

Reduction Processes in the Course of Mechanochemical Synthesis of $\text{Li}_{1+x}\text{V}_3\text{O}_8$

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Mechanical activation (MA) of the $\text{LiOH} + \text{V}_2\text{O}_5$ and $\text{Li}_2\text{CO}_3 + \text{V}_2\text{O}_5$ mixtures followed by brief heating at 673 K was used to prepare dispersed $\text{Li}_{1+x}\text{V}_3\text{O}_8$. It was shown that structural transformations during MA are accompanied by reduction processes. EPR spectra of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ are attributed to vanadyl VO^{2+} ions with weak exchange interaction. The interaction of localized electrons (V^{4+} ions) with electron gas (delocalized electrons), which is exhibited through the dependence of EPR line width of vanadium ions versus measurement temperature (C–S–C relaxation), is revealed. It is shown that C–S–C relaxation is different for intermediate and final products. The properties of mechanochemically prepared $\text{Li}_{1+x}\text{V}_3\text{O}_8$ are compared with those of HT- $\text{Li}_{1+x}\text{V}_3\text{O}_8$, obtained by conventional solid state reaction. Mechanochemically prepared $\text{Li}_{1+x}\text{V}_3\text{O}_8$ is characterized by a similar amount of vanadium ions, producing electron gas, but a higher specific surface area. © 2001 Academic Press

Key Words: lithium–vanadium oxide; $\text{Li}_{1+x}\text{V}_3\text{O}_8$; mechanochemical reactions; EPR; electron structure; vanadyl ions; C–S–C relaxation.

$\text{Li}_{1+x}\text{V}_3\text{O}_8$ is a well known candidate for cathode material in rechargeable lithium batteries (1–3). Some attempts have been made to find new low-temperature methods, instead of the conventional high-temperature one, in order to improve its electrochemical characteristics (2, 3). It was shown that the solution technique, producing more disperse or even amorphous material, should lead to higher capacity and better cycling behavior (2, 3). It is achieved, in the authors' opinion, by decreasing of particles' size, degree of crystallinity, and an absence of the long-range order, reducing the pathway through lithium ions diffusion.

In the present study the method of mechanical activation (MA) combined with low-temperature heating was used to prepare dispersed $\text{Li}_{1+x}\text{V}_3\text{O}_8$ material. Since $\text{Li}_{1+x}\text{V}_3\text{O}_8$ is

known to be a bronze-type compound, in which a part of the V^{5+} ions is reduced to V^{4+} (4), its synthesis, starting from V^{5+} -containing compounds, should be accompanied by reduction processes. It was interesting to investigate these processes against the different initial reagents and different conditions of MA and following heating. The amount and the electronic state of V^{4+} ions in mechanochemically prepared $\text{Li}_{1+x}\text{V}_3\text{O}_8$ were compared by EPR spectroscopy with those of $\text{Li}_{1+x}\text{V}_3\text{O}_8$, obtained by conventional solid state reaction.

EXPERIMENTAL

LiOH , Li_2CO_3 , and V_2O_5 (quality "pure for analysis") were used as the initial reagents. Mechanical activation was carried out in an AGO-2 activator with water cooling and corundum jars and balls (5 mm diameter, 660 rpm) in air. The mass ratio of material and balls was 1/20. The molar ratio Li/V in the starting mixtures corresponded to a stoichiometry of $\text{Li}_{1.07}\text{V}_3\text{O}_8$. The time of activation varied from 30 sec to 10 min. Activated samples were then heated at 673 K for 4 hours in air.

High-temperature $\text{Li}_{1+x}\text{V}_3\text{O}_8$ (a standard) was prepared by melting of the mixture of V_2O_5 with Li_2CO_3 at 953 K in air.

