

Structurally Characterized Erbium Alkoxides for Use as an Amphoteric Dopant in PErZT Ceramic Thin Film and Nanoparticles

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A family of erbium alkoxides [Er(OR)₃] was prepared from the reaction of Er[N(SiMe₃)₂]₃ with a series of alcohols (HOR) in selected solvents and crystallographically characterized as: [Er(μ-Onep)₂(Onep)]₄, (**1**), [Er₄(μ₄-O)(μ₃-Onep)(μ-Onep)₅-(Onep)₄(py)₃] (**3**), Er₃(μ₃-OtBu)₂(μ-OtBu)₃(OtBu)₄(HOtBu)₂ (**4**), Er₃(μ₃-O)(μ-OtBu)₄(OtBu)₃(py)₃ (**7**), Er(dmp)₃(solv)₃ [solv = thf (**9**), py (**10**)], [Er(η-dip)(dip)₂]₂ (**11**), Er(dip)₃(thf)₂ (**12**), [Er(μ-OH)(dbp)₂(thf)]₂ (**15**), Er(dbp)₃(py)₂ (**16**), [Er(μ-tps)(tps)₂]₂ (**17**), Er(tps)₃(solv)₃ [solv = thf (**18**) and (py) (**19**)] where Onep = neopentoxide (OCH₂CMe₃), OtBu = *tert*-butoxide (OCMe₃), dmp = 2,6-dimethylphenoxide [OC₆H₃-(Me)₂-2,6], dip = 2,6-diisopropylphenoxide [OC₆H₃-(CHMe₂)₂-2,6], dbp = 2,6-di-*tert*-butylphenoxide [OC₆H₃-(CMe₃)₂-2,6], tps = triphenylsiloxide [OSi(C₆H₅)₃], tol = tolu-

ene, thf = tetrahydrofuran, and py = pyridine. The structures observed and data collected for the Er family of compounds are, in general, consistent with those reported previously for the Dy congeners over the range of solvated mono-, di-, tri-, and tetranuclear species. Representative members of the Er(OR)₃ precursors were used for the production of a PErZT precursor solution, which was subsequently used to generate thin films and nanoparticles. Further, these select Er precursors were used to generate Er₂O₃ nanoparticles. The full characterization of this family of compounds is reported along with the results of the materials investigations.

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Introduction

The perovskite phase of lead zirconium titanate (PZT) has found utility in a wide range of applications including ferroelectric nonvolatile random access memories, sports equipment, window tinting, sensors, smart cards, and numerous other electronic applications.^[1–6] However, PZT ceramic materials demonstrate rapid fatigue when cycled on standard platinized silica (Pt/Si) supports. Recently, we reported on the “aliovalent cation effect” (ACE) where the PZT thin films fatigue properties were improved through selective doping with lanthanide (Ln) cations that could occupy either the A or B site.^[7,8] In particular, the Dy-doped PZT films (PDyZT) were found to possess high remanent polarization (*P_r*), high dielectric constant (*ε'*), and reduced fatigue when cycled on Pt/Si wafers.^[7,8] Due to the void of acceptable dysprosium alkoxide [Dy(OR)₃] precursors (see Table 1), it was necessary to synthesize and characterize a series of systematically varied Dy(OR)₃ compounds (21 new

compounds) to determine the optimal Dy-dopant precursor.^[8] From this novel family of compounds, the 2,6-diisopropylphenoxide (dip) derivative yielded the highest quality PDyZT films with impressive fatigue resistance. In an effort to further explore this phenomenon we were interested in determining where the edges of the ACE stopped. Fortunately, the Ln series possesses a systematic change in the +3 Ln cations, which allows for a controlled probing of the ACE phenomenon in PZT ceramic thin films. However, for the smaller lanthanides, there are surprisingly few structurally characterized alkoxides available in the literature.^[9–11]

Therefore, to further develop this neglected area and identify new sol-gel precursors, we undertook the synthesis and characterization of a systematically varied family of Er(OR)₃ in a variety of solvents. These compounds were isolated following Equation (1), where the alcohol (H-OR) ranged from H-Onep = neopentyl alcohol (H-OCH₂CMe₃), H-OtBu = *tert*-butyl alcohol (H-OCMe₃), H-dmp = 2,6-dimethylphenol [H-OC₆H₃(Me)₂-2,6], H-dip = 2,6-diisopropylphenol [H-OC₆H₃(CHMe₂)₂-2,6], H-dbp = 2,6-di-*tert*-butylphenol [H-OC₆H₃(CMe₃)₂-2,6], H-tps = triphenylsilanol [H-OSi(C₆H₅)₃] using a variety of solvents: tol = toluene, thf = tetrahydrofuran, and py = pyridine. The general matrix used in this study led to the synthesis of compounds **1–19** and is shown in Table 1 along with a comparison to the Dy(OR)₃ compounds that were previously

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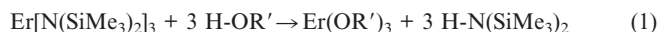
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Table 1. List of structure types isolated for the matrix of ligands and solvents used to explore $\text{Er}(\text{OR})_3$ and $\text{Dy}(\text{OR})_3$ structures. The nuclearity is listed and in parentheses the type of interaction used by the ligands to form the molecule and/or the number of solvent molecules bound.

Er	tol	thf	py	HOR
Onep	1 tetra (μ , 0)	[a]	3 tri (μ and μ_3 ; 3)	[a]
OrBu	[a]	[a]	7 tri (μ and μ_3 ; 3)	4 tri (μ and μ_3 ; 2)
dmp	[a]	9 mono (3)	10 mono (3)	[a]
dip	11 di (π ; 0)	12 mono (2)	[a]	[a]
dbp	[a]	15 di (2)	16 mono (2)	[a]
tps	17 di (μ , 0)	18 mono (3)	19 mono (3)	
Dy	tol	thf	py	NH_3
Onep	tetra (μ , 0)	tri (μ and μ_3 ; 2)	tri (μ and μ_3 ; 2)	hex
OrBu	tri (μ and μ_3)	tri (μ and μ_3 ; 2)	tri (μ and μ_3 ; 2)	[a]
dmp	di (π ; 0)	mono (3)	mono (3)	linear tri (2)
dip	di (π ; 0)	mono (2)	mono (3)	mono (2)
dbp	mono (0)	mono (1)	mono (2)	mono (1)
tps	di (μ)	mono (3)	mono (3)	[a]

[a] No acceptable crystal solutions reported.

isolated.^[8] From this matrix, the following $\text{Er}(\text{OR})_3$ compounds were crystallographically characterized as: $[\text{Er}(\mu\text{-Onep})_2(\text{Onep})_4]$ (**1**), $[\text{Er}_4(\mu_4\text{-O})(\mu_3\text{-Onep})(\mu\text{-Onep})_5(\text{Onep})_4(\text{py})_3]$ (**3**), $\text{Er}_3(\mu_3\text{-OrBu})_2(\mu\text{-OrBu})_3(\text{OrBu})_4(\text{HOtBu})_2$ (**4**), $\text{Er}_3(\mu_3\text{-O})(\mu\text{-OrBu})_4(\text{OrBu})_3(\text{py})_3$ (**7**), $\text{Er}(\text{dmp})_3(\text{solv})_3$ [$\text{solv} = \text{thf}$ (**9**), py (**10**)], $[\text{Er}(\eta\text{-dip})(\text{dip})_2]$ (**11**), $\text{Er}(\text{dip})_3(\text{thf})_2$ (**12**), $[\text{Er}(\mu\text{-OH})(\text{dbp})_2(\text{thf})_2]$ (**15**), $\text{Er}(\text{dbp})_3(\text{py})_2$ (**16**), $[\text{Er}(\mu\text{-tps})(\text{tps})_2]$ (**17**), $\text{Er}(\text{tps})_3(\text{thf})_3$ (**18**), $\text{Er}(\text{tps})_3(\text{py})_3$ (**19**). The synthesis and full characterization of these compounds are discussed. Suitable crystals were not isolated for compounds **2** (Onep/thf), **5** (OrBu/tol), **6** (OrBu/thf), **8** (dmp/tol), **13** (dip/py), **14** (dbp/tol) and additional discussion of these compounds will not be pursued since their structures were not unequivocally established.



Representative species from this novel family of compounds were used to explore their utility for the production of ceramic materials. The ACE for PERZT thin films was probed using **11** as the dopant precursor due to the similarity with the Dy counterpart (Table 1).^[7,8] Further, since new properties were expected on the nanoscale, attempts were made to generate Er_2O_3 and PERZT nanoceramics. With this wide variety of structurally varied species, it was possible to further explore the “precursor structure argument” (PSA)^[12–16] for nanoparticle morphology predictions. A solution route to nanoparticles of Er_2O_3 was discovered using **1** and **11**. Full details of the synthesis, characterization, and subsequent properties of these precursors and materials are presented.

