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LOW-TEMPERATURE SOLID-STATE ROUTES TO TRANSITION METAL OXIDES VIA METATHESIS REACTIONS INVOLVING LITHIUM OXIDE

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Abstract—Thermolysis of a mixture of lithium oxide and anhydrous transition metal halide, MX_n (M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Co, Ni, Cu, Zn, X = Cl; M = Mn, X = I), at oven temperatures of 450°C for 5 h produces crystalline transition metal oxide via a solid-state metathesis reaction. DSC studies show that the reaction is initiated at 300°C for M = Hf and Nb. When M = Ta or Nb the product is $LiMO_3$. The metal oxides and lithium-metal oxides were characterized by X-ray powder diffraction, S.E.M., EDAX, FT-IR and magnetic moment measurements.

Metal oxides of various formulations are known for all the transition elements.[1] They have widespread technological importance as powders for catalysts,[2] ceramics,[3] engineering materials[4] and as thin films for reflectance coatings. Recently the use of mixed metal oxides as high-temperature superconductors[5] has seen rapid growth and could lead to great improvements in power transmission.

Metal oxides have been made by heating the metal in air, often at high temperature. The refractory nature of some metal oxides means that annealing has often been required to produce a crystalline material. New developments in metal oxide and mixed metal oxide synthesis have involved the use of either molecular precursors or hydrothermal processes.[6] The thermal decomposition of metal nitrates or alkoxides has allowed lower temperature preparation of oxides either as bulk solids or as thin films via MOCVD. Occasionally competitive degradation pathways incorporate other elements in the oxide lattice in these lower temperature preparations.[7] Hydrothermal processes have allowed lower temperature mixed-metal oxide synthesis and have several advantages, including intimate mixing of the reagents and stoichiometric composition control.

Solid-state "self-propogating high-temperature synthesis" (SHS) routes to ceramic materials including nitrides, sulphides, phosphides and oxides have been developed by Russian workers.[8] Kaner[9–12] has elegantly developed this work for metathesis type reactions and has synthesized a range of main group and transition metal pnictides, mixed pnictides and mixed chalcogenides. Solid-state metathesis routes have some advantages when compared to traditional methods of metal oxide synthesis: firstly, no solvent is involved in the reaction; secondly, low synthesis temperatures are required often with the reaction exhibiting high exothermicity once initiated; thirdly, the by-products in the reactions are removeable from the oxide lattice allowing ready separation of products. Additionally, stoichiometric control of the reagents allows the possibility of making a range of mixed metal oxides.

An early example of a metathesis route to metal oxides was developed in 1932 by Hilpert and Wille,[13] who reported the preparation of mixed-metal ferrates at moderate temperature (400–500°C) by reaction of metal dichlorides with lithium ferrate. Recently, reaction[10,14] of sodium peroxide with CuF was found to produce Cu_2O.

We report here the reaction of lithium oxide with anhydrous transition metal halides, to produce crystalline transition metal oxides.

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EXPERIMENTAL

All reactions and preparations were conducted under vacuum or in a dinitrogen filled dry-box. Glass ampoules were made out of either pyrex, borosilicates or quartz glass and were either flame dried under vacuum or heated to 400°C for 6 h prior to reaction. All solvents were degassed; THF was distilled from sodium/benzophenone and stored over 4 Å molecular sieves prior to use. Metal halides and lithium oxide were purchased from Aldrich Chemical Company. The metal halides were dried over thionyl chloride prior to use. X-ray powder diffraction patterns were obtained using a Siemens D5000 diffractometer using nickel filtered Cu-K_α radiation (1.5406 Å); SEM and EDAX analyses were obtained on a Jeol JSM 820 instrument equipped with the Kevex program;[15] FT-IR spectra were obtained as pressed KBr pellets on a Nicolet 205(CsI); GC were obtained on a Pye–Unicam 204 with 5 Å molecular sieves using a thermal conductivity detector with helium carrier gas; magnetic moment measurements were determined by a Johnson–Matthey balance. DSC analyses were performed in open aluminum pans under argon flow on a Polymer Laboratories DSC using a ramp rate of 5°C $\min^{-1}$ from 200 to 620°C. Thermal initiation of the reactions was performed in a Lenton Thermal Design tube furnace. Microanalyses were performed by Medac LTD, Brunel University.