Structural transformations and reduction processes in the course of mechanochemical synthesis of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ were studied by X-ray, IR, and EPR spectroscopy. X-ray patterns were obtained by using a DRON-3.0 diffractometer ($\text{CuK}\alpha$ radiation) and IR spectra by using a Bruker FTIR spectrometer (pellets with CsI). Thermal analysis was performed with an MOM derivatograph (Hungary) using Pt crucibles, in air. The rate of heating was 10 K/min. Concentration of V^{4+} ions in the samples was analyzed by the method described in (4). The specific surface area was measured by the BET method. EPR spectra were recorded by using a Bruker EPR spectrometer ($\lambda = 3$ cm) at 293 and 77 K. The values of g -factors were determined in comparison to a DPPH standard. The error was equal to ± 0.003 .

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Integral intensity was measured by double integration in comparison with the standard and with an error of about 30%.

RESULTS AND DISCUSSION

Thermal analysis data show that interaction between initial reagents takes place directly in the course of MA. On DTA curves of the $\text{LiOH} + \text{V}_2\text{O}_5$ and $\text{Li}_2\text{CO}_3 + \text{V}_2\text{O}_5$ mixtures activated for 10 min the thermal effects of phase transformations of starting materials ($T_{\text{LiOH}} = 718 \text{ K}$, $T_{\text{Li}_2\text{CO}_3} = 973 \text{ K}$, $T_{\text{V}_2\text{O}_5} = 963 \text{ K}$) are absent (Fig. 1). Instead of them, an endothermal effect appears at 293–473 K, accompanied by releasing of weakly bound molecules of H_2O and CO_2 . At 473–623 K it transforms into a strong exothermal effect, connected with energy elimination as the chemical reaction is completed. At 868–873 K the melting effect of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ is observed for both mixtures. It is accompanied by mass gain ($\sim 0.5 \text{ mass}\%$) as a result of the oxidation process of V^{4+} ions (4).

Figure 2 shows X-ray patterns of the $\text{LiOH} + \text{V}_2\text{O}_5$ mixtures after MA and following thermal treatment at 673 K, compared with initial V_2O_5 and HT- $\text{Li}_{1+x}\text{V}_3\text{O}_8$. The intensity of reflections of V_2O_5 in activated samples is decreased. The reflections of initial LiOH are present at the background level due to its amorphization and the weak scattering ability of lithium atoms. On X-ray patterns of the mixtures activated for 1 min one can see the appearance of new weak reflections assigned to lithium–vanadium bronzes in addition to reflections of V_2O_5 . After 10 min of MA the

reflections of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ are present on the patterns. It indicates that structural transformations take place starting from the early stage of MA. After heating of the mixtures activated for different times, all reflections observed belong to $\text{Li}_{1+x}\text{V}_3\text{O}_8$. Note that heating of nonactivated mixtures at 673 K for 4 hours leads to partial interaction of reagents only. Thus, the preliminary MA, even for a short time (30 sec), essentially decreases the final temperature of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ synthesis, providing formation of product in a highly dispersed state (see below).

Figure 3 displays IR spectra of the $\text{LiOH} + \text{V}_2\text{O}_5$ samples after MA and thermal treatment in comparison with the initial V_2O_5 and HT- $\text{Li}_{1+x}\text{V}_3\text{O}_8$. The intensity of the absorption band at 1020 cm^{-1} , corresponding to stretching vibrations of double vanadyl bonds $\nu(\text{V}=\text{O})$ in V_2O_5 , decreases. New bands appear in the $900\text{--}1000 \text{ cm}^{-1}$ range for both types of activated mixtures. The spectra of heated samples coincide with those of HT- $\text{Li}_{1+x}\text{V}_3\text{O}_8$. According to (5), three bands at 920, 950, and 995 cm^{-1} should be assigned to $\text{V}=\text{O}$ stretching vibrations. The change of the vibration frequency of $\text{V}=\text{O}$ bonds in activated samples and final product $\text{Li}_{1+x}\text{V}_3\text{O}_8$, in comparison with pure V_2O_5 , probably is a result of incorporation of lithium ions into the cell.

