A novel sol–gel route to synthesize $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ ceramics with enhanced electrocaloric effect

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$(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ ultra-fine powders were synthesized by a novel sol–gel route, and the mechanism of the reaction was discussed. SrCO_3 , BaCO_3 , oxalate niobium and citric acid were used to initiate the sol–gel process, and ethylene glycol (EG) was added to further polymerize the cross-linking structure. The evolution of the $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ phase, the reaction process and the microstructures were investigated by X-ray diffraction (XRD), Raman spectroscopy, Fourier transform infrared spectroscopy, DSC-TG and scanning electron microscopy. The synthesis temperature of the $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ powders reached as low as 1200°C , and the size and morphology of the powders were controlled by temperature. By adjusting the calcination temperature, we obtained $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ powders with uniform sizes of 20 nm to 500 nm. Then, dense $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ ceramics were successfully prepared using these ultrafine powders. Finally, an enhanced electrocaloric effect (ECE) value of 0.35°C was obtained at 100 kV/cm.

Keywords: Sol–gel process; $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$; ultrafine powders; electrocaloric effect.

1. Introduction

The electrocaloric effect (ECE) refers to the reversible change in temperature that occurs when a polar material is applied to an electrical field under adiabatic conditions. This effect is considered as a promising cooling technology because of its high-efficiency and environment-friendly working system.^{1–3} In the 21st century, a massive ECE was detected in $\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ and $\text{P}(\text{VDF-TrFE})$ thin films, successively.^{4,5} To date, related studies have been conducted on numerous ferroelectric films,^{6–8} polymers,^{9,10} and ceramics.^{11–13} In these works, the maximum ECE was calculated in $\text{Pb}_{0.8}\text{Ba}_{0.2}\text{ZrO}_3$ thin films.¹⁴ Unfilled tungsten bronze oxide strontium barium niobate $((\text{Sr}_x\text{Ba}_{1-x})\text{Nb}_2\text{O}_6, 0.25 \leq x \leq 0.75)$ drew considerable interest because of its excellent behavior as microwave resonator, ferroelectric RAM and pyroelectric detector.^{15–17} Recently, Hamad¹⁸ simulated the ECE of $(\text{Sr}_x\text{Ba}_{1-x})\text{Nb}_2\text{O}_6$ single-crystal thin films and certified that $(\text{Sr}_x\text{Ba}_{1-x})\text{Nb}_2\text{O}_6$ is a potential candidate for solid-state refrigeration.

In most cases, $(\text{Sr}_x\text{Ba}_{1-x})\text{Nb}_2\text{O}_6$ powders are synthesized through the conventional solid-state reaction method.^{19–21} The process is simple but requires a high temperature. Thus, the particle sizes of the synthesized powders tend to be large and nonuniform. To lower the synthesis temperature and decrease the particle size, scholars proposed the use of wet chemical methods. Co-precipitation reaction²² and the sol–gel route^{23,24} have been employed previously. In these methods, expensive and unstable organic metallic compounds

are used, and dry argon gas is flushed into the reaction container to protect the solution from water. Potassium hydroxide was added in some experiments.²⁵ If K^+ remains in the precursors, the ion would worsen the dielectric properties of $(\text{Sr}_x\text{Ba}_{1-x})\text{Nb}_2\text{O}_6$ ceramics. The sol–gel method is widely adopted because molecules and ions can react thoroughly in this approach, which then generates a uniform and transparent gel. Furthermore, the involved reaction easily proceeds to a sol–gel route. The sol–gel method has been proved to be a practical technique for preparing new materials. In our work, we utilized the sol–gel method to prepare $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ precursors. The sol–gel method reported previously was enhanced in the present study, and a novel sol–gel route was created. As a substitute for Nb_2O_5 , soluble oxalate niobium was introduced, eliminating the need to use HF solution or sulfuric acid.^{26,27} In the experiment, we employed simple inorganic salts and organic carboxylic acid to initiate the sol–gel process. We also added ethylene glycol (EG) to further polymerize the cross-linking structure.

