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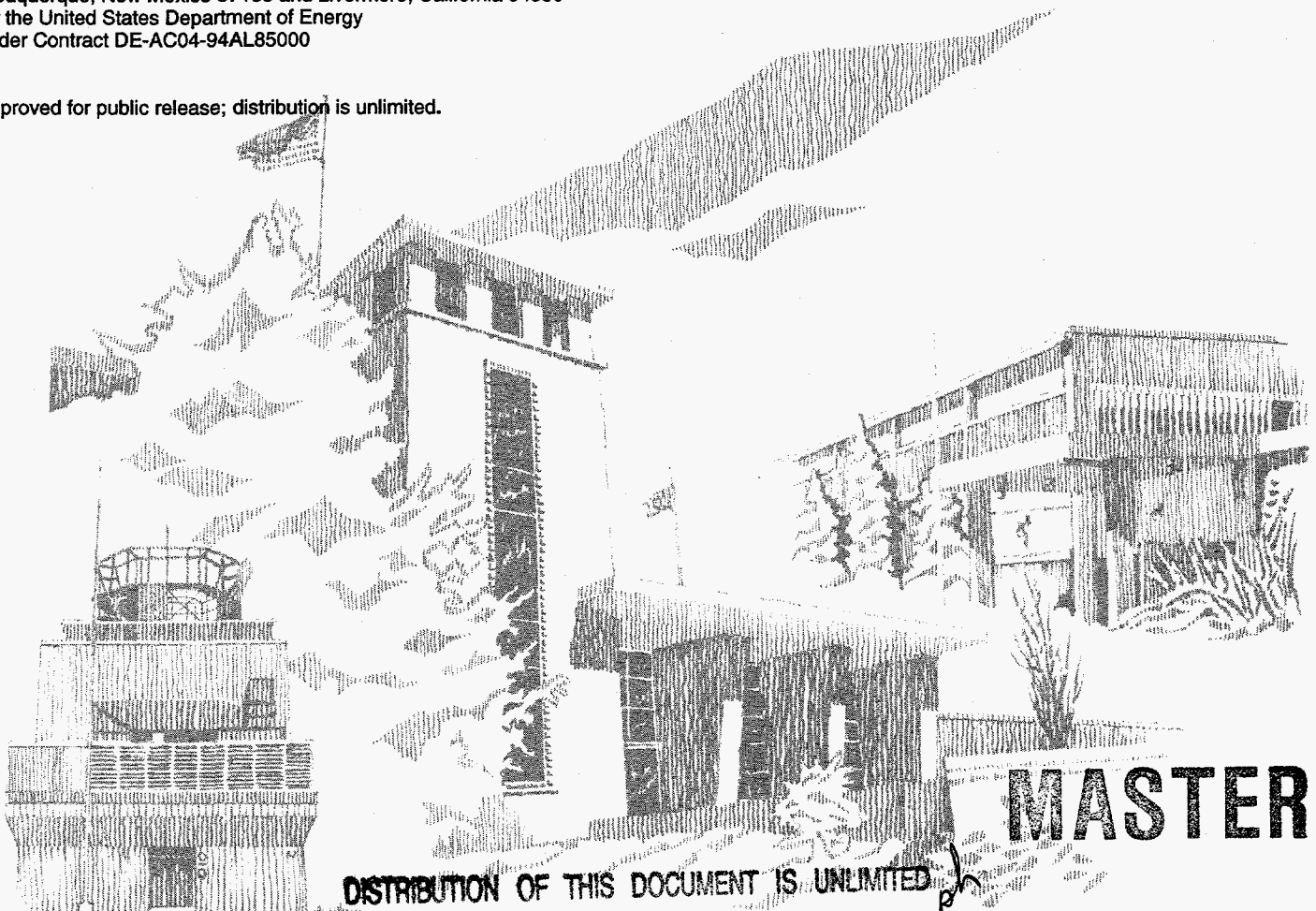
Synthesis and Regeneration of Lead (IV) Acetate

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Synthesis and Regeneration of Lead (IV) Acetate

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Abstract

Lead acetate [Pb(O₂CMe)₄] was easily synthesized from a warm solution of Pb₃O₄, HO₂CMe and O(OCMe)₂ following literature preparations *when* the appropriate measures to minimize water contamination were followed. Furthermore, Pb(O₂CMe)₄ which has been decomposed (evidenced by the appearance of a purple color due to oxidation) can be regenerated using a similar preparatory route. Introduction of Pb(O₂CMe)₄ from the two routes outlined above into the IMO process for production of PZT thin films gave films with comparable ferroelectric properties to commercially available Pb(O₂CMe)₄ precursors. However, the freshly synthesized material yields PZT films with better properties compared to the recycled material.

