

Mechanochemical way for preparation of disordered lithium–manganese spinel compounds

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Abstract

The influence of mechanical activation of mixtures of MnO_2 with LiOH and Li_2CO_3 , combined with the following short thermal treatment at different temperatures, on the structure, the processes of disordering, oxygen stoichiometry and dispersion of lithium–manganese spinel has been investigated. It was shown that the mechanochemically prepared compounds are characterized by high dispersion, strongly compressed lattice, the increased amount of Mn (4+) ions and two types of disordering (cation vacancies and cation mixing). The amount of defects and dispersion of product decreases and the crystallinity increases with the temperature of the following thermal treatment. The nature of reagents and the conditions of mechanical activation (MA) influence on parameters of spinel, especially at moderate temperatures. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Lithium–manganese oxide compounds with spinel structure attract a great deal of interest in both theoretical and applicative aspects. A great ability of manganese ions to change easily their valence state in lithium–manganese spinels and possibility for cation mixing are the origin of interesting physical properties of these compounds. On the other hand, lithium–manganese spinels were found to be promising cathode materials for lithium batteries. Structural characteristics, particle size and crystallinity of these materials play very important role in their electrochemical behavior [1–3].

Mechanochemistry is one of the most promising low temperature method of synthesis. In this method nanoscale mixing of reagents occurs. Nucleation process is initiated at room temperature, exhibiting more homogeneous distribution, larger specific surface area and smaller particle size of products as compared with those, prepared by conventional solid state method. The method allows to obtain disordered compounds. In spinels, disordering is achieved either through cation mixing (inverse spinel) or through cationic and anionic non-stoichiometry (deficient spinel). Disordered

lithium–manganese spinels are assumed to improve reversibility and to increase capacity while cycling as cathode in lithium batteries.

Recently [4], we showed the possibility of direct mechanochemical synthesis of LiMn_2O_4 with poor crystallinity and specific surface area of about 50–100 m^2/g .

In the present work we investigated the influence of mechanical activation (MA), combined with the following short thermal treatment at different temperatures, on the structure, processes of disordering, oxygen non-stoichiometry and dispersion of LiMn_2O_4 samples.

2. Experimental

MA was carried out in AGO-2 planetary mill with water cooling, using stainless jars and balls (8 mm diameter, 660 rpm). The mass ratio of materials to balls was 1/40. MnO_2 , LiOH and Li_2CO_3 with qualification “pure for analysis” were used as starting reagents. The molar ratio $\text{Li}/\text{Mn} = 1/2$. Two groups of mixtures activated for 1 and 10 min were under the study. MA was followed by thermal treatment of mixtures at 450, 600 and 800°C for 4 h.

Phase analysis, change of lattice parameters and oxygen stoichiometry, as well as local structure and cationic environment have been performed using X-ray powder diffraction

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(DRON-3.0 diffractometer, Cu $K\alpha$ irradiation), thermal analysis (“MOM” derivatograph, Hungary), ^7Li NMR (solid state NMR spectrometer of wide lines, $B_0 = 1.2$ T, 300 K) and IR spectroscopy (Specord-75, pellets with CsI). Specific surface area was measured by BET method.

3. Results and discussion

3.1. Mechanochemical interaction

Fig. 1 shows the X-ray patterns of the mixtures of MnO_2 with LiOH activated for 1 (a) and 10 (b) min and thermally treated at different temperatures. In the mixture activated 1 min noticeable interaction between reagents is not observed. The reflexes of MnO_2 are slightly changed. The reflexes of initial lithium compounds are present at the background level due to their amorphization and weak scattering ability of lithium atoms. On contrary, in the mixture activated 10 min profound interaction between reagents occurs. The broadening of LiMn_2O_4 reflexes is connected with the decreased size of particles and residual strains. The following thermal treatment of activated samples, starting from 450°C , brings to formation of crystalline spinel. All the patterns could be indexed using cubic spinel cell, space group $Fd3m$. The samples prepared from Li_2CO_3 are characterized by better crystallinity of spinel.

