High-Pressure Investigations of spinel-type LiTM_2O_4 (TM = transition metal) cathode materials

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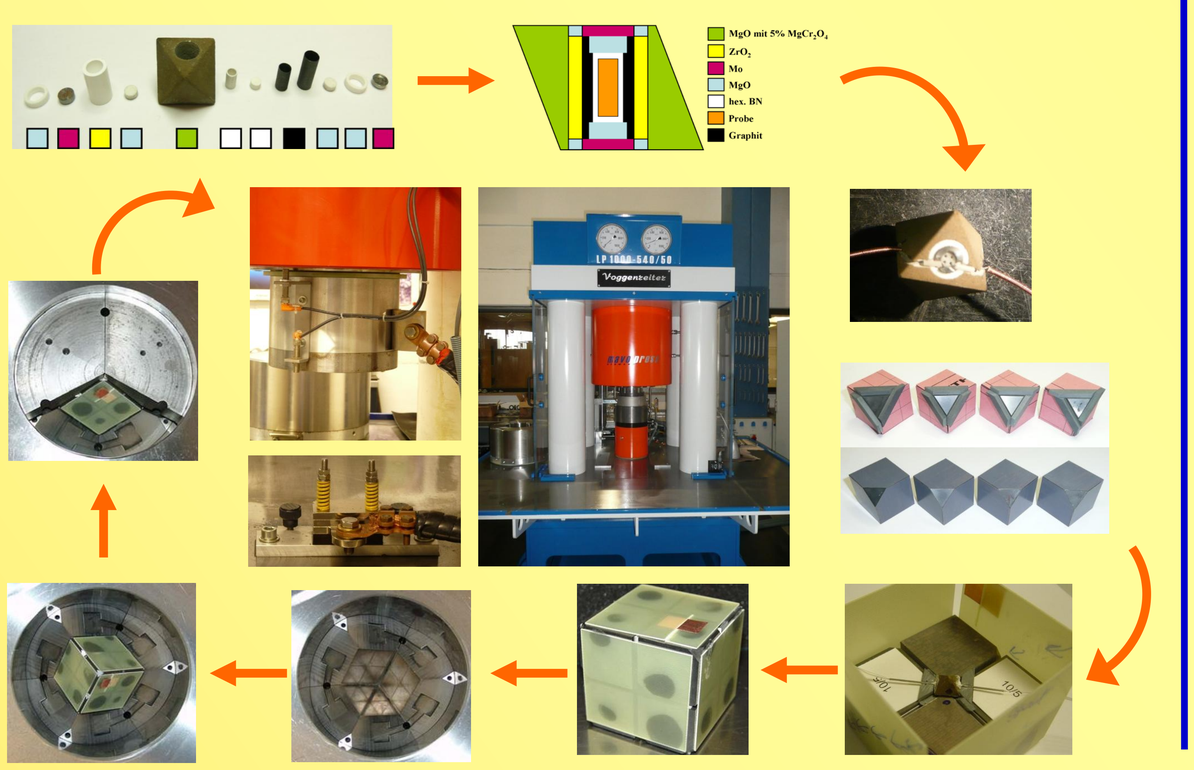
Introduction

New synthesis strategies are needed to prepare novel electrode materials for lithium-ion batteries. High-pressure / high-temperature routes are widely used within other fields of Solid State Chemistry to induce structural transformations of materials, conducting to novel polymorphs possessing structures not accessible at ambient pressure. The high pressure treatment changes both the crystal structure as well as the electronic characteristics of the material. High pressure driven transformations of several electrode materials have been studied and reported, for example Li_xFePO_4,[1,2] V_2O_5,[3] Li_2MSiO_4 (M = Mn, Co).[4,5] It is proven that after exposure to high pressure/high temperature conditions, the electrochemical properties varied compared to the ambient pressure materials. For $LiMn_2O_4$ various studies report structural examinations at high pressure of these spinel phase[6-9]. But, only little is known about the electrochemical behaviour of these phases, when they are used as intercalation compound for an electrode in a lithium ion battery.[10] In this work we investigate the pressure driven structural and electrochemical modifications of spinel LiTM_2O_4 (TM = transition metal) cathode materials.

