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THERMODYNAMIC STABILITY OF THE LITHIUM ZIRCONATES AND LITHIUM YTTRATE

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Abstract—The thermodynamic data of the lithium zirconates (Li_2ZrO_3, $Li_6Zr_2O_7$, Li_4ZrO_4 and Li_8ZrO_6) were calculated based on the Neumann–Kopp rule and the third law. The equilibrium lithium oxide vapor pressures and lithium loss values due to evaporation at different temperatures and in different environments were obtained. Thermal decomposition of Li_8ZrO_6 was assessed by theoretical calculations and weight loss and XRD experiments. The experimental results are in agreement with the theoretically predicted ones. The Gibbs free energies of reaction of lithium zirconates and lithium yttrate with water vapor and the corresponding equilibrium vapor pressures of water were calculated. The stability of pure and yttrium-doped Li_8ZrO_6 with respect to water vapor is assessed from weight gain measurement in air.

Keywords: Thermodynamic stability, lithium zirconates, lithium yttrate.

1. INTRODUCTION

Li_8ZrO_6 and $LiYO_2$ are two of the few lithium ion conductors that are thermodynamically stable against pure lithium (1), and may be suitable as solid electrolytes in lithium batteries. Li_8ZrO_6 and Li_2ZrO_3 are also potential tritium breeding materials in a fusion reactor because of the low tritium solubility and a reasonably rapid diffusion of tritium (2). However, a systematic study on the preparation of Li_8ZrO_6 has not been reported. This material is difficult to synthesize as a single phase because of the high content of the volatile lithium component. A knowledge of the thermal stability and the stability against attack by water vapor is important for processing and applications of Li_8ZrO_6, Li_2ZrO_3 and $LiYO_2$.

2. EXPERIMENTAL

Sample preparation

The starting materials were reagent grade ZrO_2 and Li_2O_2 and analytical grade Y_2O_3. The appropriate amounts of oxides were weighed, mixed and ground in an agate mortar with a suitable amount of acetone. The ground powders were fired in alumina crucibles in air first at 130–150°C for 1 day, then at 900°C for 3 days. The reacted samples were ground again and pressed into pellets of 13 mm diameter by 2–5 mm thick at 70 MPa. The pellets were sintered in an alumina crucible in air at 500°C for 1 day, then 800°C for 8 h and finally at 930°C for 30 min to obtain samples of $Li_{8+x}Y_xZr_{1-x}O_6$.

The crystal structure was studied via X-ray powder diffraction using CuKα Ni-filtered radiation. The weight loss at different temperatures and weight gain on exposure to air were determined by an analytical balance. The reacted products after exposure to air were analyzed by i.r. spectra and DTA.

3. THEORETICAL CALCULATIONS AND RESULTS

3.1. *Thermodynamic data calculations*

Enthalpies of formation of $Li_6Zr_2O_7$ and $LiYO_2$ are not available, but the enthalpies for Li_2ZrO_3, Li_4ZrO_4 and Li_8ZrO_6 have been measured by Neubert and Guggi (3). Based on the compilation of standard enthalpies of formation of inorganic compounds by Swalin (4) and Kubaschewski *et al.* (5), there is an excellent correlation between the enthalpies and the molar volume changes of the compounds formed from the elements. This correlation originates from the relationship between bond strength and bond length. The correlations for Li_8ZrO_6, Li_4ZrO_4 and Li_2ZrO_3 are shown in Fig. 1. From this correlation and the values of the molar volume changes of Li_6ZrO_7 and $LiYO_2$, the standard enthalpies of formation were determined to be $-2680\ kJ\ mol^{-1}$ for $Li_6Zr_2O_7$ and $-1420\ kJ\ mol^{-1}$ for $LiYO_2$. Good agreement was found when this method was applied to check the enthalpy of

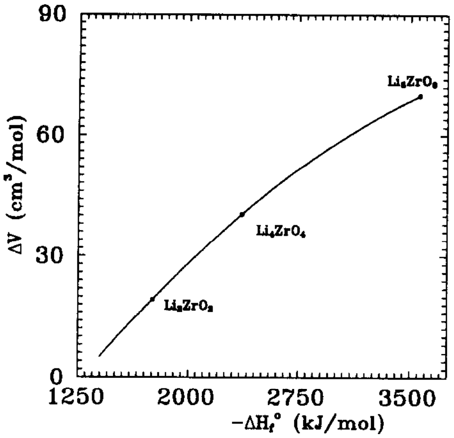

Fig. 1. The correlation between standard enthalpy of formation and molar volume change after forming compounds from their components for lithium compounds.