According to thermal analysis (Fig. 2), the samples activated 1 and 10 min differ from the initial ones. On

DTA-curves of initial MnO_2 –LiOH and MnO_2 – Li_2CO_3 mixtures endothermal effects, corresponding to phase transitions of reagents ($T_{\text{LiOH}} = 440^\circ\text{C}$, $T_{\text{Li}_2\text{CO}_3} = 700^\circ\text{C}$, $T_{\text{MnO}_2} = 540^\circ\text{C}$), are present. After MA these effects practically disappear. The endoeffects at 50 – 600°C are observed. Besides, a sharp exothermic peak appears for the mixture with LiOH after 10 min MA.

Thus, considering X-ray and thermal analysis data, one can conclude that a short MA of the mixtures (1 min in our case) brings to a fine grinding and mixing of reagents. As a result, the substantial acceleration of the interaction process between solids under the following heating at temperatures 200 – 300°C lower than the melting point of lithium reagents takes place. Moreover, prolonged MA of mixtures brings to realization of direct solid state mechanochemical interaction of reagents, which is almost completed after 10 min. During the following thermal treatment the processes of crystallization of spinel and elimination of residual gaseous products (H_2O , CO_2) occur.

The acceleration of solid state reactions under mechanical loading is promoted by the formation of the molecular-dense mechanocomposites. Two different kinds of mechanocomposites are formed, depending upon structural and mechanical properties of lithium reagents. When LiOH, having a layered structure and exhibiting good plasticity, is used, a quick amorphization of this compound occurs, followed by its “smearing” on the surface of firmer MnO_2 particles [4,5]. The adhesion forces at the contact of LiOH and MnO_2 particles exceed the cohesion forces inside MnO_2 particles.

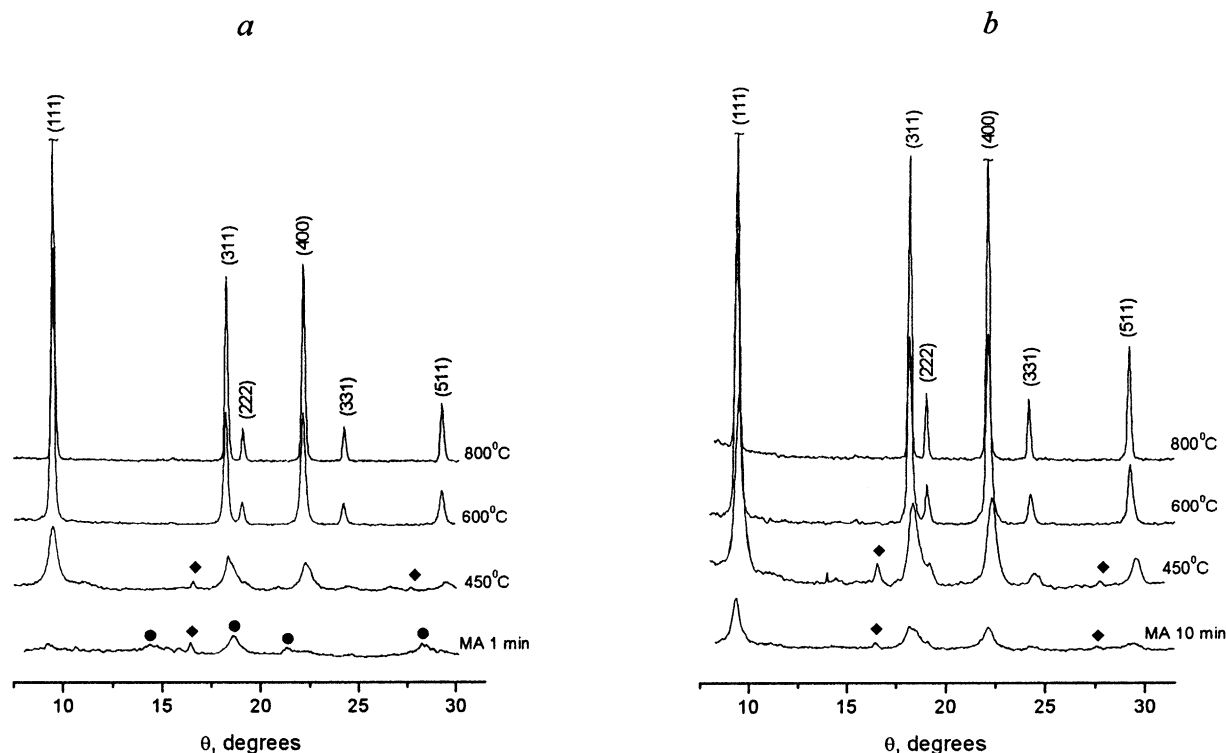


Fig. 1. X-ray patterns of the mixtures of MnO_2 with LiOH, activated 1 (a) and 10 (b) min and heated at different temperatures. (●) MnO_2 ; (◆) Mn_2O_3 .