Results and Discussion

A systematically varied series of $\text{Er}(\text{OR})_3$ was required in order to initiate the material evaluation of Er ceramics with controlled properties. A search of the literature reveals only two $\text{Er}(\text{OR})_3$ had been previously crystallographically

characterized including $\text{Er}_5(\mu_5\text{-O})(\mu_3\text{-OiPr})_4(\mu\text{-OiPr})_4(\text{OiPr})_5$ ^[10,11] and $\text{Er}(\text{dip})_3(\text{thf})_2$.^[9] The remainder of alkoxy-like species possess other metals,^[17–21] halides,^[22] or poly-functional ligands^[23] which prevents use for generation of high quality ceramic oxide materials due to the potential cross cation, anion, and/or residual ligand contamination. Due to the lack of available $\text{Er}(\text{OR})_3$ compounds, it was necessary to synthesize a series of precursors to determine the optimal species. A study of a matrix of sterically varied precursors in different solvents was undertaken (see Table 1). For this report, only those compounds that were crystallographically characterized will be discussed.

Synthesis

On the basis of our previous experience with the problems associated with the ammoniacal route, we elected to use the amide/alcohol metathesis route that proved beneficial for the Dy system.^[8] The $\text{Er}(\text{NR}_2)_3$, where $\text{NR}_2 = \text{N}(\text{SiMe}_3)_2$, was synthesized according to established routes involving the metathesis reaction between ErCl_3 and 3 equiv. of KNR_2 in thf.^[8,24–29] The resultant powder isolated from the metathesis route was sublimed and crystallized to ensure pure starting material. It is of note that purification of the $\text{Er}(\text{NR}_2)_3$ is critical to the successful isolation of crystalline material. Once isolated, this precursor was treated with a variety of alcohols as shown in Equation (1) (Table 1).

The majority of samples remained clear after stirring for 12 h; however, those that formed a precipitate, typically the more sterically demanding ligands, were warmed slightly to redissolve the powder. Crystals were either isolated by slow evaporation or rotary evaporation of the volatile portion of the reaction mixture followed by cooling the reaction mixture to -35°C , if necessary.

FTIR data of the resultant powders revealed no amide stretches and, for the majority of samples no $-\text{OH}$ stretches, which implies complete substitution had occurred between the amide and the alcohol. Two exceptions to this were the spectra noted for compound **4** and **15**, which showed broad IR stretches around 3000 cm^{-1} associated with the bound H-OrBu and the $-\text{OH}$, respectively. In general, elemental analyses were found to be consistent with the single-crystal X-ray structures isolated (vide infra) for these compounds. Those that were off slightly from expected values were solvated species and the high volatility of the bound solvent often causes significant problems in obtaining accurate analyses.^[8,30] Due to the paramagnetic nature of the Er metal center, we were unable to get meaningful NMR spectroscopic data either in solution or solid-state. Therefore, single-crystal X-ray diffraction studies were undertaken to assist in elucidating the identity of the final products isolated.

Crystal Structures

As mentioned only two structures of $\text{Er}(\text{OR})_3$ have previously been reported.^[9–11] Obviously, no general trends can

be discerned from this limited set of precursors but comparisons to literature compounds will be made when appropriate. Figures 1, 2, 3, and 4 are the structure plots of representative crystal structures for this family of compounds. The various compounds are discussed below in order of the ligand increasing steric bulk of the ligand.

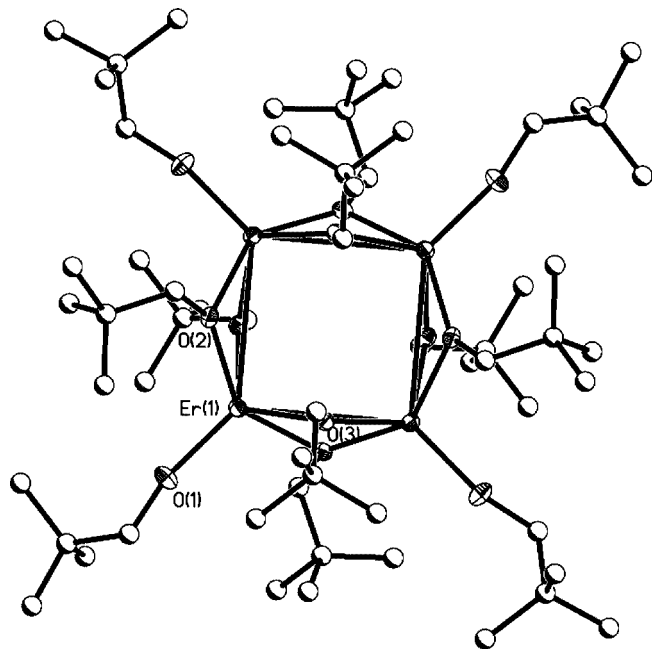


Figure 1. Structure plot of **1**. Thermal ellipsoids of heavy atoms are drawn at the 30% level and carbon atoms are shown as stick and ball for clarity. Selected bond lengths [Å]: Er(1)–O(1) 2.033(5); Er(1)–O(2) 2.241(6); Er(1)–O(3) 2.244(6). Selected bond angles [°]: O(1)–Er(1)–O(3) 122.8(3); O(1)–Er(1)–O(2) 112.9(3); O(3)–Er(1)–O(2) 72.7(2); O(1)–Er(1)–O(3) 118.3(3); O(2)–Er(1)–O(3) 89.5(3); O(1)–Er(1)–O(2) 105.8(3); O(3)–Er(1)–O(2) 86.9(2); O(3)–Er(1)–O(2) 71.7(2).

Using the more sterically demanding Onep ligand reduced the nuclearity and prevented the formation of an oxo ligand as noted for the smaller *OiPr* derivative $\text{Er}_5(\mu_5\text{-O})(\mu_3\text{-}i\text{Pr})_4(\mu\text{-}i\text{Pr})_4(\text{O}i\text{Pr})_5$.^[10,11] The resultant species, identified as $[\text{Er}(\mu\text{-Onep})_2(\text{Onep})]_4$ (**1**), is consistent with the other Ln- and Group 3 neopentoxide species (Figure 1)^[31] wherein, each of the four trigonal bipyramidal (TBP) Er metal centers possess two $\mu\text{-Onep}$ and one Onep ligand. Attempts to isolate this compound using the Lewis basic solvents thf (**2**) did not lead to X-ray quality crystals; however, from py the tetramer observed in **1** was reduced to a trinuclear species surprisingly forming an oxo species, $[\text{Er}(\mu_3\text{-O})(\mu\text{-Onep})_6(\text{Onep})_4(\text{py})_3]$ (**3**). The source of the oxo species is not known as of yet and typically not observed for the Onep derivatives, unless esterification mechanisms from side reactions with carboxylic acids occur but may be due to adventitious water in the solvent.^[30–32]

Increasing the steric bulk to the *OtBu* groups, led to crystallization of the trinuclear **4** which had additional *HOtBu* bound to it, as shown in Figure 2. Previously, we isolated a Ce/*OtBu* tetramer^[30] that did not possess any

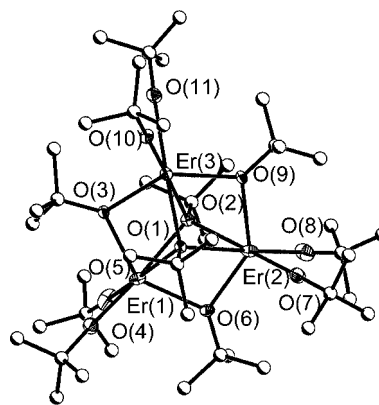


Figure 2. Structure plot of **4**. Thermal ellipsoids of heavy atoms are drawn at the 30% level and carbon atoms are shown as stick and ball for clarity. Selected bond lengths [Å]: Er(1)–O(1) 2.305(3); Er(1)–O(2) 2.371(3); Er(1)–O(3) 2.269(3); Er(1)–O(4) 2.525(4); Er(1)–O(5) 2.067(3); Er(1)–O(6) 2.250(3). Selected bond angles [°]: O(5)–Er(1)–O(6) 106.17(13); O(5)–Er(1)–O(3) 104.93(13); O(6)–Er(1)–O(3) 143.78(12); O(5)–Er(1)–O(1) 109.45(13); O(6)–Er(1)–O(1) 76.35(12); O(3)–Er(1)–O(1) 76.16(12); O(5)–Er(1)–O(2) 177.71(13); O(6)–Er(1)–O(2) 74.47(12); O(3)–Er(1)–O(2) 73.78(12); O(1)–Er(1)–O(2) 68.48(11); O(5)–Er(1)–O(4) 74.73(14); O(6)–Er(1)–O(4) 101.31(13); O(3)–Er(1)–O(4) 104.40(12); O(1)–Er(1)–O(4) 175.59(12); O(2)–Er(1)–O(4) 107.37(12).

