HEBM synthesis of nanocrystalline $LiZn_{0.5}Ti_{1.5}O_4$ spinel and thermally induced order–disorder phase transition($P4_332 \rightarrow Fd\bar{3}m$)

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ABSTRACT

Nanocrystalline $LiZn_{0.5}Ti_{1.5}O_4$ disordered spinel (S.G. $Fd\bar{3}m$) was synthesized by high energy ball milling (HEBM). TEM analysis of the sample has shown that the particle size distribution is broad ranging from 10 to 60 nm. By X-ray line broadening analysis, the average apparent size of the crystallites is found to be 19(1) nm, while the average apparent strain is $26(4) \times 10^{-4}$. The cation distribution was found to be metastable, with Zn in octahedral $16d$ and Ti in tetrahedral $8a$ position, against their known site preference. After annealing the sample at 650 °C for 3 h and slow cooling down to room temperature, superstructure reflections (1 1 0), (2 1 0), (2 1 1) have been observed, indicating a cation ordering in the octahedral sublattice and a combined symmetry reduction (S.G. $P4_332$). The reverse symmetry change $P4_332 \rightarrow Fd\bar{3}m$ caused by increasing the temperature was studied by *in situ* XRPD, DSC/DTA, Landau's theory of phase transitions and Raman spectroscopy. An analysis of the topology of the order parameter vector space indicates a biquadratic or linear-quadratic coupling between the order parameters Q_1 and Q_2. In $LiZn_{0.5}Ti_{1.5}O_4$ dilatation expansion of crystal lattice as well as spontaneous strain values are rather small (order of 10^{-4}), comparing to e.g. $Li_{1.33x}Co_{2-2x}Ti_{1+0.67x}O_4$.

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1. Introduction

Transition metal oxide spinels have been studied for many years for their potential in electrochemical, catalytic, magnetic and ceramic applications [1–3]. Due to novel methods of synthesis and the possibility of notably reducing crystallite sizes to a nanometric level, new electronic and chemical properties of materials have been obtained. Recently, several investigations have been devoted to find out how these properties depend on structure and microstructure parameters of the materials (e.g. cation distribution, particles size, shape and microstrain) which – to some extent – can be controlled by the synthesis procedures [4–7]. Consequently, the interest in understanding the correlation between crystal structure/microstructure, and materials properties is increased.

The spinel structure represents one of the most important structure families among the double oxides with general composition AB_2O_4, where the oxygen ions form a cubic close packed array with tetrahedrally (T_d) and octahedrally (O_h) coordinated interstices. In more detail, one-eighth of the tetrahedral and one-half of octahedral sites are occupied with cations (A and B). Depending on the distribution of the cations between the T_d and O_h vacancies, different principal spinel types can be distinguished: normal, $(A)^{tet}[B_2]^{oct}$; inverse, $(B)^{tet}[AB]^{oct}$; or random, $(A_{0.33}B_{0.67})^{tet}[A_{0.67}B_{1.33}]^{oct}$. At room temperature, the cation distribution is mainly determined by the cation site preferences, but it can vary with the changes in temperature, pressure and/or due to cation substitutions. In a more general form, the cation distribution among the two cation sites can be expressed with the formula $(A_{1-i}B_i)^{tet}[A_iB_{2-i}]^{oct}$, where i denotes the degree of inversion. In the case when sublattices (T_d and/or O_h) are occupied by at least two different types of cations and a particular stoichiometric ratio is achieved, there is possibility of cation ordering. Any ordering of cations into one or both sublattices is followed by lowering of the crystal symmetry. In case of a 1:3 ordering in the octahedral sublattice, the space group changes from $Fd\bar{3}m$ to $P4_332$ (a subgroup of index 8). The symmetry reduction is accompanied with the following splitting of the Wyckoff positions: (T_d) $8a \rightarrow 8c$; (O_h) $16d \rightarrow 4b + 12d$; $32e$ (oxygen position) $\rightarrow 24e + 8c$ [8]. It has to be stressed that the preferences of a certain cation species for a particular site [9] may change significantly when bulk

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spinel compounds are compared with their nanoscale counterparts [10].