Li_5AlO_4, another lithium ion conductor. The experimental value of the standard enthalpy of formation of Li_5AlO_4 was $-2365\ \mathrm{kJ\ mol^{-1}}$ (6), whereas the value obtained from the correlation in Fig. 1 was $-2366\ \mathrm{kJ\ mol^{-1}}$.

The data for heat capacities and entropies of Li_6ZrO_7, Li_4ZrO_4, Li_8ZrO_6 and $LiYO_2$ are also not available. Since the heat capacities and entropies for Li_2ZrO_3, Li_2O, ZrO_2 and Y_2O_3 are known (6), the missing values can be calculated from the third law and Kopp's rule which states that the heat capacity of a solid compound is the weighted sum of the heat capacities the elements forming the compound, i.e. for the compound of A_xB_y formed by the reaction

$$xA(s) + yB(s) = A_xB_y(s),$$

the heat capacity of A_xB_y, $(C_P)_{A_xB_y}$ can be expressed approximately as

$$(C_P)_{A_xB_y} = x(C_P)_A + y(C_P)_B.$$

The results are shown in Table 1. For Li_2ZrO_3, the calculated results are compared with the experimental values. It is seen that the relative errors of C_P and S^0 are less than 5%.

3.2. *Thermal stability calculations*

Lithium zirconates and lithium yttrate will decompose on heating because of the evaporation of lithium oxide. The major decomposition reactions are as follows:

$$Li_8ZrO_6 = Li_4ZrO_4 + 2Li_2O(g) \quad (1)$$

$$Li_8ZrO_6 = 0.5Li_6Zr_2O_7 + 2.5Li_2O(g) \quad (2)$$

$$Li_8ZrO_6 = Li_2ZrO_3 + 3Li_2O(g) \quad (3)$$

$$Li_8ZrO_6 = ZrO_2 + 4Li_2O(g) \quad (4)$$

$$Li_4ZrO_4 = Li_2ZrO_3 + Li_2O(g) \quad (5)$$

$$Li_2ZrO_3 = 2Li_2O(g) + ZrO_2 \quad (6)$$

$$LiYO_2 = 1/2Li_2O(g) + 1/2Y_2O_3. \quad (7)$$

The equilibrium vapour pressure of Li_2O, P_i (i represents the reaction number), for the above reaction is expressed as follows:

$$P_1 = \exp(-\Delta G_1^0/2RT)$$

$$P_2 = \exp(-2\Delta G_2^0/5RT)$$

$$P_3 = \exp(-\Delta G_3^0/3RT)$$

$$P_4 = \exp(-\Delta G_4^0/4RT)$$

$$P_5 = \exp(-\Delta G_5^0/RT)$$

$$P_6 = \exp(-\Delta G_6^0/2RT)$$

$$P_7 = \exp(-2\Delta G_7^0/RT),$$

where ΔG_i^0 is the standard Gibbs free energy for reaction i, R is the gas content and T is the absolute temperature. From Table 1 and thermodynamic data

Table 1. Calculated or experimental thermodynamic data for lithium zirconates and lithium yttrate at 298 K

	C_p (J mol^{-1} K^{-1})	S^0 (J mol^{-1} K^{-1})	ΔH^0 (kJ mol^{-1})
Li_2ZrO_3	110.3 110.3†	88.0 91.6†	−1756‡
$Li_6Zr_2O_7$	274.6	220.8	−2678
Li_4ZrO_4	164.4	129.2	−2364‡
Li_8ZrO_6	272.6	204.4	−3562‡
$LiYO_2$	78.3	68.3	−1423

†Experimental values from [6].
‡Experimental values from [3].