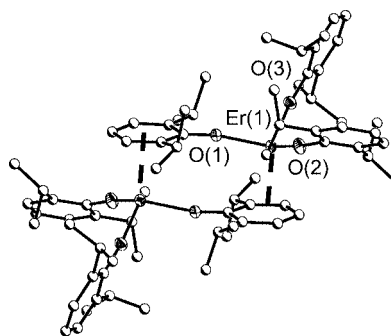


Figure 3. Structure plot of **11**. Thermal ellipsoids of heavy atoms are drawn at the 30% level and carbon atoms are shown as stick and ball for clarity. Selected bond lengths [Å]: Er(1)–O(1) 2.096(18); Er(1)–O(3) 2.069(17); Er(1)–O(2) 2.095(18); Er(1)–ring 2.81 Å. Selected bond angles [°]: O(2)–Er(1)–O(1) 109.3(7); O(2)–Er(1)–O(3) 102.5(7); O(3)–Er(1)–O(1) 106.3(7); O(1)–Er(1)–ring 108.1(9); O(2)–Er(1)–ring 83.9(9); O(3)–Er(1)–ring 140.6(8).

Lewis basic solvents (i.e., thf, py, or *HOtBu*) however, the Er corollary could not be isolated without bound solvents as noted for the pyridine adduct, $\text{Er}_3(\mu_3\text{-O})(\mu\text{-}i\text{Pr})_4(\text{O}i\text{Pr})_5(\text{py})_3$ (**7**). Again, the py adduct appears to produce the oxo which argues for water present in the py; however, numerous structures using the same solvent did not yield the oxide, so the origin of the oxo is still unproven. This complex is similar to **4** and other trinuclear species where the terminal ligands are now replaced by these stronger.

Aryl oxides are often used to control nuclearity because the steric bulk around the metal center can be easily altered.^[8,12,13,30,33–36] We routinely use the most sterically demanding di-*ortho*-substituted phenoxide ligands to induce as large an effect as possible. The resulting products are again discussed in increasing steric demand (dmp, dip,

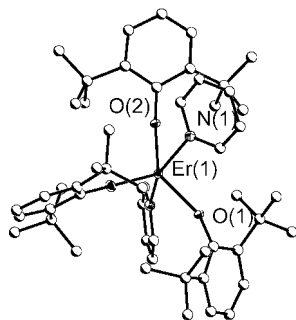


Figure 4. Structure plot of **16**. Thermal ellipsoids of heavy atoms are drawn at the 30% level and carbon atoms are shown as stick and ball for clarity. Selected bond lengths [Å]: Er(1)–O(2) 2.095(4); Er(1)–O(1) 2.161(3); Er(1)–O(1A) 2.161(3); Er(1)–N(1) 2.469(4); Er(1)–N(1A) 2.469(4). Selected bond angles [°]: O(2)–Er(1)–O(1) 112.54(8); O(2)–Er(1)–O(1A) 112.54(8); O(1)–Er(1)–O(1A) 134.92(16); O(2)–Er(1)–N(1) 101.96(9); O(1)–Er(1)–N(1) 81.96(12); O(1)–Er(1)–N(1A) 88.91(13); O(2)–Er(1)–N(1A) 101.96(9); O(1A)–Er(1)–N(1A) 88.91(13); O(1A)–Er(1)–N(1) 88.96(12); N(1)–Er(1)–N(1A) 156.08(18).

dbp). For the dmp derivative, large clear crystals were easily isolated from toluene but the diffraction was poor and an acceptable structure solution could not be garnered for **8**. Therefore, we employed the Lewis basic solvents to assist in growing acceptable crystals. For both thf and py, mononuclear species with three solvents to form an octahedral geometry were isolated as Er(dmp)₃(solv)₃ [solv = thf (**9**) and py (**10**)].

Increasing the steric bulk of the *ortho* substituent to isopropyl groups led to the isolation of **11** (Figure 3). The η -interaction noted for **11** is the same as previously noted for the La,^[37] Nd,^[9] and Dy^[8] systems. Again, the η -interaction was easily disrupted using Lewis basic solvents forming the trigonal bipyramidal (TBP) monomeric species **12** for the thf adduct.

Using the most sterically demanding dbp ligand, crystals of the unsolvated species **14** could not be isolated in high quality; however, in the presence of a Lewis base, two very different species were characterized. Out of thf, a dinuclear thf adduct was isolated as **15**. Surprisingly, the dinuclear species possesses a μ -OH group which was not identified for the Dy series^[8] but have been reported for other lanthanides species including, [(μ -OH)Yb(OAr)₂(thf)]₂ (OAr = dbp,^[38] dbp-But-4,^[38,39]) and [(μ -OH)Sm(dbp-Me-4)₂(OPPh₃)]₂.^[40] Increasing the Lewis basicity of the solvent to py led to the TBP monomer **16** (Figure 4). It is most likely not due to adventitious water in the solvent or it would have been observed in the Dy system.^[8]

Siloxide ligands offer the potential for the production of Si-containing materials and slightly different ligand properties both sterically and electronically. Therefore, we added the tps ligand into our structural investigation. The tps derivatives isolated for the Er system are consistent with the Dy(tps)₃ structure^[8] wherein a dinuclear complex was isolated from tol (**17**) with μ -tps and terminal tps in standard edge-shared tetrahedral-bound metal centers. Subsequent monomers were isolated from Lewis basic solvents as **18**

and **19**, for thf and py. The bulky tps ligands allow for tetrahedral (Td) arrangements for the metal centers of **17** and octahedral (Oh) geometries for **18** and **19** through the binding of three solvent molecules.

In general, the structures noted for the Er system were consistent with the Dy(OR)₃ precursors previously reported;^[8] however, **15** does prove that unaccounted variations are possible, and probable. Surprisingly, a number of compounds could not be successfully isolated for the Er system that were easily isolated for the Dy system.^[8] Subtle effects that dictate crystal growth are at play and require further investigations.

Materials

With these compounds successfully characterized, a sufficient number and variety of species were available for systematic materials structure–property investigations. Two systems were investigated: Er-doped PZT (or PErZT) thin films for electronic properties and nanomaterials of Er₂O₃ and PErZT.

Film Characteristics

The precursor solutions of Pb_{0.98}(Er)_{0.04}(Zr_{0.3}Ti_{0.7})_{0.98}O₃ [PErZT(4/30/70)] and Pb_{0.98}(Er)_{0.04}(Zr_{0.52}Ti_{0.48})_{0.98}O₃ [PErZT(4/52/48)] were prepared as described in the experimental section. Selection of the Er dopant on the B site of the perovskite is based on previous studies and a dopant concentration of 4% Er was selected to maximize the possible effects of the dopant without creating unwanted secondary phases. Dektak profilometer film thickness measurements were 150–180 nm after the deposition of 4 layers. X-ray diffraction patterns and hysteresis loops are shown in Figure 5, a–d. Both films were found to be polycrystalline, single-phase perovskite films (Figure 5, b and d) with an enhanced (111) orientation, attributed to the templating effects of the Pt(111)/Ti/SiO₂/Si substrates. The PErZT(4/30/70) films also showed a more pronounced (100) peak than PErZT(4/52/48) films. This is consistent with the room temperature tetragonal structure of a PZT(30/70) film compared to the room temperature morphotropic structure of a PZT(52/48) film. The previously reported PZT(30/70) films isolated under identical conditions used for the PErZT films, had narrow and square loops with reasonable properties: spontaneous polarization (P_r) = 24 μ C/cm², coercive field (E_c) = 93 kV/cm², a dielectric constant (ϵ') = 396, and $\tan \delta$ = 0.007 (10 kHz, 100 mV). For the PErZT(4/30/70) films, comparable values were obtained: P_r = 26 μ C/cm², E_c = 126 kV/cm, ϵ' = 343, and $\tan \delta$ = 0.009 (10 kHz, 100 mV).^[8]

After top-electrodes were sputter-deposited, the ferroelectric properties were discerned for PErZT films. Hysteresis loops for the PErZT(4/30/70) and PErZT(4/52/48) films are shown in Figure 5a and Figure 5c, respectively. In agreement with the Dy-doped films, the PErZT(4/30/70) films displayed a P_r = 30 μ C/cm², E_c = 171 kV, ϵ' = 366 and $\tan \delta$ = 0.03. For the PErZT(4/52/48) films slightly lower ferroelectric property values were obtained, with a P_r =

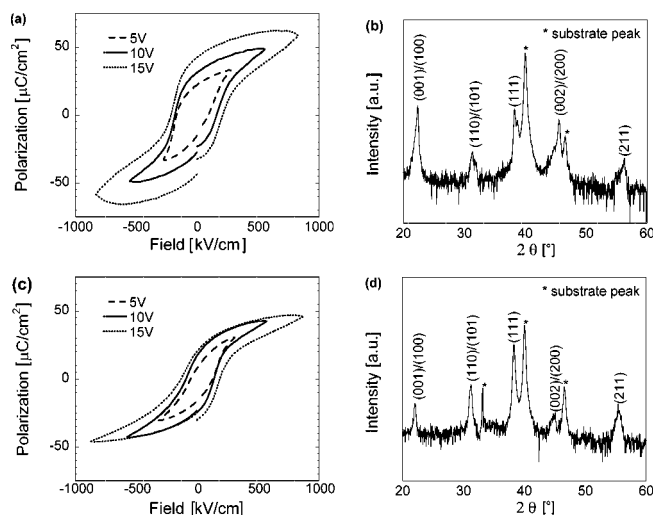


Figure 5. Characterization of PErZT(4/30/70): (a) hysteresis loop, (b) XRD; and characterization of PErZT(4/52/48): (c) hysteresis loop, (d) XRD.

