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Pr³⁺-Doped Lithium Niobate and Sodium Niobate with Persistent Luminescence and Mechano-Luminescence Properties

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Abstract: In this research, a comprehensive series of Pr³⁺-doped lithium niobate and sodium niobate materials were obtained at different temperatures via solid-state sintering, and their structures and properties were compared. NaNbO₃: 0.75% Pr³⁺ phosphors were synthesized by sintering at 1150 °C for 2 h and emitted red persistent luminescence for more than 1200 s, peaking at 612 nm under UV excitation, which was a typical long persistent luminescence phenomenon. Furthermore, the sample glowed when pressurized, and a red bright luminescence which lasted for several seconds was visible to the naked eye. This was a typical mechanical luminescence phenomenon of samples under mechanical stress, directly converting mechanical energy into light energy. It was determined that NaNbO₃:Pr³⁺ and LiNbO₃:Pr³⁺ both possess multimode luminescence. Owing to their red long persistent luminescence (LPL) and mechano-luminescence (ML) properties, Pr³⁺ phosphors can be employed in fields, such as display technologies, stress sensing, structural damage detection, and other complex applications.

Keywords: phosphors; red persistent luminescence; multimodal luminescence



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1. Introduction

When a material absorbs external excitation energy, such as light, electric fields, or electron beams, if it does not undergo chemical changes, it returns to its original equilibrium state; however, in this process, excess energy is emitted in the form of light, which is luminescence [1,2]. Luminescence is an ancient and mysterious phenomenon. With the passage of time, it has gradually entered people's vision and been deeply studied. Long persistent luminescence (LPL) refers to a phenomenon whereby luminescent materials can continue to emit light after excitation is halted, which plays an important role in the biological, medical, military, and anti-counterfeiting industries [3–6]. LPL materials can be divided into excessive metal-ion-doped luminescent materials (Cr³⁺, Mn²⁺, Mn⁴⁺, and Ni²⁺), S² electronic structure ion-doped luminescent materials (Bi³⁺ and Pb²⁺), rare-earth metal-ion-doped luminescent materials (Eu²⁺, Eu³⁺, Ce³⁺, Sm³⁺, Tb³⁺, Dy³⁺, Er³⁺, Yb³⁺, Nd³⁺, Pr³⁺, Ho³⁺, and Tm³⁺) and others, according to the luminescent center [5–9]. There are also excessive metal-ion-doped luminescent materials; for example, in the Ga₂O₃ matrix, Cr³⁺ produces a sharp line emission near 700 nm due to the energy level transition of ²E → ⁴A₂. In the La₃Ga₅GeO₁₄ matrix, Cr³⁺ has a broadband emission at 650–1000 nm due to the ⁴T₂ → ⁴A₂ transition. S² electronic structure ion-doped luminescent materials, for example, ZnS:Cu⁺, can emit yellow persistent luminescence near 530 nm for more than 1 h after excitation. The blue persistent luminescence of CdSiO₃:In³⁺ at 435 nm

after excitation can be more than 2 h. $\text{MgAl}_2\text{O}_4:\text{V}^{3+}$ emits yellow persistent luminescence around 520 nm after excitation for more than 1 h. Rare-earth metal-ion-doped luminescent materials are one of the earliest forms of long-afterglow luminescence; particularly, in 1996, T. Matsuzawa realized $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ and Dy^{3+} emit green LPL after 20 h by co-doping Dy^{3+} . Due to the variety of rare-earth ions and the variety of preparation methods, the luminescent color, luminescent intensity, and luminescent properties of these rare-earth metal-ion-doped luminescent materials are also varied, and these their preparation method is mature, with excellent performance. Praseodymium ion, as a rare earth ion in luminescent materials because of its unique energy level characteristics, is also of great significance. Pr^{3+} can produce a variety of emissions in different matrix materials with varying emission properties, and an emission wavelength that can be extended from the ultraviolet (UV) to the infrared region, attracting significant academic interest [10–16]. Recently, a significant number of Pr^{3+} -doped phosphors, scintillators, and LPL materials have been reported [10–16].

Xue et al. prepared a $\text{Sr}_3\text{TaAl}_3\text{Si}_2\text{O}_{14}:\text{Pr}^{3+}$ blue-green LPL material using a high-temperature solid-state method. The photoluminescence emission coincided with the persistent luminescence emission spectrum. The emission peak at 489 nm corresponds to the $^3\text{P}_0 \rightarrow ^3\text{H}_4$ transition of Pr^{3+} , and it has a long persistence time above 900 s [10]. In the same year, they reported that the emission peaks of a $\text{Sr}_2\text{Ta}_2\text{O}_7:\text{Pr}^{3+}$ blue LPL luminescent sample at 486 and 498 nm were attributed to the $^3\text{P}_0 \rightarrow ^3\text{H}_4$ transition, and the LPL decay time was determined to be >1200 s [11]. In Mg^{2+} and Pr^{3+} co-doped LiNbO_3 perovskite single crystals, Lin et al. found persistent bright-red LPL generated by a wide range of near-UV excitation; they then proposed a charge relaxation mechanism based on the transition between the intermediate defect states [12]. NaNbO_3 doped with Pr^{3+} ions could be excited in the near-UV region of approximately 350 nm, resulting in a bright single red emission at room temperature, which was attributed to the transition between the excited state, $^1\text{D}_2$, and the ground state, $^3\text{H}_4$, of the Pr^{3+} ions [13]. In summary, the electronic transitions corresponding to the red and near-infrared emissions of Pr^{3+} mainly include $^1\text{D}_2 \rightarrow ^3\text{H}_4$ (610 nm), $^1\text{D}_2 \rightarrow ^3\text{H}_5$ (720 nm), $^1\text{D}_2 \rightarrow ^3\text{H}_6$ (900 nm), and $^1\text{D}_2 \rightarrow ^3\text{F}_{3,4}$ (1080 nm). Also, Pr^{3+} -doped luminescent materials had stable red LPL properties. Pr^{3+} , as the luminescent center of red LPL, had broad application prospects in several fields, such as scintillators, emergency lighting, and biomedicine, and has been widely studied in the past [14,15].