Table 2. Lithium and lithium oxide vapor pressure at different temperatures for Li_8ZrO_6, Li_4ZrO_4, Li_2ZrO_3 and $LiYO_2$

	T(K)	1173	1473	1773
Reaction†	P_{Li_2O} (atm)	7.86×10^{-10}	6.46×10^{-6}	
Reaction‡	P_{Li} (atm)	7.70×10^{-10}	1.67×10^{-6}	
Reaction§	P_{Li} (atm)	5.18×10^{-12}	8.00×10^{-8}	
Reaction‖	P_{Li} (atm)	8.92×10^{-15}	1.27×10^{-10}	
Reaction¶	P_{Li} (atm)	1.78×10^{-18}	5.48×10^{-13}	
Reaction††	P_{Li_2O} (atm)	5.16×10^{-11}	5.20×10^{-7}	2.24×10^{-4}
Reaction‡‡	P_{Li_2O} (atm)	2.21×10^{-13}	8.00×10^{-9}	8.56×10^{-6}
Reaction§§	P_{Li_2O} (atm)	1.93×10^{-25}	4.71×10^{-14}	1.80×10^{-9}

†$Li_8ZrO_6 = Li_4ZrO_4 + 2Li_2O(g)$.
‡$Li_8ZrO_6 = Li_4ZrO_4 + 4Li(g) + 2O_2(g)$ (in vacuum or in an atmosphere with initial $P_{O_2} = 0$).
§$Li_8ZrO_6 = Li_4ZrO_4 + 4Li(g) + 2O_2(g)$ (in air).
‖$Li_8ZrO_6 = 1/2Li_6Zr_2O_7 + 5Li(g) + 5/4O_2(g)$ (in vacuum or in an atmosphere with initial $P_{O_2} = 0$).
¶$Li_8ZrO_6 = 1/2Li_6Zr_2O_7 + 5Li(g) + 5/4O_2(g)$ (in air).
††$Li_4ZrO_4 = Li_2ZrO_3 + Li_2O(g)$.
‡‡$Li_2ZrO_3 = 2LiO(g) + ZrO_2$.
§§$LiYO_2 = 1/2Li_2O(g) + 1/2Y_2O_3$.

in [6], it is known that at the same temperature, $P_1 > P_3 > P_4$. Moreover, although Li_2O vapour can decompose further into lithium gas and oxygen, the calculations of Li_2O decomposition are orders of magnitude smaller than decomposition to LiO_2 and ZrO_2. Therefore, only reactions 1 and 2 need to be considered in thermal stability calculations.

From the thermodynamic data in Table 1 and [6], the equilibrium vapor pressure values of lithium oxide and lithium for Li_8ZrO_6, Li_4ZrO_4, Li_2ZrO_3 and $LiYO_2$ can be calculated (Table 2).

3.3. *Stability against water vapor*

Many lithium compounds tend to be attacked by water vapor in wet air. The ultimate case is hydrolysis of lithium compounds to form LiOH. In order to study the stability against water vapor for lithium zirconates due to hydrolysis, the following reactions have to be considered.

$$1/2Li_8ZrO_6 + H_2O(g) = 2LiOH + 1/2Li_4ZrO_4 \quad (W1)$$

$$2/5Li_8ZrO_6 + H_2O(g) = 2LiOH + 1/5Li_6Zr_2O_7 \quad (W2)$$

$$1/3Li_8ZrO_6 + H_2O(g) = 2LiOH + 1/3Li_2ZrO_3 \quad (W3)$$

$$1/4Li_8ZrO_6 + H_2O(g) = 2LiOH + 1/4ZrO_2 \quad (W4)$$

$$Li_4ZrO_4 + H_2O(g) = 2LiOH + Li_2ZrO_3 \quad (W5)$$

$$Li_6Zr_2O_7 + H_2O(g) = 2LiOH + 2Li_2ZrO_3 \quad (W6)$$

$$Li_2ZrO_3 + H_2O(g) = 2LiOH + ZrO_2 \quad (W7)$$

$$2LiYO_2 + H_2O(g) = 2LiOH + Y_2O_3. \quad (W8)$$

From the thermodynamic data in Table 1 and [6], the standard Gibbs free energies of the above reactions were calculated as follows:

$$\Delta G^0_{W1} = -120.67 + 0.1521T - 0.01149T \times \ln(T/298)$$

$$\Delta G^0_{W2} = 169.53 + 0.1521T - 0.01149T \times \ln(T/298)$$

$$\Delta G^0_{W3} = -117.60 + 0.1521T - 0.01149T \times \ln(T/298)$$

$$\Delta G^0_{W4} = -103.62 + 0.1531T - 0.1149T \times \ln(T/298)$$

$$\Delta G^0_{W5} = -111.47 + 0.1521T - 0.1149T \times \ln(T/298)$$

$$\Delta G^0_{W6} = -1553.4 + 0.1521T - 0.01149T \times \ln(T/298)$$

$$\Delta G^0_{W7} = -61.70 + 0.1559T - 0.01153T \times \ln(T/298)$$

$$\Delta G^0_{W8} = 219.99 + 0.1521T - 0.01149T \times \ln(T/298).$$

The equilibrium water vapor pressure for these reactions is listed in Table 3. In air, the typical water vapor pressure is 10^{-2} atm. Then the Gibbs free

Table 3. The equilibrium water vapor pressure for lithium zirconates and lithium yttrate at various temperatures

T(K)	298	373	473	673	773	873
P_{W1}† (atm)	6.29×10^{-14}	8.22×10^{-10}	2.21×10^{-6}	1.24×10^{-2}	1.67×10^{-1}	1.20
P_{W2}‡ (atm)	4.59×10^{37}					
P_{W3}§ (atm)	2.16×10^{-13}	2.00×10^{-9}	4.82×10^{-6}	2.15×10^{-2}	1.83	0.76
P_{W4}‖ (atm)	6.82×10^{-11}	2.30×10^{-7}	1.80×10^{-5}	0.26	2.60	
P_{W5}¶ (atm)	2.58×10^{-12}	1.50×10^{-8}	2.30×10^{-7}	6.43×10^{-2}	0.70	4.30
P_{W6}†† (atm)	4.50×10^{-265}					
P_{W7}‡‡ (atm)	2.10×10^{-4}	0.23	11.3			
P_{W8}§§ (atm)	3.20×10^{57}					

energies of reactions W1 to W8 can be calculated as given in Table 4.

4. DISCUSSION

4.1. *Thermal stability*

From the thermodynamic calculations in section 3.2, it is known that reaction 1 is more favourable than reactions 2, 3 and 4 for the decomposition for Li_8ZrO_6. Therefore, for calculating the lithium loss due to evaporation, only reaction 1 will need to be considered. Based on the Hertz–Langmuir expression (7) and Table 2, the maximum lithium loss from reactions 1, 6 and 7 can be calculated as listed in Table 5.

Considering a spherical perfect crystal with an initial radius of R_0, and for convenience, neglecting the anisotropy of its decomposition and also the affects of products on the reaction rate, then the minimum time for the full decomposition of the material can be derived as

$$t = \rho R_0 / v,$$

where ρ is the density of the crystal and v is the effusion rate of the decomposition vapor.

As an example, at 1200°C, a 1 g spherical crystal Li_8ZrO_6 would decompose fully via reaction 1 in less than 9 h, and at 1100°C it would require about 116 h, but, at 900°C, Li_8ZrO_6 decomposes very slowly, requiring 6.5×10^4 h. Based on this information, it is recommended that the reaction temperature in the preparation of Li_8ZrO_6 be below 1100°C. In the present work, the solid state formation parameters of Li_8ZrO_6 from the Li_2O_2 and ZrO_2 raw materials were chosen as 900°C and 72 h. XRD results in Fig. 2 show that pure phase Li_8ZrO_6 was obtained after the reaction.

The decomposition experiments for Li_8ZrO_6 sintered disc samples with diameter 13 mm and thickness 2–3 mm were carried out in air at 1000 and 1200°C. The XRD results shown in Fig. 2 indicate that the sample heated at 1200°C for 8 h in air retains Li_8ZrO_6 as a minor phase. For the sample heated at 1000°C for 20 h, Li_4ZrO_4 appeared in the sample. The lithium loss at 1000°C in air was measured for a sample with 13 mm diameter and 3.5 mm thickness

Table 4. The Gibbs free energies of reaction of lithium zirconates and lithium yttrate with water vapor in air with $P_{H_2O} = 0.01$ atm

