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The standard enthalpy of formation of superionic solid electrolyte $Li_7La_3Zr_2O_{12}$

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ABSTRACT

The standard enthalpy of formation of perspective solid electrolyte $Li_7La_3Zr_2O_{12}$ is determined using thermodynamic cycles based on the measurement of its enthalpy of dissolution. The standard molar enthalpies of dissolution in aqueous solution of 1 mol dm^{-3} HCl, formation from binary oxides and formation from elements for tetragonal form of $Li_7La_3Zr_2O_{12}$ are found to be −1547.6, −168.0 and −7152.6 kJ mol^{-1}, respectively.

1. Introduction

Recently a lithium and lithium-ion batteries are considered to be the high performance power sources for portable and promising energy storage devices, hybrid electric vehicles, et al. Application of metallic lithium as an anode of chemical power sources gives some advantages, such as high values of electromotive force (EMF) and specific capacity [1,2]. To avoid a dendrite formation in such power sources one can use a solid electrolyte. The main requirements for solid electrolytes for such batteries are the high lithium-ion conductivity, stability against anode and cathode materials and a low value of the electronic component of conductivity. Chemical instability means that the electrolyte can react with the electrodes. This process leads to the materials degradation, electroactive component loss and even short-circuits of a power source by conducting products of the interaction. However, most known solid electrolytes with high lithium-ion conductivity, such as Li_3N and titanates with a perovskite-related structure are unstable in direct contact with electroactive materials [3]. On the other hand, many stable electrolytes have low lithium-ion conductivity at moderate temperatures [4–6]. Some times ago a new lithium-ion solid electrolyte $Li_7La_3Zr_2O_{12}$ (LLZ) with cubic syngony was discovered by Murugan et al. [7]. The interest in LLZ is due to the fact that this electrolyte has a relatively high Li^+-conductivity (~10^{-4} S/cm) at room temperature [7] and, according to Wepner it is stable against metallic lithium in liquid lithium immersion tests. Later the test of stability was carried out by Keriyama et al. by studying the electrochemical cell Li | LLZ | Li by cyclic voltammetry and chronopotentiometry [8]. It was shown that the transfer of lithium ions with a current density up to 10 μA cm^{-2} through the solid electrolyte does not lead to its degradation. Moreover, such all-solid-state electrochemical cells as Li | LLZ | $LiCoO_2$ [9,10], Li | LLZ | $Cu_{0.1}V_2O_5$ [11,12] and Li | LLZ | TiS_4 [13] were successfully designed and operated.

However in all such experiments LLZ stability can be provided by kinetic reasons, especially if one points out that all studied electrochemical measurements were carried out at very low current density that did not exceed 10 μA cm^{-2}. Such kinetic reasons mean that the reaction is energetically favorable but there is a high energetic barrier between the final and the initial state, such as for the diamond-graphite transition. At the same time only the thermodynamic data of $Li_7La_3Zr_2O_{12}$ allow us exactly determine its genuine stability to metallic lithium and other electrode materials and components of environment in a wide temperature range. These data are necessary input parameters for a thermodynamic simulation to find optimal conditions for a synthesis or to predict chemical interaction with different materials and media, as in [14].

In this study we have aimed to determine the standard enthalpy of formation of tetragonal $Li_7La_3Zr_2O_{12}$ because this structural form of LLZ can be stabilized at room temperature without any doping additive [15,16]. Cubic structure has higher conductivity than tetragonal modification at room temperature however the conductivity values are comparable at the temperature of 573 K [17,18]. To determine the standard enthalpy of LLZ formation we have measured its enthalpy of dissolution by direct calorimetry technique and performed calculations using the thermodynamic cycles.

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Table 1
Summary of sample descriptions.

Chemical Name	Formula	Source	Purity according to Supplier, %
Lithium carbonate	Li_2CO_3	Vekton	99.30[a]
Lanthanum oxide	La_2O_3	Vekton	99.99[a]
Zirconyl nitrate	$ZrO(NO_3)_2{\cdot}2H_2O$	Khimreaktivsnab	99.8[a]
Nitric acid	HNO_3	Khimreaktivsnab	99.9[a]
Citric acid	$C_6H_8O_7{\cdot}H_2O$	Khimreaktivsnab	99.99[a]
Aqueous solution of hydrochloric acid	1 mol dm^{-3} HCl in H_2O (3.59 wt.% of HCl)	prepared here from 1 M fixanal of HCl (Ekroshim, LTD) and distilled water	3.59[a]
Argon	Ar	Urarkriogas	99.993[b]
Helium	He	Urarkriogas	99.99[b]
Zirconate Lanthanum Lithium	$Li_7La_3Zr_2O_{12}$	prepared here	98.0[a,c]

[a] Mass fraction purity.

[b] Mole fraction purity.

[c] Purity according to XRD and volumetric measurements.

2. Experiment

Li_2CO_3, La_2O_3 and aqueous solution of $ZrO(NO_3)_2{\cdot}2H_2O$ were used as starting components for the citrate-nitrate synthesis of tetragonal $Li_7La_3Zr_2O_{12}$ (Table 1). The reagents were mixed in the stoichiometric ratio except Li_2CO_3 which was taken with 10 wt% excess. A smaller excess of lithium carbonate leads to a formation of the $La_2Zr_2O_7$ impurity. These components were dissolved in the mixture of the dilute nitric and citric acids. The resulting solution was evaporated at 353 K to transparent gel. Then the gel was dried and pyrolized at ~473 K. The synthesis was performed by increasing the temperature stepwise (973 K for 1 h; 1073 K for 1 h; 1173 K for 1 h). First two steps were carried out under air. The final temperature step was carried out under argon atmosphere (Ar, special purity). After each stage of the synthesis, the mixture of reagents was thoroughly ground in an agate mortar. Before calorimetric measurements, the synthesized powder was annealed in a helium atmosphere (He, special purity) at 973 K for 1 h to remove adsorbed gases. To remove traces of CO_2 from helium the gas was bubbled through an adsorber containing KOH and activated carbon. After annealing, all samples were placed in a desiccator with askarite (a mixture of KOH and asbestos) to prevent carbonisation.