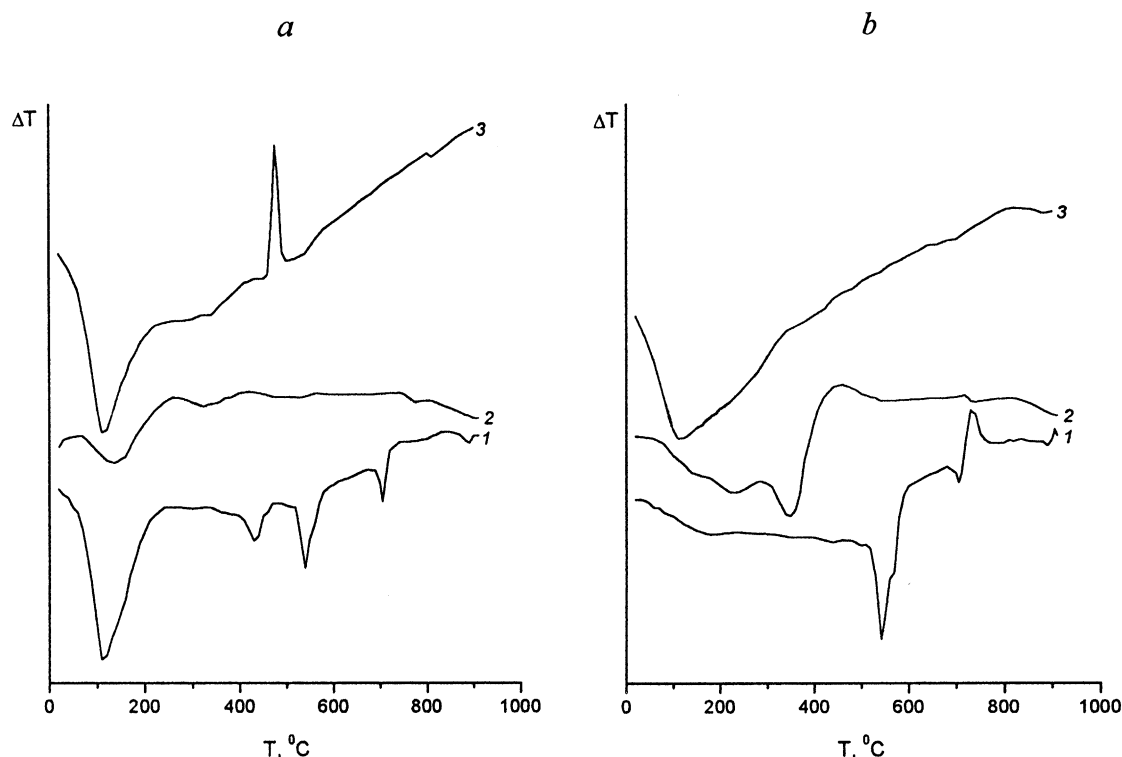


Fig. 2. DTA-curves of heating of initial (1) and activated mixtures of MnO_2 with LiOH (a) and Li_2CO_3 (b): 2–10 min, 3–10 min.

A thin film of amorphous LiOH acts as surfactant, accelerating the dispersion of MnO_2 particles. Dense contact between reagents brings to the formation of numerous micronuclei of a new phase of product. In the case of Li_2CO_3 , having ionic structure and exhibiting brittle properties, the brittle fracture of both components is observed. Probably, the amount of contacts is lower in the last case. In the course of the following heating of both samples, the growth of nuclei of a new phase takes place. The more is the amount of micronuclei, the higher must be the dispersion of the final crystal product.