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Introduction

Recently, it has been difficult to obtain lead (IV) acetate [commercial-Pb(O₂CMe)₄] from commercial vendors in a reasonable time frame (typically a 3 month delay). This causes significant worry due to the high rate of consumption of this material in the production of precursor solutions for thin films of lead containing ferroelectric materials, such as PZT.¹⁻⁶ It is necessary to understand what is causing these materials to decompose and how to stop or regenerate the decomposed commercial-Pb(O₂CMe)₄ to minimize waste. This study has further prompted us to investigate the possibility of synthesizing our own Pb(O₂CMe)₄ to insure continuation of various projects. This short report details the synthesis of Pb(O₂CMe)₄ from red-lead (Pb₃O₄), attempts to recycle Pb(O₂CMe)₄ to minimize waste, and the ferroelectric properties of thin films produced therefrom.

Results and Discussion

Pb(O₂CMe)₄ is a well characterized monometallic material⁷ wherein four acetate ligands are chelated to a single metal center, Figure 1. The FT-IR spectra of commercial-Pb(O₂CMe)₄ (Aldrich) is shown in Figure 2a. A literature report⁸ for the synthesis of this material is quite simple involving Pb₃O₄ (starting materials were from Aldrich or Fisher and used without further purification) and is as follows: (i) a 10:2 mL mixture of acetic acid (HO₂CMe) and acetic anhydride (O(OCMe)₂) is warmed to 50-55°C, (b) Pb₃O₄ (3 g) is added to the warm mixture in small enough aliquot to insure dissolution of the oxide, (3) upon complete dissolution the reaction mixture is cooled in an ice bath to grow crystals and (4) the crystalline material is filtered away from the mother liquor using a Buchner funnel.

Following this preparation, an off-brown colored solution of highly contaminated Pb(O₂CMe)₄ was typically produced. This decomposition is associated with the un-intended introduction of water into the system. Typically all of the starting materials are stored in ambient atmosphere of which both the Pb₃O₄ and HO₂CMe are extremely hygroscopic. Introduction of excess O(OCMe)₂ is intended to account for the majority of excess water, wherein, it reacts forming more HO₂CMe. This requires a delicate balance of exposure and addition of the Pb₃O₄ so that the undesired decomposition is not observed. We found under these conditions a successful synthesis occurred about 1 out of 10 times.

A. Preparation. To improve our yield, strict drying conditions were observed. O[O₂CMe]₂ (Fisher) was used as received. Pb₃O₄ (Aldrich) was dried under vacuum at 60°C, overnight. HO₂CMe (Fisher or Aldrich) was dried over and freshly distilled from CrO₃/acetic anhydride.⁹ These materials were all transferred to an inert atmosphere glove box and further handled with rigorous exclusion of air or moisture.

Preparations using 30 g Pb₃O₄ were undertaken as previously detailed (*vide supra*) with little or no decomposition products observed. The crystals of this synthesized-Pb(O₂CMe)₄ were grown by simply allowing the warm solution to cool. It is of note that even with the dry HO₂CMe, we needed to add O(OCMe)₂ to insure a successful synthesis due to supposed trapped water in the Pb₃O₄. A typical batch of crystals can appear quite "wet" (i.e., HO₂CMe remains). This excess HO₂CMe was substantially reduced by washing the crystalline material with hexanes. The isolation of synthesized-Pb(O₂CMe)₄ was verified by FT-IR (KBr pellet,