20 $\mu\text{C}/\text{cm}^2$ and an $E_c = 137$ kV; however, the dielectric properties improved: $\epsilon' = 564$ and $\tan \delta = 0.01$. The higher P_r observed in the PErZT(4/30/70) is attributed to the room temperature tetragonal composition of this film while the higher ϵ' observed in the PErZT(4/52/48) is attributed to the film's room temperature morphotropic boundary composition. Unfortunately, the fatigue testing for the Er-doped films did not show the significant improvement noted for the Dy doping.^[7,8] However, this sets a lower limit for the ACE phenomenon and the slightly larger Y and Ho cations are now under investigation.

Nanoparticles

With this family of well-characterized compounds in hand, it was decided to investigate their utility as precursors for nanomaterials. Nanoparticles are of interest due to the novel properties expected for materials on this size scale. In the literature, 5 to 30 nm sized erbium(III) oxide nanocrystals dispersed in titania have been previously isolated by employing $\text{Er}(\text{NO}_3)_3$ in an inverse microemulsion process followed by a heat treatment at 600 °C.^[41,42] The resulting materials were identified as Er_2O_3 by powder XRD and photoluminescent measurements.^[41,42] Recently, a solution route using decomposition of lanthanide acetylacetonate in oleic acid, oleylamine, and octadecene at 310 °C yielded Er_2O_3 nanoparticles.^[43] We are interested in controlling the properties of nano- Er_2O_3 for electrooptic applications. Therefore, we undertook two different approaches to generate nanoparticles that were more amenable to large-scale syntheses: (a) solution precipitation and (b) solvothermal using our novel representative $\text{Er}(\text{OR})_3$ precursors **1** and **11**. Both of the processing routes are greatly simplified in comparison to the microemulsion route,^[41,42] are amenable to large scale synthesis, and require significantly lower pro-

cessing temperatures than the Ln-acac route.^[43] The results for solution precipitation of **1** and **11** are presented, followed by the results of the solvothermal routes.

Solution Precipitation

The reaction pathway for both of the alkoxides appeared to follow identical pathways, wherein the pale pink solution of the precursor immediately formed a white precipitate upon injection into the refluxing solution. The subsequent isolation also proceeded in an identical manner. Therefore, all of the observed differences in the generated manner can only be attributed to the variations in pendant hydrocarbon chain of the alkoxide ligand.

For **1**, the resulting powder was found to be made of 7–8 nm highly crystalline Er_2O_3 (see Figure 6) particles, as found by TEM imaging, the observed SAED pattern, and only Er and O observed in the EDS spectrum (Cu is background from the grid). The PXRD spectrum was fairly broad but consistent with Er_2O_3 nanoparticles of 1.7 nm, based on the Scherrer equation calculations. In comparison, using **11** (Figure 7) 3–4 nm nanoparticles of Er_2O_3 were formed as characterized by TEM and EDS analyses with a noted decrease in crystallinity by SAED. For select grains, HRTEM images clearly show the lattice fringes of Er_2O_3 . The PXRD was broad peaks consistent with Er_2O_3 wherein calculations indicated nanoparticles of 1.9 nm were formed.

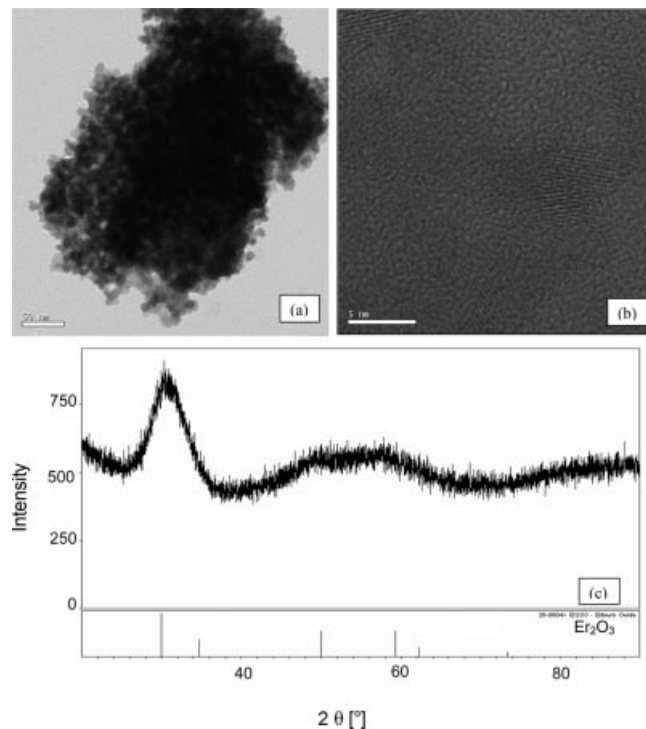


Figure 6. TEM images of Er_2O_3 generated from **1** using the solution precipitation route: (a) TEM image (50 nm scale bar), (b) HRTEM (5 nm scale bar), and (c) PXRD.

The difference in the observed particle sizes between the TEM and XRD measurements may be due to several factors in the X-ray diffraction measurement. Particle size affects the PXRD pattern by broadening the peak. Several

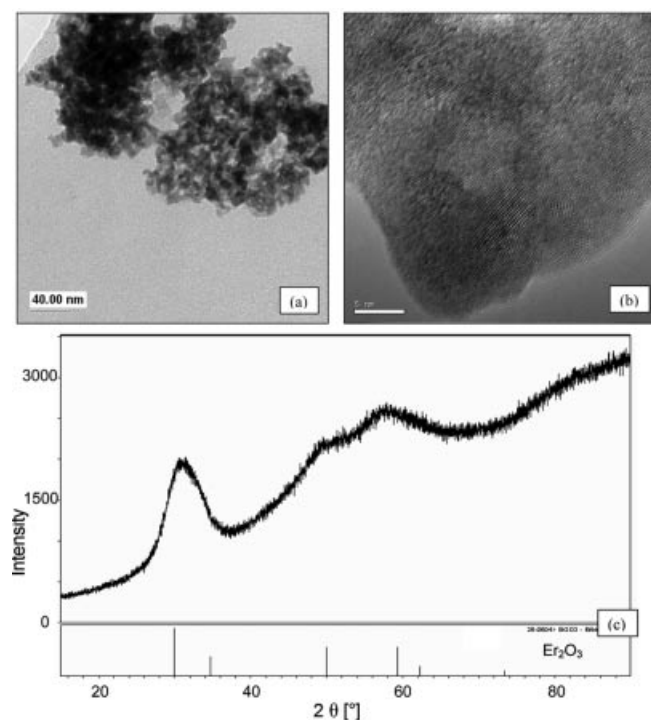


Figure 7. TEM images of Er_2O_3 generated from **11** using the solution precipitation route: (a) TEM image (40 nm scale bar), (b) HRTEM (5 nm scale bar), and (c) PXRD.

factors contribute to this peak broadening, including instrument line broadening, reduction in particle size, variation in particle composition, and microstrain. Of these possible effects, variation in particle composition and some instrument line broadening may account for the systematic underestimation of the particle size from the PXRD measurement. Despite this difference, the PXRD measurement of particle size is useful for efficient measurement of many samples and for particle size measurement on materials with strong agglomeration.

In general, from this study the formation of crystalline Er_2O_3 was more easily achieved with **1** than **11**. Upon introduction of a Lewis base, both compounds alter their original structure forming a trinuclear solvated species for **1** (as evidenced by **4**, and **7**) and a solvated monomer for **11** (**9**, **10**, **12**, **16**, **18**, and **19**). Using the PSA, the size of the resultant nanoparticles could be reasoned; however, the morphologies did not follow any trends. The faster and more uniform the nanoparticles form, the longer they will have to crystallize under the conditions we used. The particle precursor for **1** is more likely to have a larger nucleation seed in comparison to that of monomeric **11**. Thus, **1** yields higher quality nanoparticles as determined by the nature of the solvated structure.

