Study of LiMgVO$_4$ electrical conductivity mechanism

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ABSTRACT

This paper deals with impedance spectroscopy on single-phase polycrystalline LiMgVO$_4$ in the temperature range of 25–500 °C. Thermogravimetric measurements show a weight loss of 2.7% in the temperature range between 25 °C and 175 °C due to humidity desorption. A conductivity mechanism along the grain boundaries (agb) is identified in the specific temperature range and is attributed to a reversible humidity absorption–desorption mechanism. Equivalent circuits are drawn using the results of the impedance measurements at each temperature. A unique conduction process within the material is assigned to each element of the equivalent circuit and Arrhenius plots are plotted. The calculation of activation energy of each conduction mechanism is based on the Arrhenius plots. The activation energy E_b of the bulk conductivity mechanism was found to be 0.62 eV. The activation energy E_{gb} of the grain boundaries conductivity mechanism was found to be 1.03 eV up to 275 °C and 0.50 eV in the temperature range of 300–500 °C. The absence of the conductivity mechanism along the grain boundaries above 175 °C can only be due to the complete removal of water from the material's grains.

1. Introduction

The first studies of LiMgVO$_4$ have been published by Blasse [1,2], who proposed an olivine structure and gave unit cell parameters based on the olivine space group D_{2h}^{16}. In Ref. [3] Paques-Ledent has shown that the X-ray powder diffraction diagram does not agree with the olivine structure. In a later paper [4] Paques-Ledent has proposed that LiMgVO$_4$ is a vanadate isomorph with Na$_2$CrO$_4$-type structure. In Ref. [5] Capsoni et al. have studied the cation distribution in LiMgVO$_4$ and LiZnVO$_4$ and obtained the room temperature cation occupancy in LiMgVO$_4$ and LiZnVO$_4$ crystallographic sites by means of the combined use of X-ray powder diffraction, ^{7}Li and ^{51}V magic angle spinning nuclear magnetic resonance (MAS NMR) and micro-Raman measurements. Interesting properties have been reported related to the luminescence which is due to the tetrahedrally coordinated V^{5+} ions [6–8].

In the category of LiMVO$_4$ materials, where M = Cu, Ni, Co, Zn, Cd, Mg, Be and Li, special attention has been paid to LiNiVO$_4$ and LiCoVO$_4$ that have an inverse spinel structure and can be reversibly lithiated [9]. In Ref. [10] we have reported an impedance analysis study on LiNiVO$_4$ and LiCoVO$_4$ and showed that a reversible water absorption–desorption mechanism over the temperature range of 25–150 °C is responsible for the behavior of the materials between the above temperatures, which is not consistent with pure ionic conductivity. A similar behavior has been found in the case of Li$_3$VO$_4$ [11] but not in the case of LiCuVO$_4$, where no water absorption has been observed [12]. In Ref. [10] it was also shown that the amount and rate of water absorption depends on microstructure of the compound and air exposure conditions. Most likely, for these materials, there exists a conduction mechanism along the grain boundaries (agb), caused by humidity. The electrical properties of LiMgVO$_4$ have not yet been reported as far as we know. As it is discussed below, the study of the electrical properties of LiMgVO$_4$ and especially the effect of humidity on its conductivity is of particular interest, since it may lead to the possibility of its use as a humidity sensor like LiZnVO$_4$ [13–15]. As a matter of fact, it is the dramatic change in conductivity due to the humidity of the surrounding atmosphere (up to seven orders of magnitude as shown below), which could be exploited in humidity sensor applications. In this paper, for the first time, we report on the conduction mechanisms of polycrystalline LiMgVO$_4$ in the temperature range of 25–500 °C by means of impedance spectroscopy measurements. It is shown that, humidity strongly affects the electric performance of LiMgVO$_4$ too, which strengthens our interpretation used in the case of LiNiVO$_4$, LiCoVO$_4$ and Li$_3$VO$_4$ [10,11].