In addition, Zhang et al. discovered that the mechanical luminescence in $\text{NaNbO}_3:\text{Pr}^{3+}$ and Er^{3+} was a physical phenomenon, whereby the material can emit light visible to the naked eye under the influence of stress, friction, scratch, fracture, and ultrasonic oscillation; they determined that it originates from the triple coupling of the piezoelectricity, trap energy level, and Pr^{3+} center [16]. Xu et al. reported a well-known multifunctional piezoelectric material that exhibited both piezoelectricity and efficient piezo-luminescence. In $\text{LiNbO}_3:\text{Pr}^{3+}$, Pr was substituted into the Li sites [17]. The prepared mechanical luminescent particles were embedded into polymers or other films into composite materials to achieve waterproofing and flexibility, and they could also provide multidimensional information that could be observed. The emergence of this multimode luminescent material enables Pr^{3+} -doped luminescent materials to offer unique insights for designing highly integrated stimuli-responsive smart devices and for applications in anti-counterfeiting, wireless detection, nondestructive analysis, stress sensing, damage diagnosis, and other fields.

During the past two decades, there were series of significant advances in the field of luminescent materials, including the discovery of new phosphors, the development of novel characterization methods, and an in-depth understanding of the mechanism of luminescence [18–22]. Among these, a series of well-known visible and infrared long persistent luminescent materials was discovered and rapidly applied in night vision monitoring, medical diagnosis, and optical information storage [23–27]. Additionally, NaNbO_3 and LiNbO_3 were promising optoelectronic lead-free insulating piezoelectric substrates, which were suitable for various applications, such as modulators, storage devices, sensors, and actuators [28,29].

Therefore, in this study, we prepared and analyzed a series of Pr^{3+} -doped niobate phosphor red LPL materials, combining the excellent properties of NaNbO_3 and LiNbO_3 matrices with Pr^{3+} luminescent centers to exhibit red LPL and ML properties. Through this study, we can further elucidate the structural properties, clarify the luminescence mechanism, and improve the luminescence performance of these materials. Owing to their red LPL and ML properties, Pr^{3+} -doped niobate phosphors can be employed in fields, such as display technologies, stress sensing, structural damage detection, image anti-counterfeiting of luminescent inks, and other complex applications.

2. Materials and Methods

$\text{NaNbO}_3:x\%\text{Pr}^{3+}$ ($x = 0.25, 0.50, 0.75, 1.00, 1.50$, and 2.00) samples were obtained using solid-phase sintering method. Nb_2O_5 (99.99%, Aladdin), Pr_6O_{11} (99.99%, Aladdin), and $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (99.99%, Aladdin) were weighed according to the ratio. They were then placed in an agate mortar, and an appropriate amount of anhydrous ethanol was added. The powders were ground and then placed into a vacuum drying oven (101.325 kPa, 80 °C, DZF-6050, Shanghai Boxun Industrial Co., Ltd. Medical Equipment Factory) for 1 h. Approximately 1 g of the dry powder was added into the mold; the pressure was 28 MPa, the holding time was 10 s, and the disc with thickness of 0.1–0.2 cm and diameter of 1.5 cm was pressed. The pressed flakes were placed in a crucible and sintered in a muffle furnace at 1150 °C. The heating rate was 5 °C/min, the holding time was 2 h, and the furnace was cooled. Using the same method, the Nb_2O_5 (99.99%, Aladdin), Pr_6O_{11} (99.99%, Aladdin), and Li_2O (99.99%, Aladdin) were weighed according to the ratio, and $\text{LiNbO}_3:\text{Pr}^{3+}$ was obtained at 1150 °C with a heating rate of 5 °C/min via solid-state sintering. The preparation of the sample also went through the steps of calculating the ratio, weighing, grinding, drying, tableting, sintering and cooling, and, finally, the sample was obtained for testing. And the two methods are very similar, such as tableting, as in the following steps. The wafer-type samples with thicknesses of 0.1–0.2 cm and diameters of 1.5 cm were formed by dry pressing. The prepared luminescent materials were tested by X-ray diffraction (XRD, Rigaku, DMAX-2500PC), and the phase compositions of the products and processes were analyzed. The microstructures and elemental compositions of the prepared luminescent materials were analyzed by field-emission scanning electron microscopy (SEM, Hitachi, JSM-6380LA). The fluorescence spectrum analysis was divided into two parts: excitation spectrum and emission spectrum, which can be used to characterize the luminescence characteristics of the sample. The persistent luminescent decay curve was the primary method used to characterize the long persistent luminescent properties of materials. The excitation and emission spectra and persistent luminescent decay curves of the samples were measured by F-7000 fluorescence spectrometer. The excitation source of the spectrometer was a 450 W xenon lamp, equipped with an R928P photomultiplier tube detector (250–900 nm). In order to avoid the influence of external light on the accuracy of the test spectrum, the sample is tested in an all-black environment. To evaluate the ML properties, round sheet (disc with thickness of 0.1–0.2 cm and diameter of 1.5 cm was pressed) samples were prepared. The samples were exposed to UV light; the ML intensity under a load was measured with a lab-made system comprising a universal testing machine (UTM, Jinanjixie, WDW-E) and a computer (Dell, AMD R5-5625U). According to the pressure and the contact area between the chuck grip and the samples, the applied pressure was calculated. Shooting was used to observe the change in the luminescence intensity of the sample like a change in stress to study the mechanical luminescence properties of the sample. Before each luminescence performance test, the sample needs to be heated at 400 °C for 30 min to empty the internal traps generated by the storage of the long persistent luminescent material, and then the excitation light is used to excite the sample.