The synthesized LLZ powder and the dry solid obtained after its dissolution were examined by X-ray diffraction analysis (XRD). XRD was performed with a Rigaku D-MAX-2200V diffractometer with a vertical goniometer, Cu K_α-radiation and $2\theta = 10–70°$.

Calorimetric measurements were performed using Calvet calorimeter DAK-1-1 (Chernogolovka, Russian Federation) at 298 K with the cell volume of 10 cm^3 and sensitivity of 10^{-6} J s^{-1}. Preliminary weighted powder samples were placed into the thin glass ampoules which were vacuum sealed after that. Calorimetric cell was filled with aqueous solution of 1 mol dm^{-3} HCl (~8 ml) and the ampoule was placed inside the cell in a special holder. The aqueous solution of HCl was prepared from fixanal at 298 K and molarity of 1 mol dm^{-3} corresponds to 3.59 wt.% of HCl (Table 1). Here and everywhere in the manuscript 1 mol dm^{-3} means 3.59 wt.%. After a few hours when thermal equilibrium was established the ampoule was broken and oxide powder began to dissolve in HCl media. The dependence of thermo-EMF versus time was registered during the dissolution process providing the heat evolution curve. Integration of heat evolution curves gave the value of enthalpy of dissolution. Typically complete dissolution of 10 mg sample took about 2 h. The calibration of calorimeter was carried out using the enthalpy of dissolution of potassium chloride in water at 298 K. The absolute error of the thermal effects integration is associated with the variations in the baseline and the side thermal effects (breaking the ampoule, mixing) and estimated during the blank experiments as 0.02 J.

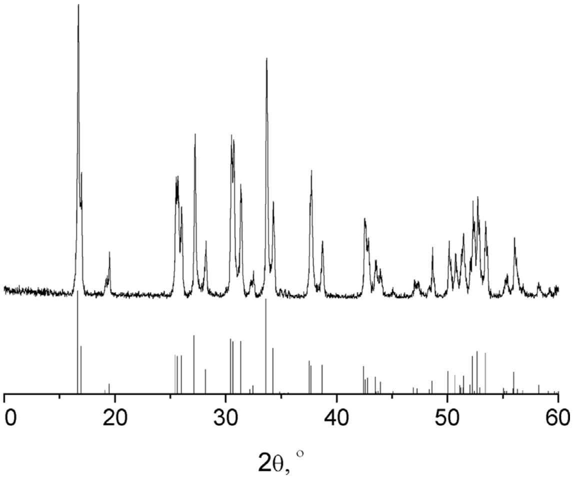

Fig. 1. The XRD pattern of the synthesized $Li_7La_3Zr_2O_{12}$. The vertical lines in the bottom indicate the theoretical diffraction positions of LLZ with tetragonal structure.

The standard errors of values obtained by adding or subtraction are calculated as a sum of standard errors of all terms with corresponding stoichiometric factors.

3. Results and discussion

The XRD pattern of the synthesized $Li_7La_3Zr_2O_{12}$ is given in Fig. 1. There are no another phases but tetragonal LLZ according to XRD. However, XRD analysis is not well suited for accurate determination of the phase composition of lithium compounds because the X-ray scattering from lithium atoms has low amplitude, especially against a background of heavy atoms, such as lanthanum. Neutron diffraction measurements are more suitable for such studies. Thus, for many lithium-containing garnets, the impurity of lithium carbonate was only detected by neutron diffraction studies. The lithium carbonate content in these systems ranged from 0.7 to 6 wt.% [19,20], although XRD analysis did not detect this impurity. Because quantitative analysis by diffraction methods contains some assumptions and is not obvious, we proposed a simple and physically valid method [21]. This method is based on the measurement of the volume of carbon dioxide produced by the interaction of the investigated material with acid. In the volumetric experiments, the solid electrolytes $Li_7La_3Zr_2O_{12}$ was determined to contain 2.00 ± 0.04 wt.% Li_2CO_3. Liberated amount of carbon dioxide is reproduced for a series of measurements. The formation of Li_2CO_3 impurity is unavoidable even with short-term contact of the $Li_7La_3Zr_2O_{12}$ with air.

To specify the products of LLZ dissolution in hydrochloric acid a powdered sample of LLZ of 2 g was dissolved in an excess of aqueous solution of 1 mol dm^{-3} HCl. The resulting mixture was evaporated to a dry solid and obtained powder was studied using X-ray diffraction method. The diffractogramm of the obtained solid is shown in Fig. 2. As one can see the solid contains lithium and lanthanum chlorides and zirconium oxide and there are no reflexes of LLZ. So we suggest the following reaction of the interaction between LLZ and aqueous HCl:

$$Li_7La_3Zr_2O_{12} + 16\ HCl_{(aq)} \rightarrow 7\ LiCl_{(aq)} + 3\ LaCl_{3(aq)} + 2\ ZrO_2\downarrow + 8\,H_2O, \tag{1}$$

where the subscript *(aq)* means "aqueous". The standard enthalpy of this reaction ($\Delta_d H_{LLZ}$) has been measured directly in the calorimeter, as described in Experimental section (Table 2). The value obtained from calorimetry was equal to −1816 ± 30 J g^{-1}.

The enthalpy of LLZ formation from single oxides is calculated according the following equation ($\Delta_{ox}H_{LLZ}$):

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