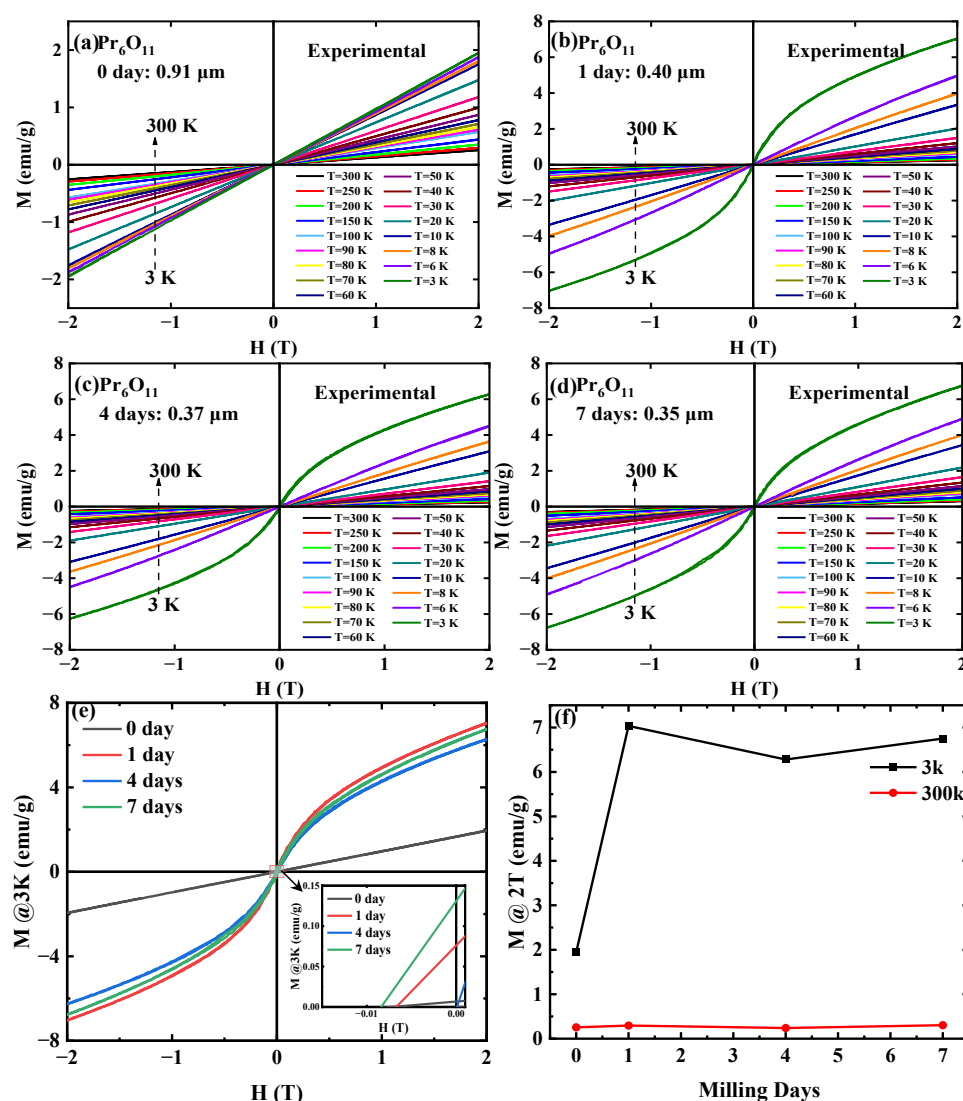


Figure 5. (a–d) Temperature magnetic hysteresis (M-H) loops of Pr_6O_{11} powders at measuring temperatures ranging from 3 K to 300 K with different wet ball-milling durations (0, 1, 4 and 7 days). (e) Comparative plot of the hysteresis loops at 3 K with magnified plot around 0 T. (f) Summary of magnetizations at 3 K and 300 K with different wet ball-milling durations.

