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Effect of allied and alien ions on the EPR spectrum of Mn^{4+}-containing lithium–manganese spinel oxides

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Abstract

Electron paramagnetic resonance spectroscopy was used for studying the effect of allied and alien ions on the EPR spectrum of Mn^{4+}-containing lithium–manganese spinel oxides. Manganese spinel oxides with paramagnetic Mn^{4+} and diamagnetic substituents in the 16d spinel sites were studied: $Li[Mg_{0.5}Mn_{1.5}]O_4$, $Li[Mg_{0.5-x}Co_{2x}Mn_{1.5-x}]O_4$, $0<x\leq 0.5$, and $Li[Li_{1/3}Mn_{5/3}]O_4$. Ni^{2+}-ions with integer-spin-ground state ($S=1$) were selected as alien ions: $Li[Mg_{0.5-x}Ni_xMn_{1.5}]O_4$ ($0\leq x\leq 0.5$), $Li[Li_{(1-2x)/3}Ni_xMn_{(5-x)/3}]O_4$ ($0\leq x\leq 0.5$), and $Li[Ni_{0.5}Mn_{1.5-y}Ti_y]O_4$ ($0\leq y\leq 1.0$). It was shown that in Ni-substituted oxides the low temperature EPR response comes from magnetically correlated Ni–Mn spins, while at high registration temperature Mn^{4+} ions give rise to the EPR profile. Analysis of the EPR line width allows differentiating between the contributions of the density of paramagnetic species and the strength of the exchange interactions in magnetically concentrated systems. The density of allied and alien paramagnetic species has no effect on the EPR line width in cases when the strengths of antiferro- and ferromagnetic interactions on an atomic site are close. On the contrary, when antiferro- or ferromagnetic interactions on an atomic site are dominant, the EPR line width increases with the density of paramagnetic species.

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1. Introduction

Lithium manganese oxides with a spinel structure are of technological interest as electrode materials for rechargeable lithium-ion batteries [1]. Substituted spinels with divalent metal ions, $LiM_{0.5}Mn_{1.5}O_4$, as well as Co-substituted spinels, belong to the promising candidates for high-voltage electrode materials [2–6]. The cationic distribution in the lithium transition metal oxides has been recognized as a factor affecting their electrochemical performance [7,8]. Complimentary to the XRD techniques, the spectroscopic methods appear to be effective for studying the local cationic environment [9].

Electron paramagnetic resonance (EPR) spectroscopy deals not only with the electronic structure of paramagnetic centres, but also with their local environments. For magnetically concentrated systems, both dipole–dipole and exchange interactions smear the effect of neighbour species, leading to the appearance of a broad symmetrical EPR line [10–12]. Depending on the spin concentration and the distance between the spins, the dipole-dipole interactions are superimposed on the Zeeman's interactions, thus leading to an increase in line width. Contrary to the dipole–dipole interactions, the exchange interactions average the local magnetic fields around the paramagnetic species, as a result of which the line width decreases. This assertion is referred to the case when antiferro- or ferromagnetic interactions

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dominate on an atomic site. When ‘alien’ paramagnetic ions appear in a close proximity of the EPR active species, the EPR spectrum undergoes strong changes. Contrary to the effect of the ‘allied’ paramagnetic ions, the effect of ‘alien’ paramagnetic ions is theoretically not well described.

However, EPR has been successfully used for studying the cationic distribution in magnetically concentrated lithium–manganese spinels [13–19]. The complexity of the EPR spectrum of pure $Li_{1+x}Mn_{2-x}O_4$ is associated with the simultaneous appearance of Mn^{3+} and Mn^{4+} ions in 16d octahedral sites. The replacement of Mn^{3+} in $Li_{1+x}Mn_{2-x}O_4$ by mono-, di- and three-valent ions (such as Li^+, Mg^{2+}, Ni^{2+} and Co^{3+}) yields solids spinel solutions containing Mn^{4+} only. It is well known that ions with half-integer spin ground state (such as Mn^{4+}, $S=3/2$) are especially suitable for studying with EPR spectroscopy at conventional microwave frequencies (9.3 GHz, X-band). Depending on the synthesis conditions, EPR spectra of $Li[CoMn]O_4$, $Li[Li_{1/3}Mn_{5/3}]O_4$ and $Li[M_{0.5}Mn_{1.5}]O_4$ compositions permit differentiation between samples in respect of the local environment of Mn^{4+} [20,21]. In addition, the changes in the local structure of transition metal ions during Li intercalation and deintercalation in $LiNi_{0.5}Mn_{1.5}O_4$ spinels has been monitored by EPR [22].