3. Results and Discussion

3.1. Temperature and Structure

The microstructure and elemental composition of the $\text{NaNbO}_3\text{:Pr}^{3+}$ samples were analyzed using SEM and energy-dispersive X-ray spectroscopy (EDS). Figure 1 shows that the size of the $\text{NaNbO}_3\text{:0.5Pr}^{3+}$ grains gradually increased from 0.5 to 5 μm (Figure 1a–d) with temperature increases from 1000 $^{\circ}\text{C}$ to 1150 $^{\circ}\text{C}$. The powder sample is not dense, and the particle size is not uniform, but the particle size generally grows with an increase in temperature. Owing to the increase in temperature, the liquid-phase content increases, resulting in particle agglomeration. Another reason is that the increase in temperature provides more energy for the solid-phase reaction, and the chemical driving force is significant, which promotes the reaction. From Figure 1e,f, it can be observed that the powder has melted and is no longer granular. There are some annular holes on the surface, which may be caused by the bubble rupture when the gas inside the material is discharged during melting at 1200 $^{\circ}\text{C}$. There is no obvious grain boundary in the microscopic area of the scanned image. It can be observed from the EDS spectra in Figure 2 that there are uniformly distributed elements, such as Nb and Pr, in the observation area, except the local “bubbles”. Furthermore, there are circular bubbles and holes with a diameter of more than 5 μm in the intercepted area owing to the melting of the sample. It is confirmed that to reduce the inhomogeneity of the sample, the reaction temperature should be maintained at <1200 $^{\circ}\text{C}$. Compared with the convenience of taking and obtaining samples at 1150 $^{\circ}\text{C}$ and 1200 $^{\circ}\text{C}$, the optimal $\text{NaNbO}_3\text{:0.5% Pr}^{3+}$ preparation temperature is 1150 $^{\circ}\text{C}$. The microstructure and elemental composition of the $\text{LiNbO}_3\text{:Pr}^{3+}$ samples were analyzed using SEM and energy-dispersive X-ray spectroscopy (EDS) in Figure 3. Similarly, we analyzed the structure of $\text{LiNbO}_3\text{:Pr}^{3+}$ materials at different temperatures from Figure 3. It can be observed from Figure 3 that the shape of the $\text{LiNbO}_3\text{:0.5Pr}^{3+}$ is irregular spherical or blocky, and the size of its grains gradually increases (Figure 3a–d) with the temperature increase from 1000 $^{\circ}\text{C}$ to 1150 $^{\circ}\text{C}$. Figure 3e, shows, similar to NaNbO_3 , “annular holes and bubbles” are also generated on the surface of the 1200 $^{\circ}\text{C}$ $\text{LiNbO}_3\text{:0.5Pr}^{3+}$ sample. In addition to the uneven distribution of elements caused by high temperature (1200 $^{\circ}\text{C}$), the sample is not easy to remove and can become stuck to the crucible, which is inconvenient for subsequent operation. We can draw a conclusion, from this study, that the reaction temperature should be maintained at 1150 $^{\circ}\text{C}$.