It was noticed that structural transformations in the $\text{Li}_2\text{CO}_3 + \text{V}_2\text{O}_5$ activated mixtures appeared to proceed more intensively.

Surprisingly, after aging for 6 months at room temperature the phase composition of activated samples (without heating) is significantly changed. The intensity of X-ray

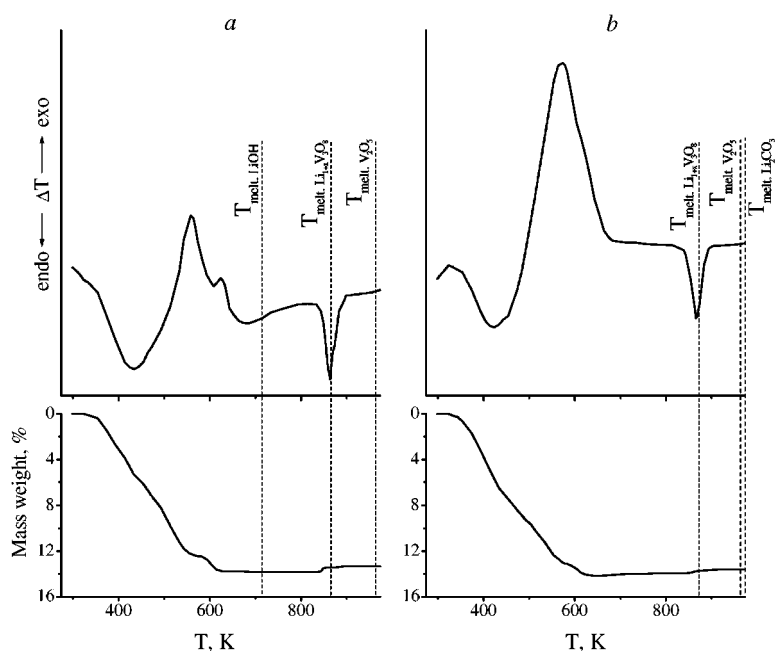


FIG. 1. DTA and TG curves for the $\text{LiOH} + \text{V}_2\text{O}_5$ (a) and $\text{Li}_2\text{CO}_3 + \text{V}_2\text{O}_5$ (b) mixtures activated for 10 min.

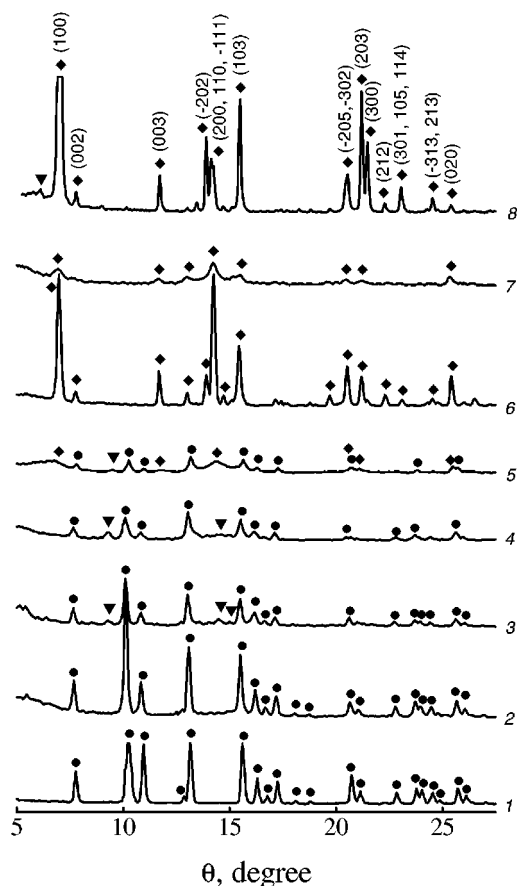


FIG. 2. X-ray of the $\text{LiOH} + \text{V}_2\text{O}_5$ mixture activated for 30 sec (2), 1 min (3), 5 min (4), 10 min (5), 10 min and heated at 673 K (6), 5 min and aged for 6 months at room temperature (7) in comparison with initial V_2O_5 (1) and HT- $\text{Li}_{1+x}\text{V}_3\text{O}_8$ (8). ●, V_2O_5 ; ◆, $\text{Li}_{1+x}\text{V}_3\text{O}_8$; ▼, Li-V bronzes.

