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HIGH-TEMPERATURE BEHAVIOR AND VIBRATIONAL SPECTROSCOPY OF SYNTHETIC $LiMg_{0.5}Ti_{1.5}O_4$ SPINEL

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The ideal spinel structure consists of a cubic close-packed array of anions with one-eighth of the tetrahedral and one-half of the octahedral interstices occupied by cations. The general formula for spinel is AB_2X_4, where A is a tetrahedrally and B an octrahedrally coordinated cation. Depending on the distribution of the cations among the two cation sites, different spinel types can be distinguished.

Polycrystalline $LiMg_{0.5}Ti_{1.5}O_4$ ordered spinel (S.G. $P4_332$) was synthesized by solid-state reactions of Li_2CO_3 (99.998%), MgO (99.9955%) and TiO_2 ($>$ 99%). Stochiometric amounts of the dried starting materials were mixed by planetary ball milling with ethanol medium. The starting mixture was filled in a platinum crucible, heated in a muffle furnace at 700 ˚C for 12 h and subsequently fired at 1025 ˚C for 24 h. The product was quenched in air from the reaction temperature. The expected order-disorder phase transition ($P4_332 \rightarrow Fd\bar{3}m$) in $LiMg_{0.5}Ti_{1.5}O_4$was studied byin situ XRPD, Raman Spectroscopy and DTA at high temperatures. In situ Raman spectra and XRPD patterns were recorded from room temperature up to 1180 ˚C. The XRPD patterns showed that between 1000 ˚C and 1025 ˚C the superstructure reflections of the ordered phase disappeared, indicating the symmetry change $P4_332 \rightarrow Fd\bar{3}m$. The reverse effect caused by cooling, occured between 1000 ˚C and 975 ˚C. In good agreement, on heating the DTA experiment showed a sharp endothermic peak at 998 ˚C. On cooling the corresponding endotherm peak occurred at 978 ˚C. The Raman spectrum recorded at room temperature exhibits strong Raman bands at 710, 405, 171, 156, 114 cm^{-1}, medium bands at 536,452, 349, 303, 270, 248, 217, 190 cm^{-1} and weak bands at 651, 628, 575 cm^{-1}. With increase of temperature all Raman bands are shifted to lower wavenumbers due to thermal expansion. At a temperature of 1050˚C only five broad bands could be observed at 125, 246, 325, 485 and 694 cm^{-1} Factor group analysis of the disordered spinel structure ($Fd\bar{3}m$ - O_h^7) predicts that only five optic modes are Raman active (A_{1g} + E_g + 3 F_{2g}). As a consequence of the 1:3 ordering in the octahedral sublattice and the lower space group symmetry the number of Raman active modes increases significantly (5 A_1 + 12 E + 17 F_2, Jović et al. 2009).

Jović, N., Vučinić-Vasić, M., Kremenović, A., Antić, B., Jovalekić, Č., Vulić, P., Kahlenberg, V., Kaindl, R. (2009) HEBM synthesis of nanocrystalline $LiZn_{0.5}Ti_{1.5}O_4$ spinel and thermally induced order-disorder phase transition ($P4_332 \rightarrow Fd\bar{3}m$). Materials Chemistry and Physics, 116, 542-549.