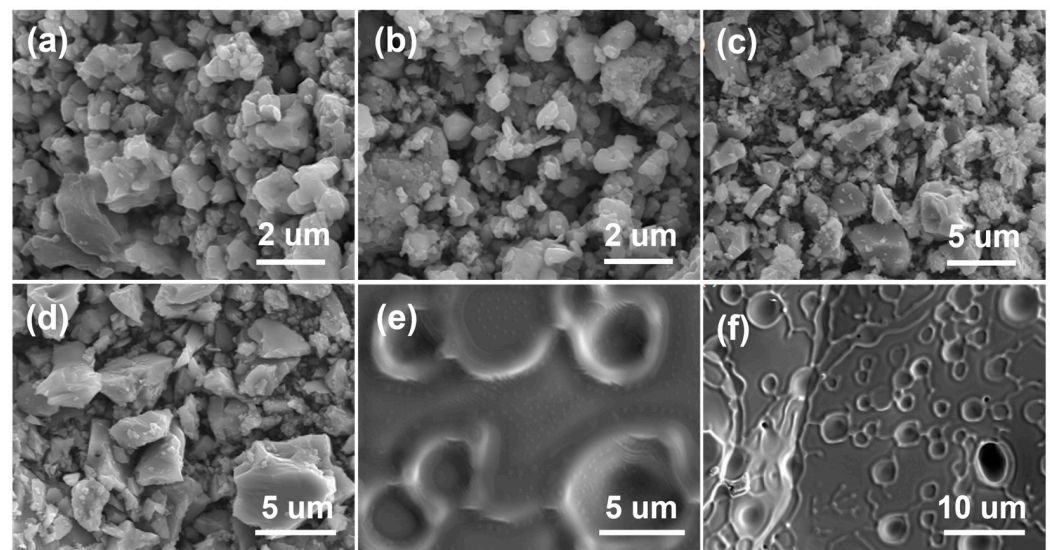


Figure 1. Microstructures of the fabricated $\text{NaNbO}_3\text{:0.5% Pr}^{3+}$ sintered at different temperatures by scanning electron microscopy (SEM). (a) 1000 $^{\circ}\text{C}$; (b) 1050 $^{\circ}\text{C}$; (c) 1100 $^{\circ}\text{C}$; (d) 1150 $^{\circ}\text{C}$; (e) 1200 $^{\circ}\text{C}$; (f) 1200 $^{\circ}\text{C}$.

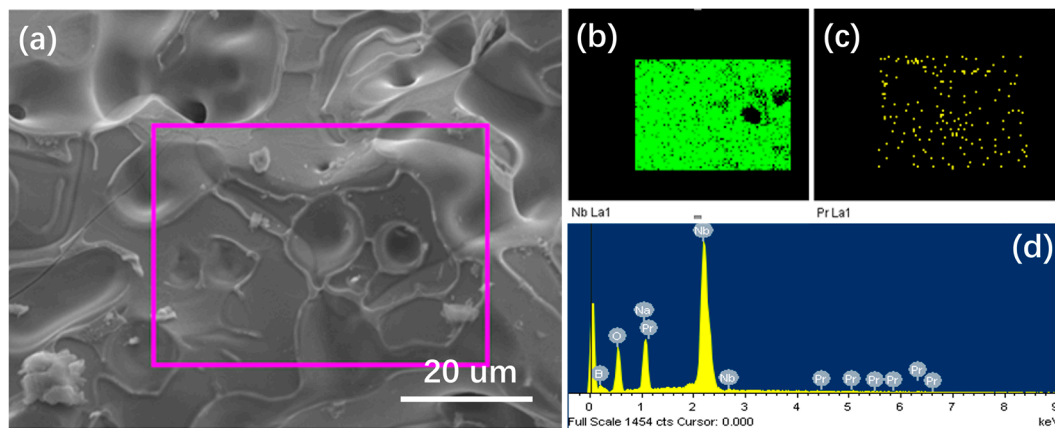


Figure 2. Energy Dispersive Spectrometer (EDS) spectrum analysis of $\text{NaNbO}_3:0.5\% \text{Pr}^{3+}$ prepared at 1200°C . (a) $\text{NaNbO}_3:0.5\% \text{Pr}^{3+}$ particles surfaces; (b) Na elemental analysis maps observed by EDX of (a); (c) Pr elemental analysis maps observed by EDX of (a); (d) a typical elemental analysis spectrum observed by EDX of (a).