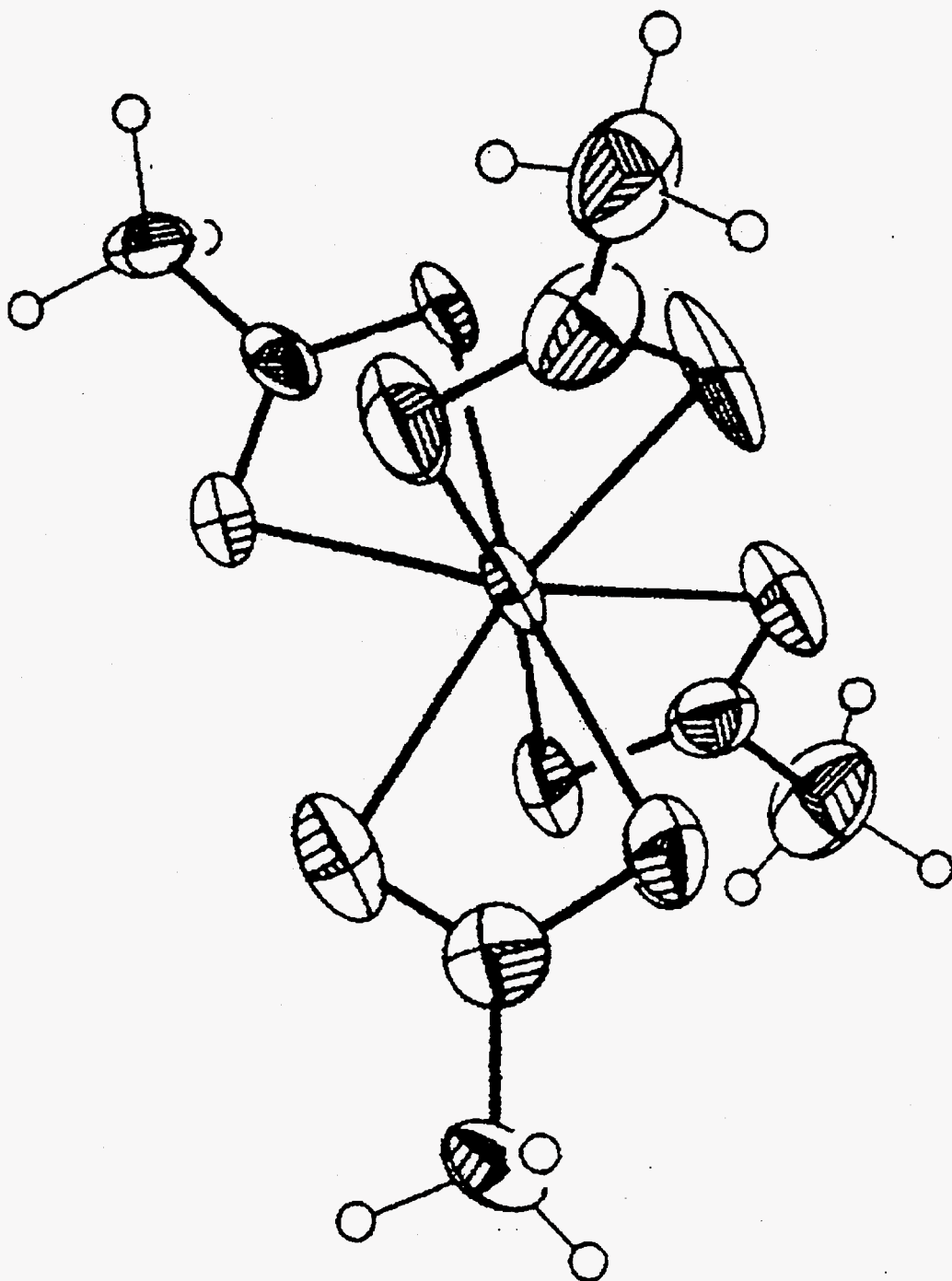


Figure 1. Thermal ellipsoid plot of $\text{Pb}(\text{O}_2\text{CMe})_4$

FIGURE 2 FT-IR spectra of :