T(K)	298	373	473	673	873
ΔG_{W1} (kJ)	−63.7	−53.5	−33.1	1.2	34.8
ΔG_{W2} (kJ)	226.3	239.6	257.1	291.4	325.0
ΔG_{W3} (kJ)	−60.9	−47.6	−30.1	4.2	37.8
ΔG_{W4} (kJ)	−46.6	−33.2	−15.6	18.9	52.7
ΔG_{W5} (kJ)	−54.7	−41.4	−24.1	10.3	43.9
ΔG_{W6} (kJ)	−1497	−1483	−1466	−1431	−1398
ΔG_{W7} (kJ)	−3.8	9.8	27.6	62.7	97.0
ΔG_{W8} (kJ)	276.7				

Table 5. The maximum lithium loss rates in Li_8ZrO_6, Li_4ZrO_4 and Li_2ZrO_3 and $LiYO_2$ at different temperatures

T(K)	1173	1273	1473	1673	1773
Δm_1($g\,h^{-1}\,cm^{-2}$) (for Li_8ZrO_6)	2.00×10^{-6}	6.11×10^{-4}	1.47×10^{-1}		
Δm_6($g\,h^{-1}\,cm^{-2}$) (for Li_2ZrO_3)	5.6×10^{-9}	3.74×10^{-7}	1.82×10^{-4}	2.43×10^{-2}	0.18
Δm_7($g\,h^{-1}\,cm^{-2}$) (for $LiYO_2$)	4.92×10^{-21}	2.45×10^{-18}	4.71×10^{-14}	8.41×10^{-11}	1.8×10^{-9}

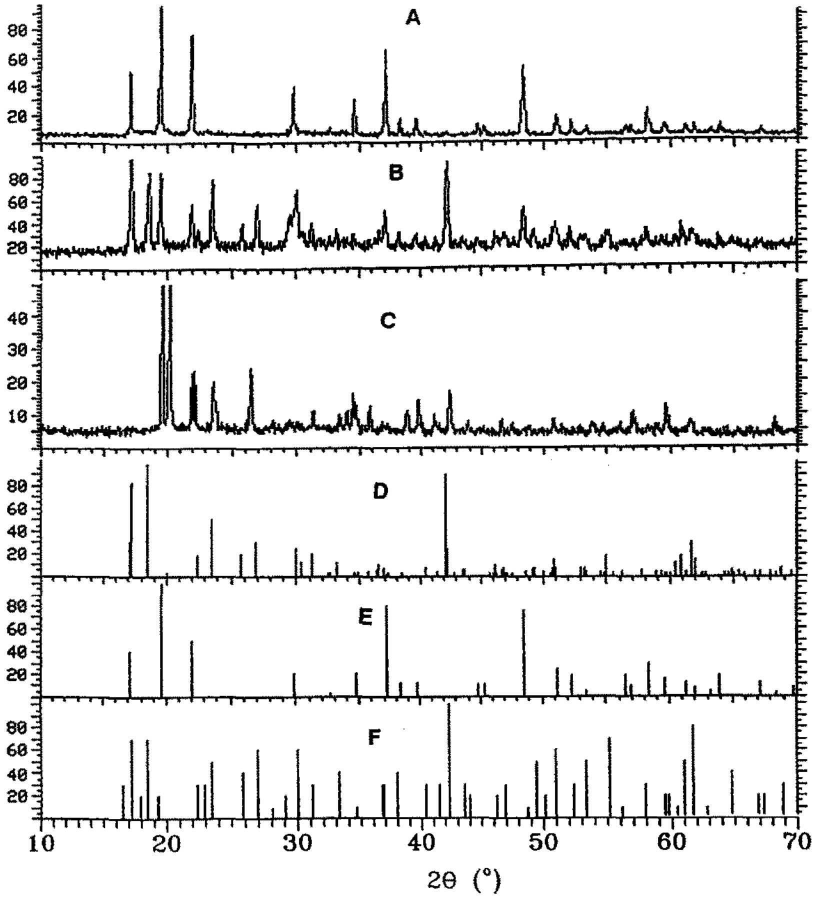

Fig. 2. The X-ray diffraction patterns for Li_8ZrO_6 heated at different temperatures, A: before heating; B: 1000°C for 20 h, C: 1200°C for 8 h; D, E and F are from JCPDS cards for Li_4ZrO_4 (#20-645), Li_8ZrO_6 (#26-867) and Li_2ZrO_3 (#33-843), respectively.