In the present work, varied sizes of $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ powders were synthesized through a novel sol–gel route, and $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ dense ceramics were prepared using these ultrafine powders derived from the proposed process. The reaction process and microstructures during the evolution of $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ phases were investigated. With a Curie temperature T_c of about 50°C , the ECE of the $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ ceramics was calculated. Enhanced ΔT and ΔS

of 0.35°C and 0.41 J/(kg·K), respectively, were obtained at 100 kV/cm.

2. Experimental Procedures

Oxalate niobium (21.35%, Ningxia Orient Tantalum Industry), ammonia (25–28%, Sinopharm Chemical Reagent), SrCO_3 (> 99.95%, Aladdin), BaCO_3 (> 99.99%, Sinopharm Chemical Reagent), citric acid (CA; > 99.8%, Sinopharm Chemical Reagent) and EG (> 99.0%, Sinopharm Chemical Reagent) were used as reagents. Deionized water from an ultrapure water system (UP Ultrapure) was used. All procedures were performed under ambient conditions.

Oxalate niobium (0.1 mol) was dissolved in deionized water (500 mL, 25°C) and stirred constantly to give a clear solution. Subsequently, excessive ammonia (100 mL) was added to precipitate Nb^{5+} . Precipitates were then aged at 80°C for 12 h, filtered, and washed with deionized water to remove excessive ammonia. The precipitate obtained was added to a citrate acid solution with stirring at 80°C until Nb–citrate acid solution was formed. On the basis of the chemical formula $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$, reagents were obtained as the mole ratios of Sr:Ba:Nb 1:1:4. SrCO_3 was added to Nb–citrate acid solution and then stirred to form a transparent solution. Next, BaCO_3 was added to the solution and then stirred continuously until a colorless solution was achieved. EG was slowly added to complete esterification. Deionized water was evaporated, after which the solution became a homogenous sol with a light-yellow color. Subsequently, the sol was vacuum dried at 80°C until transformation into a highly viscous precursor gel. Precursors were heated from 600°C to 1200°C at a ramp rate of 5°C/min, and then the temperature was maintained for 3 h.

The powders synthesized by the sol–gel route after calcination were pressed as a cylinder-shaped sample of 12 mm diameter and 2–3 mm thickness under a pressure of about 98 MPa. $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ ceramics were obtained by sintering in air at 1275°C and 1300°C for 3 h.

Crystal structures and phase purities were identified by powder X-ray diffraction (XRD) analysis with $\text{CuK}\alpha$ radiation (D/max 3B; Rigaku Co., Tokyo, Japan) at room temperature. XRD data were collected over the 2θ range 10°–80°. The Raman spectra of the product powders were measured by a Nicolet ALMEGA Raman spectrometer with an existing line at 523 nm of a Nd:YAG laser at room temperature. The exposure time for every sample was 2.00 s, and the number of exposures was two times. NETZSCH STA 449F3 was used to detect thermal evolution at a heating rate of 5°C/min to 1350°C in nitrogen. The microstructures and morphology of the product powders and ceramics were observed by scanning electron microscopy (SEM; SU-70, HI-0026-0002). ECE measurements were performed using a broadband dielectric spectrometer (Turnkey Concept 50, Novocontrol Technologies GmbH & Co. KG, Hundsangen Germany) and a precision analyzer (RT Premier II, Radiant Technologies, Inc., NM).