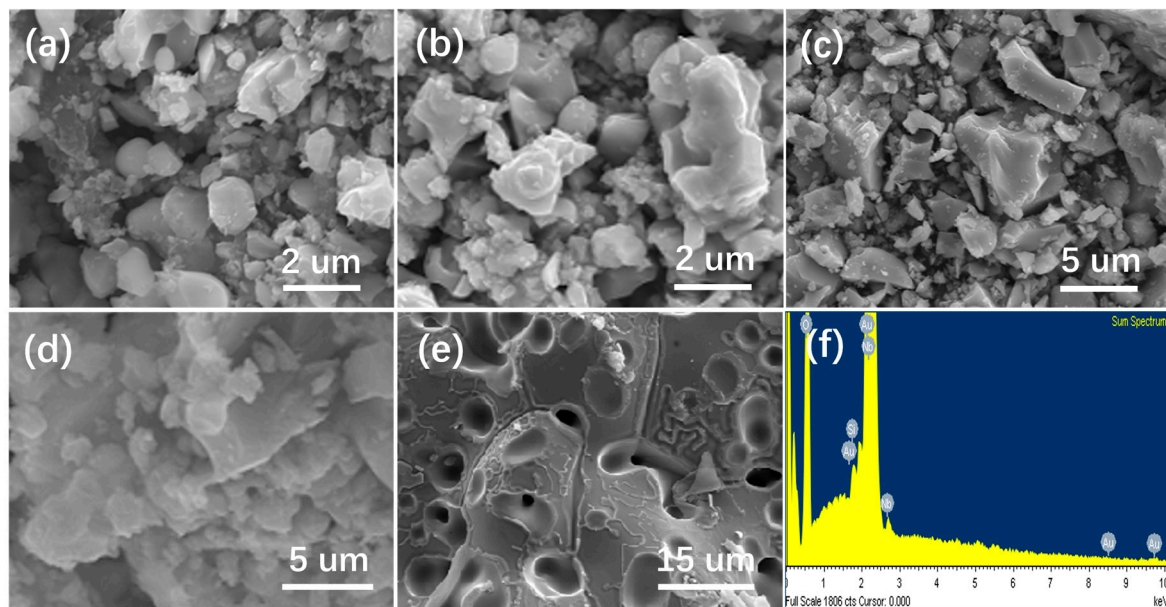


Figure 3. Microstructures of the fabricated $\text{LiNbO}_3:0.5\% \text{Pr}^{3+}$ sintered at different temperatures by scanning electron microscopy (SEM). (a) 1000°C ; (b) 1050°C ; (c) 1100°C ; (d) 1150°C ; (e) 1200°C ; (f) a typical elemental analysis spectrum observed by EDX of (e).

Figure 4 shows the XRD pattern of the $\text{NaNbO}_3:\text{Pr}^{3+}$ and $\text{LiNbO}_3:\text{Pr}^{3+}$ samples sintered at different temperatures. As shown in Figure 4a, the lattice diffraction peaks of the samples correspond well with the standard diffraction peaks of NaNbO_3 (No. 33-1270) in the PDF database, indicating that the formed crystal phases are NaNbO_3 crystal phases belonging to the orthorhombic system and Pbma space group [28,30]. As shown in Figure 4b, the lattice diffraction peaks of the samples correspond well to the PDF cards (No. 20-0631) of the crystal form of LiNbO_3 , and the formed LiNbO_3 crystal phases belong to the hexagonal crystal system and R3c space group [12]. With the increase in temperature, the crystallinity of $\text{NaNbO}_3:0.5\%\text{Pr}^{3+}$ and $\text{LiNbO}_3:0.5\%\text{Pr}^{3+}$ is gradually enhanced. No impurity phase was produced under different preparation conditions.

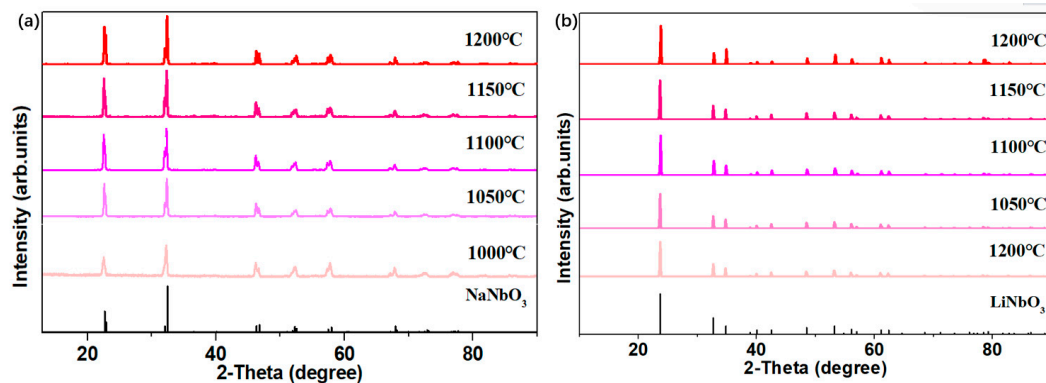


Figure 4. X-ray diffraction (XRD) pattern of $\text{NaNbO}_3:0.5\%\text{Pr}^{3+}$ and $\text{LiNbO}_3:0.5\%\text{Pr}^{3+}$ sintered at different temperature, (a) $\text{NaNbO}_3:0.5\%\text{Pr}^{3+}$; (b) $\text{LiNbO}_3:0.5\%\text{Pr}^{3+}$.

3.2. Persistent Luminescence Properties

The emission and excitation spectra and long persistent luminescence decay curves of $\text{NaNbO}_3:0.75\%\text{Pr}^{3+}$ are shown in Figure 5. From Figure 5a, it can be observed that the maximum excitation and emission peaks of the sample are at 329 and 612 nm, respectively. The luminescent properties of the materials are typically related to two factors: the crystal field provided by the matrix material and the electron transition and energy transfer of the doped ions. That is, owing to the deviation from stoichiometry and the lack of Na atoms, V_{Na}^- is universal, and excess Nb^{5+} will enter the Na site as $\text{Nb}_{\text{Na}}^{4+}$ to achieve charge compensation [13,31] owing to the $^1\text{D}_2 \rightarrow ^3\text{H}_4$ energy level transition of the Pr^{3+} ions. Therefore, red light can be observed by irradiating the sample with a 300–350 nm UV lamp. Figure 5b illustrates the luminescence intensities of the samples prepared at different sintering temperatures, which is excited at 329 nm. It can be observed that as the sintering temperature increases, the LPL intensity of the sample increases. This may be observed because the higher the temperature, the better the degree of crystallization becomes. Furthermore, the crystal field of the matrix material is affected, and the electron transition of the doped ions is improved. To investigate the luminescence of the samples, the LPL properties of the samples are shown in Figure 5c, which displays the LPL decay curves of $\text{NaNbO}_3:x\text{Pr}^{3+}$ ($x = 0.25, 0.50, 0.75, 1.00, 1.50$) ($\text{NaNbO}_3:\text{Pr}^{3+}$) obtained by monitoring at 612 nm for 1200 s after the 329 nm UV excitation was stopped for 10 min. It can be observed that when $x = 0.25, 0.50, 0.75, 1.00$, and 1.50 , the afterglow intensity of the material is not significantly different. When $x = 0.75$, the afterglow of the material is optimal. When $x < 0.75$, the LPL intensity increases with increasing x . When $x > 0.75$, the LPL intensity decreases with increasing x . Therefore, it is inferred that the optimal doping amount of Pr^{3+} in NaNbO_3 is 0.75 mol%. This also provides a good reference and the available process conditions for the preparation of this $\text{NaNbO}_3:\text{Pr}^{3+}$ material.

