

**STUDIES OF THE REACTIONS OF ZIRCONIUM
TETRAKIS(ACETYLACETONATE) IN ALCOHOLS MEDIA**

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ABSTRACT. The reactions of zirconium tetrakis(acetylacetonate) in alcohols media have been studied. It has been shown that with the primary alcohols: n-butanol, iso-butanol, ethylene glycol, 2-methoxyethanol the zirconium alkoxides, containing at least one acetylacetonate group, are formed. Reaction with iso-propyl alcohol results in the formation of a stable cluster soluble both in polar and non-polar solvents, containing stabilizing acetylacetonate ligands. Heat treatment of the cluster due to the X-ray diffraction analysis leads to the formation of zirconium dioxide of cubic symmetry. The scheme of the reactions has been put forward that includes subsequent catalytic reactions, taking place in co-ordination sphere of zirconium. The reactions comprise the exchange of alkoxide ligands, hydride shift that results in the reduction of acetylacetone into pentanediol-1,4 with simultaneous formation of aldehyde. The zirconium precursors thus obtained were used in sol-gel process of preparation of ferroelectric lead zirconate titanate(PZT) thin films.

INTRODUCTION

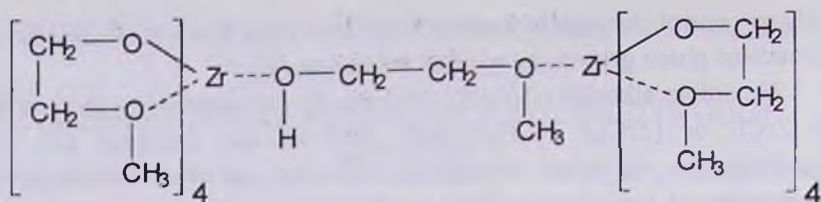
The considerable interest to the chemistry of zirconium-organic compounds particularly alkoxides can be explained by the progress for recent decade of chemical methods of preparation of ferroelectric thin films of crystalline structure. The structure of the alkoxides in the solution has significant influence on the initial stages of crystallization of ferroelectric films. The proper selection of alkoxides makes it easy not

only to control the stoichiometry of the thin films but also facilitates the crystalline phase growth on selected substrates [1].

Zirconium alkoxides (alcoholates) usually are prepared by the reaction of ZrCl_4 or $[\text{ZrCl}_6] 2\text{C}_2\text{H}_5\text{N}$ with alcohols and ammonia [2]. The disadvantages of using zirconium alkoxides in the technology of preparation of ferroelectric films are their extreme reactivity as well as tendency to hydrolysis in air. Nesmeyanov and coworkers described a method of preparation of zirconium alkoxides based on the exchange reaction of zirconium tetrakis(acetylacetonate) with alcohols, particularly with *n*-propyl, iso-propyl, *n*-butyl, and benzyl alcohols [3-5]. The authors assigned the tetralkoxide structure to the products of the exchange reaction with *n*-butyl and benzyl alcohols and structure with mixed ligands to the products of the reaction with *n*-propyl and iso-propyl alcohols, basing only on the elementary analysis data. The objective of the present work is to study regularities of the reactions of zirconium tetrakis(acetylacetonate) in alcoholic media as well as to develop methods of preparation of active precursors for synthesis of ferroelectric films in sol-gel process.

Results and discussions

It has been found that zirconium tetrakis(acetylacetonate)- $\text{Zr}(\text{acac})_4$ is an active reagent for preparation of ferroelectric thin films. The pure reagent useful for preparation of PZT films has been prepared by recrystallization of the initial reagent grade $\text{Zr}(\text{acac})_4$ from absolute iso-propyl alcohol. It appears to be a useful and stable reagent for preparation *in situ* of different zirconium alkoxides. Regularities of the reactions of $\text{Zr}(\text{acac})_4$ in alcoholic media have been studied, and, depending on alcohol's nature, zirconium alkoxides of different composition have been obtained. On the basis of ^1H NMR and IR spectral data it has been established that the main product of the reaction of $\text{Zr}(\text{acac})_4$ in 2-methoxyethanol environment is alkoxide of the following composition $\text{Zr}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3(\text{acac})$. The complexes of the same structure have been obtained in the case of *n*-butyl and *iso*-butyl alcohols. ^1H NMR and IR spectral analysis data are in good accordance with the elementary analysis data for synthesized compounds. Zirconium (2-methoxyethanolato-O,O'), without acetylacetonate ligands, has been obtained by chemical exchange of OR groups in $\text{Zr}(\text{OR})_4$ by 2-methoxyethanolate groups. ^1H NMR, IR spectral and elementary analysis data show that the dimmer form of the compound is the most feasible:



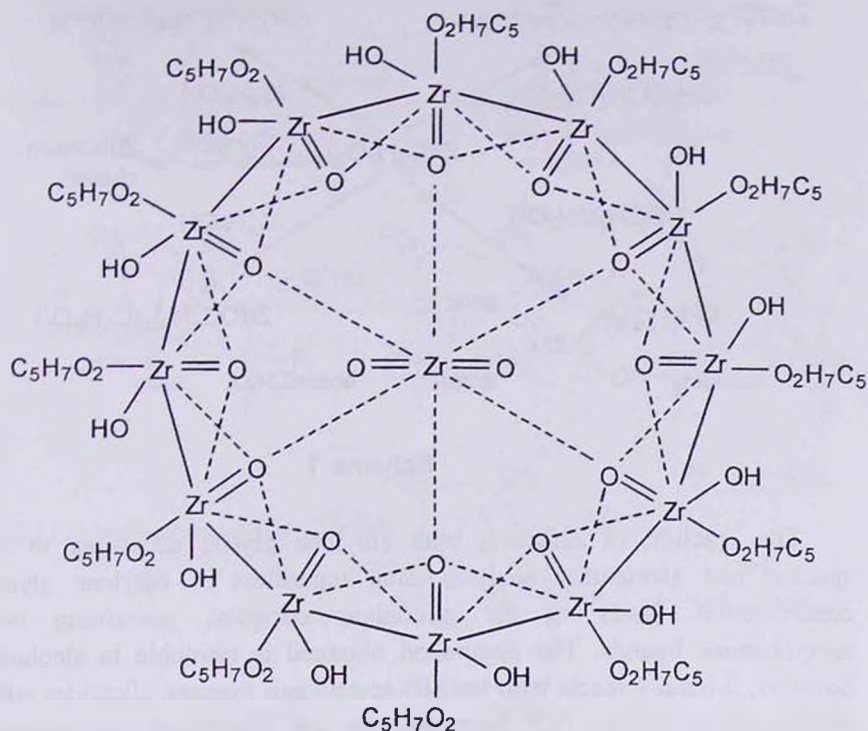
The reactions of zirconium tetraacetylacetonate in alcoholic media are presented in scheme 1. It has been mentioned above that iso-propyl alcohol is an appropriate solvent for recrystallization of zirconium tetraacetylacetonate, and no significant changes of composition of the latter compound even under reflux for many hours take place. However, it has been found that at 125°C $\text{Zr}(\text{acac})_4$ readily reacts with iso-propyl alcohol resulting in the formation of a complex with the metal content of $\approx 41\%$. On comparing the X-ray diffraction patterns of $\text{Zr}(\text{acac})_4$ and those of the unknown zirconium containing complex similarity in values of interplanar distances d was found (Table).

Table

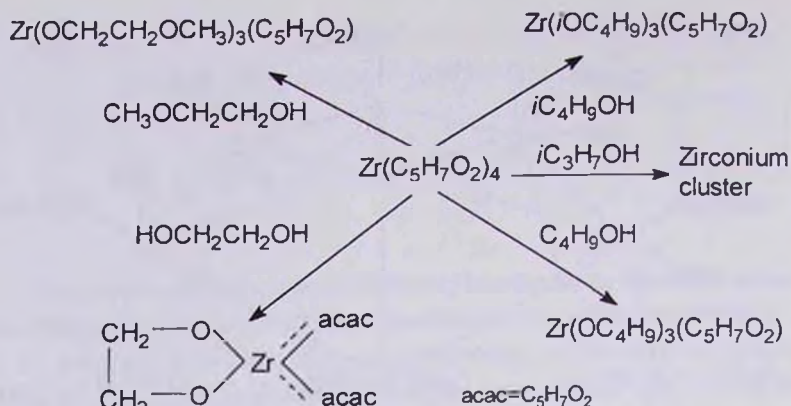
Interplanar Distances d , (and Peaks Intensities I ,% for Zirconium Tetrakis(acetylacetonate) and the Zirconium Cluster

$\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_4$		Zirconium	cluster
$d, \text{\AA}$	$I/I_0, \%$	$d, \text{\AA}$	$I/I_0, \%$
9.56	100	9.60	100
7.65	9	7.69	63
7.07	3	7.17	12
5.06	2	6.89	10
3.78	2		
3.60	8	3.61	33
3.47	3	3.49	11

This is the evidence of certain resemblance of their structures and of presence of the same acetylacetonate ligands, which was proved by IR and ^1H NMR spectral data. However, contrasting to the zirconium tetrakis(acetylacetonate), the latter compound contains $\text{O}=\text{Zr}=\text{O}$ and $\text{Zr}=\text{O}$ groups within the cluster type complex, which contains acetylacetonate ligands:



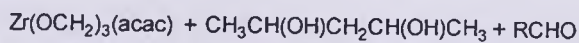
This was proved by X-ray diffraction studies of the samples undergone heat treatment at 300°C throughout 15-20 minutes resulting in the formation of zirconium dioxide of cubic symmetry. Their XRD data ($d=2.93, 1.80, 1.54$) are in good accord with ASTM 27-997 data. Since the cubic modification of zirconium dioxide is formed above 2300°C from common tetragonal zirconium dioxide, structure of dodecahedral type, containing zirconium dioxide, can be supposed for the cluster. X-ray analysis of $\text{Zr}(\text{acac})_4$ treated under the same conditions shows the absence of the peaks of cubic ZrO_2 and the presence of remaining acetylacetonate ligands, which is the evidence that just the highly organized zirconium cluster is the source of cubic ZrO_2 . The insoluble cluster with $\approx 60\%$ metal content was obtained at 140°C .



Scheme 1

The reaction of $\text{Zr}(\text{acac})_4$ with ethylene glycol, according to IR spectral and elementary analysis data, regardless of ethylene glycol concentration, leads to the zirconium complex, containing two acetylacetonate ligands. The compound obtained is insoluble in alcohols, however, it readily reacts with lead(II) acetate and titanium alkoxides with the formation of the PZT homogeneous sol. Zirconium bis-(ethylene glycolate) without acetylacetonate ligands can be obtained by the reaction of zirconium tetra(iso-propoxide) with ethylene glycol [6].

In the course of studies of regularities of the reactions of zirconium tetrakis(acetylacetonate) in alcoholic media we observed an unknown in the literature catalysis related to the metal ligand interaction and transformations of the acetylacetonate ligands. The earlier detected reaction of FeCl_3 with the distillation products Nesmeyanov and coworkers explained by iron tris(acetylacetonate) formation [4,5]. According to the GLC analysis data irrespective of alcohol nature we detected the presence of pentane-1,4-diol and complete absence of acetylacetonate in the reaction mixture. Moreover in the products of $\text{Zr}(\text{acac})_4$ reaction with n-butyl alcohol, according to the GLC analysis data and the positive test for the reaction of image forming silver, butyric aldehyde has been detected. The data obtained indicate on the possibility of proceeding the stepwise catalytic reaction in the co-ordination sphere of zirconium, involving the exchanges of alkoxide ligands, hydride shifts, resulting in the reduction of acetylacetonate and simultaneous formation of the aldehyde:



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EXPERIMENTAL

Zirconium tetrakis(acetylacetonate) was prepared according to the method described in [7], and was purified by recrystallization from isopropyl alcohol. Zirconium tetra(isopropoxide) was prepared from pyridinium hexachlorozirconate according to the method described in [8]. 2,4-Pentandiol was synthesized according to the method described in [9].

IR spectral measurements were made with "Specord IR-75" spectrometer in Nujol. ^1H NMR spectral measurements were carried out with "Varian-60" spectrometer, using CCl_4 as solvent and HMDS as a standard. XRD analyses of crystalline samples were made with "Dron-2" (λCuK_α) spectrometer.

Zirconium tris(buthoxide)acetylacetonate was prepared by dissolving 1.22 g (0.0025 mole) of zirconium tetrakis(acetylacetonate) in 30 ml of boiling butyl alcohol and refluxing the mixture for 30 min. After it the volatile products were removed by distillation in nitrogen flow at 100-120°C. After threefold repeating of this procedure the test for FeCl_3 of the fractions distilled were negative. After removing the volatiles in vacuum/20 torr at 50-80°C the viscous light yellow liquid was obtained. Yield is 0.93 g (93%). Found %: Zr 23.07, C 49.34, H 7.95; $\text{C}_{17}\text{H}_{34}\text{O}_5\text{Zr}$, calculated %: Zr 22.27, C 49.84, H 8.37.

IR spectrum, ν , cm^{-1} : 1120, 1160 (C-O-C), 1525, 1595 (symmetric and asymmetric valence frequencies of C=O group coordinated with zirconium).

^1H NMR (δ , ppm): 1.1 (9H, t, CH_3), 1.42-1.6 (12H, m, CH_2), 2.1 (6H, s, CH_3CO), 3.8 (6H, m, CH_2OZr), 5.7 (H, s, $=\text{CH}-$).