Solvothermal Synthesis

Under solvothermal conditions, a Parr digestion bomb of the same solution was investigated to determine processing variations for the same compounds. For **1**, spheroidal nanoparticles of Er_2O_3 were isolated ranging from 10–

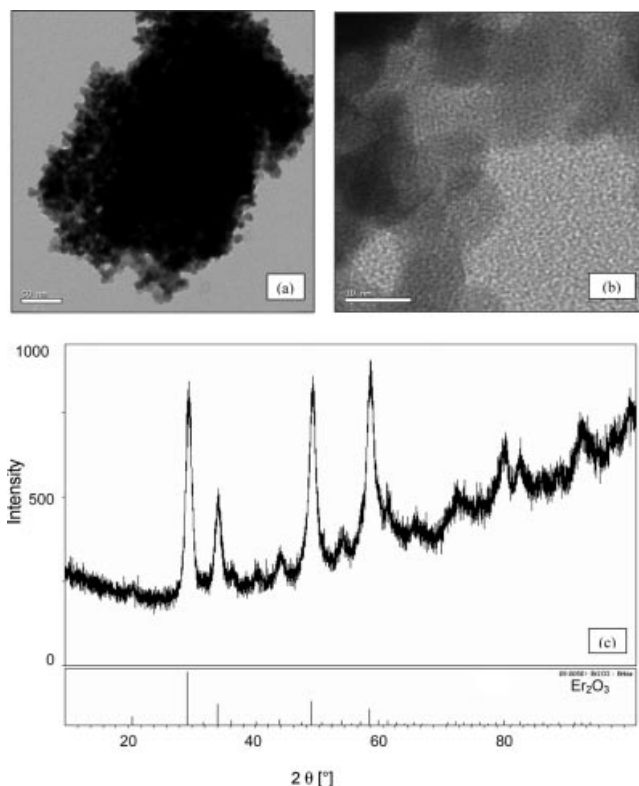


Figure 8. Nanoparticles from Parr bomb using **1**: (a) TEM image (50 nm scale bar), (b) HRTEM (10 nm scale bar), and (c) PXRD.

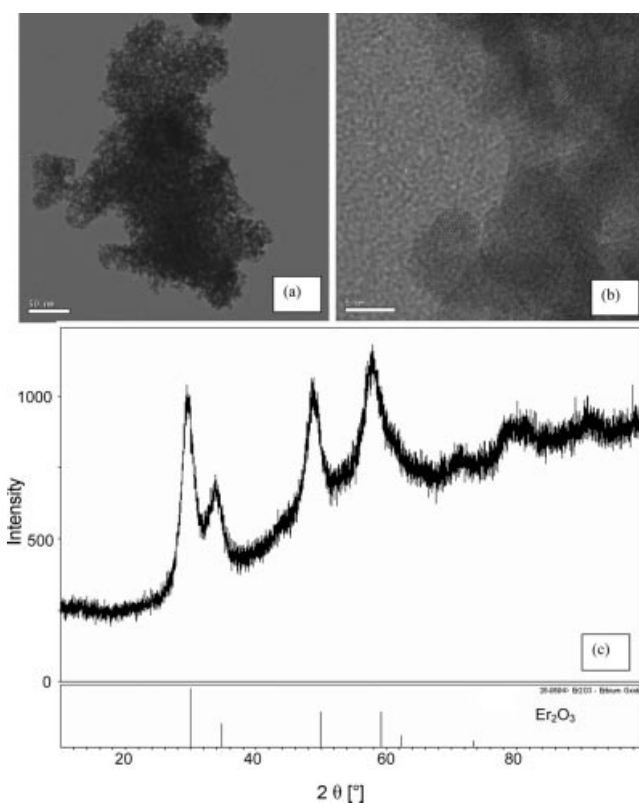


Figure 9. Nanoparticles from Parr bomb using **11**: (a) TEM image (50 nm scale bar), (b) HRTEM (5 nm scale bar), and (c) PXRD.

15 nm in size verified by EDS and PXRD (Figure 8). Surprisingly, the PXRD pattern was much sharper with calculated sizes of 7.0 nm. For **11**, more spherical shaped nanoparticles were isolated in the same approximate size range of 10–15 nm (Figure 9). The particles were more uniform in morphology and size in comparison to **1** but the particles appear less crystalline by PXRD pattern; however, HRTEM reveals the crystalline lattice planes. The broad peaks of PXRD pattern were calculated to generate particles of 3.7 nm. The TEM images and those calculated from the XRD pattern have a significant difference again the issues discussed previous (vide infra) may account for this variance.

In general, the structures of the precursors do not appear to play as large a role in determining the morphology of the final Ln-based nanomaterials isolated as noted for transition metals.^[12–16] However, there are significant differences based on the structural considerations of **1** vs. **11**. The crystallinity of the final material appears to be higher with the bomb preparative routes vs. the solution precipitation methods.

PErZT Nanoparticles

Due to the success with the simple Er system, it was of interest to determine if more complex nanoparticles could be generated from the same solution under similar conditions. Attempts to generate PErZT nanomaterials were undertaken using the same precursor thin film solution with **1** as the dopant and the process for preparing nano-Er₂O₃ as discussed above. The solution precipitation route yielded large nanoparticles on the order of 30 nm in size (Figure 10). EDS indicates each of the cations is present; how-

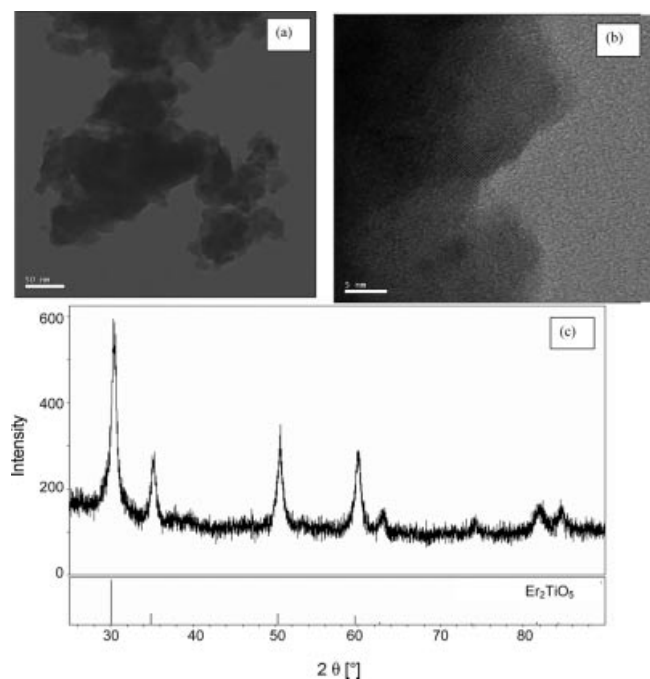


Figure 10. PErZT nanoparticles MeIM/H₂O prep: calcined at 650 °C: (a) TEM image (50 nm scale bar), (b) HRTEM (5 nm scale bar), and (c) PXRD.

ever, the PXRD pattern shows only ErTiO₃ is present as a crystalline material. The absent Pb and Zr cations are probably phase separated as amorphous PbZrO₃, which requires significantly higher temperatures to crystallize. Alternatively, the solvothermal route led to the isolation of particles on the size of 5–10 nm (Figure 11) with each of the cations present in the EDS. Interestingly, highly crystalline particles (HRTEM with *d* spacing ca. 3.0 Å) were observed in the PbTiO₃ structure that is consistent with PZT (3.1 Å). Further work to improve the uniformity and consistency of the multication nanomaterial in order to explore the properties of these electroceramic materials is underway.

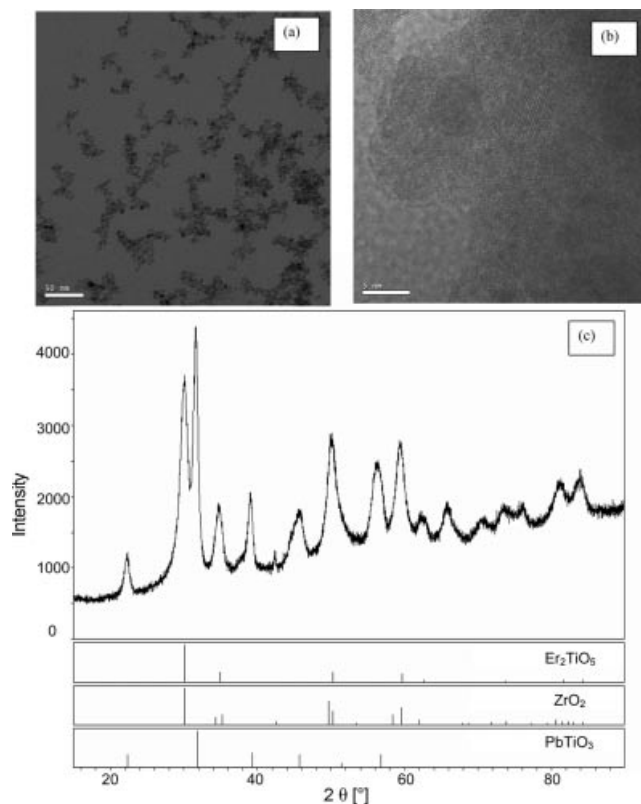


Figure 11. PErZT nanoparticles bomb prep: calcined at 650 °C: (a) TEM image (50 nm scale bar), (b) HRTEM (5 nm scale bar), and (c) PXRD.