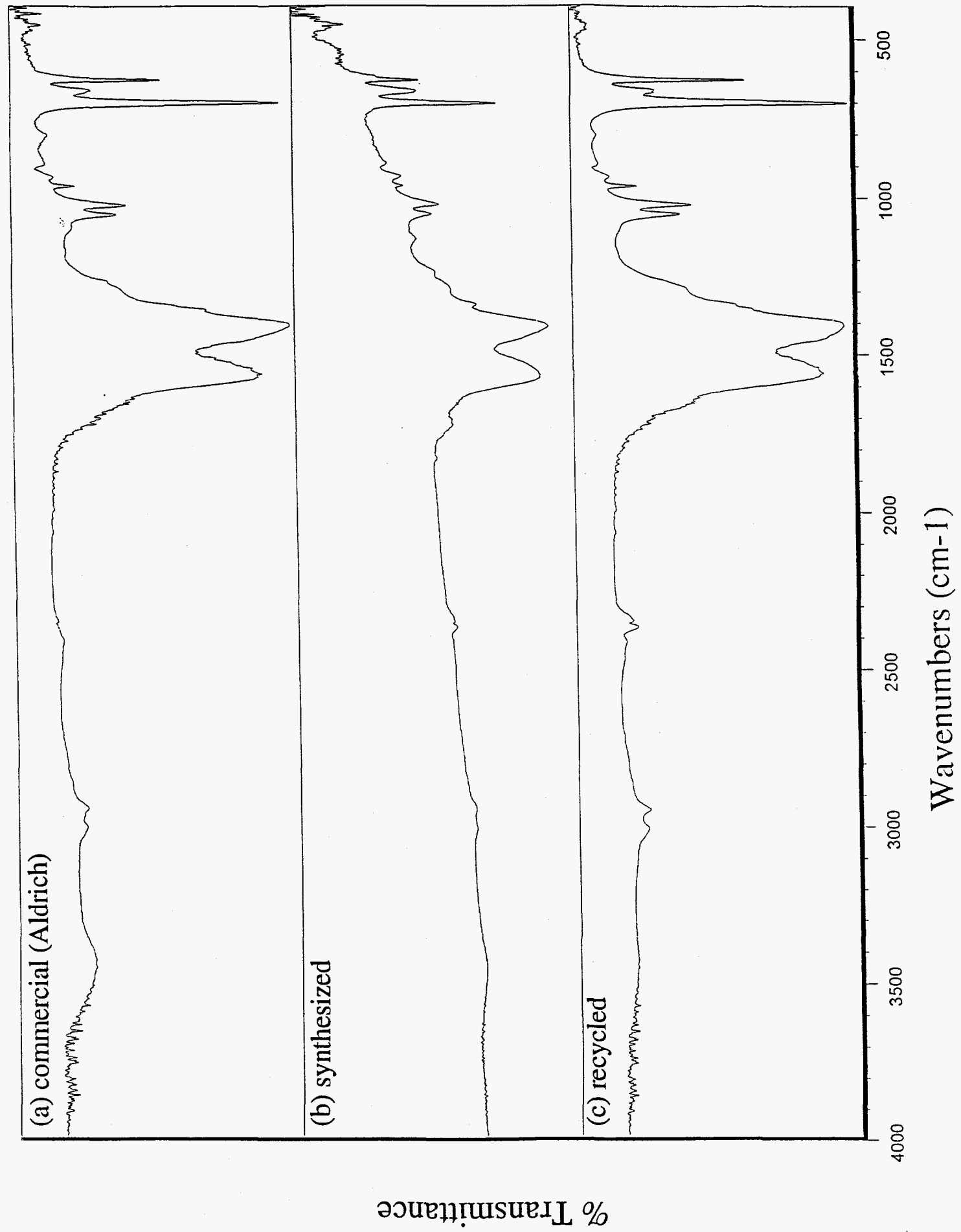


Figure 2 b). As can be observed, the spectra of the synthesized and commercial-Pb(O₂CMe)₄ appear nearly identical.