3. Results and Discussion

Initially, CA was added to dissolve the precipitated hydroxide and carbonates. During neutralization, the CA chelated Nb^{5+} , Sr^{2+} and Ba^{2+} . The mole ratio of CA:metallic cation was 2:1, and the mass ratio of CA:EG was 40:60. The ratio of organic acids and EG played a critical role in the experimental procedure. Smaller mass ratios led to weaker precursor sol stability. As a result, molecules aggregated and precipitation occurred. In contrast, larger mass ratios contributed to the stability of the cross-linked structure but released a substantial amount of organic molecules during heating. Considering all the factors, we selected the mass ratio of 40:60 (Table 1 (A/B/C)). The solution pH was adjusted to pH 1–2 by dropping nitric acid. CA is a weak organic acid. Hence, when a solution contains massive H^+ amounts, CA does not easily ionize H^+ from its $-\text{COOH}$ and poor chelation with cations ensues. Meanwhile, if $\text{pH} > 10$ through ammonia addition, the reaction attains alkaline conditions, and metallic cations tend to precipitate. However, excessive ammonia would generate a transparent solution because NH_4^+ sequesters metallic cations from CA to form complex ions. The precursor gel then becomes black brown and solidification occurs after vacuum drying. Consequently, the gel becomes unavailable for spin coating.

CA is often employed in the Pechini method because the majority of metallic cations can be complexed with CA. The two $-\text{OH}$ s in EG hold a high tendency to complex with metallic cations, and this complexation is further stabilized by esterification. Three $-\text{COOH}$ s are present in CA, as displayed below, and two $-\text{OH}$ s exist in EG; these compounds are commonly used in pair.²⁸ CA initially participates in a neutralization reaction, where $\text{Nb}(\text{OH})_5$ is converted to Nb^{5+} , whereas Ba^{2+} and Sr^{2+} are complexed with CA.

The XRD patterns of the precursor powders derived from the sol–gel route and calcined at 600°C to 1200°C for 3 h are shown in Fig. 1. This figure reveals that the $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ major phase formed at the relatively low temperature of 600°C, under which H_2O and the organic compounds were decomposed and released. Some minor secondary phases did not disappear until the calcination temperature was raised to 1200°C.

The four minor peaks of the secondary phase located at 28°–31° are apparent in Fig. 1(b). These peaks were attained at 600°C. When the temperature was increased, the

Table 1. Precursor appearances with different mass or mole ratio reactants in various ambient conditions.

Solution	CA	EG	pH	Precursor
A	60	40	1–2	increased cracking after calcination
B	50	50	1–2	unstable gel
C	40	60	1–2	bright-yellow gel
D	40	60	> 10	dark brown, solidified

All solutions: Sr 0.025 mol; Ba 0.025 mol; Nb 0.1 mol; CA/Mⁿ⁺ 2:1.

Fig. 1. XRD patterns of the $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ powders synthesized through the sol-gel route after calcination at increasing temperatures in air: (a) 15° – 80° and (b) 25° – 35° .

diffraction peaks at $\sim 29^\circ$ and $\sim 31.5^\circ$, which were attributed to SrNb_2O_6 and BaNb_2O_6 , respectively, intensified gradually but completely disappeared at 1200°C . When the pH was 1–2, CA existed in two forms, namely, as free molecule and primary ionization ion, H_2Cit^- . Three structural arrangements of RCOO^- and metal cation were present (Fig. 2). The levels of HCit^{2-} and Cit^{3-} were decreased in the solution; thus, most metal ions remained as one-tooth complexing or bridge complexing compounds. Given the random M, these ions could be Ba^{2+} , Sr^{2+} and Nb^{5+} .

Fig. 2. Three probable structures of M-citrate: (a) one-tooth complexing, (b) two-tooth complexing and (c) bridge complexing.

The three types of polymerization include (i) $\text{Nb}(\text{H}_2\text{Cit})_n\text{--Sr}(\text{H}_2\text{Cit})_n\text{--Ba}(\text{H}_2\text{Cit})_n$, (ii) $\text{Nb}(\text{H}_2\text{Cit})_n\text{--Sr}(\text{H}_2\text{Cit})_n$ and (iii) $\text{Nb}(\text{H}_2\text{Cit})_n\text{--Ba}(\text{H}_2\text{Cit})_n$. Among these types, type (i) tends to form $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ and types (ii) and (iii) tend to develop SrNb_2O_6 and BaNb_2O_6 , respectively. In addition, two modes could coexist. Figure 3 displays the probable complexed structure and reaction equation. Under high temperatures, the samples transformed from their amorphous state to form crystals. Thus, the intensities of the XRD peaks of $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$, SrNb_2O_6 and BaNb_2O_6 all increased. When the ion distribution in the system was homogeneous and Sr^{2+} and Ba^{2+} are present in equivalent amounts, the reaction in (3.1) occurred at 1100°C . Accordingly, both SrNb_2O_6 and BaNb_2O_6 disappeared when the ion distribution increased to 1200°C .