Transition metal oxide preparation (M = Ti, Zr, Hf, V, Cr, Mo, W, Mn, Fe, Co, Ni, Cu, Zn, Hg)

Lithium oxide (50–100 mg) and anhydrous metal halide, MX_y (equimolar quantities of lithium and halide), were ground together using an agate pestle and mortar in a nitrogen filled dry-box. The powder was added to a thick-walled glass ampoule, sealed under vacuum and sonicated with ultrasound for 10 min. The ampoule was then wrapped in glass wool and placed in a conventional oven at 450°C for 2–10 h, during which time the solids invariably fused into a large lump and changed colour. The ampoule was removed from the oven, allowed to cool to room temperature and broken open in a dinitrogen filled glove-box. Trituration of the fused solid with THF (3×20 cm^3) for 10 h produced a coloured precipitate and a cloudy THF layer. Evaporation of the THF filtrate produces lithium chloride. The coloured powders were identified as transition metal oxides by X-ray powder diffraction (Table 1), EDAX analysis, FT-IR and magnetic moment measurements. Ceramic yields, based on the metal after THF trituration varied from 60 to 90% dependent on the sample.

Table 1. Crystalline phases observed from reaction of MX_n and Li_2O

Initial metal halide	Crystalline phase detected	Colour	Yield (%)	Reaction time (h)	Observed lattice *a* spacing[20]	Literature lattice *a* spacings
$TiCl_4$	TiO_2 (Li_2TiO_3)	White	60	2	4.585 (5.06)	4.593 (5.072)
$TiCl_3$	TiO_2	White/grey	60	2	5.069	5.067
$ZrCl_4$	ZrO_2	Grey	65	2	5.32	5.313
$HfCl_4$	HfO_2	Grey	65	2	5.12	5.12
VCl_4	VO_2 (Li_3VO_4)	Black	55	2	9.083 (5.499)	9.083 (5.447)
VCl_3	V_2O_3 ($LiVO_2$)	Black	60	2	5.42	5.43
$NbCl_5$	$LiNbO_3$	Light grey	90	2	5.149	5.149
$TaCl_5$	$LiTaO_3$	Grey	90	2	5.167	5.153
$CrCl_3$	Cr_2O_3	Grey	60	10	4.955	4.958
$MoCl_5$	MoO_2	Brown	65	10	5.609	5.607
$MoCl_3$	MoO_2	Black	70	10	5.610	5.607
WCl_4	WO_2	Black	70	2	5.575	5.575
MnI_2	MnO (Mn_3O_4)	Brown	85	2	4.440	4.445
$FeCl_3$	Fe_3O_4 (Fe_2O_3)	Dark brown	80	2	8.396	8.396
$CoCl_2$	CoO	Brown	85	10	5.040	5.036
$NiCl_2$	NiO	Light green	75	10	4.277	4.260
CuI	Cu_2O	Yellow	40	2	4.177	4.176
$ZnCl_2$	ZnO	Light grey	90	2	4.271	4.270
$HgCl_2$	HgO	Yellow	45	10	3.257	3.350

Note: not all lattices are cubic; only the *a* value is reported. Minor phases detected are shown in parentheses.

Alternative procedure

(1) An identical procedure to that outlined above can be carried out by initiating the reaction using a 750 W industrial microwave oven with a variable heating period dependent on the sample. The work-up and properties of the materials obtained were identical to those initiated in the conventional oven.

(2) The metal oxides could also be washed free of lithium chloride by-products by washing with degassed water for 10 min.

(3) Attempts at making mixed metal oxides were investigated under the same reaction and work-up conditions as above, except equimolar quantities of the starting metal halide powders were ground together before mixing in the ground lithium oxide powder.

CAUTION! Reaction of hydrated metal halides with lithium oxide can lead to an explosion of the ampoules on thermolysis. Care must be taken in the reactions of Li_2O with metal halides because a vigorous exothermic reaction can result. All preparations should be routinely performed behind a toughened glass safety screen.