reflections of V_2O_5 is sharply decreased, while that of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ is increased, especially in the mixtures with LiOH (Fig. 2). In IR spectra the bands' intensity increases (Fig. 3). The complex line in the $900\text{--}1050\text{ cm}^{-1}$ range is narrowed, with a clear maximum at 950 cm^{-1} and a shoulder at 970 cm^{-1} .

Structural transformations observed in the mixtures under study after their MA and following heating or aging are accompanied by reduction processes, as evidenced by EPR spectroscopy data.

MA of the $\text{V}_2\text{O}_5 + \text{LiOH}$ and $\text{V}_2\text{O}_5 + \text{Li}_2\text{CO}_3$ mixtures leads to the change in EPR spectra as the time of MA increases. The spectra observed for the first mixture can be described as a superposition of two signals (Fig. 4a). The first signal makes a major contribution at a short time of MA (it is more clearly displayed at 5 min MA), but after activation for 10 min this signal disappears. The values of g_{\perp} and g_{\parallel} (1.98 and 1.92, correspondingly) and HFS ($A_{\perp} = 65\text{ G}$, $A_{\parallel} = 185\text{ G}$) well correspond to parameters of EPR spectra of isolated $\text{V}=\text{O}^{2+}$ ions, which were observed

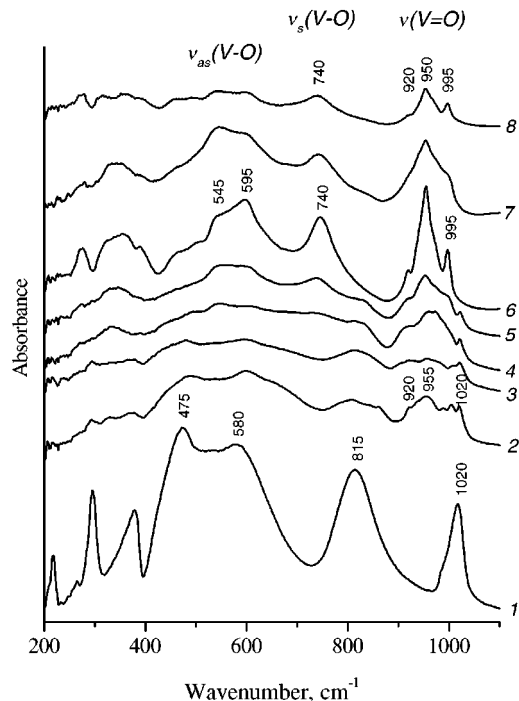


FIG. 3. IR spectra of the $\text{LiOH} + \text{V}_2\text{O}_5$ mixture activated for 30 sec (2), 1 min (3), 5 min (4), 10 min (5), 10 min and heated at 673 K (6), 5 min and aged for 6 months at room temperature (7) in comparison with initial V_2O_5 (1) and HT- $\text{Li}_{1+x}\text{V}_3\text{O}_8$ (8).

for mechanically activated V_2O_5 (6) and lithium-doped V_2O_5 single crystals (7). Assignment of this signal to activated V_2O_5 was confirmed by the following observation. It was found that after 6 months of aging this signal practically disappears in the spectrum of the $\text{V}_2\text{O}_5 + \text{LiOH}$ mixture activated for 5 min due to consumption of activated V_2O_5 in reaction with LiOH, which occurs, according to X-ray and IR data (see above), at room temperature. Note that at the same time the aging of the sample activated for 10 min leads to weak changes in the EPR spectrum. In the case of the $\text{V}_2\text{O}_5 + \text{Li}_2\text{CO}_3$ activated samples, the contribution of the EPR signal of activated V_2O_5 into the total spectrum is not so significant, probably due to the higher rate of its consumption in the mechanochemical reaction with Li_2CO_3 , compared with LiOH (Fig. 4b).