(1.1585 g). The experimental and calculated values are shown in Table 6. It is seen that calculated values are slightly larger but in good agreement with experimental results.

4.2. *Stability against water vapor*

It is useful to be able to predict whether lithium zirconates will be attacked by water vapor through hydrolysis in specific situations and also to determine the final products of the reaction of lithium zirconate with water vapor. From Tables 3–5, it is known that if the partial pressure of water vapor is larger than 6.29×10^{-14} atm at room temperature, Li_8ZrO_6 will be thermodynamically unstable. At 400°C, Li_8ZrO_6 will be unstable when the partial pressure of water vapor is larger than 0.0124 atm. In air, since the water vapor content is quite variable up to 5% (vol.), then Li_8ZrO_6 could be unstable in air even at 400°C.

Table 6. The experimental and calculated values of lithium loss at 1000°C for a sintered Li_8ZrO_6 sample with 13 mm diameter and 3.5 mm thickness (1.1585 g)

Time (h)	10	20	30	50	72
Experimental (g)	0.0131	0.0231	0.0336	0.0528	0.0821
Calculated (g)	0.0168	0.0336	0.0504	0.0840	0.1210

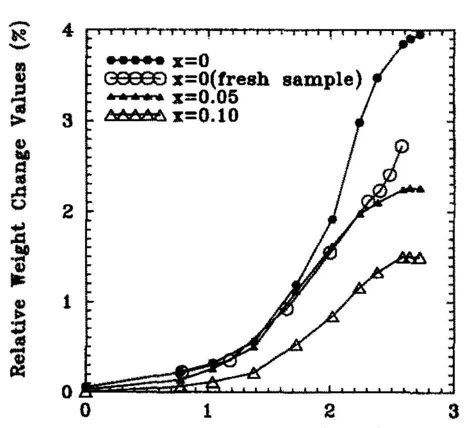

Fig. 3. The dependence of the relative weight-gain values on time in air for yttrium-doped Li_8ZrO_6 ($Li_{8+x}Y_xZr_{1-x}O_6$) stored in dry air for 2 months with $x = 0$, 0.05, and 0.1, where the weight-increase values are multiplied by 0.1.

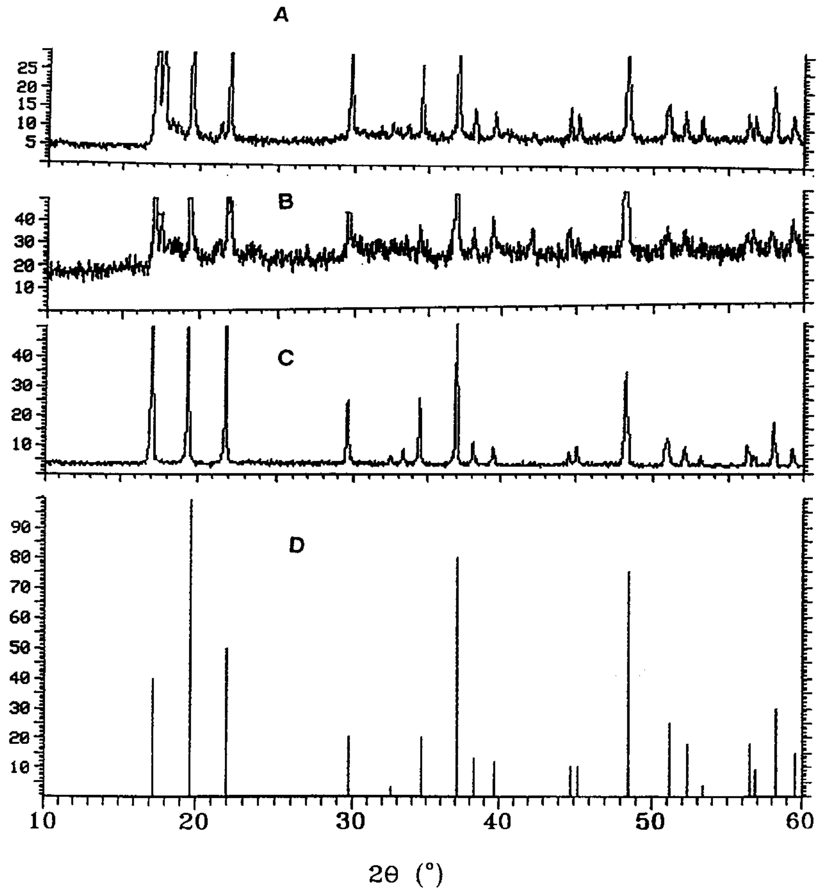

Fig. 4. The X-ray patterns of for Li_8ZrO_6 exposed to air, A: for 440 h after the sample was stored in dry air for 2 months, B: for 24 h immediately following sintering, C: before exposing to air, D: JCPDS card for Li_8ZrO_6 (#26-867).