RESULTS AND DISCUSSION

Reaction of ground powders of Li_2O and anhydrous transition metal halides at an oven temperature of 450°C in sealed ampoules produce crystalline transition metal oxides and lithium halides via a solid state metathesis reaction, eqs (1), (2), (3) and (4).

$$MCl_4 + 2Li_2O \longrightarrow MO_2 + 4LiCl \quad (M = Hf, Zr, W) \qquad (1)$$

$$MX_2 + Li_2O \longrightarrow MO + 2LiX \quad (M = Zn, Hg, Cd, Co, Ni, X = Cl; \; M = Mn, X = I) \qquad (2)$$

$$FeCl_3 + Li_2O \longrightarrow Fe_2O_3 + Fe_3O_4 + 3LiCl \qquad (3)$$

$$2CuI + Li_2O \longrightarrow Cu_2O + 2LiCl \qquad (4)$$

The product of the reactions [eqs (1), (2), (3) and (4)] was often contained as a fused grey lump and a small amount of a white solid was sublimed onto the walls of the ampoule. The white sublimed solid was analysed as lithium halide (either LiCl or LiI dependent on the initial reagents) by X-ray powder diffraction (XRPD), lithium flame test and EDAX analysis. The grey fused material showed a smooth morphology by S.E.M., Fig. 1(a); metal, oxygen and a small amount of halide (15 mol%) by EDAX analysis, both of which are consistent with the formation of a metal oxide that is coated with sublimed lithium halide. The metal oxide was purified by either washing with THF or water; this removed the co-product lithium halide. The metal oxides after trituration were characterized by X-ray powder diffraction (Table 1), FT-IR, magnetic moment measurements, S.E.M., EDAX analysis and microanalysis.

The S.E.M. profile of the triturated metal oxides showed micron sized particles with sharp angles and faces as illustrated in Fig. 1(b), whilst the EDAX analysis revealed only metal and oxygen with no halides present (2–3% detection limit). The samples of ZnO and Cr_2O_3 made in this study showed less than 0.5% lithium by microanalysis, indicating that the metal oxide lattices do not contain appreciable amounts of LiX after trituration. The FT-IR spectra of the metal oxides showed a broad band at *ca* 450 cm^{-1} due to M—O stretches. The magnetic moment measurements were typical for each of the metal oxides and showed no deviation from literature values.[16]

The X-ray powder diffraction data for the transition metal oxides formed from reaction of Li_2O and metal halide are summarized in Table 1. In general, after a reaction time of 5 h at 450°C a crystalline transition metal oxide was formed, however, the degree of crystallinity as judged by the Scherrer equation[17] varied from crystallite sizes of 800 Å (ZnO) to 150 Å (HfO_2). The metal oxides after trituration showed no lithium halide present and only one phase of metal oxide (by XRD), with the exception of iron and manganese where two phases, Fe_2O_3, Fe_3O_4 and MnO, Mn_3O_4, were detected. Representative XRD patterns for ZnO and MnO, Mn_3O_4 made in this study, are shown in Figs 2(a) and 2(b).

The phase of metal oxide detected by XRD invariably showed the metal in the same oxidation state as in the initial metal halide. In general no reduction or oxidation of the metal occurred and no gases (O_2) were detected from the reaction by GC, however, for reactions involving $TiCl_3$ and $MoCl_3$, TiO_2 and MoO_2 were detected indicating an oxidation at the metal. For reactions involving VCl_3 and VCl_4 the metal oxides formed were V_2O_3 and VO_2, respectively. A small amount of the phases associated with $LiVO_2$ and Li_3VO_4 were also detected in these reactions by XRD. Analogous solid-state reactions of Li_3N and metal halides do lead to reduction at the metal and formation of dinitrogen,[18] with the tendency increasing across the periodic table such that when starting with $HfCl_4$ partial reduction occurs at the metal and HfN and N_2 are formed. To the right of the *d*-block reduction becomes increasingly more important