3.2. Structural properties of prepared samples

Fig. 3 shows the dependence of the specific surface area S of LiMn_2O_4 samples after MA and heating. (It is impossible to estimate correctly S for non-heated samples by BET method because of the formation of secondary aggregates of primary particles with surface unpenetrable for gaseous molecules.) S of heated samples decreases with the temperature rising and the time of MA. In accord with our assumption, S appears to be higher for samples, prepared from LiOH at 450°C , than for those, prepared from Li_2CO_3 . At 600 and 800°C no noticeable differences in S value between hydroxide and carbonate samples and between those activated for a different time are observed.

According to Fig. 4, spinels, prepared by MA and following heating, are characterized by very low lattice parameter a , which increases versus temperature rising. (It is impos-

sible to estimate correctly the lattice parameter for activated samples without being heated because of very broad reflections on X-ray patterns.) One can see slight tendency for increasing of a in samples prepared from hydroxide. It is well known that the radius of Mn^{4+} ions is lower than of Mn^{3+} , and they are more stable at lower temperatures. Thus, low values of a parameter for the samples with molar ratio $\text{Li}/\text{Mn} = 1/2$ point to the increased amount of Mn^{4+} ions comparing with that of stoichiometric spinel [3]. It is clear that in the samples prepared from Li_2CO_3 the amount of Mn^{3+} ions and the value of a are higher than in the case of LiOH samples because of reducing character of CO_2 , eliminating in the course of interaction under MA and heating, especially at 450°C [5].

Besides, a low cell parameter of spinels as prepared could be caused by the presence of substantial disordering of cationic sublattices. One of well known lithium–manganese spinels with $\text{Li}/\text{Mn} = 1/2$ molar ratio is $\text{Li}_2\text{Mn}_4\text{O}_9$, or $(\text{Li}_{0.89}\square_{0.11})_{\text{tet}}[\text{Mn}_{1.78}\square_{0.22}]_{\text{oct}}\text{O}_4$ (where \square is a vacancy) in spinel notation [3]. It is characterized by a pressed lattice ($a = 8.16 \text{ \AA}$ instead of 8.24 for LiMn_2O_4) and has all Mn ions in (4+) oxidation state. The composition of mechanochemically prepared spinels, probably, can be described by a similar formula $(\text{Li}_{1-x}\square_x)[(\text{Mn}^{4+}\text{Mn}^{3+})_{2-y}\square_y]\text{O}_4$ or $\text{LiMn}_2\text{O}_{4+z}$. The temperature being risen, the process of reduction of manganese ions and annealing of defects occurs.

The excess of oxygen in mechanochemically prepared spinels is released under heating (Fig. 5). For all samples this