The comparatively open character of the spinel structure is an interesting feature for those materials which require high mobility of lithium ions, as electrodes and electrolytes in Li-ion batteries. $Li_{1.33}Ti_{1.67}O_4$ spinel, for example, has attracted considerable interest as a negative electrode material due to its remarkable electrochemical characteristics and lack of dilation during the charge/discharge process [11–15]. The effect of a partial substitution of lithium and/or titanium ions with transition metals (e.g. Fe, Co, Mn, Cr) on the electrochemistry of $Li_{1.33}Ti_{1.67}O_4$ has also been studied [16–18]. From a crystallographic point of view, a special interest was dedicated to the compositions $LiM_{0.5}Ti_{1.5}O_4$, M = Co, Zn, Ni, Fe, Mg, which possess an ordered structure of M^{2+} and Ti^{4+} ions on the O_h sublattice [16,19–21]. Consequently, our motivation to study the title compound has its technological importance as well as investigation of crystal structure changes with thermal annealing and order–disorder phase transition.

In the present paper we have investigated the microstructure of $LiZn_{0.5}Ti_{1.5}O_4$ obtained by high energy ball milling, as well as the evolution of the crystal structure after thermal annealing of the sample. The mechanism of the observed order–disorder phase transition in $LiZn_{0.5}Ti_{1.5}O_4$ has been studied by *in situ* X-ray powder diffraction, Raman spectroscopy and Landau's theory of phase transition.

2. Experimental

Polycrystalline samples of $LiZn_{0.5}Ti_{1.5}O_4$ were produced by high energy ball milling using a Fritsch Pulverisette 5 planetary mill with vials and balls made of hardened steel. An appropriate mixture of commercial Li_2CO_3, ZnO and TiO_2 powders (purity >99%) was used as starting material. The mass of the powder mixture was 10 g, the ball-to-powder weight ratio was 20:1. Mechanochemical treatment was carried out in air for 20 h. During the milling process the vial was opened for a few times in order to relieve the CO_2 gas produced during the mechanochemical reaction. The as-prepared sample was subsequently heated at 650 °C for 3 h and slowly cooled down to room temperature (cooling speed was around 2 °C min^{-1}).

X-ray powder diffraction (XRPD) patterns of the as-prepared and the annealed samples were recorded at room temperature on a Philips PW1710 diffractometer using graphite monochromatized Cu Kα radiation and a Xe-filled proportional counter. Data for the mechanochemically synthesized sample were collected in the angular range between 15.5° and 140° 2θ, with a step size of 0.02° and a counting time of 10 s per step. The measurement conditions for the annealed specimen were as chosen as follows—2θ-interval: 10–120°, step size: 0.02°, counting time: 20 s.

The change of the crystal symmetry was investigated by *in situ* XRPD in the temperature range from 900 to 1100 °C in temperature steps of 20 °C. XRPD patterns for Rietveld structural refinements were collected in the 2θ interval 10–110°, with a step size of 0.02° and a scanning time of 5 s per step on a SIEMENS D5005 diffractometer equipped with an Anton Paar HTK 1200 high temperature chamber (Cu Kα radiation, θ–θ geometry, parallel beam optics, secondary Soller slits and scintillation counter) in synthetic air atmosphere. Before starting a single run of the high temperature series the sample was kept at the appropriate temperature for a sufficiently long time to insure thermodynamical equilibrium.

Transmission electron microscopy (TEM) has been performed on a Philips M400 instrument allowing for a magnification of up to 310,000×. Differential thermal (DTA) and calorimetric (DSC) analyses were carried out up to 1180 °C in air with a TA SDT 2060 device using heating and cooling rates of 15 °C min^{-1}.

To investigate the presence of impurities as well as to check the homogeneity of the distribution of elements a JEOL 8100 microprobe analyzer was employed.

Raman spectra were recorded by a HORIBA JOBIN YVON LabRam-HR800 spectrometer. Samples were excited by the 514.5 nm emission line of a Ar^+-laser through a 50× long-working distance objective (numerical aperture 0.5). Size and power of the laser spot on the sample surface were approximately 3 μm and ranged around 5 mW. The spectral resolution, experimentally determined by measuring the full width at half maximum of the Rayleigh line, was about 1.8 cm^{-1}. The dispersed light was collected by a 1024 × 256 open electrode CCD detector. Confocal pinhole was set to 1000 μm. Spectra were recorded unpolarized. All spectra were corrected assuming linear or second order polynomial function background and deconvoluted by Gauss–Lorentz functions using the built-in spectrometer software Labspec 4. Raman shifts were calibrated by regular adjusting the zero-order position of the grating and the Rayleigh line of a (1 0 0) polished single-crystal silicon wafer. Accuracy of the determined band positions should be better than 0.5 cm^{-1}.