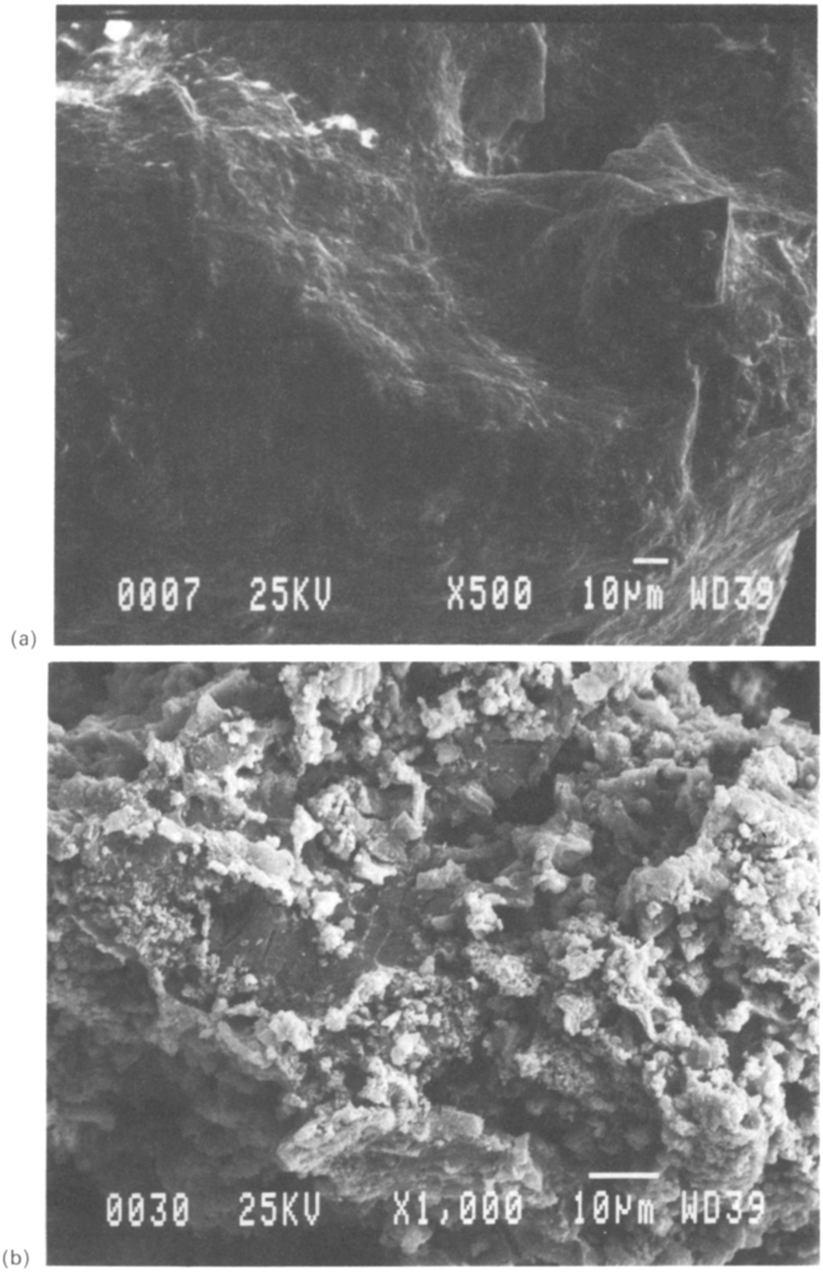

Fig. 1. S.E.M. profiles of the solid produced by reaction of MnI_2 and Li_2O (a) without and (b) after trituration with water.

and the reaction between $ZnCl_2$ and Li_3N yields only zinc metal and dinitrogen. This trend is not seen for the reactions of Li_2O and transition metal halides where metal oxides (or lithium metallates) are formed for all the metal halides studied independent of the position of the metal in the periodic table. The reason for the difference in reactivity for similar solid-state reactions involving Li_2O and Li_3N and metal halides may be due to the fact that many of the late transition metal nitrides are thermally unstable and undergo facile reduction to metal and dinitrogen, whereas metal oxides are comparatively more thermally stable.