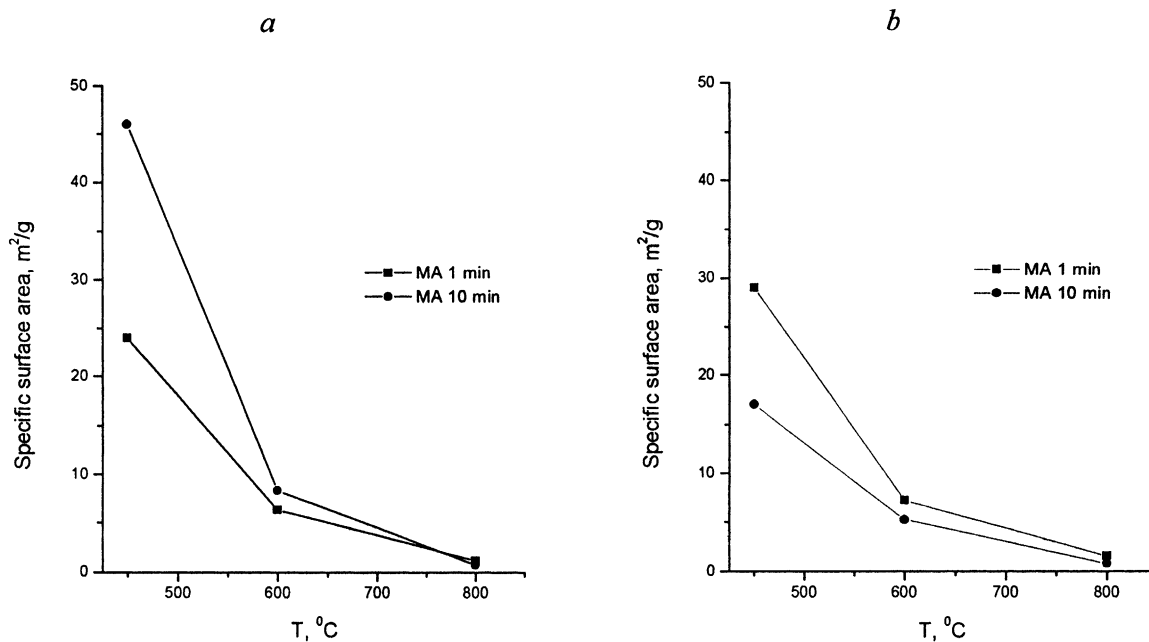


Fig. 3. Specific surface area of LiMn₂O₄ vs. time of MA and the temperature of heating: (a) prepared from LiOH; (b) from Li₂CO₃.

is a two-step process. The starting temperature of the second step coincides for all samples and is equal to 800°C. On contrary, the temperature of the first step is different and comprises 400°C for sample prepared at 450 and 650°C, for the others. The cooling process is followed by mass gain. In the 800–1000°C region the process is reversible and at lower temperatures is irreversible. According to [6,7], the value of irreversible mass loss can be associated with the changing of average oxidation degree of manganese ions, i.e. it must be equal to the amount of defects (cation vacancies). Our

estimations showed that the amount of vacancies for samples being heated at different temperatures varies from 0.07 to 0.02 per formula for tetra-(x) and from 0.14 to 0.04 for octa-positions (y) versus the temperature increasing. Note, that the samples heated even at 800°C conserve some amount of defects.

IR spectroscopy data point to the other type of disordering. Fig. 6 shows IR spectra of MnO₂–LiOH mixtures activated for 1 (a) and 10 (b) min and heated at different temperatures. Two asymmetric bands are present in all

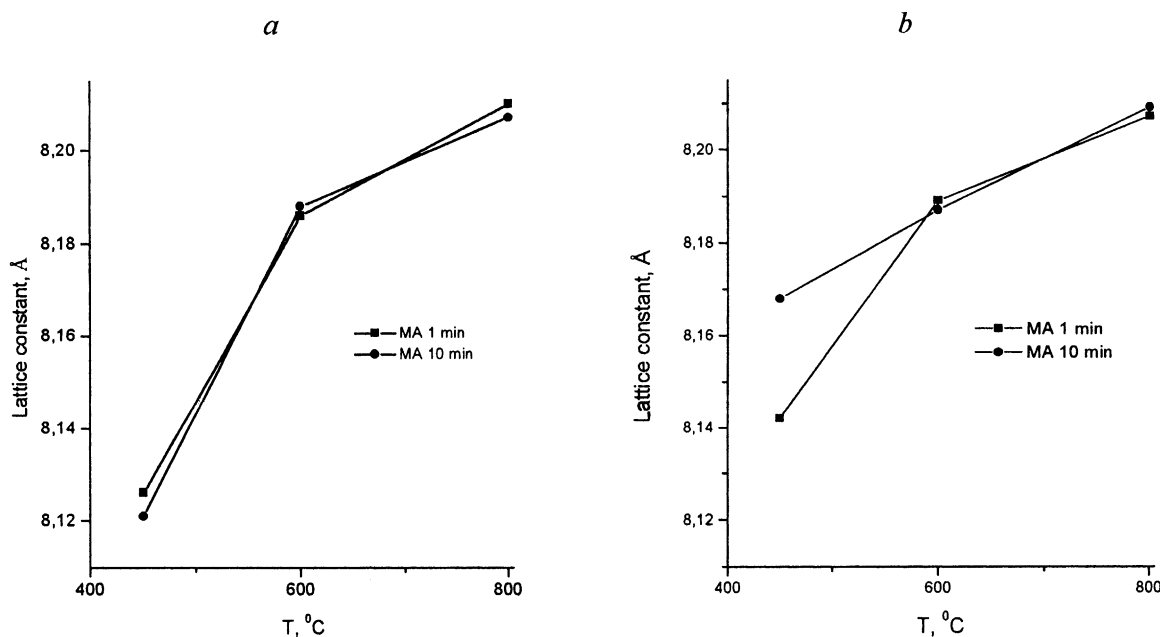


Fig. 4. Lattice parameter of LiMn₂O₄ vs. time of MA and the temperature of heating: (a) prepared from LiOH; (b) from Li₂CO₃.