Zirconium tris(iso-buthoxide)acetylacetonate as yellow viscous glass like mass was obtained similarly except that iso-butanol was used as alcohol. Yield 0.98 g (96%). Found %: Zr 21.50, C 50.42, H 8.63; $\text{C}_{17}\text{H}_{34}\text{O}_5\text{Zr}$, calculated %: Zr 22.27, C 49.84, H 8.37.

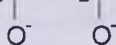
IR spectrum, ν , cm^{-1} : 1120, 1150 (C-O-C), 1525, 1595 (symmetric and asymmetric valence frequencies of C=O group coordinated with zirconium).

^1H NMR (δ , ppm): 0.9 (18H, d, CH_3), 1.8 (3H, m, CH), 2.0 (6H, s, CH_3CO), 3.64 (6H, m, OCH_2), 5.6 (H, s, $=\text{CH}-$).

Zirconium tris(2-methoxyethanolato-O,O')acetylacetonate as viscous glass like mass was obtained similarly except that 2-methoxyetanol was used as alcohol. Volatile products were removed by distillation in nitrogen flow at 70-80°C at 40 torr. The residue after removal of the volatile products was dissolved in light petroleum, filtered out, and dried

for 2 h at 50°C and 20 torr. Yield 0.89 g (86%). Found %: Zr 22.80, C 39.72, H 6.60; $C_{14}H_{28}O_8Zr$, calculated %: Zr 21.95, C 40.46, H 8.37.

IR spectrum, ν , cm^{-1} : 1120, 1160 (C-O-C), 1525, 1595 (symmetric and asymmetric valence frequencies of C=O group coordinated with zirconium). H^1NMR (δ , ppm): 2.1 (6H, s, CH_3CO), 3.30 (9H, s, OCH_3), 3.35 (6H, m, CH_2O), 3.9 (6H, m, $Zr-OCH_2$), 5.65 (H, s, $=CH-$), weak signals at 1.1-1.3 ppm, which can be related to the protons of CH_3 and CH_2 groups of $CH_3CHCH_2CHCH_3$ remaining zirconium ligands.



Zirconium ethylene glycolate bis(acetylacetonate) was synthesized by refluxing 1.22 g (0.0025 mole) of zirconium tetrakis(acetylacetonate) in 25 ml of dry iso-propyl alcohol and 0.31 g (0.0005 mole) of ethylene glycol in 10 ml of dry benzene for 1 h. The resultant compound as insoluble residue was filtered off, washed with dry benzene and dried in nitrogen flow at 50°C/20 torr for 4 h. Yield 0.72 g (82%). Melting point $\approx 300^\circ C$ with decomposition. The product is insoluble in benzene, 2-methoxyethanol, dissolved in 2-methoxyethanol on introducing pyridine or triethanolamine as complex forming agents. Found %: Zr 26.10, C 40.98, H 5.20; $C_{12}H_{18}O_6Zr$, calculated %: Zr 26.10, C 41.24, H 5.19.

IR spectrum, ν , cm^{-1} : 1100, 1165 (C-O-C), 1525, 1595 (symmetric and asymmetric valence frequencies of C=O group coordinated with zirconium).

Bis[zirconium tetrakis(2-methoxyetanolato-O,O')], complex with 2-methoxyethanol. 0.57g (0.0015 mole) of zirconium tetrakis(*iso-propoxide*)-*iso-propyl* alcohol complex, 0.9 ml (0.012 mole) of 2-methoxyethanol, and 8 ml of benzene were placed in a distillation columned flask and the azeotrope mixture of benzene with *iso-propyl* alcohol was removed at 71°C. The residue was dissolved in pentane, was filtered out, pentane was removed at reduced pressure at room temperature. The residue the glass like mass was dried in vacuum. Yield 0.43 g (73%). Found %: Zr 21.25, C 37.19, H 7.82; $C_{27}H_{64}O_{18}Zr_2$, calculated %: Zr 21.23, C 37.74, H 7.51.

IR spectrum, ν , cm^{-1} : 1130, 1070 (C-O-C), 3300-3500 (OH). H^1NMR (δ , ppm): 3.40 (27H, s, OCH_3), 3.80 (18H, m, CH_2O), 4.10 (18H, m, $Zr-OCH_2$).

The zirconium cluster was prepared by heating 1.22 g (0.0025 mole) of zirconium tetrakis(acetylacetonate) in 20 ml of dry *iso-propyl* alcohol in a sealed glass ampoule for 3 h. The resultant mixture was cooled, crystals of initial zirconium tetrakis(acetylacetonate) were filtered

off. The filtrate was distilled under reduced pressure for removal of the volatile products. The residue, the light yellow crystals, was dried at $50^{\circ}\text{C}/20$ torr. Yield 0.35 g. The product is soluble in benzene and alcohols, decomposes above 250°C . Found %: Zr 42.00, C 24.38, H 3.73; $\text{C}_{60}\text{H}_{96}\text{O}_{50}\text{Zr}_{13}$, calculated %: Zr 42.30, C 25.60, H 3.40.