The reaction of $HfCl_4$ with Li_2O was studied by DSC, which revealed a large exotherm at 310–325°C (Fig. 3). Similar results were also obtained for reaction of $NbCl_5$ and Li_2O. The energy released (120–300 kJ mol^{-1}) corresponds to the expected heat of reaction on forming metal oxide and LiCl. Interestingly the exotherm takes place over a time scale of a few minutes, indicating that the reaction is not as violently exothermic as reactions of $MoCl_5$–

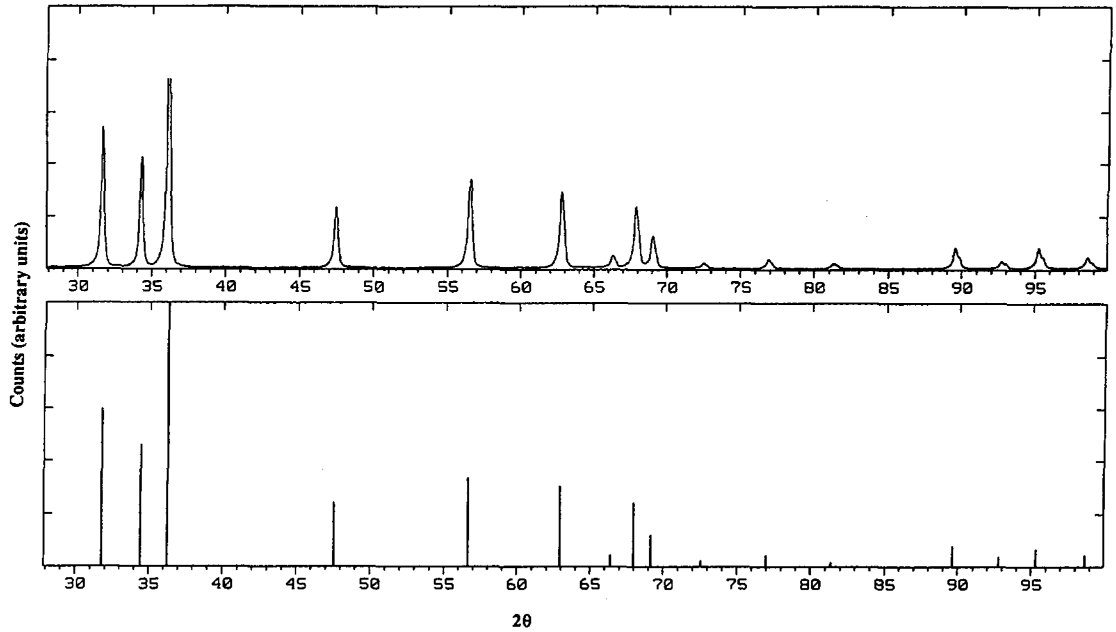

Fig. 2(a). Upper trace X-ray powder diffraction pattern for the solid produced from reaction of $ZnCl_2$ and Li_2O ; lower trace standard X-ray powder diffraction line pattern for ZnO.