Conclusions

We have synthesized and fully characterized a family of Er(OR)₃ from the reaction of Er[N(SiMe₃)₂]₃ and a variety of commercially available alcohols that systematically varied in steric bulk. The isolated compounds are structurally similar to the Dy(OR)₃ species^[8] isolated previously with nuclearity ranging from mono- (**9**, **12**, **16**, **18**, **19**), to bis- (**11**, **15**, **17**), to tri- (**6**) to tetranuclear (**1**) species. From this set of Er(OR)₃ compounds **11** was used to generate PErZT. The ferroelectric properties were consistent with the Dy doped PZT; however, the fatigue properties were not improved as noted for the Dy species.^[7,8] Additional work to elucidate the ACE demarcation line is in progress with

other large Ln cations. Nanoparticles of Er_2O_3 were successfully synthesized and isolated; however, the more complex ternary PERZT yielded mixed size particles of various compositions.

Experimental Section

All compounds described below were handled with rigorous exclusion of air and water using standard Schlenk line and glove box techniques. All solvents were stored under argon and used as received (Aldrich) in sure seal bottles, including hexanes (hex), toluene (tol), thf, and py. The following chemicals were used as received (Aldrich): ErCl_3 , $\text{KN}(\text{SiMe}_3)_2$ (KNR_2), H-Onep, H-OrBu, H-dmp, H-dip, H-dbp, H-tps, $[\text{Zr}(\text{O}i\text{Pr})_4(\text{HO}i\text{Pr})_2]$, $\text{Ti}(\text{O}i\text{Pr})_4$ was distilled immediately prior to use and stored under an inert atmosphere. $\text{Er}(\text{NR}_2)_3$ was synthesized from the reaction of ErCl_3 and three equivalents of LiNR_2 in thf and purified by sublimation and subsequent crystallization from hexanes.^[8] FT-IR data were obtained on a Bruker Vector 22 Instrument using KBr pellets under an atmosphere of flowing nitrogen. Elemental analysis was performed on a Perkin-Elmer 2400 CHN-S/O Elemental Analyzer.

General Synthesis: The appropriate HOR was added by a pipette to a stirring mixture of $\text{Er}(\text{NR}_2)_3$ that was dissolved in desired solvent. After 12 h, if a precipitate formed, the solution was warmed until the precipitate redissolved. After cooling to room temperature, the volatile material was allowed to slowly evaporate or the volume of the reaction was drastically reduced via rotary evaporation. The reaction was then set aside or cooled to -35°C , if necessary until crystals formed.

[Er(μ -Onep) $_2$ (Onep)] $_4$ (1): See ref.^[31]

Er(μ -O)(μ_3 -Onep)(μ -Onep) $_5$ (Onep) $_4$ (py) $_3$ (3): Used KNR_2 (0.500 g, 0.771 mmol), H-Onep (0.204 g, 0.231 mmol) and ca. 10 mL of py. Yield 0.215 g (62.1%). FT-IR (KBr): $\tilde{\nu}$ = 2957 (s), 2906 (w), 2902 (m), 2809 (m), 2747 (w), 2681 (m), 2368 (m), 2348 (m), 1481 (s), 1462 (m,sh), 1394 (s), 1364 (s), 1334 (w), 1266 (m), 1216 (w), 1059 (s), 1061 (s), 1017 (s), 974 (w), 935 (m), 896 (m), 826 (m), 701 (m), 700 (m), 670 (w), 606 (s), 517 (m), 481 (s), 418 (s) cm^{-1} . $\text{C}_{65}\text{H}_{126}\text{Er}_4\text{N}_3\text{O}_{11}$ (1794.76): calcd. C 43.5, H 7.08, N 2.34, for $\text{C}_{75}\text{H}_{136}\text{Er}_4\text{N}_5\text{O}_{11}$ (3 + 2py): calcd. C 46.1, H 7.02, N 3.59; found C 46.5, H 7.20, N 3.05.

Er $_3$ (μ_3 -OrBu) $_2$ (μ -OrBu) $_3$ (OrBu) $_4$ (HOOrBu) $_2$ (4): Used KNR_2 (0.500 g, 0.771 mmol), H-OrBu (0.171 g, 0.231 mmol) and ca. 10 mL of toluene. Yield 0.220 g (65.5%). FT-IR (KBr): $\tilde{\nu}$ = 2968 (s), 2362 (s), 2344 (s,sh), 1375 (m), 1356 (w,sh), 1203 (s), 1153 (w), 1142 (w), 1071 (w), 1039 (w,sh), 1004 (s), 938 (m), 920 (m,sh), 845 (m), 766 (w), 753 (w), 700 (m), 681 (m), 636 (w), 527 (m), 479 (m) cm^{-1} . $\text{C}_{44}\text{H}_{99}\text{Er}_3\text{O}_{11}$ (1306.04): calcd. C 40.47, H 7.64, for $\text{C}_{40}\text{H}_{89}\text{Er}_3\text{O}_{11}$ (4-1 H-OrBu): calcd. C 38.49, H 7.18; found C 38.6, H 6.93.

Er $_3$ (μ_3 -O)(μ -OrBu) $_4$ (OrBu) $_3$ (py) $_3$ (7): Used KNR_2 (0.500 g, 0.771 mmol), H-OrBu (0.171 g, 0.231 mmol) and ca. 10 mL of py. Yield 0.25 g (76.5%). FT-IR (KBr): $\tilde{\nu}$ = 2961 (s), 2362 (s), 2344 (m), 1618 (s), 1561 (m), 1509 (m), 1378 (w), 1242 (m), 1206 (m), 1108 (s), 1061 (s), 1016 (m), 933 (w,sh), 829 (s), 748 (m), 669 (s), 594 (w), 474 (w) cm^{-1} . $\text{C}_{43}\text{H}_{78}\text{Er}_3\text{N}_3\text{O}_8$: calcd. C 40.76, N 3.316, H 6.20. $\text{C}_{28}\text{H}_{63}\text{Er}_3\text{O}_8$ (7-3 py): calcd. C 32.70, H 6.17; found C 32.4, H 6.81.

Er(dmp) $_3$ (thf) $_3$ (9): Used KNR_2 (0.500 g, 0.771 mmol), H-dmp (0.282 g, 0.231 mmol) and ca. 10 mL of thf. Yield 0.350 g (60.8%). FT-IR (KBr): $\tilde{\nu}$ = 3621 (s), 3066 (w,sh), 3039 (w,sh), 3010 (w,sh), 2957 (s), 2920 (w,sh), 2853 (w,sh), 2722 (w), 2585 (w), 2368 (w),

2345 (w), 1593 (s), 1469 (s), 1441 (s), 1428 (S), 1374 (m,sh), 1290 (s), 1269 (m,sh), 1226 (m), 1153 (m), 1092 (s), 1068 (m), 1039 (m), 1007 (m), 978 (m), 917 (m), 871 (w,sh), 849 (s), 757 (s), 748 (s), 623 (m), 569 (w), 532 (s), 489 (w), 462 (w) cm^{-1} . $\text{C}_{36}\text{H}_{51}\text{ErO}_6$ (747.06): calcd. C 57.9, H 6.90; found C 58.31, H 6.92.

Er(dmp) $_3$ (py) $_4$ (10): Used KNR_2 (0.500 g, 0.771 mmol), H-dmp (0.282 g, 0.231 mmol) and ca. 10 mL of py. Yield 0.450 g (68.9%). FT-IR (KBr): $\tilde{\nu}$ = 2960 (m,sh), 2918 (s), 2850 (s), 2363 (w), 2345 (w), 1592 (m), 1466 (s), 1443 (w,sh), 1428 (w,sh), 1378 (w), 12889 (w,sh), 1264 (s), 1220 (w), 1092 (s), 1070 (w,sh), 1038 (w), 918 (w,sh), 874 (m), 847 (m), 801 (s), 756 (m), 720 (w), 704 (s), 623 (w), 534 (m) cm^{-1} . $\text{C}_{44}\text{H}_{47}\text{ErN}_4\text{O}_3$ (847.14): calcd. C 2.4, H 5.59, N 6.61; found C 62.1, H 5.67, N 6.68.

[Er(η -dip)(dip) $_2$] (11): Used KNR_2 (0.500 g, 0.771 mmol), H-dip (0.412 g, 0.231 mmol) and ca. 10 mL of toluene. Yield 0.450 g (84.7%). 1.0618 g FT-IR (KBr): $\tilde{\nu}$ = 3063 (w,sh), 3020 (w,sh), 2961 (s), 2869 (m), 2362 (m), 2344 (w), 1601 (m,sh), 1591 (m), 1460 (w,sh), 1433 (s), 1382 (m), 1361 (m), 1333 (s), 1267 (s), 1202 (m), 1155 (w), 1069 (m), 1068 (w), 1059 (w), 1042 (m), 1007 (m), 978 (w), 924 (s), 889 (m), 864 (m,sh), 843 (*s), 797 (m), 692 (w,sh), 669 (w), 650 (w), 627 (w), 567 (m), 489 (w), 470 (w) cm^{-1} . $\text{C}_{71}\text{H}_{93}\text{Er}_2\text{O}_6$ (1377.03): calcd. C 61.9, H 6.82; found C 62.4, H 6.89.