The second signal observed corresponds to the EPR spectrum without HFS with resolved anisotropy of the g -factor.

The spectra of the $\text{V}_2\text{O}_5 + \text{LiOH}$ and $\text{V}_2\text{O}_5 + \text{Li}_2\text{CO}_3$ mixtures activated for 10 min and those activated for 5 min and aged are similar to each other and can be practically described by a second signal of weakly anisotropic form (sloping at g_{\parallel} range) and with $g_{\perp} = 1.96$, and without traces of HFS and fine structure. The parameters and the form of this signal are in complete correspondence with those of HT- $\text{Li}_{1+x}\text{V}_3\text{O}_8$ (8). Heating of activated samples at 673 K

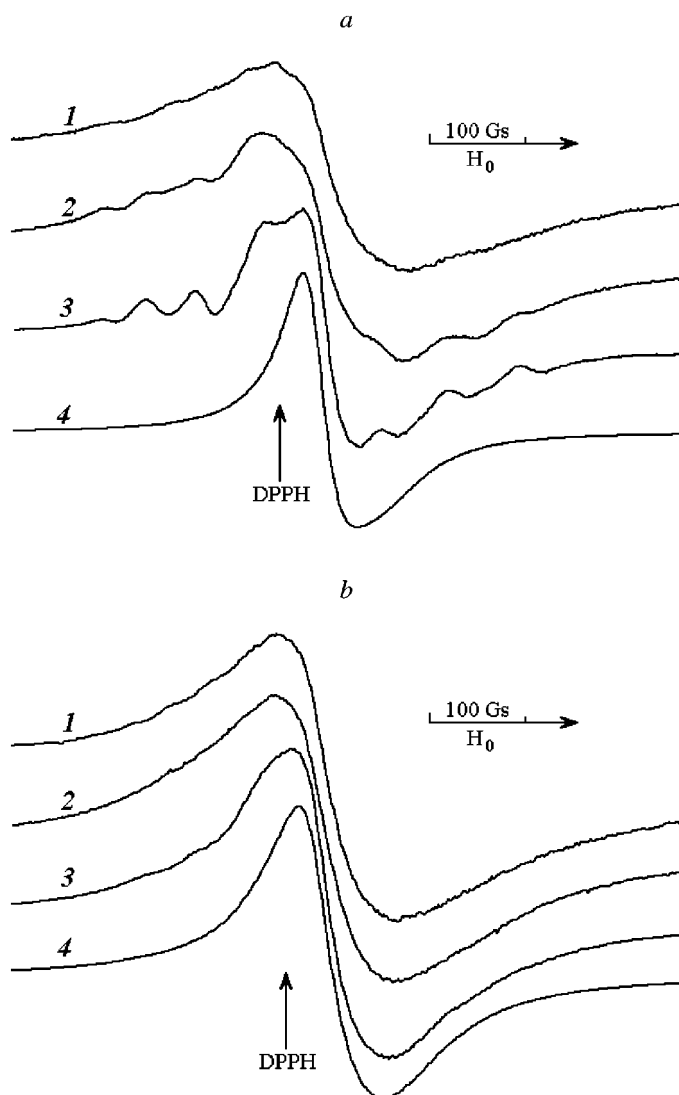


FIG. 4. EPR spectra of the $\text{LiOH} + \text{V}_2\text{O}_5$ (a) and $\text{Li}_2\text{CO}_3 + \text{V}_2\text{O}_5$ (b) mixtures activated for 30 sec (1), 1 min (2), 5 min (3), and 10 min (4) ($T = 77$ K).

does not lead to a significant change in the EPR spectra. The g_{\perp} value of the signal observed allows its assignment to VO^{2+} ions with a vanadyl bond. A high value of g_{\perp} is a characteristic feature of these ions (8). Yet, this signal has some unusual features that demand more detailed consideration.