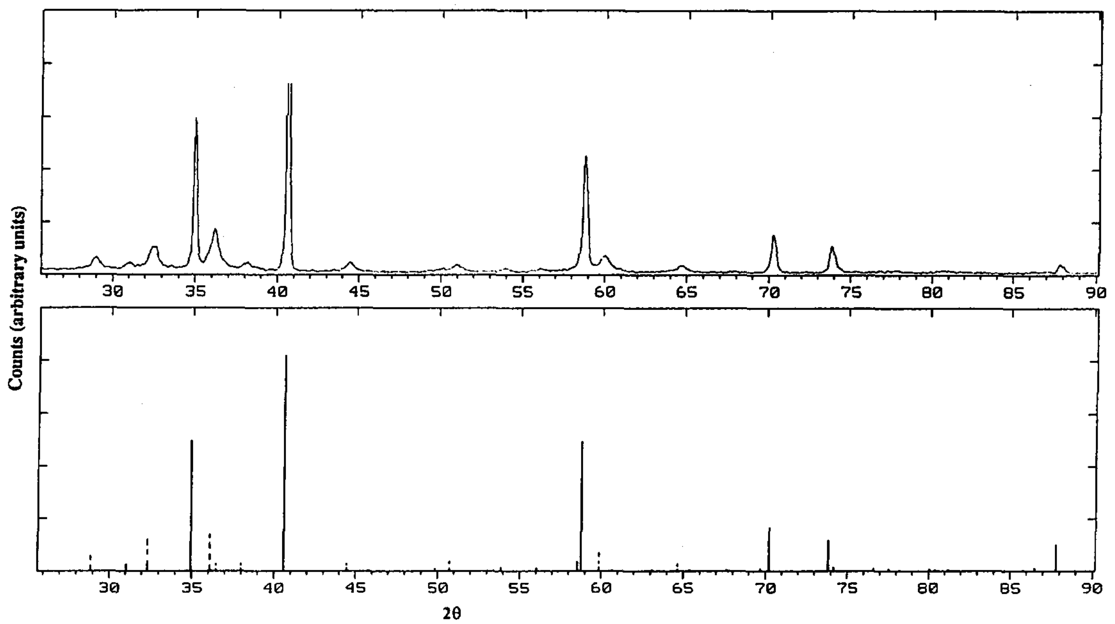

Fig. 2(b). Upper trace X-ray powder diffraction pattern for the solid produced from reaction of MnI_2 and Li_2O ; lower trace standard X-ray powder diffraction line pattern form MnO (——) and Mn_3O_4 (----).

Na_2S and Li_3N–$HfCl_4$ which are over in a few seconds.[9,18] However, the reaction of $ZnCl_2$ and Li_2O is extremely exothermic with the products spraying the inside of the DSC cell ; initiation temperature in this case proved to be around 250°C. It is probable that heat transfer in the DSC cell is easier than in the glass ampoule reactions and that the observed tube furnace initiation temperatures of 400–450°C actually correspond to 310–325°C at the sample surface after the effects of thermal gradient through the glass and the bulk sample are taken into account. Blank runs of Li_2O and $HfCl_4$

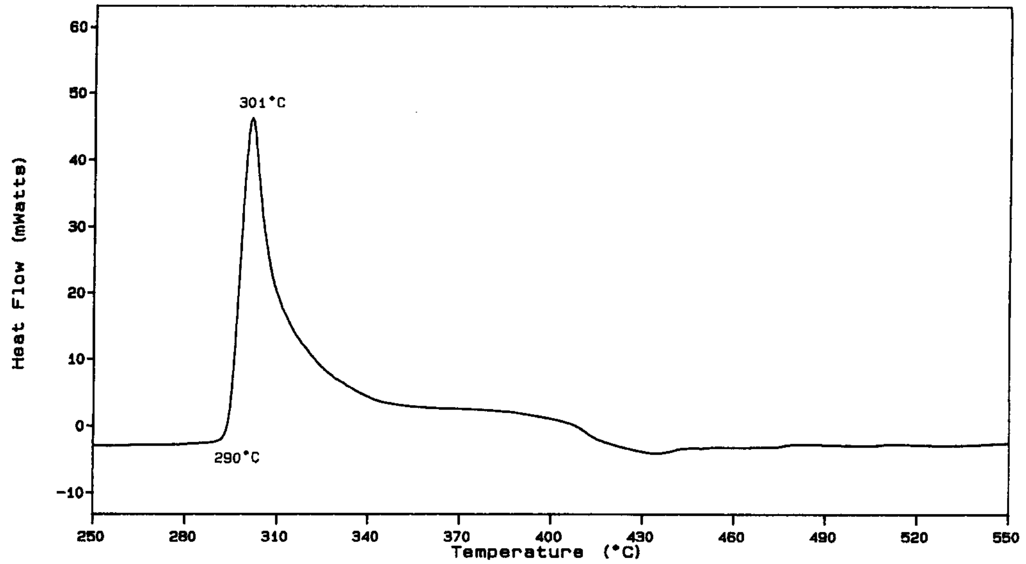

Fig. 3. Differential scanning calorimetry trace for reaction of $HfCl_4$ and Li_2O.

in the same apparatus showed no features of the same magnitude from 200 to 650°C. A sample of $HfCl_4$ and Li_2O held at 295°C showed heat evolved over a 15 min period, corresponding approximately to the calculated heat of reaction. The heat evolved from the reaction suggests high temperatures are generated; this is confirmed by the crystallinity of the product. Analogous reactions of lithium nitride or lithium sulphide with transition metal halides are very exothermic, inducing temperatures[9,18] in excess of 1000°C.