2. Experimental

Polycrystalline LiMgVO$_4$ was prepared with conventional solid-state reaction as described in Ref. [9].

$$Li_2CO_3 + 2MgO + 2NH_4VO_3 \xrightarrow{650\,^\circ C, 4days} 2LiMgVO_4 + 2NH_3 + H_2O + CO_2$$
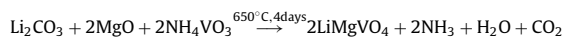
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Chemical characterization of the material was accomplished by using electron microprobe (EDAX). Photographs taken by scanning electron microscopy (SEM) were used to study its morphology. X-ray powder diffraction (XRD) using Cu Kα$_1$ radiation was used to confirm the structure. SETARAM SETSYS TG/DTA equipment was used to carry out thermogravimetric measurements. Impedance data was collected on cylindrical pellets (~16 mm in diameter with a thickness of 2 mm), obtained by applying pressure of 5 ton/cm^2 for 30 s in a 16 mm die. The density of the samples was found to be 83% of the crystallographic density. Nickel plate electrodes were used. An impedance analyzer HIOKI 3532-50 was used over the frequency range of 42 Hz to 1 MHz to collect the impedance data. Initially, measurements were carried out in order to examine whether the material displays a linear behavior. It was found that the material displays a linear behavior when the applied voltage is above 150 mV. All measurements were taken by applying a constant voltage of 200 mV. The impedance of the pellets was measured at frequencies 50 Hz, 100 Hz, 1 KHz, 10 KHz, 100 KHz and 1 MHz, as the pellet was being heated up to 500 °C at a rate of 50 °C/h and then cooled down to room temperature. These measurements were taken in order to check the reproducibility and hysteresis phenomena. The impedance of the samples was measured at 100 different frequency values, logarithmically distributed in the range from 42 Hz to 10^6 Hz, at temperatures from 25 °C to 500 °C, in 25 °C steps. During the measurements a constant pressure was applied, using an adjustable spring mechanism on the electrode-sample system. When the desired temperature was reached, there was a delay of 1 h until impedance measurements were taken. During this stabilization time the temperature varied less than 1 °C.

3. Results and discussion

The proportion of atoms indicated by electron microprobe was the same with the proportion predicted by the chemical formula of the compound, with the exception of Li, the proportion of which could not be calculated because of its low atomic number. From the SEM photographs of the compound it was estimated that the diameter of the grains ranges between 10 μm and 40 μm (Fig. 1). The XRD pattern of the prepared powder (Fig. 2) shows that no additional lines were found that could be assigned to the presence of impurities. The XRD pattern confirms the presence of a single-phase LiMgVO$_4$ (PDF #380275).