Er(dip) $_3$ (thf) $_2$ (12):^[9] Used KNR_2 (0.500 g, 0.771 mmol), H-dip (0.412 g, 0.231 mmol) and ca. 10 mL of thf. Yield 0.320 g (49.2%). FT-IR (KBr): $\tilde{\nu}$ = 3057 (w), 2960 (s), 2890 (w,sh), 2362 (w), 2345 (w), 1588 (s), 1450 (w,sh), 1432 (s), 1381 (m), 1357 (m,sh), 1333 (s), 1274 (s), 1210 (s), 1174 (w), 1109 (m), 1097 (m), 1042 (s), 1016 (m), 953 (w), 934 (w,sh), 888 (m,sh), 864 (s), 804 (m), 754 (s), 691 (s), 617 (w), 566 (s) cm^{-1} . $\text{C}_{44}\text{H}_{67}\text{ErO}_5$ (843.27): calcd. C 62.7, H 8.03; found C 61.9, H 7.98.

[Er(μ -OH)(dbp) $_2$ (thf)] $_2$ (15): Used KNR_2 (0.500 g, 0.771 mmol), H-dbp (0.477 g, 0.231 mmol) and ca. 10 mL of thf. Yield 0.380 g (73.9%). FT-IR (KBr): $\tilde{\nu}$ = 2957 (s), 2917 (w,sh), 2872 (w,sh), 2362 (s), 2344 (s), 1476 (w), 1459 (m), 1407 (s), 1385 (m,sh), 1316 (w), 1244 (s), 1200 (m), 1122 (m), 1104 (s), 1045 (w), 1007 (m), 922 (w), 865 (s), 821 (s), 796 (w), 748 (s), 708 (m), 656 (s), 527 (m), 429 (m) cm^{-1} . $\text{C}_{64}\text{H}_{100}\text{Er}_2\text{O}_8$ (1332.01): calcd. C 57.7, H 7.56; found C 57.1, H 7.37.

Er(dbp) $_3$ (py) $_2$ (16): Used KNR_2 (0.500 g, 0.771 mmol), H-dbp (0.477 g, 0.231 mmol) and ca. 10 mL of py. Yield 0.390 g (53.7%). FT-IR (KBr): $\tilde{\nu}$ = 2959 (s), 2366 (w), 2345 (s), 1442 (m,sh), 1408 (s), 1384 (m,sh), 1360 (w), 1251 (s), 1219 (m,sh), 1200 (m), 1154 (w), 1104 (m), 1068 (w), 1042 (m), 866 (s), 822 (m), 749 (s), 703 (s), 655 (s), 629 (m), 545 (w), 431 (s) cm^{-1} . $\text{C}_{52}\text{H}_{73}\text{ErN}_2\text{O}_3$ (941.42): calcd. C 66.3, H 7.82, N 2.98; found C 66.8, H 8.10, N 2.42.

[Er(μ -tps)(tps) $_2$] (17): Used KNR_2 (0.500 g, 0.771 mmol), H-tps (0.639 g, 0.231 mmol) and ca. 10 mL of toluene. Yield 0.480 g (59.9%). FT-IR (KBr): $\tilde{\nu}$ = 3069 (s), 3043 (m,sh), 3021 (w), 3008 (w), 2998 (m), 2958 (s), 2366 (m), 2342 (m), 1975 (w,sh), 1958 (m), 1902 (w,sh), 1886 (m), 1818 (s), 1773 (m), 1652 (m), 1588 (s), 1560 (w), 1482 (s), 1426 (s), 1329 (w), 1301 (w,sh), 1259 (s), 1251 (w,sh), 1115 (s), 1093 (s,sh), 1027 (m,sh), 995 (w,sh), 857 (w,sh), 842 (s), 746 (s), 710 (s,sh), 698 (s), 621 (w), 571 (m), 486 (s) cm^{-1} . $\text{C}_{115}\text{H}_{98}\text{Er}_2\text{O}_6\text{Si}_6$ (2079.07): calcd. C 66.4, H 4.75; found C 66.6, H 5.26.

Er(tps) $_3$ (thf) $_3$ (18): Used KNR_2 (0.500 g, 0.771 mmol), H-tps (0.639 g, 0.231 mmol) and ca. 10 mL of thf. Yield 0.720 g (72.9%). FT-IR (KBr): $\tilde{\nu}$ = 3063 (m), 3045 (m), 2994 (w), 2882 (w), 1459 (m), 1450 (m), 1428 (s), 1342 (w), 1331 (w), 1296 (w), 1257 (m), 1185 (s), 1111 (s), 1068 (m), 1047 (w,sh), 1027 (s), 1000 (w,sh), 984 (s), 916 (w), 875 (s), 742 (s), 704 (s), 672 (w), 519 (s), 508 (w,sh), 452 (m), 432 (m), 413 (m) cm^{-1} . $\text{C}_{66}\text{H}_{69}\text{ErO}_6\text{Si}_3\cdot\text{C}_4\text{H}_8\text{O}$: calcd. C

65.6, H 6.05; for $C_{66}H_{69}ErO_6Si_3$ (**18**–1 thf): calcd. C 65.5, H 5.76; found C 65.1, H 5.96.

Er(tps)₃(py)₃ (19**):** Used KNR_2 (0.500 g, 0.771 mmol), tps (0.639 g, 0.231 mmol) and ca. 10 mL of py. Yield 0.680 g (71.7%). FT-IR (KBr): $\tilde{\nu}$ = 3063 (m), 3044 (m,sh), 3006 (w), 2363 (m), 2345 (m), 1599 (s), 1579 (w, sh), 1524 (w), 1483 (s), 1442 (s), 1427 (s), 1273 (w), 1257 (w), 1231 (w), 1217 (m), 1185 (m), 1154 (w), 1109 (s), 1067 (s), 1038 (s), 1001 (m,sh), 985 (s), 745 (s), 701 (s), 622 (s), 602 (w, sh), 520 (s), 507 (w,sh), 453 (m), 433 (m), 411 (m) cm^{-1} . $C_{69}H_{60}ErN_3O_3Si_3$ (1230.77): calcd. 67.3C, 4.91H, 3.42N. $C_{64}H_{55}ErN_2O_3Si_3$ (**19**–1 py): C 66.7, H 4.81, N 2.43; found C 67.0, H 4.91, N 2.80.

General X-ray Crystal Structure Information: [44] Crystals were mounted onto a glass fiber from a pool of Fluorolube™ and immediately placed in a cold N_2 vapor stream, with a Bruker AXS diffractometer equipped with a SMART 1000 CCD detector using graphite-monochromatized Mo- K_α radiation (λ = 0.7107 Å). Lattice determination and data collection were carried out using SMART Version 5.054 software. Data reduction was performed using SAINTPLUS Version 6.01 software and corrected for absorption using the SADABS program within the SAINT software package.

Structures were solved by direct methods that yielded the heavy atoms, along with a number of the lighter atoms or by using the PATTERSON method, which yielded the heavy atoms. Subsequent Fourier syntheses yielded the remaining light-atom positions. The hydrogen atoms were fixed in positions of ideal geometry and refined using SHELXS software. The final refinement of each compound included anisotropic thermal parameters for all non-hydrogen atoms. It is of note that crystal structures of $M(OR)_x$ often contain disorder within the atoms of the ligand chain causing higher than normal final correlations.^[24–29]

Data collection parameters for **1**–**19** are given in Table 2. Specific issues associated with individual structures are discussed below. Fully refined structures of **3** and **7** could not be obtained due to significant disorder in the Onep and OtBu ligands, respectively; however, the connectivity of both compounds were unequivocally established and are in agreement with the $Dy(OR)_3$ structures reported. Structure **11** had significant disorder in the isopropoxide ligands that resulted in oblong thermal ellipsoids and a slightly higher R_1 value; however, the overall structure observed is in agreement with $[Dy(\eta\text{-dip})(\text{dip})_2]_2$ in both unit cell and connectivity. For **17**, it was necessary to squeeze disorder electron density of 317.1 Å³ which is in agreement with ca. 1 tol molecule. Noncentrosymmetric settings were chosen for **1**, **7**, **12**, and **18** even though a mirror plane appears to exist for these molecules. By further investigation of these species, disruption in the symmetry due to nonrigid ligands, such as Onep (**1** and **7**) or disorder in coordinating solvent thf (**12** and **18**) ultimately requires refinement in noncentrosymmetric settings.

CCDC-641110 to -641120 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Film Production: Standard spin-coat deposition routes^[45] were used to generate the PErZT thin films with a brief description of the preparation and processing described below. The PZT (30/70 or 48/52) films were produced following the established “basic route to PZT” (BRP) route,^[45,46] in which $Pb(OAc)_2 \cdot (HOAc)$ (Aldrich, 95%) dissolved in pyridine (py) was added to a mixture of $Ti(OiPr)_4$ and $[Zr(OiPr)_4(HOiPr)]_2$ dissolved in tol to form the PZT precur-

sor mixture. The appropriate $Er(OR)_3$ precursor was dissolved in py and then added to the PZT mixture to form the ca. 0.4 M PErZT precursor solution.