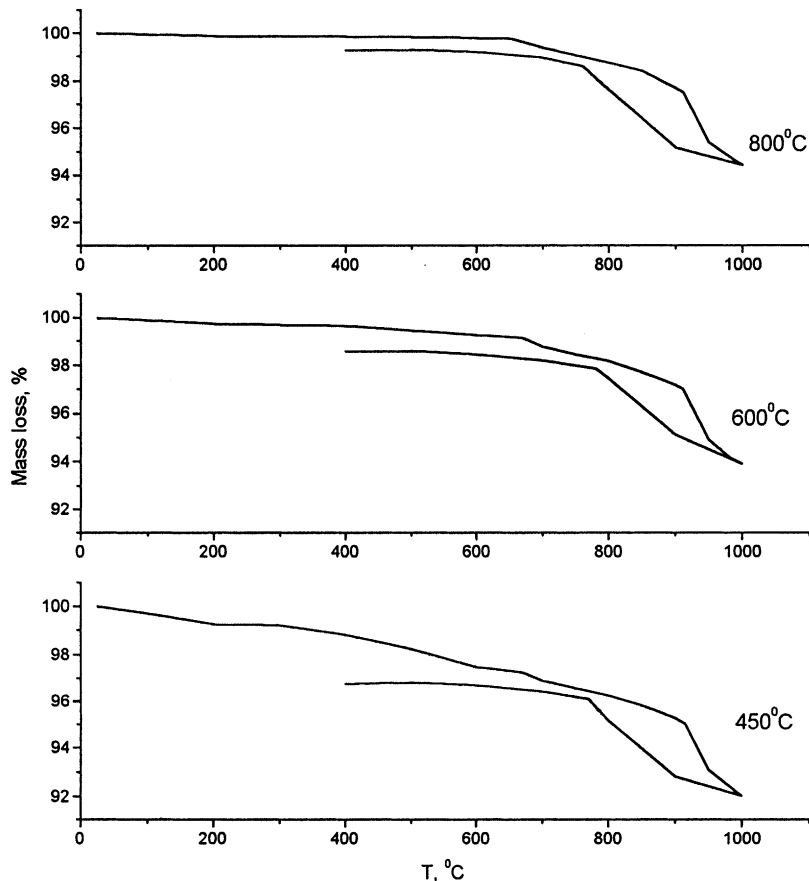


Fig. 5. TG-curves of heating and cooling of the mixtures of MnO_2 with Li_2CO_3 , activated 10 min and heated at different temperatures.