The absence of HFS in the EPR spectrum of localized centers for $\text{Li}_{1+x}\text{V}_3\text{O}_8$, formed after 10 min MA, points to the appearance of an exchange interaction between vanadium ions. It could be explained by their dimerization as $\text{V}^{4+}-\text{O}-\text{V}^{4+}$. But the distance between paramagnetic ions in such dimers is so small and, correspondingly, an exchange interaction is so large that dimers with spin $S = 1$ and a fine structure should be observed in the EPR

spectrum, but they are absent. At the same time, if dimerization does not occur, the average distance between V^{4+} ions should be rather large. Indeed, the measurement of integral intensity shows that, for example, in the case of samples activated for 5 min, the concentration of V^{4+} ions is equal to 10% from the estimated value for $\text{Li}_{1+x}\text{V}_3\text{O}_8$ at $x = 0.07$. Paramagnetic ions with such low concentration (less than 1% per formula) should be observed as isolated ions without exchange interaction with each other; i.e., HFS should be present in the EPR spectrum in this case. But this does not occur. Probably, the absence of HFS can be explained as a result of a weak magnetic exchange interaction between localized centers through electron gas. An electron gas is formed from V^{4+} ions by delocalization of unpaired electrons.

The observation of a temperature dependence of the line width of EPR spectra of localized paramagnetic centers is a direct consequence of the presence of an electron gas in oxides and its interaction with these centers. In the case of centers located in crystal fields of low symmetry (V^{4+} ion with a short vanadyl bond is one such center), the line width is independent of temperature. Hence, the appearance of such dependence can be considered as a direct evidence of the appearance of electron gas (7). Table 1 shows that the line width of the samples activated for 5 and 10 min with spectra represented only by an anisotropic signal is changed as the measurement temperature is increased from 77 to 293 K.

As follows from Table 1, a classical example of line broadening with measurement temperature increasing, connected with the rise of the amount of unpaired electrons on the Fermi level of an ideal crystal, is realized for samples

TABLE 1
Line Width ΔH and Integral Intensity I (in Relative Units) of EPR Signals of Activated Samples

Sample	After MA		After aging		Measurement temperature (K)
	$\Delta H, \text{G}$	I^a	$\Delta H, \text{G}$	I	
$\text{LiOH} + \text{V}_2\text{O}_5$, 5 min MA			92	1.6	77
			70	0.45	293
$\text{LiOH} + \text{V}_2\text{O}_5$, 5 min MA + 673 K	50	7.1			77
	84	2.8			293
$\text{LiOH} + \text{V}_2\text{O}_5$, 10 min MA	57	0.21	78	8.8	77
	69	3.2	67	2.2	293
$\text{Li}_2\text{CO}_3 + \text{V}_2\text{O}_5$, 5 min MA	107	3.1	113	3.4	77
	100	0.9	84	0.7	293
$\text{Li}_2\text{CO}_3 + \text{V}_2\text{O}_5$, 5 min MA + 673 K	49	9.6			77
	86	3.7			293
$\text{Li}_2\text{CO}_3 + \text{V}_2\text{O}_5$, 10 min MA	92	15	89	20	77
	99	4	90	4.6	293

^a For $\text{Li}_{1.07}\text{V}_3\text{O}_8$, when all reduced vanadium ions are represented by V^{4+} , $I = 8$ at 293 K.

heated at 673 K. The line broadening is also observed for the $V_2O_5 + LiOH$ mixture activated for 10 min, but in contrast to the case mentioned above, a sharp rise of the integral intensity of the EPR spectra (15 times) occurs in this case, indicating that the Curie law is not obeyed. This fact demands special discussion. For the other samples (including the $V_2O_5 + LiOH$ mixture activated for 10 min and aged for half a year), the line broadening, in contrast, is observed as measurement temperature decreases. At the same time, for the latter samples, as well as for that after heating, the Curie law is adequately carried out (see Table 1).