The aim of this communication is to study the effect of allied and alien ions on the EPR spectrum of Mn^{4+}-containing lithium–manganese spinel oxides. The magnetic structure of the lithium manganese spinel is a result of competition between 90° direct Mn^{4+}–Mn^{4+} antiferromagnetic and 90° superexchange Mn^{4+}–O^{2-}–Mn^{4+} ferromagnetic interactions [23]. Therefore, the spinels can be regarded as systems where antiferro- and ferromagnetic interactions act on an atomic Mn site. We have selected Ni^{2+} paramagnetic ions with integer-spin-ground state ($S=1$) as alien ions. In the X-band, these ions remain usually ‘EPR-silent’ due to the fact that the magnitude of the zero field splitting parameter is larger than the available microwave frequency [24]. To rationalize the EPR of magnetically concentrated systems, the EPR study was first focused on spinels, where Mn^{4+} ions only are EPR active. Then the study was extended to the Ni-substituted analogues, where both Ni^{2+} and Mn^{4+} are paramagnetic.

2. Experimental

Three groups of Mn^{4+} containing spinel oxides are chosen. The first group consist of oxides where Mn^{4+} and diamagnetic substituents are distributed in the 16d spinel sites: $Li[Mg_{0.5}Mn_{1.5}]O_4$, $Li[Mg_{0.5-x}Co_{2x}Mn_{1.5-x}]O_4$, $0<x\leq 0.5$, and $Li[Li_{1/3}Mn_{5/3}]O_4$. The second group comprises nickel substituted analogues: $Li[Mg_{0.5-x}Ni_xMn_{1.5}]O_4$ and $Li[Li_{(1-2x)/3}Ni_xMn_{(5-x)/3}]O_4$ with $0\leq x\leq 0.5$. Finally, Ti substituted $Li[Ni_{0.5}Mn_{1.5}]O_4$ oxides have been studied. It has been shown that Ti^{4+} substitutes for Mn^{4+}, $Li[Ni_{0.5}Mn_{1.5-y}Ti_y]O_4$ being obtained for $0\leq x\leq 1.0$ [25].

For the preparation of spinel oxides, we used the acetate precursor method. This method consists in freeze-drying of acetate salts of the corresponding metal ions, followed by thermal decomposition at 450 °C in air. To ensure the synthesis of a XRD pure phase, the decomposed products are pelleted, heated at 600 °C in oxygen atmosphere for 48 h and, then, cooled to room temperature with 1°/min. Under these synthesis conditions, ordered $LiM_{0.5}Mn_{1.5}O_4$ phases are obtained. For the synthesis of Ti-substituted $LiNi_{0.5}Mn_{1.5}O_4$ we used the synthesis procedure described in [25]. Stoichiometric mixtures of $LiOH\cdot H_2O$, $Ni(OH)_2$, γ-MnOOH and TiO_2 were pressed into pellets and heat treated at 900 °C for 5 h in air. After the grinding, the resulting mixture was pressed again to pellets and heated at 700 °C for 48 h in air.

The lithium content of the samples was determined by atomic absorption analysis. The total content of manganese, nickel, cobalt and magnesium was established by atomic absorption analysis. The mean oxidation state of manganese ions was established permanganometrically after dissolution of the powdered sample in a mixture of $VOSO_4$ and H_2SO_4 by titrating the excess of V^{4+} in the solution.

X-ray phase analysis was made by a Philips diffractometer with Cu K_α radiation. Unit cell parameters were obtained from least-square fitting of all peak positions. The IR spectra were recorded with a Nicolet Avatar-32 spectrometer using KBr pellets. The EPR spectra were recorded as a first derivative of the absorption signal of an ERS-220/Q spectrometer within the temperature range of 90–400 K. The g-factors were determined with respect to a Mn^{2+}/ZnS standard. The signal intensity was established by double integration of the experimental EPR spectrum.

3. Results and discussion

3.1. Cationic distribution in Mn^{4+}-containing spinels

For divalent metal ions substituted spinels ($LiM_{0.5}Mn_{1.5}O_4$), the main structural feature is the 1:3 order of M^{2+}:Mn^{4+} ions in the 16d spinel sites [8]. The observed 1:3 cationic order leads to reduction of $Fd3m$ symmetry to $P4_332$. IR spectroscopy has been shown to be a suitable experimental tool for studying the cationic ordering in complex compositions, even in cases when it is not accessible to XRD techniques [26,8]. Fig. 1 compares the IR spectra of $Li[Mg_{0.5-x}Ni_xMn_{1.5}]O_4$, $Li[Li_{(1-2x)/3}Ni_xMn_{(5-x)/3}]$ O_4 and $Li[Ni_{0.5}Mn_{1.5-y}Ti_y]O_4$. The two IR modes typical of a spinel structure are split into several bands, indicating $Mg^{2+}{}_{0.5-x}Ni^{2+}{}_x/Mn^{4+}$ ordering in $Li[Mg_{0.5-x}Ni_xMn_{1.5}]O_4$ compositions. The ordering bands are clearly resolved for $Li[Li_{(1-2x)/3}Ni_xMn_{(5-x)/3}]O_4$ with $0.2\leq x\leq 0.5$ and $Li[Ni_{0.5}Mn_{1.5-y}Ti_y]O_4$ with $x\leq 0.5$. For 1:3 spinel ordering, every 4b octahedron occupied by M^{2+} is surrounded by six 12d octahedra containing Mn^{4+} only, while four Mn^{4+} and two M^{2+} form the first metal shell of Mn^{4+} occupying 12d