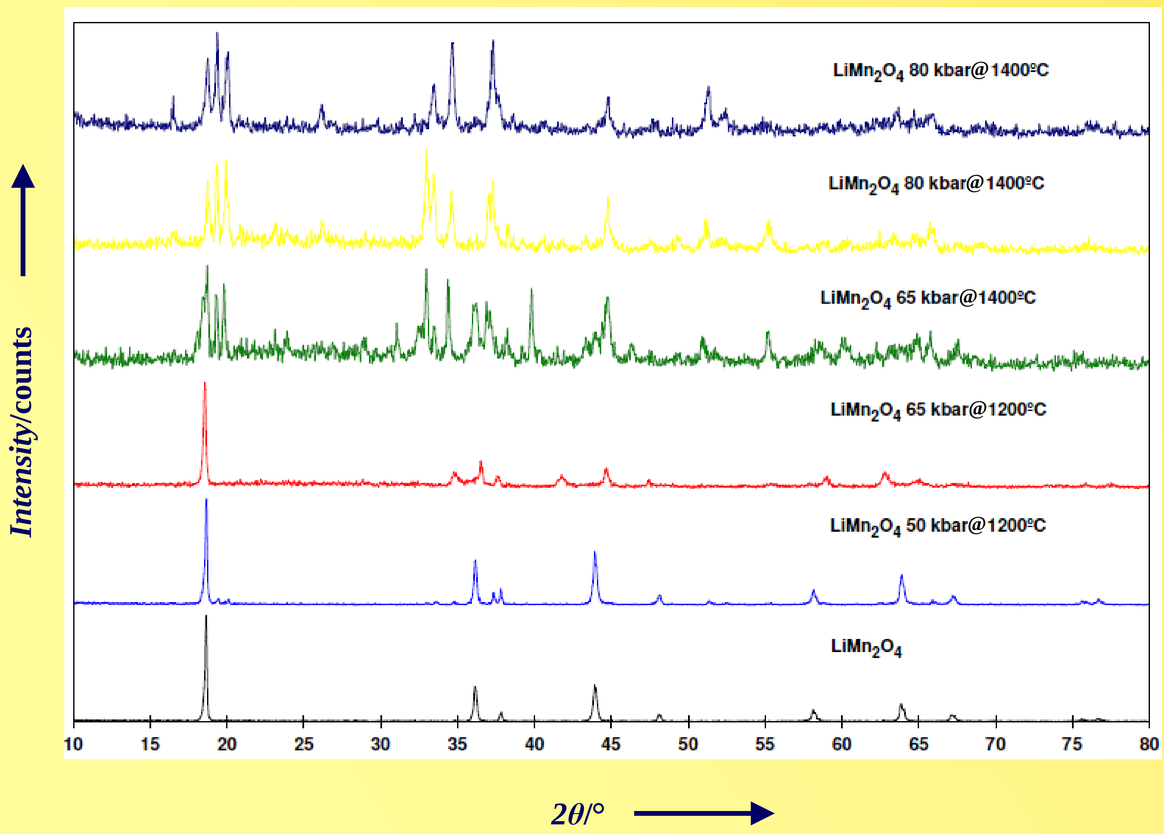
Experimental Approach:

Multianvil-Press



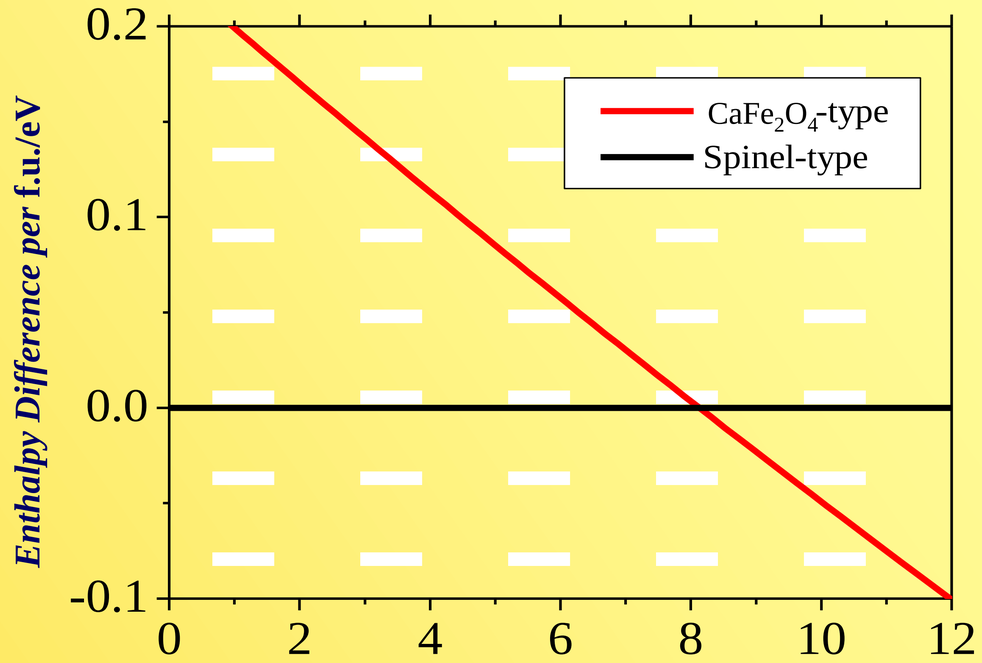
High-pressure experiments are performed in a 1000 tons Walker-type multianvil press. The figure shows the step by step process of mounting the assembley.

