

STRUCTURAL PHASE TRANSITIONS IN TWO LITHIUM TANTANYL COMPOUNDS

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Structural phase transitions have been observed in LiTaOXO₄ with X=Si,Ge by means of X-ray single crystal and powder diffraction, differential scanning calorimetry and ⁷Li MAS-NMR spectroscopy. The crystal structure of both compounds is characterized by parallel chains of trans corner sharing TaO₆ octahedra, connected via isolated XO₄ tetrahedra. The same structural topology is found in the mineral titanite, CaTiOSiO₄, but the TaO₆ octahedra form nearly eclipsed chain conformations in LiTaOXO₄. In analogy to the antiferroelectric to paraelectric phase transition that occurs near 500 K in titanite, the space group symmetry changes from P2₁/c to C2/c and both transitions are close to a tricritical point. The critical temperatures are T_c=231 K (X=Ge) and T_c=439 K (X=Si). Li occurs in distorted tetrahedral oxygen coordination and it remains disordered over two equivalent 4-coordinated sites in the paraphase of LiTaOGeO₄, as is evident from the ⁷Li-MAS-NMR spectra as a function of temperature and from X-ray structure refinements. The transitions in LiTaOXO₄ are compared to similar structural phase transitions in other AMOXO₄ compounds in terms of cation displacements and generated spontaneous strain. Critical temperatures are evaluated as a function of cation displacement using an adapted form of the Abrahams-Kurtz-Jamieson criterion.

Keywords: PHASE TRANSITIONS, TITANITE, ANTIFERROELECTRIC

VARIABLE TEMPERATURE STUDIES OF COMPOUNDS WITH NOVEL TEMPERATURE - RESISTIVITY CHARACTERISTICS, STUDY OF [(ET)₄[(H₃O)Ga(C₂O₄)₃]PHNO₂]

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Crystals with ET molecules (bisethylene dithio-tetrafulvalene) and coordinated metal species have been synthesised successfully and have been shown to exhibit interesting conduction properties. The mechanistic pathway for the conduction variance is hitherto unknown. We hope that detailed structural information will lead to a better understanding of the physical properties.

[(ET)₄[(H₃O)Ga(C₂O₄)₃]PhNO₂] is almost isomorphous with a series of Cr or Fe paramagnetic superconductors(1), however it is not a simple metal. The ET molecules are essentially planar with disordered terminal C-C positions. Variable temperature experiments were conducted on Bruker SMART 1K and 6K diffractometers and data were collected between temperatures of 25 K and 293 K. The electrical resistivity variance with temperature was measured between 1 K and 300 K using an Oxford Instruments Maglab 2000 with EP probe. [(ET)₄[(H₃O)Ga(C₂O₄)₃]PhNO₂] becomes a superconductor below 7.5 K, at higher temperatures however, several shifts are seen in the gradients of the resistivity variance with temperature. The relative arrangement of the molecules is found to be a crucial parameter in determining the electrical properties of the compound, although the changes in this structure for the most part were small. Results of this variable temperature structural study will be presented here.

(1) A.W. Graham; M. Kurmoo; P. Day (1995) J. Chem. Soc. Chem. Commun 2061-20

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X-RAY STRUCTURAL INVESTIGATIONS OF PHASE TRANSITIONS IN SPINELS IN THE Fe-Mn-O SYSTEM IN AIR

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One of the main features of the Fe-Mn-O system is deformation structural transition, due to the orbital degenerate Mn(III) ions, and caused by the cooperative Jahn-Teller effect. To forecast the material properties, it is necessary to study in details the effects of external parameters and Jahn-Teller ions' substitution on crystal lattice distortion and the nature of phase transitions induced. According to the phase equilibrium diagram of the Fe-Mn-O system in air Fe_xMn_(3-x)O₄ spinels (x<1.5) were synthesized in the temperature range of 1273-1473 K with following cooling in three different ways. Using the X-ray analysis the dependences of unit cell parameters and tetragonal distortion degree for spinel and hausmannite phases in equilibrium (*in situ*) and non-equilibrium conditions on composition, sintering temperature and cooling way were investigated. The linear temperature and composition dependences of unit cell parameters of spinel and hausmannite in equilibrium conditions were established. At the same time, unit cell parameters of homogeneous phase with hausmannite structure arising therein instead of these two phases upon cooling are described by a power function with the exponent of 0.5 through the characteristics of undistorted quenched spinel (concentration of non-Jahn-Teller ions and the unit cell parameter), and defined uniquely by sintering temperature and cooling rate. Thus, upon cooling the Fe-Mn-O system in the manganese-rich part, tends to segregation, while one of the separated phases is distorting tetragonally and its distortion degree is defined by the uniformity of distribution of Jahn-Teller ions in the equilibrium homogeneous solid solution and their motion upon cooling.

Keywords: X-RAY DIFFRACTION, MANGANESE FERRITE, PHASE TRANSITIONS

PHASE TRANSITION DATA BASE TEN YEARS AFTER

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Exactly ten years ago the crystallographic database on structural phase transitions have been appeared as a special issue of 'Phase Transitions' (38, 127-220 (1992)). Now, the new edition of the Phase Transition Database, PTDB-2002, is presented. This version is enriched by a new types of data requested by users of PTDB and contains the critically reviewed and corrected data on about 5300 phase transitions observed in 3500 crystals with respect to 3500 transitions in 2200 crystals for previous edition. Each entry for given crystal contains the space group symbols with number of formula units, Z, separated by the temperature of phase transition and it is presented in order of growing temperature. No more than two references are also listed there. Some supplementary data on properties of phases (ferroelectric, incommensurate) and phase transitions (irreversible, melting, decomposition or amorphization) are also presented by using a different fonts. The underlined symbol of the space group shows that the full structure data are presented in the Inorganic Crystal Structure Database (ICSD). The crystals with known high-pressure phase transition(s) are also marked. Some statistical analyses, e.g. a frequency of occurrence of phase transition with the given change of crystal system, will be also presented at the poster.

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Keywords: DATABASE, PHASE TRANSITIONS