In situ high temperature Raman experiments were performed in a Linkam THMS 1500 heating-stage with a quartz window and a ceramic crucible. Measurements were performed between 500 and 1200 °C in steps of 100 °C. Temperature precision
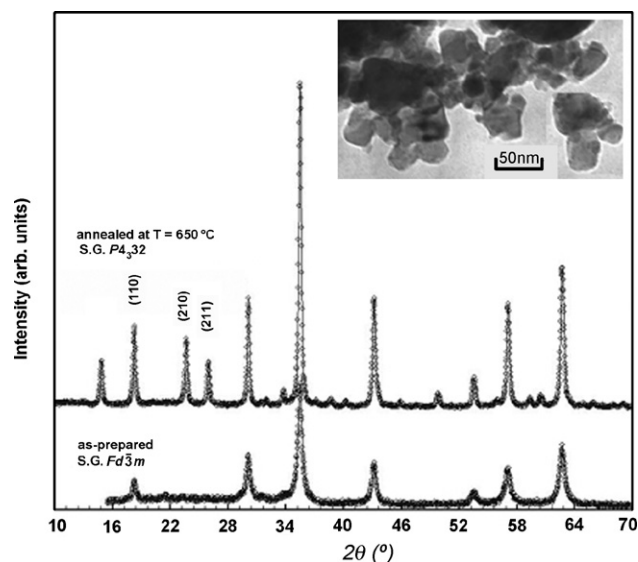

Fig. 1. XRPD patterns of $LiZn_{0.5}Ti_{1.5}O_4$ (as-prepared and after annealing at 650 °C), recorded at room temperature. TEM picture of the as-prepared sample (inset).

and accuracy, checked by measuring the thermal shift of the TO-LO phonon of a (1 0 0) polished single-crystal silicon wafer, was around ±5 °C.

3. Results and discussion

3.1. Structural characterization

The powder X-ray diffraction pattern of $LiZn_{0.5}Ti_{1.5}O_4$ obtained by direct mechanochemical reaction (i.e. as-prepared) confirms the presence of a disordered spinel structure (S.G. $Fd\bar{3}m$). After annealing at 650 °C for 3 h and slow cooling down to room temperature, the superstructure reflections (1 1 0), (2 1 0), (2 1 1) were observed (Fig. 1), indicating a cation ordering in the O_h sublattice and a symmetry reduction to S.G. $P4_332$. Broadening of XRPD reflections of the as-prepared $LiZn_{0.5}Ti_{1.5}O_4$ sample point out to a pronounced influence of microstructural effects (size and strain) on the line profiles. The absence of cation ordering in this sample is probably a consequence of the preparation method, since high energy ball impacts can produce a lot of defects and lead to peculiar cation distributions. On the contrary, it was recently shown that a $LiZn_{0.5}Ti_{1.5}O_4$ material synthesized by a modified polymeric precursor method [22], crystallized in an ordered spinel structure (S.G. $P4_332$), with particles size about 90 nm.

X-ray powder diffraction data have been used to refine the crystal structure of the as-prepared as well as the annealed samples. Microprobe analysis of the sample has shown the presence of impurities that were due to the sample preparation method (source of iron) and unreacted rests of the reactant: two small peaks at 21.4° and 23.5° 2θ in the XRPD pattern of as-prepared sample indicate the presence of a small amount of Li_2CO_3, which was added in excess (about 5 wt.%) during the synthesis procedure. Any trials to take into account presence of the second phase during the crystal structure refinement has not improved refinement, so as-prepared sample was considered as a single phase and the crystal structure refinement has been performed in the $Fd\bar{3}m$ space group using the Rietveld profile method and Fullprof program [23]. The lattice constant for the as-prepared $LiZn_{0.5}Ti_{1.5}O_4$ material has been determined to be 8.3759(1) Å at room temperature, which is consistent with already reported values for the same composition [22]. It is interesting to notice that analyzing lithium, zinc and titanium cation distributions over the tetrahedral 8*a* and the octahedral 16*d* positions revealed presence of all cations in both crystallographic