High-Pressure Synthesis of $LiMn_2O_4$

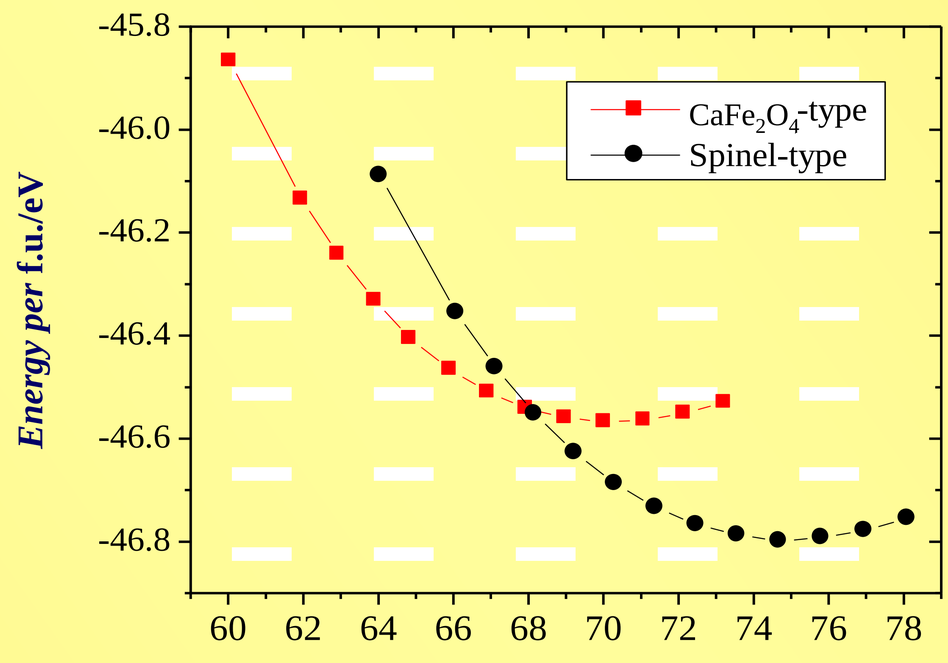


Phasetransition to the high-pressure phase of $LiMn_2O_4$ ($CaFe_2O_4$-type) from 6 GPa on visible.

DFT-Calculations



Enthalpy-pressure diagram for the transition of $LiMn_2O_4$.



Energy-volume diagram of $LiMn_2O_4$

	B (GPa)	B'	V (A^3)	E (eV)
Spinel	108.1	4.2	74.95	46.795
$CaFe_2O_4$	108.9	5.1	70.23	46.564

[1] M. E. Arroyo de Dompablo, N. Biskup, J.M. Gallardo-Amores, E. Morán, H. Ehrenberg, U. Amador, *Chem. Mater.* **2010**, *22*, 994.
[2] M. E. Arroyo de Dompablo, J.M. Gallardo-Amores, U. Amador, *Electrochem. Solid St.* **2005**, *8*, A564-A569.
[3] M. E. Arroyo de Dompablo, J. M. Gallardo-Amores, U. Amador, E. Morán, *Electrochem. Commun.* **2007,** *9*, 1305-1310.
[4] M. E. Arroyo de Dompablo, U. Amador, J.M. Gallardo-Amores, E. Morán, H. Ehrenberg, L. Dupont, R. Dominko, *J. Power Sources* **2009**, *189*, 638.
[5] M. E. Arroyo de Dompablo, R. Dominko, J.M. Gallardo-Amores, L. Dupont, G. Mali, H. Ehrenberg, J. Jamnik, E. Moran, *Chem Mater* **2008**, *20*, 5574-5584.
[6] P. Piszora, W. Nowicki, J. Darul, B. Bojanowski, S. Carlson, Y. Cerenius, *Radiat. Phys. Chem.* **2009**, *78*, S89-S92.
[7] J. Darul, W. Nowicki, C. Lathe, P. Piszora, *Radiat. Phys. Chem.* **2011**, *80*, 1014-1018.
[8] A. Paolone, A. Sacchetti, P. Postorino, R. Cantelli, A. Congeduti, G. Rousse, C. Masquelier, *Solid State Ionics* **2005,** *176*, 635-639.
[9] K. Tokiwa, K. Matsukura, S. Kasahara, S. Tsuda, S. Mikusu, K. Takeuchi, A. Iyo, Y. Tanaka, J. Akimoto, J. Awaka, N. Kijima, Y. Takahashi, T. Watanabe, *J. Phys.: Conf. Ser.* **2009**, *150*, 042210.
[10] K. Yamaura, Q. Huang, L. Zhang, K. Takada, Y. Baba, T. Nagai, Y. Matsui, K. Kosuda, E. Takayama-Muromachi, *J. Am. Chem. Soc.* **2006**, *128*, 9448-9456.