lating ϕ from association constants obtained by whatever analytical technique. Comparing such calculated values with the experimentally measured ϕ values, discrepancies due to the neglected solute–solvent interactions might be revealed.

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Synthesis of lead(II)titanate and related compounds with the perovskite structure

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AS PART of a solid state investigation of leadzirconate–titanate systems, different methods of synthesis are being used, such as heating of the well-mixed oxides [1], pyrolysis of amorphous organic precursors [2] and thermal decomposition of oxalate complexes [3].

After a successful synthesis of the ilmenite-structure compounds $FeTiO_3$, $MgTiO_3$ etc. and solid solutions thereof by thermal decomposition of the well-defined aquohexafluorotitanate complexes of the type $Fe(H_2O)_6TiF_6$ [4], the authors tried to apply the same method to the synthesis of compounds having the perovskite structure such as $PbTiO_3$ via the complex $Pb(H_2O)_3TiF_6$. The principle of the method is given by the stoichiometric equations,

$$PbCO_3 + H_2TiF_6 = Pb(H_2O)_3TiF_6 \text{ [5]}$$

$$Pb(H_2O)_3TiF_6 = PbTiO_3 + 6HF.$$

After thermogravimetric analysis of the aquofluoro complex it appeared that normal heating in air resulted in a mixture of $PbTiO_3$, PbF_2, PbO and TiO_2. Therefore slow decomposition in nitrogen, nitrogen/steam and nitrogen/hydrogen/steam atmospheres was applied which, however, also resulted in contaminated $PbTiO_3$ residues. But it was found that heating in air only, using a very slow heating program, to prevent evaporation of TiF_4 at 284°C, does result in pure $PbTiO_3$.

An example of such a heating program is: 2 hr 250°C, 2 hr 300°C, 2 hr 400°C, 8–16 hr 550°C, $\frac{1}{4}$ hr 600°C, $\frac{1}{4}$ hr 700°C, $\frac{1}{2}$ hr 800°C. It is noticed that heating at lower temperatures and at 550°C is carried out for a relative long period. Care has to be taken that the synthesis of the $Pb(H_2O)_3TiF_6$ leads to a pure product. In preparing an aqueous solution of H_2TiF_6 by dissolving TiO_2 in aqueous 42% HF on a hot waterbath it is advisable to add an excess of TiO_2 in order to prevent a precipitate of PbF_2 in the next step due to the presence of unreacted F^--ions. A less than equational amount of solid $PbCO_3$ added to the filtered H_2TiF_6 solution, dissolves with effervescence, at the same time giving a white precipitate of $Pb(H_2O)_3TiF_6$, which can be washed with acetone. It was found that solutions of lead nitrate or acetate used in place of solid lead carbonate did not give as good results, because contamination by extra lead ions occurred. The reason might be that $Pb(H_2O)_3TiF_6$ is easily hydrolysed in a too great amount of water and/or that nitrate and acetate give adducts with the fluorotitanate.

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Analysis of the products showed:

$Pb(H_2O)_3TiF_6$: Pb 49·10% (gravimetric as chromate), Ti 11·40% (gravimetric as cupferronate), (theoretical Pb 48·97%, Ti 11·32%).

$PbTiO_3$: Pb 68·20% (gravimetric as lead sulphate after melting with potassium pyrosulphate [6]). Ti 15·96% (gravimetric as *p*-hydorxyphenylarsonate), (theoretical Pb 68·36%, Ti 15·80%). Found by X-ray fluorescence analysis: Pb 68·0%, Ti 16·0%.

In the table the X-ray diffraction pattern of $PbTiO_3$ obtained with CuK_α-radiation in a diffraction spectrometer Philips PW 1320/1310 is compared with that given in the X-ray powder data file, card no. 6–0452[7]. There is complete correspondence, which indicates that the used method yields pure $PbTiO_3$.

Table 1. Comparison of X-ray diffraction patterns

	ASTM 6–0452		This work	
hkl	*d* (Å)	I/I_1	*d* (Å)	Intensity
001	4·150	26	4·149	24
100	3·899	49	3·897	47
101	2·842	100	2·846	100
110	2·758	52	2·756	49
111	2·297	40	2·301	38
002	2·076	15	2·074	13
200	1·950	32	1·955	33
102	1·833	13	1·829	11
201	1·765	10	1·767	8
210	1·744	11	1·748	10
112	1·6581	19	1·6592	21
211	1·6075	42	1·6090	39

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