Hess' Law calculations[19] of the reaction of Li_2O with metal halides indicate that the reaction is exothermic with ΔH_f varying from -100 to -600 kJ mol^{-1} dependent on the metal. Initiation of the reaction in a small region of the solid may occur, but propagation throughout the bulk material may not be as facile in these uncompressed mixed Li_2O/MX_n powders than with analogous Li_3N reactions. Thus, a number of independent propagations throughout the solid could account for the observed fused crystalline product and partially sublimed metal halide.

The major exceptions to the formation of metal oxides in the reactions of Li_2O with transition metal halides were those involving niobium and tantalum pentachlorides, where $LiNbO_3$ and $LiTaO_3$ were the only phases detected [eq. (5)]. However, in reactions involving titanium and vanadium halides with Li_2O a small amount of crystalline lithium metallate was observed in addition to the main metal oxide phase by XRPD. The X-ray powder diffraction patterns of $LiTaO_3$ and $LiNbO_3$

$$MCl_5 + 3Li_2O'LiMO_3 + LiCl$$

$$(M = Ta, Nb) \qquad (5)$$

were phase pure (Fig. 4) after THF trituration and the EDAX analysis showed only metal and oxygen with no chlorine present (lithium could not be determined by EDAX analysis on the instrument used). The samples of $LiMO_3$ were diamagnetic as expected, indicating that the metals had not been reduced.

Attempts at making mixed-metal oxides, $M_xM_yO_z$, by reaction of preground metal halides and lithium oxide did not prove successful at oven temperatures of 450°C. This is illustrated in Fig. 5 for the reaction of equimolar amounts of $ZnCl_2$ and MnI_2 with Li_2O, which produced both ZnO and MnO rather than a mixed metal oxide, Zn_xMn_yO.

The oxygen incorporated in the transition metal oxides formed from metathesis reactions involving Li_2O comes predominantly from the lithium oxide, because blank experiments under exactly the same conditions produced only unreacted metal halide (as demonstrated by XRPD and EDAX analysis). However, for the reactions involving $TiCl_3$ and $MoCl_3$, where oxidized products TiO_2 and MoO_2 are produced, some oxygen is probably incorporated in the product either due to work-up or from the glassware. One specialist utility of this reaction could be in incorporating isotropically labelled oxygen into a metal oxide lattice by starting with initially labelled lithium oxide.