The emission and excitation spectra and long persistent luminescence decay curves of $\text{LiNbO}_3:\text{Pr}^{3+}$ are shown in Figure 5d–f. From Figure 5d, it can be observed that the maximum excitation and emission peaks of the sample are at 365 and 620 nm, respectively. There is a broad peak at 300–440 nm in the excitation spectrum, corresponding to the absorption of the LiNbO_3 host lattice, and the corresponding energy transfer is light source $\rightarrow \text{LiNbO}_3$ host lattice $\rightarrow \text{Pr}^{3+}$ luminescence center. The emission spectrum indicates that the sample emitted a bright-red light with high purity under excitation of 365 nm. The strongest emission peak of the emission spectrum is located at 620 nm, which corresponds to the energy level transition from $^1\text{D}_2$ to the ground state $^3\text{H}_4$ of Pr^{3+} . In addition, a secondary peak generated by the energy level splitting at 635 nm can also be observed. Otherwise, comparing $\text{NaNbO}_3:\text{Pr}^{3+}$ and $\text{LiNbO}_3:\text{Pr}^{3+}$, it can be seen that the highest positions of their excitation peaks and emission peaks are basically similar. This means that they have similar energy levels, electron transitions, and release pathways. This may be because Li^+ and Na^+ belong to the same main group in the periodic table of chemical elements, which means they have the same piezoelectric properties and trap energy, although their crystal structures are

different. On the other hand, $\text{NaNbO}_3\text{:Pr}^{3+}$ and $\text{LiNbO}_3\text{:Pr}^{3+}$, two materials that are doped rare-earth ions Pr^{3+} , have certain similarities in luminescence. And it provides effective help and information to analyze and study of luminescent materials. In addition, from Figure 5e,f, combined with the previous analysis and the luminescence characteristics of $\text{NaNbO}_3\text{:Pr}^{3+}$, similar conclusions are drawn: the most suitable sintering temperature of $\text{LiNbO}_3\text{:Pr}^{3+}$ is 1150°C , and the optimal doping amount of Pr^{3+} in LiNbO_3 is 2.00 mol%. This also provides a credible reference for the future comparison and application of these $\text{NaNbO}_3\text{:Pr}^{3+}$ and $\text{LiNbO}_3\text{:Pr}^{3+}$ materials in the future. We also analyze this in detail of $\text{LiNbO}_3\text{:Pr}^{3+}$ through Figure 5e,f. Figure 5e illustrates the luminescence intensities of the samples prepared at different sintering temperatures, which is excited at 365 nm. It can be observed that as the sintering temperature increases, the LPL intensity of the sample increases. To investigate the luminescence of the samples, the LPL properties of the samples are shown in Figure 5f, which displays the LPL decay curves of $\text{LiNbO}_3\text{:Pr}^{3+}$ obtained by monitoring at 620 nm for 1200 s after the 365 nm UV excitation is stopped for 10 min. Although the LPL intensity of the sample gradually decreases with time, the LPL intensity of the sample $\text{LiNbO}_3\text{:2%Pr}^{3+}$ is higher than that of other samples from beginning to end. It can be observed that the optimal doping amount of Pr^{3+} in LiNbO_3 is 2.00 mol%. Through the structural characteristics and luminescence properties of the samples, the most suitable sample preparation was determined, especially for the two points of good sample morphology and good luminescence intensity.