The room temperature Raman spectra for the powders are summarized in Fig. 4. The spectra of the $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ precursor powders are similar to those of the $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ single crystals.²⁹ Three broad and strong $\text{A}_1(\text{TO})$ phonon peaks at 96, 243 and 631 cm^{-1} were observed. The strong peak at 635 cm^{-1} was assigned to the elongation of the O–Nb bond. However, the peaks located at 128, 176 and 198 cm^{-1} weakened and became hardly detectable in the $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ powders calcined at 1200°C . Meanwhile, the other three split peaks at 591, 628 and 683 cm^{-1} merged into one peak. These transformations were caused by the vanishing of SrNb_2O_6 , which reacted to $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$.³⁰ These results suggest that the $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ samples contained a small amount of incompletely reacted SrNb_2O_6 and BaNb_2O_6 at low calcination temperatures. At 1200°C , these minor secondary phases reacted to form $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$, and the Raman peaks located at wave numbers consequently disappeared. In general, the Raman spectroscopy results are consistent with the XRD findings.

A typical DSC trace is shown in Fig. 5(a) for the decomposition of SrCO_3 powders. The two endothermic transitions at 932.1°C and 1017.6°C are related to the different decomposition stages of carbonate in the reaction equation. The weight loss observed (30.76%) is consistent with the calculated value (29.8%).

The formation processes of SrNb_2O_6 and $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ are illustrated in Figs. 5(b) and 5(c), respectively. The weight losses resulting from the oxide formation may be calculated from the synthesis reaction as follows:

Fig. 3. (a) Probable structure of the M-citrate and (b) scheme for the polymerization reaction process on M-metal ions.

Fig. 4. Raman spectra of the $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ powders synthesized through the sol-gel route after calcination under increasing temperatures in air.

The good agreement between the calculated and experimental weight losses indicate that in the conventional solid-state method, SrNb_2O_6 and $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ could only be obtained at a high temperature ($\sim 1200^\circ\text{C}$).

Figure 5(d) presents the DSC-TG curves of the $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ precursor powders synthesized through the novel sol-gel route and calcined at 600°C . The curves only display an endothermic peak at 1233.9°C , which may correspond to the phase change of $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ at high temperature. A low weight loss percentage (1.07%) was detected when the $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ powders were heated at 1350°C . This result suggests that a phase change occurred at a high temperature but the details are unclear.

Surface and particle morphology micrographs are shown in Fig. 6. Uniform spherical-shaped $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$

Fig. 5. DSC and TG curves of reactant powders (a) SrCO_3 , (b) $\text{SrCO}_3 + \text{Nb}_2\text{O}_5$, (c) $\text{SrCO}_3 + \text{Nb}_2\text{O}_5 + \text{BaCO}_3$ and (d) $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ precursor synthesized through a novel sol-gel route and calcined at 600°C .

Fig. 6. SEM micrographs of $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ powders synthesized through a sol-gel route and calcined in air at (a) 600°C, (b) 700°C, (c) 800°C, (d) 900°C, (e) 1000°C, (f) 1100°C and (g) 1200°C compared with $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ powders prepared through the conventional solid-state reaction method at (h) 1200°C.

powders with an average size of about 20 nm were obtained after calcining at 600°C. With increasing calcination temperature from 600°C to 1200°C, the particles enlarged gradually. The average particle size was below 50 nm for the powders calcined at 600°C to 800°C, whereas a larger size of 500 nm was detected for the powders calcined at 900°C to 1100°C. Compared with the powders prepared through the solid-state method with sizes as large as above 1 μm , those synthesized through the sol-gel route were considerably advantageous in particle size. The suitable grain size and morphology of fine powders are valuable in optimizing the dielectric characteristics of sintered ceramics³¹; hence, the novel sol-gel route is superior to the solid-state method in this aspect.