Multilayered films of the desired composition were spin-coat deposited, in air, onto Pt(1700 Å)/Ti(300 Å) coated, thermally oxidized SiO_2/Si substrates using a photoresist spinner (3000 rpm for 30 s). After each deposition, the films were heated on a hot plate (300 °C for ca. 5 min) and cooled to room temperature before the deposition of the next layer. After the final layer received the 300 °C treatment (for this study 2–4 layers were used), the film was crystallized in a tube furnace at 650 °C for 30 min in air. X-ray diffraction (XRD) was used to confirm the phase purity and orientation of the final films.

Ferroelectric Testing: To measure the electrical properties of the films, gold top electrodes (ca. $250 \times 250 \mu m$) were sputter-deposited onto the films using a shadow mask to create a parallel-plate capacitor geometry. Capacitor top electrode areas were individually measured with a calibrated optical microscope and film thicknesses were measured using a Dektak profilometer. The low-field dielectric properties were measured at 10 kHz (100 mV p-p) using an HP 4284A impedance analyzer (Palo Alto, CA). The ferroelectric properties of the PLnZT films were measured using an RT66A ferroelectric tester from Radiant Technologies (Albuquerque, NM). Accelerated ferroelectric fatigue tests were performed using a 1-MHz bipolar square wave pulse, with the applied electric field normalized to ca. 700 kV/cm.

Nanoparticle Synthesis: Nanoparticles of Er_2O_3 were formed following one of two methods using **1** or **11** which were chosen as representative members of the alkyl- and aryloxy derivatives, respectively. The BRP method was also used to generate the PErZT precursor solution for the multication nanoparticles.

Two general routes were explored to synthesize nanoparticles: (a) solution precipitation and (b) solvothermal routes. (a) *Solution Precipitation.* The first route used a mixture of 1-methyl imidazole and water (MeIm/ H_2O) having a 14.5/0.5 mL ratio. This solution was placed in a two-neck round bottom equipped with a reflux condenser and a septum. Under flowing argon, the MeIm/ H_2O solution was brought to reflux conditions (ca. 200 °C) and the desired precursor dissolved in tol was injected via syringe. A white precipitate formed immediately and the mixture was stirred for 30 min at 197 °C then cooled to room temperature. The as prepared particles were collected by centrifugation and rinsed with ethanol and then calcined in a tube furnace under flowing argon at 600 °C for 1 h. (b) *Solvothermal.* The second route used was a 45 mL Parr Acid Digestion Bomb. In the glove box, the desired precursors were dissolved in ca. 15 mL of benzyl alcohol (BzOH) and the clear solutions were transferred to the Teflon™ liners and placed in the bomb. The bomb was taken out of the glove box and the reaction was heated to 200 °C for 48 h. The white precipitate was collected by centrifugation and rinsed with ethanol.

The resulting nanopowders were slurried in tol followed by placing a drop of the solution onto a holey-carbon copper grid and allowing it to air dry. Upon complete drying for the samples were then examined with a transmission electron microscope (TEM) Philips CM30 with acceleration voltage of 300 KeV to obtain images, as well as selected area electron diffraction (SAED) data when necessary. Elemental composition information was obtained with a Noran energy dispersive X-ray detector (EDX) using system 6 software. In addition, the powder was characterized using a PANalytical powder diffractometer using $Cu-K_\alpha$ radiation with step size 0.0167 degree, with 53.340 seconds dwelling time.

Table 2. Crystallographic data collection parameters for **1–19**.

Compound	1	3	4	7	9
Empirical formula	C ₁₅ H ₃₃ ErO ₃	C ₆₅ H ₁₂₆ Er ₄ O ₁₁ N ₃	C ₄₄ H ₉₉ Er ₃ O ₁₁	C ₄₃ H ₇₈ Er ₃ N ₃ O ₈	C ₃₆ H ₅₁ ErO ₆
Formula weight	428.67	1794.74	1306.01	1266.86	747.03
Temp. [K]	168(2)	203(2)	168(2)	203(2)	203(2)
Space group	tetragonal <i>P</i> $\bar{4}$ ₂ /c	monoclinic <i>P</i> 2 ₁ /c	monoclinic <i>P</i> 2 ₁ /c	hexagonal <i>P</i> 6 ₃ /mc	monoclinic <i>P</i> 2 ₁ /n
<i>a</i> [Å]	20.1985(14)	16.801(3)	19.2913(13)	17.239(4)	9.8147(7)
<i>b</i> [Å]	20.1985(14)	13.371(2)	10.7831(8)	17.239(4)	27.6997(19)
<i>c</i> [Å]	12.0226(16)	35.136(6)	27.2513(19)	11.269(6)	13.1323(9)
β [°]		90.479(3)	99.2430(10)		93.4720(10)
<i>V</i> [Å ³]	4905.0(8)	7893(2)	5595.2(7)	2900.2(17)	3563.6(4)
<i>Z</i>	8	4	4	2	4
<i>D</i> _{calcd.} [Mg/m ³]	1.161	4.530	1.550	1.421	1.392
μ (Mo- <i>K</i> α) [mm ⁻¹]	3.424	4.259	4.506	4.341	2.395
<i>R</i> ₁ ^[a] (%) (all data)	4.10(4.77)	12.05(12.76)	4.41(6.33)	7.77(9.999)	3.03(4.34)
<i>wR</i> ₂ ^[b] (%) (all data)	14.60(15.26)	26.57(26.86)	8.45(9.25)	19.99(22.21)	7.18(7.69)
Compound	10	11	12	15	16
Empirical formula	C ₄₄ H ₄₇ ErN ₄ O ₃	C ₇₁ H ₉₃ Er ₂ O ₆	C ₄₄ H ₆₇ ErO ₅	C ₆₄ H ₁₀₀ Er ₂ O ₈	C ₅₂ H ₇₃ Er N ₂ O ₃
Formula weight	847.12	1376.97	843.24	1331.96	941.38
Temp. [K]	203(2)	203(2)	203(2)	203(2)	203(2)
Space group	triclinic <i>P</i> $\bar{1}$	monoclinic <i>P</i> 2 ₁ /c	monoclinic <i>P</i> 2 ₁	orthorhombic <i>Pbca</i>	orthorhombic <i>Pbcn</i>
<i>a</i> [Å]	10.8524(11)	17.399(9)	9.6910(6)	19.419(4)	20.394(3)
<i>b</i> [Å]	14.0287(15)	21.796(12)	19.3993(12)	15.633(3)	13.736(2)
<i>c</i> [Å]	27.954(3)	9.796(5)	12.2166(8)	20.710(4)	17.450(3)
α [°]	81.924(2)				
β [°]	87.581(2)	105.827(7)	109.6430(10)		
γ [°]	74.401(2)				
<i>V</i> [Å ³]	4058.4(7)	3574(3)	2149(3)	6287(2)	4888.4(14)
<i>Z</i>	4	2	2	4	4
<i>D</i> _{calcd.} [Mg/m ³]	1.386	1.280	1.295	1.407	1.279
μ (Mo- <i>K</i> α) [mm ⁻¹]	2.110	2.377	1.980	2.701	1.758
<i>R</i> ₁ (%) (all data)	4.65 (7.24)	14.33 (24.99)	2.29 (2.34)	2.32 (2.94)	4.67 (9.25)
<i>wR</i> ₂ (%) (all data)	8.87 (9.63)	28.59 (36.04)	6.17 (6.20)	5.77 (6.22)	8.21 (9.50)
Compound	17	18	19		
Empirical formula	C ₁₁₅ H ₉₈ Er ₂ O ₆ Si ₆	C ₆₆ H ₆₉ ErO ₆ Si ₃ ·C ₄ H ₈ O	C ₆₉ H ₆₀ ErN ₃ O ₃ Si ₃		
Form. weight	2079.16	1281.85	1230.73		
Temp. [K]	168(2)	203(2)	203(2)		
Space group	triclinic <i>P</i> $\bar{1}$	monoclinic <i>P</i> 2 ₁	rhombohedral <i>R</i> 3c		
<i>a</i> [Å]	13.6370(15)	14.5349(15)	20.8803(5)		
<i>b</i> [Å]	14.0918(15)	16.4587(17)	20.8803(5)		
<i>c</i> [Å]	14.4596(15)	14.9029(15)	20.8803(5)		
α [°]	75.603(2)		66.54		
β [°]	70.595(2)	115.687(2)	66.54		
γ [°]	71.970(2)		66.54		
<i>V</i> [Å ³]	2459.0(5)	3212.8(6)	7343.8(3)		
<i>Z</i>	1	2	4		
<i>D</i> _{calcd.} [Mg/m ³]	1.342	1.251	1.113		
μ (Mo- <i>K</i> α) [mm ⁻¹]	1.820	1.409	1.232		
<i>R</i> ₁ (%) (all data)	3.49 (4.11)	6.69 (8.77)	7.08 (9.50)		
<i>wR</i> ₂ (%) (all data)	7.66 (7.87)	17.15 (18.62)	23.48 (26.26)		

[a] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| \times 100$. [b] $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma (w |F_o|^2)^2]^{1/2} \times 100$.

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