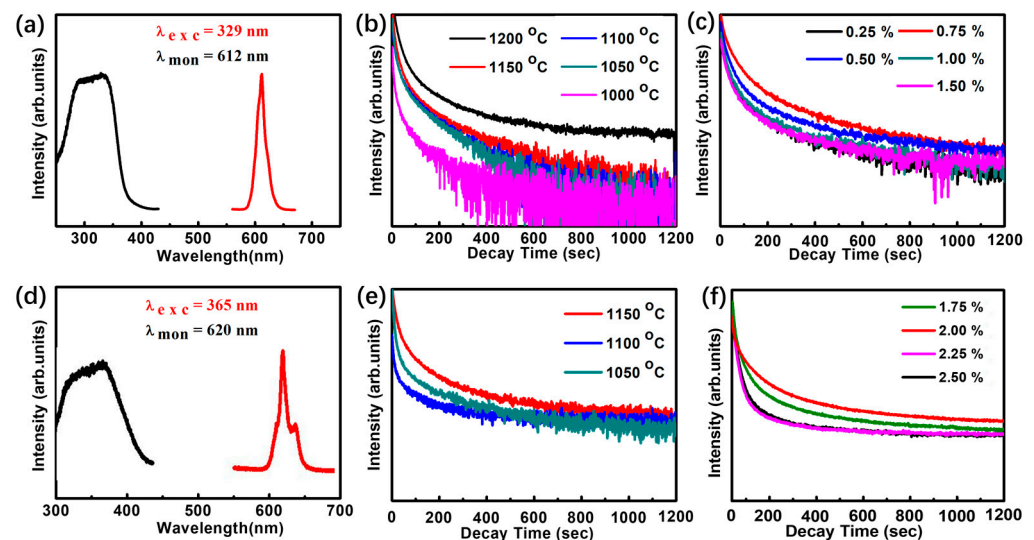


Figure 5. The emission and excitation spectra and long persistent luminescence decay curves. (a) $\text{NaNbO}_3\text{:0.75% Pr}^{3+}$: photoluminescence emission spectrum under 329 nm laser excitation and excitation spectrum monitoring at 612 nm; (b) the long persistent luminescence decay curves of $\text{NaNbO}_3\text{:0.75% Pr}^{3+}$ with different sintering temperature, luminescence decay curves under a 329 nm excitation for 10 min; (c) the long persistent luminescence decay curves of NaNbO_3 with different Pr^{3+} doping, luminescence decay curves under 329 nm excitation and excitation spectrum monitoring at 612 nm. (d) $\text{LiNbO}_3\text{:2.00% Pr}^{3+}$: photoluminescence emission spectrum under 365 nm laser excitation and excitation spectrum monitoring at 620 nm; (e) the long persistent luminescence decay curves of $\text{LiNbO}_3\text{:2.00% Pr}^{3+}$ with different sintering temperatures, luminescence decay curves under a 365 nm excitation for 10 min; (f) the long persistent luminescence decay curves of LiNbO_3 with different Pr^{3+} doping, luminescence decay curves under 365 nm excitation and excitation spectrum monitoring at 620 nm. The Y axis in (b,c,e,f) is in log scale.

3.3. Mechano-Luminescence Properties

After determining the most suitable preparation conditions, we fabricated the corresponding small discs to observe their mechanical luminescence properties. Under UV light, we can observe that the sample emits red light, and the sample is placed approx-

imately 4 cm after 10 min of excitation; the light source is then turned off, and the red afterglow can be observed. As shown in Figure 6, after 20 min of excitation under UV light, the disc edges are clamped using pliers. After the excitation light is removed, the disc demonstrates persistent luminescence. When the persistent luminescence weakens (stop excitation light for 1 min) and the grip strength of pliers' force grows (to 100 MPa), the edge of the sample suddenly becomes bright along specific textures and cracks and then darkens. This indicates that when the macroscopic sample is very thick and the luminescent center is sufficiently aggregated, an external force will affect the intensity of luminescence. Figure 6a demonstrates that the sample emits bright-red light under UV irradiation. The luminescence of the sample at the moment of turning off the UV lamp can be observed at this time in Figure 6b. Figure 6c shows the afterglow of the sample after closing the UV lamp for 1 min; it can be observed that the afterglow became weak. Figure 6d shows the change in the sample when the edge is clamped with a force of 100 MPa. When stress is applied, the edge luminescence intensity of the sample suddenly increases, and a bright-red light appears. Figure 6e,f show the luminescence intensities of the samples after 1 and 2 s, respectively. It can be observed that $\text{NaNbO}_3:\text{Pr}^{3+}$ exhibits mechanical luminescence, which the sample emits bright-red light that can be sustained with a force of 100 MPa. The long persistent luminescence lasts at least 2 s and can be strengthened by applying stress. This phenomenon is caused by the release of carriers trapped by stress [16]. This shows that $\text{NaNbO}_3:\text{Pr}^{3+}$ has a luminescence phenomenon of materials under mechanical stress, which provides the possibility for visual mechanical sensing.