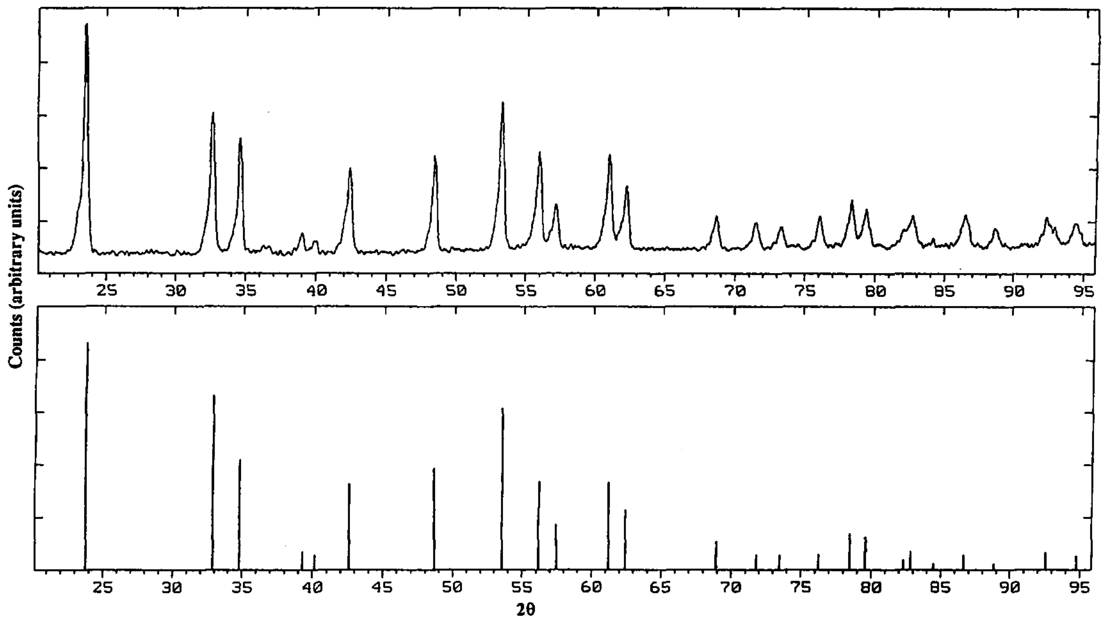

Fig. 4. Upper trace X-ray powder diffraction pattern for the solid produce from reaction of $TaCl_3$ and Li_2O; lower trace standard X-ray powder diffraction line pattern for $LiTaO_3$.

CONCLUSIONS

Current routes to metal oxides either by direct combination of the elements or by hydrothermal molecular precursor routes often involve high-temperature pyrolysis of the materials or prolonged annealing to produce a crystalline material. The solid-state metathesis routes described here to form metal oxides are at a reasonably low initiation temperature (300°C) and comparatively short reaction times (5 h for ampoule reactions, 6–10 min in a DSC cell). Unfortunately mixed-metal oxides seem

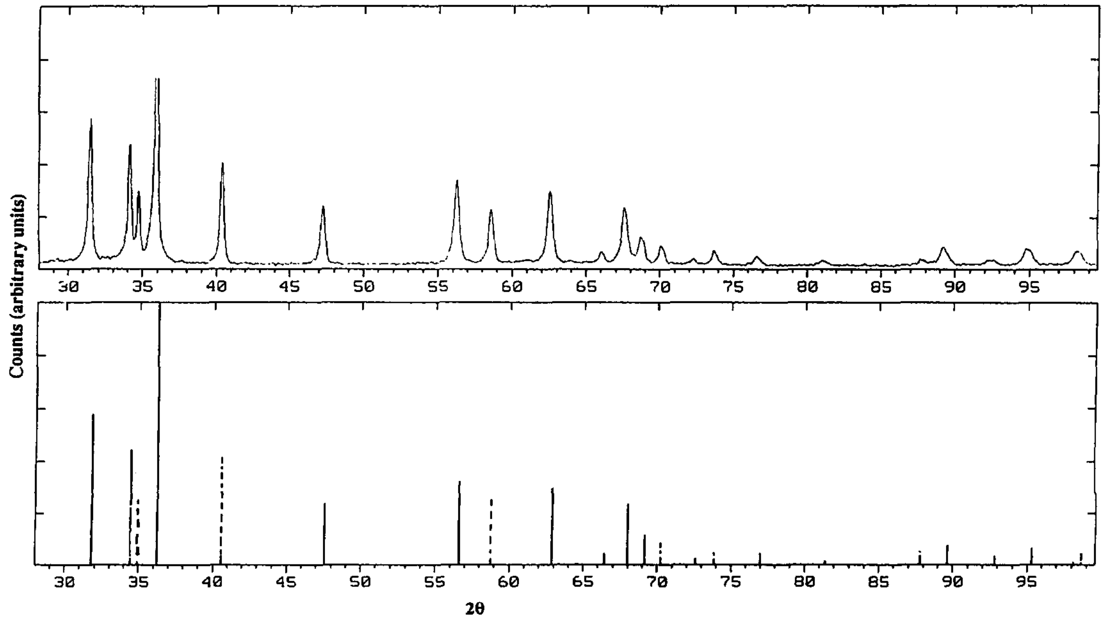

Fig. 5. Upper trace X-ray powder diffraction pattern for the solid produce from reaction of equimolar amounts of $ZnCl_2$ and MnI_2 with Li_2O; lower trace standard X-ray powder diffraction line pattern for ZnO (——) and MnO (– – – –).

difficult to form by this low external energy route, probably because of a lack of intimate mixing of the reagents. All the transition metal halides studied react with Li_2O to form metal oxide with little redox chemistry at the metal, however, for Ta and Nb the only phase produced is $LiMO_3$ and for V and Ti a small amount of $LiMO_x$ phases are also seen. The solid-state metathesis reaction of Li_2O and MX_n offers a convenient, rapid, low external energy route to industrially useful metal oxides such as TiO_2 and ZnO.

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