Considering that activated samples are badly crystallized oxide phases, probably with a lot of structural defects, including low-ordered regions, the broadening of the EPR line of paramagnetic $V=O^{2+}$ ions with measurement temperature decreasing can be explained as a result of transformation of a part of unpaired electrons of electron gas (without their pairing) from the fully delocalized state to a notably short-range delocalized state. If the efficiency of their exchange interaction with localized centers is increased at the same time, the corresponding increase of line width of the latter should occur as a result of decreasing time of their spin-lattice relaxation T_1 . Since the time of spin relaxation of mobile electrons is very short, the broadening of the EPR spectrum for a part of localized centers, occurring under strong increasing of the efficiency of their interaction with mobile electrons, in principle, can be very large. In this case, the line, corresponding to localized electrons, must disappear in the spectrum at low measurement temperature; i.e., the integral intensity of the recorded spectrum is strongly decreased as observed for the $V_2O_5 + LiOH$ mixture activated for 10 min. The observed phenomenon of short-range delocalization needs more detailed study.

The unusual feature of the EPR spectra of $Li_{1+x}V_3O_8$ obtained by MA and heating, as well as of $HT-Li_{1+x}V_3O_8$, is in the sloping form in the $g_{||}$ range without a corresponding $g_{||}$ with a clear peak (Fig. 5). As was shown in (8), such a spectrum could be interpreted as a spectrum of the system of localized $V=O^{2+}$ centers of two types, differing by direction of the crystal field axis of a short $V=O$ bond and with magnetic exchange interaction between them. Probably, the reason for the change in the crystal field axis of about 50% of $V=O^{2+}$ ions is the presence of Li^+ ions in the first coordination sphere, located around vanadyl oxygen.

Thus, MA of mixtures of V_2O_5 with $LiOH$ and Li_2CO_3 combined with low-temperature treatment leads to formation of a reduced $Li_{1+x}V_3O_8$ phase with two types of $V=O^{2+}$ ions with localized electrons and a lot of conductive electrons.

Chemical analysis data show that the amount of V^{4+} ions in $Li_{1+x}V_3O_8$, prepared by heating of activated mixtures at 673 K, is of the same order as in $HT-Li_{1+x}V_3O_8$ (Table 2). On the other hand, comparing two samples, prepared by

