

05.1-27 THERMAL DISORDER IN THE COOPERATIVE JAHN-TELLER EFFECT: TETRAGONAL-CUBIC TRANSITION IN Mn_3O_4 .

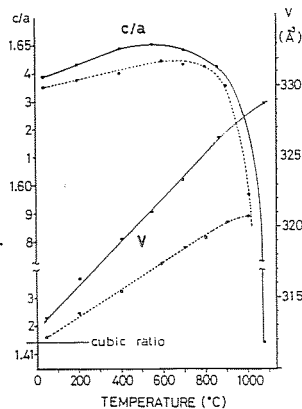
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At room temperature Mn_3O_4 is a tetragonal spinel ($I4_1/amd$, $a=5.763\text{\AA}$, $c=9.444\text{\AA}$) due to the cooperative Jahn-Teller effect of Mn^{3+} ($3d^4$). By using natural and synthetic samples of Mn_3O_4 grown by a method of the chemical transport, X-ray determination of electron density distribution from the D-Fourier synthesis onto (001) and (100) shows the deficiency of electron density on $d_{x^2-y^2}$ configuration of Mn^{3+} at the octahedral sites.

A variation of the lattice constant c shows a noticeable thermal expansion at the outset of temperature rise, but an extreme contraction just before the temperature of the transition to the cubic spinel ($Fd3m$).

In contrast, a variation curve of c/a shows a slow ascent and rapid rise near the transition temperature.

Therefore, the ratio c/a initially grows large, but drastically falls in the proximity of 900°C , and indicates $c/a=\sqrt{2}$ above the transition temperature of 1070°C . As the content of Mn^{3+} decreases, values of c/a , as well as the transition temperature, are lowered. Thermal expansion of the volume of Mn_3O_4 linearly increases regardless of the variation of c/a . Heating temperatures above 900°C were provided with a newly designed gas flame heater (Yamanaka et al, 1981).



Referring to only two variable coordinates, that is, u and v parameters of oxygen atoms ($0, u, v$), structure refinements ($R=0.021 - 0.044$) at temperatures of 20, 400, 700, 900 and 1100°C indicate that the u parameter increases at elevated temperatures, while the v parameter is almost constant ($x=0.384$). Four-equivalent bond length of Mn-O, at the octahedral sites is gradually extended from 1.928\AA to 2.099\AA in the cubic spinel structure, and two residual equivalent bond is exceedingly elongated by thermal expansion in the initial temperature rise and suddenly contracted just before the transition temperature. Mn-O bond distances at the tetrahedral sites are also expanded in the first stage and later contracted. According to r.m.s. displacement of atoms, an anisotropy of thermal vibration changes in parallel with the variation of c/a probably due to the positional disorder.

Studies of the Mössbauer effect (Yamanaka, 1972) and infrared spectra (Ishii et al, 1972) on the solid solution of $(Mn,Fe)_3O_4$ proved the presence of the local tetragonal symmetry even in the cubic spinel structure, and showed a continuous change of electric field gradient around octahedral cations and a gradual shift of modes of vibrations. It is assumed from these facts that even when Mn_3O_4 is transformed into a cubic spinel, the respective domains in Mn_3O_4 still retain a tetragonal symmetry but that the orientation of each domain changes from cooperative to random type. Consequently, Mn_3O_4 presents an isometric structure in a statistical sense. The cubic symmetry of Mn_3O_4 does not probably result from the degeneration of electron state.

05.1-28 STRUCTURAL PROPERTIES OF SHOCK-LOADED LITHIUM NIOBATE.* By B. Morosin and R. A. Graham, Sandia National Laboratories, Albuquerque, New Mex.†

Stanton and Graham (J. Appl. Phys. 50, 6892 (1979)) have reported a succession of unusual compressional features in lithium niobate crystals shocked above the ~ 2.4 GPa Hugoniot elastic limit. The reported drastic reductions of shear strength and an anomalously large pressure derivative of the bulk modulus suggest localized shock-heating effects are important. Such heating results from localized yielding along certain crystallographic planes which, because of the low thermal conductivity, may result in local temperatures in excess of the melting temperature persisting for the duration of the shock experiment ($\sim 10^{-6}$ sec). Recovered single crystals subjected to planar shock waves below and above the 13.9 GPa polymorphic phase transition have been examined by X-ray diffraction techniques. No glassy or high pressure phases were detected; however, the single crystals were found to be converted to micron-sized crystallites. Further these crystallites are found to be highly oriented with respect to the original crystal axes, suggesting that the entire recovered specimen resulted from some twin-boundary growth mechanism. Superposition of [110] and [104] appears to dominate the apparent, solid state recrystallization process. Diffraction photographs have been compared with those from thermally quenched single crystals subjected to temperatures near or at the melting point without reproducing the shock results. The present observations provide further evidence for catastrophic rather than benign interactions in shock-loaded solids. The relationship of the crystal structure to such a catastrophic interaction will be discussed.

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05.1-29 OPTICAL BIREFRINGENCE STUDIES OF FERROIC CRYSTALS USING MODULATION METHODS. By I.G. Wood and A. M. Glazer, Clarendon Laboratory, Parks Road, Oxford OX1 3PU.

Measurement of optical birefringence provides a rapid and accurate method for the detection and study of structural phase transitions in solids. Recently Wood and Glazer (J. Appl. Cryst. (1980) 13, 217-223) described apparatus for the continuous monitoring of birefringence as a function of temperature, specimen position etc. Simultaneous high-pressure, high-temperature studies have also been carried out. (Wood, Welber, David and Glazer, J. Appl. Cryst. (1980) 13, 224-229). In this paper further developments of this technique are described, including modifications to the instrument which enable it to operate as a continuously-monitoring Sénarmont compensator - a method well suited to the accurate measurement of moderate ($\sim \lambda$) changes in optical retardation. The experimental results presented will include measurements made on ferroelastic $BiVO_4$ - $BiNbO_4$ solid solutions and ferroelectric $LiTaO_3$ - $LiNbO_3$.