IR spectrum, ν , cm^{-1} : 1525, 1595 (symmetric and asymmetric valence frequencies of C=O group coordinated with zirconium), 3200-3450 (OH).

The insoluble zirconium cluster was prepared similar except that the reaction was carried out at 140°C . Found %: Zr 59.78.

ACKNOWLEDGEMENT

This work was supported by the International Science and Technology Center under grant №022-96.

ՍՊԻՐԱՅԻՆ ՄԻՋԱՎԱՅՐՈՒՄ ՑԻՐԿՈՆԻՈՒՄԻ ՏԵՏՐԱԱՅԵՏԻԼԱՅԵՏՈՆԱՏԻ ՓՈԽԱՐԿՄԱՆ ՈՒՍՈՒՄԱՍԻՐՈՒԹՅՈՒՆԸ

Ս. Գ. ԳՐԻԳՐՅԱՆ, Լ. Գ. ՌԱՇԻԴՅԱՆ, Ս. Վ. ԱՌԱՔԵԼՈՎԱ, Ն. Ե. ՄԿՐՏՅԱՆ,
Ա. Մ. ԱՐԶՈՒՄԱՆՅԱՆ և Ա. Լ. ՄԱՆՈՒԿՅԱՆ

Ուսումնասիրվել են ցիրկոնիումի տետրաացետիլացետոնատի փոխարկումները սպիրտային միջավայրում: Ցույց է տրվել, որ առաջնային սպիրտների հետ (ն-բուտիլ, իզոբուտիլ, էթիլնոգլիկոլ, էթիլենգլիկոլի մոնոմեթիլեթեր) առաջանում են ցիրկոնիումի ալկոհոլատներ, որոնք պարունակում են գոնե մեկ մնացորդային ացետիլացետոնատային խումբ: Ցիրկոնիումի տետրաացետիլացետոնատը իզոպրոպիլ սպիրտի հետ առաջացնում է կայունացնող ացետիլացետոնատային լիգանդ պարունակող կայուն, ինչպես պոլյար, այնպես էլ ոչ պոլյար լուցիչներում լուծվող կլաստեր: Կլաստերի ջերմամշակումը, ըստ ռենտգենաֆազային անալիզի տվյալների, բերում է խորանարդային մոդիֆիկացիա ունեցող ցիրկոնիումի երկօքսիդի առաջացմանը: Առաջարկվել է սպիրտային միջավայրում ցիրկոնիումի տետրաացետիլացետոնատի փոխարկման սխեմա, որն իր մեջ ներառում է ցիրկոնիումի կոորդինացիոն ոլորտում ընթացող հաջորդական կատալիտիկ ռեակցիաներ, այդ թվում ալկօքսիդային լիգանդների փոխարկում, ացետիլացետոնը մինչև 2,4-պենտադիոլի վերականգնմանը և միաժամանակ ալդեհիդի առաջացմանը բերող հիդրիդային տեղաշարժ:

ИССЛЕДОВАНИЕ ПРЕВРАЩЕНИЯ ТЕТРААЦЕТИЛАЦЕТОНАТА ЦИРКОНИЯ В СПИРТОВЫХ СРЕДАХ

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А. М. АРЗУМАНЯН и А. Л. МАНУКЯН

Исследованы превращения тетраацетилацетоната циркония в спиртовых средах. Показано, что с первичными спиртами: н-бутиловым, изобутиловым, этиленгликолем, монометиловым эфи-

ром этиленгликоля образуются алкоголяты циркония, содержащие по крайней мере одну остаточную ацетилацетонатную группу. Тетраацетилацетонат циркония с изопропиловым спиртом образует устойчивый и растворимый как в полярных, так и неполярных растворителях кластер, содержащий стабилизирующие ацетилацетонатные лиганды. Термообработка кластера, по данным рентгенофазного анализа, приводит к образованию двуокиси циркония кубической модификации. Предложена схема превращения тетраацетилацетоната циркония в спиртовых средах, включающая последовательные каталитические реакции, протекающие в координационной сфере циркония, включающие обмен алкоксидных лигандов, гидридный перенос, приводящий к восстановлению ацетилацетона в 2,4-пентандиол и одновременному образованию альдегида. Синтезированные циркониевые прекурсоры использованы в золь-гель технологии получения сегнетоэлектрических тонких пленок цирконата титаната свинца.

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