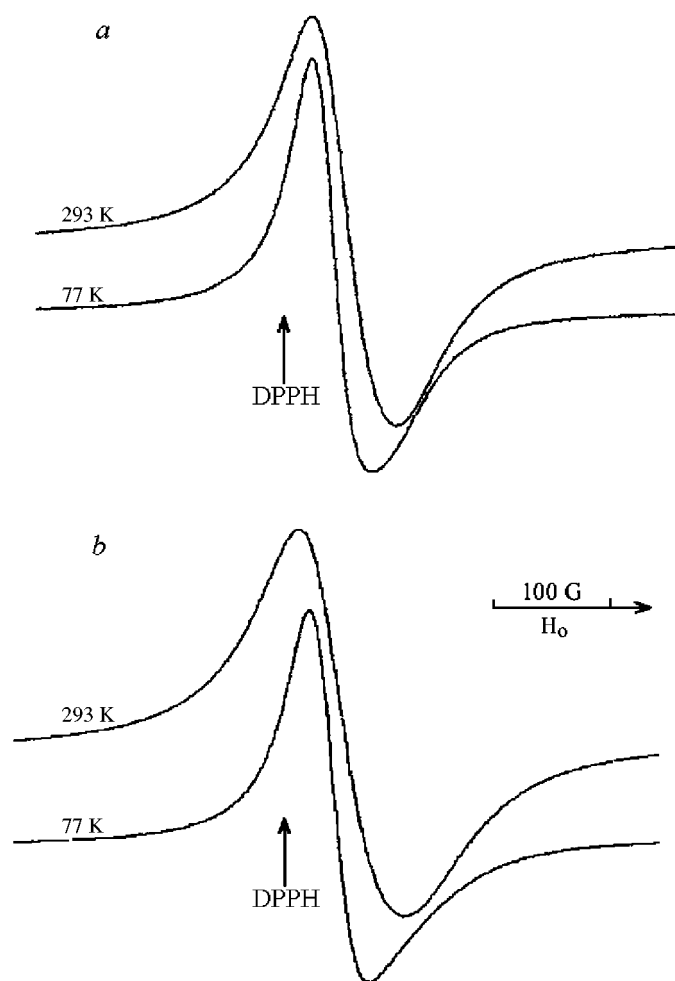


FIG. 5. EPR spectra of $Li_{1+x}V_3O_8$ prepared by MA and heating at 673 K (a) and $HT-Li_{1+x}V_3O_8$ (b), recorded at 77 and 293 K.

MA starting from $LiOH$ and Li_2CO_3 , one can see a slightly higher degree of reduction of the latter. This is a result of the reducing influence of CO_2 , which is formed in the course of interaction of Li_2CO_3 with V_2O_5 during both MA and the following heating and is supported by EPR data.

Specific surface area values of mechanochemically prepared samples appeared to be higher than of $HT-Li_{1+x}V_3O_8$ (Table 2).

TABLE 2
Data of Chemical Analysis and Specific Surface Area

Sample	Amount of V^{4+} , mol%	Specific surface area, m^2/g
1 $LiOH + V_2O_5$ (10 min MA + 673 K)	6.15	2.3
2 $Li_2CO_3 + V_2O_5$ (10 min MA + 673 K)	6.65	3.3
3 $HT-Li_{1+x}V_3O_8$ (standard)	6.15	0.9

CONCLUSION

Thus, dispersed $\text{Li}_{1+x}\text{V}_3\text{O}_8$ can be prepared using mechanical activation of the $\text{LiOH} + \text{V}_2\text{O}_5$ and $\text{Li}_2\text{CO}_3 + \text{V}_2\text{O}_5$ mixtures, followed by brief heating at 673 K. Mechanical activation is accompanied by reduction processes. According to EPR spectroscopy data, intermediate and final products are characterized by different amounts and behavior of localized and delocalized electrons, which appear in the system. $\text{Li}_{1+x}\text{V}_3\text{O}_8$ as prepared has a similar amount of vanadium ions, producing an electron gas, but a higher specific surface area, compared with HT- $\text{Li}_{1+x}\text{V}_3\text{O}_8$.

EPR spectroscopy appeared to be a good tool for the study of intermediate states formed in the course of solid

state synthesis of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ and could be used for control of the quality of the final product.

REFERENCES

1. S. Panero, M. Pasquali, and G. Pistoia, *J. Electrochem. Soc.* **130**, 1225 (1983).
2. G. Pistoia, M. Pasquali, G. Wang, and L. Li, *J. Electrochem. Soc.* **137**, 2365 (1990).
3. J. Dai, S. F. Li, Z. Gao, and K. S. Siow, *J. Electrochem. Soc.* **145**, 3057 (1998).
4. D. G. Wickham, *J. Inorg. Nucl. Chem.* **27**, 1939 (1965).
5. Y. Kera, *J. Solid State Chem.* **51**, 205 (1984).
6. E. G. Avvakumov, V. F. Anufrienko, S. V. Vosel, *et al.*, *Izv. 50 AN SSSR, Seria Khim.* **1**, 41 (1987).
7. V. A. Ioffe and I. B. Patrino, *Solid State Phys.* **10**, 815 (1968).
8. N. V. Kosova, V. F. Anufrienko, N. T. Vasenin, *et al.*, to be published.