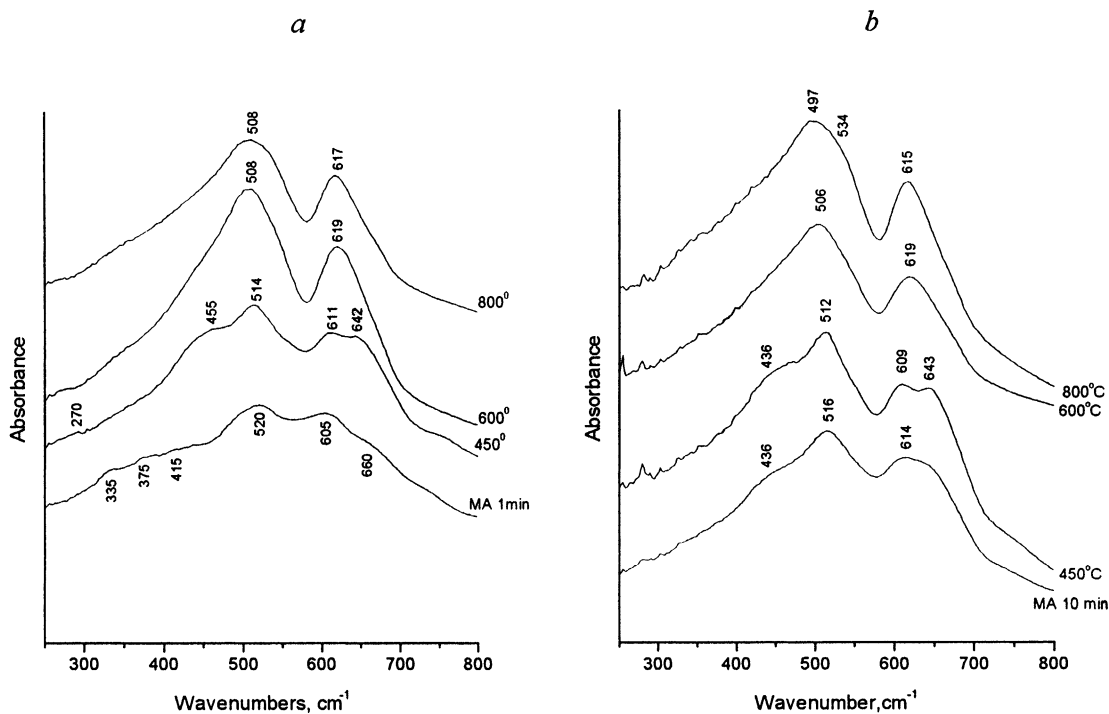


Fig. 6. IR spectra of the mixtures of MnO_2 with $LiOH$, activated for 1 (a) and 10 (b) min and heated at different temperatures.

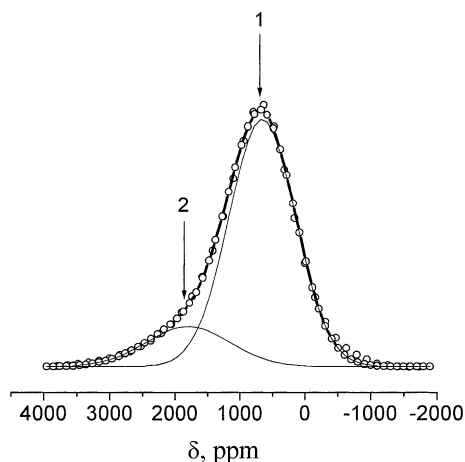


Fig. 7. ${}^7\text{Li}$ NMR spectrum of LiMn_2O_4 , prepared from $\text{MnO}_2\text{-Li}_2\text{CO}_3$ mixture (10 min MA and heated at 800°C): (1) lithium ions in tetra-positions; (2) in octa-positions.

spectra at $300\text{--}800\text{ cm}^{-1}$ region. They are degenerated for samples, heated at 600 and 800°C . The degeneration is removed for activated samples without heating and for those, heated at 450°C . Similar changes are observed for $\text{MnO}_2\text{-Li}_2\text{CO}_3$ mixtures. According to [8], such splitting of bands, as well as their asymmetry, can be explained by distribution of homogeneous manganese and lithium ions through non-equivalent crystallographic positions, i.e. the formation of mixed spinels.

The lithium ion distribution over different crystallographic sites was confirmed by ${}^7\text{Li}$ NMR spectroscopy. ${}^7\text{Li}$ NMR spectrum of LiMn_2O_4 , prepared by activation and heating of $\text{MnO}_2\text{-Li}_2\text{CO}_3$ mixture at 800°C , is presented by asymmetric line (Fig. 7). To our opinion, the observed asymmetry arises from an increasing number of neighboring oxygen atoms and indicates two different positions for lithium ions: tetrahedral and octahedral. It was considered that if all lithium ions occupy high symmetric tetrahedral $8a$ sites, NMR spectrum is presented by a narrow symmetric line. If all lithium ions occupy octahedral sites, the broadening of line must appear owing to electric field gradient.

Estimations showed that $\sim 5\text{--}7\%$ of lithium ions occupy octahedral sites.

4. Conclusion

Thus, the method of mechanical activation, combined with short heating at moderate temperatures, can be used for preparing of lithium–manganese spinels with unusual properties. Mechanochemically prepared spinels are characterized by high dispersion, poor crystallinity, strongly compressed lattice, increased amount of Mn ions in $(4+)$ oxidation state and, at least, two types of disordering: cation vacancies and cation mixing. The dispersion, the amount of defects and Mn $(4+)$ ions decrease and crystallinity increases under following thermal treatment. The nature of reagents and the conditions of MA influence the parameters of spinel, especially at moderate temperatures. This provides possibility to regulate the properties of final products, providing 3 or 4 V cathode materials. To our opinion, high disperse and disordered LiMn_2O_4 as prepared must display good cathode characteristic at fast discharged cells.

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