Figure 5e compares the 3 K hysteresis curves of all samples, with an enlarged inset near zero field to compare subtle magnetic differences. The details of the extracted magnetic parameters are shown Table 1. Although the coercivity and remanence of the hysteresis loops are observable in milled samples, they are too small and close to the experimental error (magnetic field increasing step is 0.005 T during measurements); thus, they cannot serve as rigorous criteria for ferromagnetic materials. Therefore, the strong magnetism observed at 3 K is more appropriately attributed to superparamagnetic behavior. Figure 5f quantitatively summarizes the maximum magnetization at 2 T magnetic field measured at 3 K and 300 K as a function of milling time. The unmilled powder (0 day) delivers the lowest magnetization at 3 K. After 1 day of milling, magnetization rises sharply. Further extending milling to 7 days only leads to a slight magnetization changes,

showing saturated magnetic regulation consistent with the saturated microstructure evolution from XRD and SEM characterizations.

Table 1. Magnetic parameters (H_c and $M@2T$) of Pr_6O_{11} powders under different wet ball-milling durations. The values are taken from the labeled results in Figure 5e,f. The magnetic field step for hysteresis loop measurements is 0.005 T.

Milling Days	$H_c@3K$ /(T)	$M@3K@2T$ /(emu/g)	$M@300K@2T$ /(emu/g)
0	None	1.94	0.25
1	0.0076	7.04	0.29
4	None	6.28	0.24
7	0.0090	6.75	0.30

Figure 6 is the temperature dependence of magnetic susceptibility (χ_m) of Pr_6O_{11} powders with different milling days ranging from 3 K to 300 K. Figure 6a shows that all samples exhibit typical paramagnetic behavior, characterized by a sharp increase in χ_m as the temperature decreases. The unmilled raw powder (0 day) possesses the lowest susceptibility over the full temperature range. The milled samples (1, 4, and 7 days) display significantly higher susceptibility values at low temperatures compared to the unmilled sample (0 day), indicating an enhancement in magnetic response induced by mechanical milling.

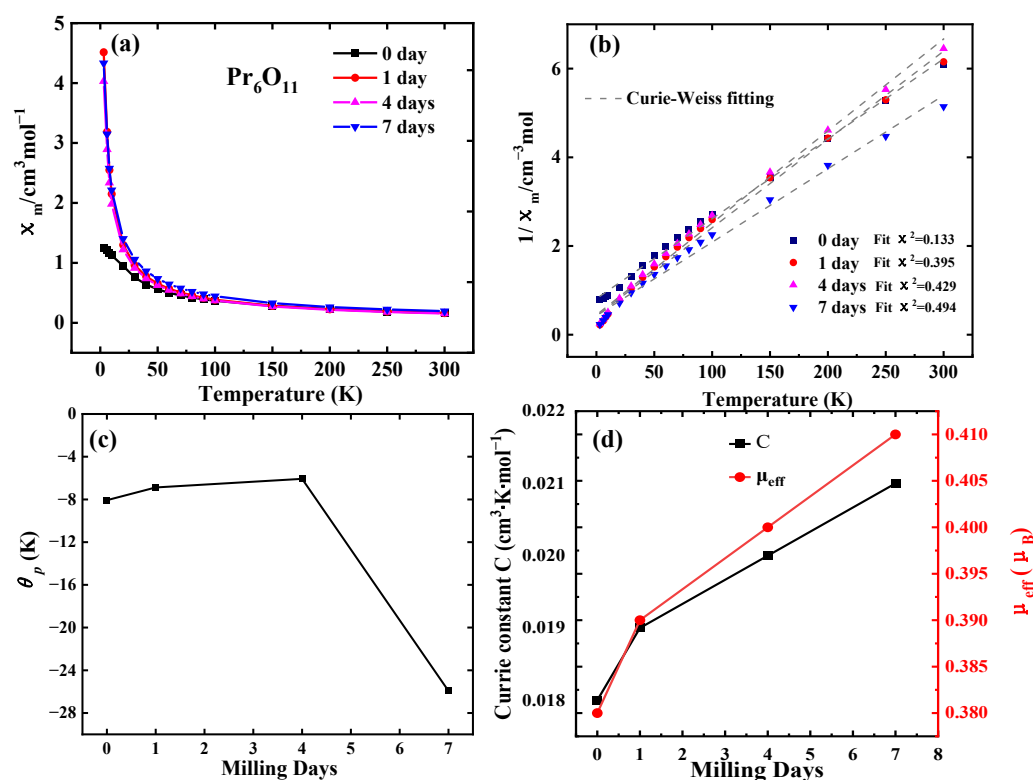


Figure 6. Temperature dependence of (a) magnetic susceptibility and (b) inverse magnetic susceptibility with Curie-Weiss law fitting of Pr_6O_{11} powders with different milling days; the fitting was taken measured from 10 K to 300 K, and the fitting errors χ^2 are indicated; (c,d) Fitted paramagnetic Curie temperature θ_p , constant C and effective moments μ_{eff} for Pr_6O_{11} powders with different milling days.