B. Recycling. Often, commercial-Pb(O₂CMe)₄ will turn an off-shade of purple while handled under dry conditions. The FT-IR of the partially decomposed or "purple" commercial-Pb(O₂CMe)₄ (Figure 3a) is significantly altered compared to the clean commercial-Pb(O₂CMe)₄ (Figure 2a). Upon exposure of either the commercial-Pb(O₂CMe)₄ (Figure 3b) or synthesized-Pb(O₂CMe)₄ (Figure 3c) to atmospheric conditions, these compounds all decompose to the same product, as evidenced by FT-IR. The final spectra shows little stretches, indicating that the ligands have been decomposed and Pb⁰ formed. Over time and exposure, the sample of the "purple" commercial-Pb(O₂CMe)₄ (Figure 3a) will eventually yield an IR spectrum identical to that of the fully exposed materials (Figure 3b and c). It is of note that the commercial-Pb(O₂CMe)₄ is oxidized more rapidly (~1 h.) than the synthesized-Pb(O₂CMe)₄ (~4 h.) as evidenced by a darkening of the white powder. After 12 hours of exposure the material is black. Again, it is apparent that a reduction of the Pb(IV) complex to Pb⁰ is occurring due to hydrolysis by ambient humidity. The purple color is really a dilution of the lead metal which would be an off-black material. In an effort to reduce waste and have another source of starting material, we have used the above synthesis to recycle this decomposed material.

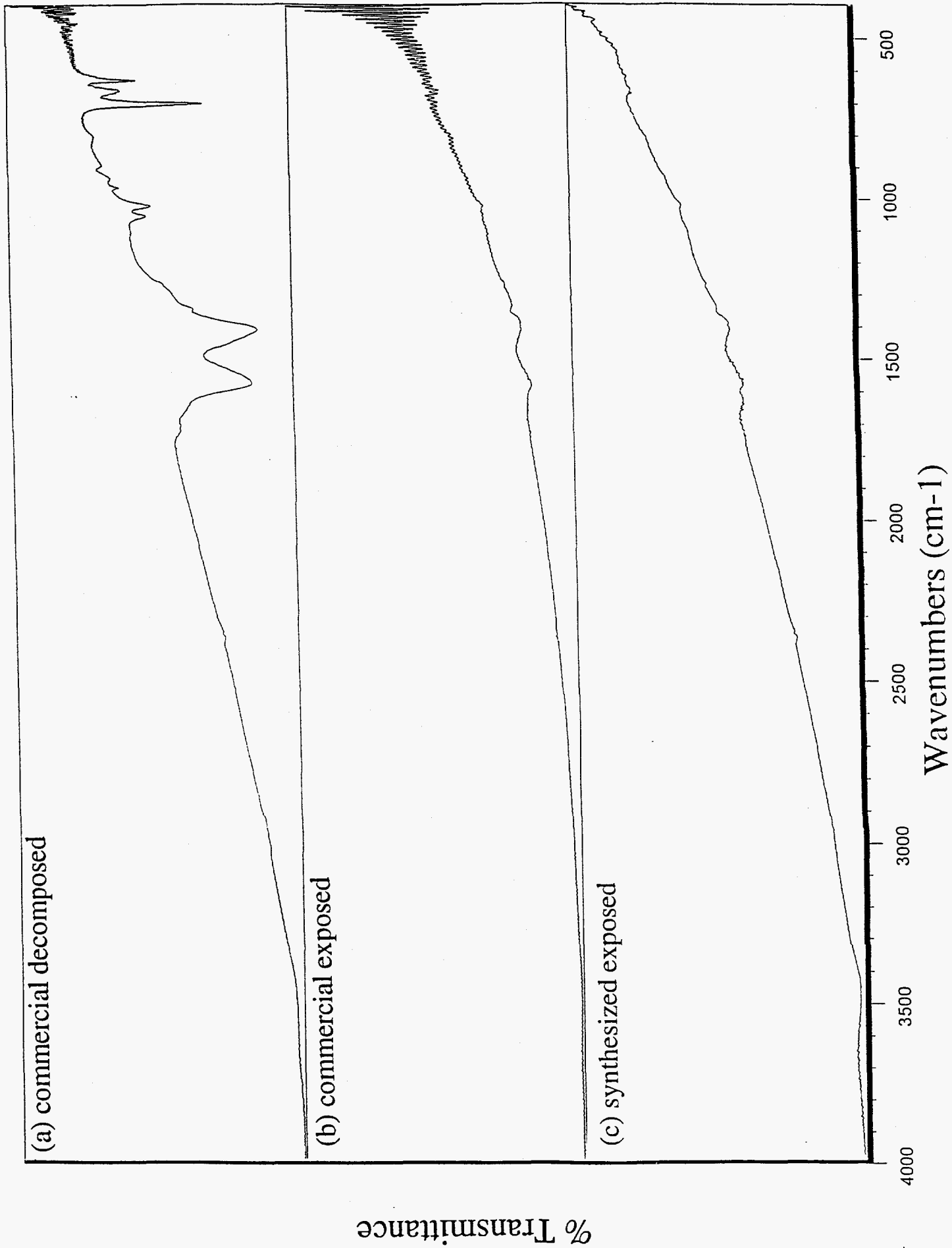
In this recycling route, acetic anhydride (Aldrich) and glacial acetic acid (Fisher) are used as received and handled under Schlenk line conditions. The contaminated Pb(O₂CMe)₄ (20 g) was put into a 1000 mL round bottom and 250 mL of acetic acid were added. Acetic anhydride (3 mL) was added to this stirring mixture and the resulting black solution was heated to 100° C until the solution clears (*note: the time for this to occur varies considerably*). After this, the heat was turned off and the solution allowed to cool to room temperature. Recycled-Pb(O₂CMe)₄ crystallizes out of solution and is isolated by vacuum filtration. The resultant powder was transferred to a Schlenk flask and dried *in vacuo* for 2 hours to remove residual HO₂CMe. *Note: It is important to limit the amount of time that the lead precursor is exposed to air.* This recycled-Pb(O₂CMe)₄ was identified by FT-IR, see Figure 2c and appears identical to the commercial- (Figure 2a) and synthesized-Pb(O₂CMe)₄ (Figure 2b). Any minor differences that can be observed by this technique are readily accounted for by the presence of excess HO₂CMe.