$(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ ceramics were prepared using powders synthesized through the proposed novel sol-gel route. $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ tungsten bronze single-phase dense ceramics were obtained from the precursor powders calcined at 600°C and 1200°C and sintered at 1275°C and 1300°C (Fig. 7). Fine and uniform microstructures were achieved in the $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ ceramics derived from the powders calcined at 600°C, whereas abnormal grain growth was noted from the $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ ceramics prepared from the powders calcined at 1200°C (Fig. 8). Meanwhile, the $(\text{Sr}_{0.5}\text{Ba}_{0.5})$

Fig. 7. XRD patterns of the $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ ceramics sintered at 1275°C and 1300°C using $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ powders calcined at 600°C and 1200°C.

Nb_2O_6 ceramics fabricated through the solid-state reaction possessed coarse grain sizes in nonuniform distribution.

Figure 9 illustrates the temperature dependence of the dielectric constant and the dielectric loss of the $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ ceramics derived from the powders calcined at 600°C at various frequencies. Slightly dispersed dielectric frequency peaks are located at $\sim 50^\circ\text{C}$ and suggests the role of

Fig. 8. SEM micrographs of the $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ ceramics sintered at 1275°C and 1300°C using the $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ powders calcined at (a) 600°C, (b) 1200°C and (c) $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ ceramics prepared by conventional solid-state reaction method.

Fig. 9. Temperature dependence of the (a) dielectric constant and (b) dielectric loss of the $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ ceramics at various frequencies.

$(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ as a relaxor ferroelectric. In Fig. 10, an electric hysteresis loop measures from 30°C to 180°C. Reversible adiabatic changes ΔT and ΔS were calculated in accordance with the indirect measurement equations

Fig. 10. P - E loops of $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ ceramics measured at 30°C–180°C.

given below:

$$\Delta T = -\frac{T}{\rho C_E} \int_{E_1}^{E_2} \left(\frac{\partial P}{\partial T} \right)_E dE$$

$$\Delta S = - \int_{E_1}^{E_2} \left(\frac{\partial P}{\partial T} \right)_E dE$$

where $(\partial P/\partial T)$ is obtained from a five-order polynomial fitted to $P(T)$ and extracted from P - E loops (Fig. 10). ρ is the density and C_E is the heat capacity. Under the temperature of interest, the density is 5.06 g/cm³, and the C_E is 465 J/(g·K). Finally, the calculated ΔT and ΔS were 0.35°C and 0.41 J/(kg·K), respectively, under an applied electric field of 100 kV/cm at 120°C (Fig. 11).

Fig. 11. ECE results of the $(\text{Sr}_{0.5}\text{Ba}_{0.5})\text{Nb}_2\text{O}_6$ ceramics at an applied electric field of 100 kV/cm: (a) reversible temperature change ΔT and (b) isothermal entropy change ΔS .

4. Conclusions

($\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$) ultrafine powders were synthesized through a novel sol-gel route that involves a polymerization reaction. Three types of polymerizations occurred and formed ($\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$, SrNb_2O_6 and BaNb_2O_6) at elevated temperature. SrNb_2O_6 and BaNb_2O_6 reacted at 1100°C and were converted into ($\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$) completely. Relative to those in the conventional solid-state reaction, the present novel sol-gel route lowered the synthesis temperature of the ($\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$) powders and the sintering temperature of the corresponding ceramics. ($\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$) powders with uniform particle sizes of 20 nm to 500 nm were obtained by calcining the precursors from 600°C to 1200°C , respectively. The ($\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$) dense ceramics prepared from the ultrafine powders exhibited fine grain sizes, a desirable property. An ECE of $\Delta T = 0.35^\circ\text{C}$ was calculated at 120°C under an applied electric field of 100 kV/cm.

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