To further investigate the magnetic interactions, the inverse susceptibility ($1/\chi_m$) was plotted against temperature and fitted using the Curie-Weiss law [25]:

$$(T - \theta_p) = C/\chi_m \quad (3)$$

where θ_p is the Curie temperature, T is the temperature, and C is a constant. The fitting results are shown in Figure 6b. The deviation from the linear temperature dependence of inverse susceptibility $1/\chi_m$ on T can clearly be seen in the milled samples (1, 4 and 7 days). For this reason, all linear fitting was taken in the temperature region from 10 K to 300 K. Figure 6b shows that for all the fittings, the fitting error χ^2 is smaller than 0.5. For the 0-day sample, the fitting has a lowest error χ^2 , suggesting typical paramagnetic behavior. For the samples with more than 1-day milling, the fitting error increases, suggesting a slight deviation from typical paramagnetic behavior.

Figure 6c shows the evolution of θ_p as a function of the milling duration. The θ_p values remain relatively stable between -8 K and -6 K for milling times up to 4 days. However, a dramatic decrease in θ_p is observed for the sample milled for 7 days, dropping to approximately -26 K. θ_p serves as an indicator of the exchange interactions between magnetic moments. This significant negative shift may be caused by the enhancement of magnetic interactions within the Pr_6O_{11} lattice after prolonged milling. However, the increased fitting error for the 7-day sample may also contribute to this abnormal θ_p . This phenomenon may possibly be attributed to milling-induced microstructural modifications, such as lattice distortion and grain refinement, which alter the magnetic property of Pr ions, as suggested by the XRD results [3,4]. The reduction of particle size may increase the specific surface area and surface defect density, which modulates the average spin correlation strength of Pr ions and further changes the paramagnetic Curie temperature. Figure 6d illustrates the evolution of Curie constant C and effective moments μ_{eff} for Pr_6O_{11} powders with different milling days derived from linear fitting. The Curie constant exhibits the highest relative increase between 0 and 1 day; after that, it keeps rising at days 4 and 7, yet the increases from 1 to 4 and from 4 to 7 are comparatively smaller. The C is proportional to the square of the effective magnetic moment per Pr ion with equation $\mu_{eff} \approx 2.88\sqrt{C}$. The growing C value suggests that milling-induced lattice defects increase the average effective magnetic moment of Pr ions, as shown in Figure 6d. This further explains the improved low-temperature magnetization observed in hysteresis loops in Figure 5.

4. Conclusions

This work systematically explores the microstructures and temperature-dependent magnetic behaviors of wet ball-milled Pr_6O_{11} powders. The XRD analysis with Williamson-Hall fittings reveal that wet ball-milling effectively reduces powder particle size and introduces controllable lattice defects without altering the intrinsic crystal structure. Magnetic measurements over a temperature range of 3–300 K demonstrate that while the unmilled powder exhibits typical paramagnetic behavior, milling-induced particle refinement significantly enhances the low-temperature magnetic moments of Pr_6O_{11} . This is accompanied by characteristic superparamagnetic hysteresis at 3 K in milled samples. Prolonged milling above 1 day cannot continuously increase the low-temperature magnetic moments. Furthermore, the fitted paramagnetic Curie temperature θ_p and Curie constant C confirm that the magnetic regulation is milling-affected and dependent on milling time. The above temperature-dependent magnetic properties of milled Pr_6O_{11} may be attributed to milling-induced grain refinement and lattice distortion, as supported by the microstructure analysis with XRD. This work provides valuable physical insights into the low-temperature magnetic properties of Pr_6O_{11} and offers guidance for its magnetic functional applications.

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Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could influence this article.

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