However, Li_8ZrO_6 should be stable against water vapor in air when the temperature is above 500°C.

From Tables 3–5, it is also known that at room temperature the final products in the reaction of Li_8ZrO_6 with water vapor in air will be ZrO_2 and LiOH (in fact LiOH will react with CO_2 and form Li_2CO_3). Tables 3–5 also show that $LiYO_2$ is thermodynamically stable against water vapor even at room temperature. In order to know whether $LiYO_2$ is stable in an environment with a combination of CO_2 and water vapor, consider the following reaction:

$$2LiYO_2 + H_2O(g) + CO_2 = Li_2CO_3 + Y_2O_3 + H_2O(l).$$

From the thermodynamic data in Table 1 and [6], we obtain a standard Gibbs free energy of 156.7 kJ at 298 K, and an entropy change less than zero. The Gibbs free energy will be even more positive at higher temperatures. Therefore, $LiYO_2$ is thermodynamically stable in an environment of both CO_2 and water vapor.

In an attempt to improve the conductivity, we prepared yttrium-doped Li_8ZrO_6 ($Li_{8+x}Y_xZr_{1-x}O_6$) solid solutions. The hydrolysis rate of Li_8ZrO_6 and yttrium-doped Li_8ZrO_6 in air at room temperature was studied by weight-gain experiments. The hydrolysis products were studied by XRD, i.r. spectra and DTA. The dependence of the relative weight-gain values of these materials on time is shown in Fig. 3. The XRD patterns for samples of Li_8ZrO_6 exposed to air, either immediately or after being stored in a dry environment for 2 months, respectively are shown in Fig. 4. It is seen that the background of the patterns for the samples exposed to air are raised, and extra peaks, which are very difficult to identify, appear, but the major XRD peaks from both LiOH and Li_2CO_3 phases are not found. This may be due to the fact that the product phases formed when Li_8ZrO_6 is exposed to air are too small or amorphous. However, the i.r. spectra and DTA results show that LiOH and Li_2CO_3 are present in the samples.

From Fig. 3, it is seen that the rate of weight increase in the fresh sample is much larger than that in the sample stored in dry air for 2 months. This may be caused by the fact that Li_8ZrO_6 will form a compact layer of carbonate on the surface during the stored period to protect it from attack by water vapor when exposed to air. It is also seen that the rates of weight-gain for samples of yttrium-doped Li_8ZrO_6 are smaller than that of pure Li_8ZrO_6.

5. CONCLUSION

Based on the Neumann–Kopp rule and the third law, the results of the calculations for thermal stability of Li_8ZrO_6 are in good agreement with the experimental ones. Li_8ZrO_6 will decompose rapidly above 1100°C, but, very slowly below 900°C. Li_2ZrO_3 will decompose rapidly above 1500°C, but it is stable below 1200°C. $LiYO_2$ decomposes very slowly even above 1500°C. Li_8ZrO_6 is thermodynamically unstable against water vapor in air with more than 1% (vol.) water vapor below 400°C and Li_2ZrO_3 is thermodynamically unstable against water vapor at room temperature. $LiYO_2$ is thermodynamically stable even in an environment with a combination of water vapor and CO_2 at room temperature. At room temperature, Li_8ZrO_6 will react to form Li_2CO_3 and ZrO_2 in air.

The hydrolysis rate of Li_8ZrO_6 stored in dry air for long periods is much slower than that of the fresh materials. Also the rate of hydrolysis of yttrium doped Li_8ZrO_6 solid solutions is slower that of pure Li_8ZrO_6.

The temperature for the synthesis and preparation in air of Li_8ZrO_6 should be in the range of 500–1100°C in order to obtain pure phase Li_8ZrO_6.

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