C. Ferroelectric Properties. Two similarly prepared inverted mixing order (IMO) (an acetic acid/MeOH chelate mixture)^{2,4} PZT 53/47 solutions were synthesized using both synthesized- and recycled-Pb(O₂CMe)₄ precursors. The ferroelectric properties of the resultant films and those typically observed for commercially derived materials are shown in Table 1.

Table 1. Ferroelectric properties of films from IMO solutions with different Pb(O₂CMe)₄. Film thicknesses were ~0.4 μm.

Pb(O ₂ CMe) ₄ Source	P _r (mC/cm ²)	P _s (mC/cm ²)	e	V _c (Volts)	dissipation factor (%)
Commercial	24	45	1200	2.5	2.0
Synthesized	25	51	1300	1.6	2.9
Recycled	28	44	850	2.3	13.7

FIGURE 3 FT-IR spectra of :



The PZT 53/47 films were grown on 1700Å Pt/300Å Ti/SiO₂/Si which were ~0.4 mm in thickness after firing at 650°C. 300 mm diameter Pt top electrodes were then deposited at room temperature to generate the Pt//PZT//Pt capacitor. The Pt top electrodes were annealed at 400°C for 5 min. prior to electrical testing. As can be discerned from this data, the electrical tests indicate that the PZT film deposited from freshly synthesized-Pb(O₂CMe)₄ was superior in many respects to the recycled-Pb(O₂CMe)₄.

During preparation of the IMO solution it was noted that the recycled-Pb(O₂CMe)₄ required higher processing temperatures to completely dissolve (~88°C) than the synthesized-Pb(O₂CMe)₄ (~80°C). Furthermore, recycled-Pb(O₂CMe)₄ had a slightly darker hue than that of the brilliantly white synthesized-Pb(O₂CMe)₄. These differences can be accounted for by the incorporation or incomplete conversion of the fully reduced lead to the +4 oxidation state. This trace impurity causes the slight off-white color, higher dissolution temperatures, and the degraded ferroelectric properties noted.

Conclusion

It has been shown that Pb(O₂CMe)₄ can be readily synthesized from red lead (Pb₃O₄), acetic acid and acetic anhydride. During the synthesis of this material it is imperative that the starting materials be kept as dry as possible otherwise undesirable decomposition will occur. Further, any oxidized Pb(O₂CMe)₄ can be recycled by warming it in acetic acid and acetic anhydride. For the recycled materials further purification methods are required to eliminate minute impurities from the final product.

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