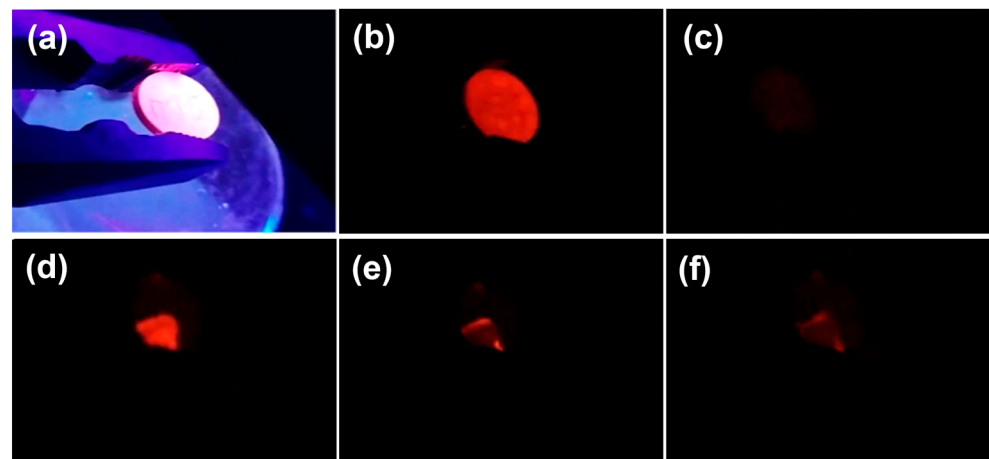


Figure 6. The digital photograph of $\text{NaNbO}_3:\text{Pr}^{3+}$ sample: (a) under UV excitation light; (b) stop UV excitation light; (c) stop excitation light for 1 min; (d) with a 100 MPa force; (e) with a 100 MPa force after 1 s; (f) with a 100 MPa force after 2 s.

In Figure 7, $\text{LiNbO}_3:\text{Pr}^{3+}$ shows the characteristics of red ML luminescence. Figure 7a,b show that, when a force of 100 MPa is applied, bright-red luminescence appears and lasts 1 s and 2 s, respectively. This is, also, consistent with the view that 'ML originates from the triple coupling of piezoelectric, trap energy and Pr^{3+} centers' [16]. From Figure 7 and previous Figures 5 and 6, we find that the two luminescent materials $\text{NaNbO}_3:\text{Pr}^{3+}$ and $\text{LiNbO}_3:\text{Pr}^{3+}$ exhibit similar red persistent luminescence and mechanical luminescence properties. This may be because, regarding $\text{NaNbO}_3:\text{Pr}^{3+}$ and $\text{LiNbO}_3:\text{Pr}^{3+}$, Li^+ and Na^+ belong to the same main group in the periodic table of chemical elements. Otherwise, comparing the two materials, although their crystal structures are different, they have the same piezoelectric properties, trap energy, and Pr^{3+} centers. Accordingly, we can also prepare and discover new LPL and ML luminescent materials according to this law, optimize the performance of LPL and ML luminescent materials, and apply luminescent materials to a broader field.

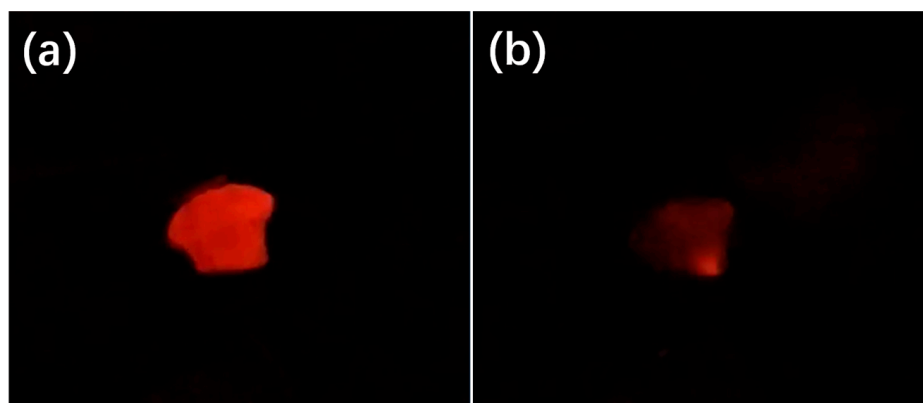


Figure 7. Mechano-luminescence properties of $\text{LiNbO}_3: \text{Pr}^{3+}$. (a) A digital photograph of luminescence intensity after 100 MPa force for 1 s. (b) A digital photograph of luminescence intensity after 100 MPa force for 2 s.

4. Conclusions

This study revealed the structure and luminescence properties of $\text{NaNbO}_3: \text{Pr}^{3+}$ materials via solid-phase sintering; the optimal parameters were determined to be 1150 °C for 2 h with a Pr^{3+} doping amount of 0.75%. The excitation and emission peaks of $\text{NaNbO}_3: \text{Pr}^{3+}$ occurred at 329 and 612 nm, respectively, corresponding to the $^1\text{D}_2 \rightarrow ^3\text{H}_4$ energy level transition. Similarly, the structure and luminescence properties of solid-phase-sintered $\text{LiNbO}_3: \text{Pr}^{3+}$ samples were clarified. The optimum process parameters were determined to be 1150 °C for 2 h, and the Pr^{3+} doping amount was 2.00%. The maximum excitation and emission peaks of the sample were at 365 and 620 nm. After excitation for 10 min, the red persistent luminescence lasted for at least 20 min for both $\text{NaNbO}_3: \text{Pr}^{3+}$ and $\text{LiNbO}_3: \text{Pr}^{3+}$. After 20 min of excitation under UV light, the sample exhibited a bright-red persistent luminescence. When the afterglow weakened, a stress of 100 MPa was applied, and the afterglow could be observed to become stronger. It was determined that $\text{NaNbO}_3: \text{Pr}^{3+}$ and $\text{LiNbO}_3: \text{Pr}^{3+}$ exhibited the properties of multimode luminescence. Based on the red persistent luminescence and mechano-luminescence properties, Pr^{3+} -doped niobate phosphors can be employed in fields such as the image anti-counterfeiting of luminescent inks and pressure-sensing transducers.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to the project is still in progress, the data is still updated.

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