The plots in Fig. 3 indicate that at each temperature level there is a frequency which corresponds to the hopping rate. Above this frequency the conductivity is a linear function of frequency in the log(σ) versus log(f) plots. Therefore the conductivity is expressed above the hopping frequency by a power law expression $\sigma(f) = Af^s$, $0 < s < 1$ [16]. The hopping frequency f_p, which is shown at each temperature level in Fig. 3, corresponds to the frequency at which the conductivity dispersion starts. As it is shown in Fig. 3, below the hopping frequency the conductivity is almost independent from frequency at any given temperature. The impedance measurements taken at 25, 100, 200, 300, 400 and 500 °C are shown in Fig. 4. The results of the impedance measurements were fitted and the equivalent circuits were drawn in 25° intervals, from room temperature to 500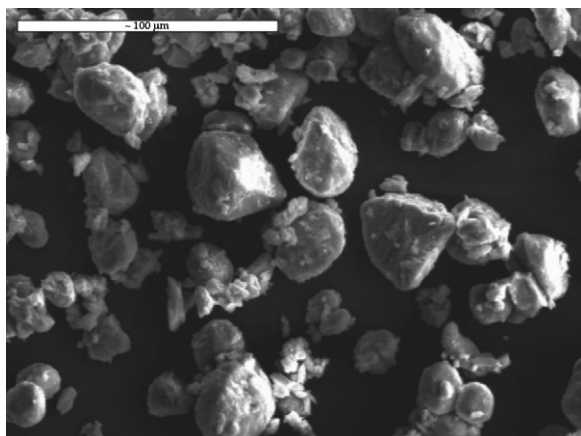 °C, using the EQUIVCRT.PAS program [17]. The equ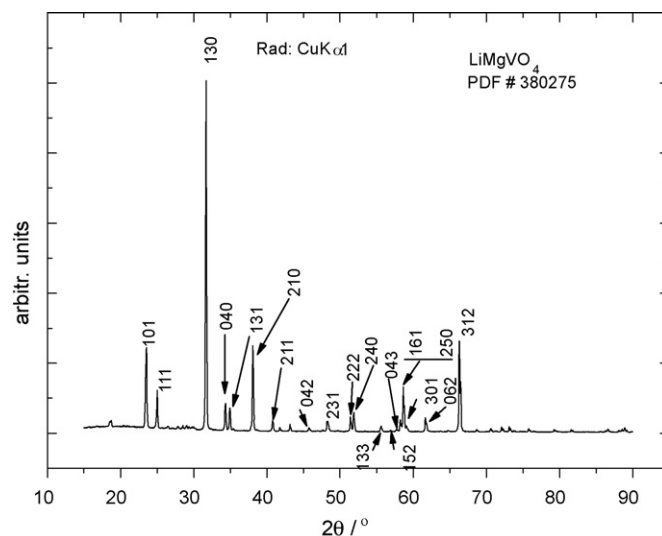ivalent circuits mentioned above at 25 °C, 100 °C, 200 °C, 300 °C, 400 °C and 500 °C and the corresponding fitting results are shown in Fig. 4. The plots drawn during the heating and cooling cycle have the same shape, indicating the same conduction mechanisms during heating and cooling. At higher temperatures hysteresis is negligible but in the low temperature region some hysteresis was observed. A slow heating and cooling rate (50 °C/h) was used between subsequent temperature levels and the sample was kept for 1 h at each temperature level before the measurement was recorded. As our measurements were taken in air atmosphere the material was able to reabsorb a large portion of humidity that had been lost during the heating cycle. The equivalent circuits which were used to fit the measurement results, using the EQUIVCRT.PAS program, consisted of (R//Q) elements in series together with a capacitance C_{dl}, and a Q_{dl} element, the origin of which is described below. The capacitance C_{dl}, named the double-layer capacitance, represents the geometric capacity between the nickel plates and the pellet and was calculated to be in the order of 10^{-1} F/cm in the whole temperature range of 25–500 °C. In the temperature range of 25–175 °C the results were fitted using an equivalent circuit, which consisted of three (R//Q) elements in series. The methodology used to assign the different conductivity processes was the same with that used in the case of LiNiVO$_4$ and LiCoVO$_4$, as it is described in Ref. [10]. The bulk conductivity is represented by the first (R//Q)
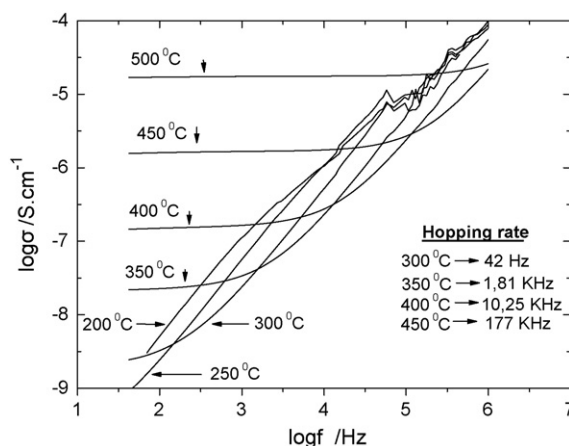

Fig. 2. XRD pattern of LiMgVO$_4$.

Fig. 1. SEM photograph of LiMgVO$_4$.

Fig. 3. Log–log plot of the specific conductivity versus frequency at different temperature levels.