

- b) Transition metal carbides with large lattice constants and strong covalent bond energy exhibit small deviations from $x = 1$ stoichiometry and form low temperature phases at $x = 0.5$ and $x = 1$. $ZrCo_{0.65}$ e.g. orders in Ti_2C structure rather than in a M_2C_3 structure because of the gain of covalent bond energy for a reduction of Zr-C bond distance by 0.03 Å (Hauck, Larson, Gruzalski, Darken & Barhorst, unpublished). $ZrC_{0.65}$ can be charged with hydrogen.
- c) Transition metal carbides with both strong Coulomb and strong covalent interactions like HfC_x and TaC_x exhibit the highest melting points of solids with about 4000 °C but exhibit very little tendency for ordering because of the small differences between Coulomb energies favouring $x = 0.83$ and covalent bond energies favouring $x = 0.5$ and $x = 1$ compositions.

05.2-12 PULSED NEUTRON DIFFRACTION STUDY OF A15

COMPOUNDS. By J.-E. Jorgensen, Aronne National Laboratory, U. S. A., A. N. Christensen and S. E. Rasmussen, Aarhus University, Denmark.

The three A15 compounds Mo_3Si , non stoichiometric Nb_3Ge and Nb_3Sn have been studied by pulsed neutron powder diffraction. These compounds represent high, medium and low temperature superconductors. The aim of the experiments was to study the relationship between superconductivity and structural instability at low temperature. The martensitic transformation (cubic to tetragonal) was observed in Nb_3Sn .

The mean squares displacements of the thermal vibrations were measured as a function of temperature. The degree of anisotropy of the transition metal vibrations will be related to structural and superconducting properties.

05.2-11 THERMAL EXPANSION OF SOME RE T_4B_4 TYPE RARE EARTH METAL BORIDES. By K. Damodar Reddy, B. Appa Rao, K. Satyanarayana Murthy and Leela Iyengar, Department of Physics, Osmania University, Hyderabad - 500 007, India

The ternary metal borides of RE T_4B_4 - type (RE=rare earth metal, T = Os, Ir) crystallize in a tetragonal structure with the space group $P4_2/n$ and are isotypic with $NdCo_4B_4$. The tetragonal unit cell parameters 'a' and 'c' of RE Os_4B_4 (RE = La, Ce, Pr, Nd and Sm) and of RE Ir_4B_4 (RE = La, Pr, Nd and Sm) have been determined accurately over the temperature range 300-800 K by X-ray powder diffraction techniques. Using the high temperature lattice parameter data the axial thermal expansion coefficients α_a and α_c have been evaluated at different temperatures. It has been found that the thermal expansion coefficients are anisotropic ($\alpha_a > \alpha_c$) and this anisotropy increases with decreasing axial ratio c/a. These results are discussed in relation to the structure and other physical properties of these materials.

05.2-13 FINE POWDER SHG-TECHNIQUE FOR THE DETERMINATION OF POLAR DISTORTION IN SUBSTANCES AND ITS APPLICATION TO THE STUDY OF SYSTEMS WITH FERROELECTRIC PHASES ($SbNbO_4$ - $BiNbO_4$ AND $SbNbO_4$ - $SbSbO_4$). By S. Yu. Stefanovich, A. P. Leonov and Yu. N. Venevtsev. L. Ya. Karpov Institute of Physical Chemistry, Moscow, USSR.

Quantitative estimations of noncentrosymmetric distortions in crystals by means of the Second Harmonic Generation (SHG) in powders are usually unsatisfactory because of the strong dependence of the intensity of the signal ($I_{2\omega}$) on the coherent length (L_C) which for various crystals varies considerably. However in the case of SHG in fine powders with the size of particles $\leq 2 \mu$ it is possible to exclude L_C from the expression for $I_{2\omega}$. Then the only parameter, on which the intensity depends, becomes the nonlinearity of the sample (d). For ferroelectrics this dependence is $I_{2\omega} \sim d^2 \sim P_s^2$, where the spontaneous polarization P_s is a measure of polar distortion of the structure.

For the detection of very weak SHG-signals, reflected from a fine-powder or ceramic sample we use a high-sensitive measuring system which also enable us to follow the changes of $I_{2\omega}$ (and P_s) vs. temperature. The results obtained by this technique when combined with the data of the usual X-ray powder analysis prove to be especially useful for the investigation of phase diagrams when ferroelectric or other non-centrosymmetric phases are present.

We have considered two systems of solid solutions based on ferroelectric $SbNbO_4$, the

second component (BiNbO_4 or SbSbO_4) belonging to the same structural type of stibiotantalate. Both fine powder and ceramic samples in the systems $(1-x)\text{SbNbO}_4 - x\text{BiNbO}_4$ and $(1-x)\text{SbNbO}_4 - x\text{SbSbO}_4$ were studied. We have shown that in the first system there is only one ferroelectric phase which exists in the region of concentrations $0 \leq x \leq 0.2$. The Curie temperature (T_C) of this phase diminishes gradually from 680 K at $x=0$ to 550 K at $x=0.2$. The phase above T_C is centrosymmetric, as well as the phase based on BiNbO_4 ($0.5 \geq x \geq 1$) above R.T. In the two-phase region ($0.2 < x < 0.5$) the intensity $I_{2\omega}$ falls off according to the linear law with the decrease of the amount of the first component in the mixture. In the second system there are two noncentrosymmetric phases: one based on the SbNbO_4 ($0 \leq x < 0.32$) and the other based on the orthorhombic α - SbSbO_4 ($0.48 < x \leq 1$), both phases coexisting at intermediate values of x . The temperature dependence of $I_{2\omega}$ in the one-phase region corresponds to the law $P_S \sim (T_C - T)^{1/2}$ specific to the ferroelectric-type phase transitions of the second order. The Curie temperature rises with x in both ferroelectric phases and reaches 920 K for α - SbSbO_4 . The comparison of intensities of SHG-signals for the extreme components of the second system at R.T. leads to the estimation: $P_S(\text{SbSbO}_4) \approx 0.1 P_S(\text{SbNbO}_4)$, which agrees with the known structural data. The monoclinic β -modification of SbSbO_4 has also been studied and found to be centrosymmetric and possess the properties of the linear dielectric.

05.2-14 THE STUDY OF THERMAL EXPANSION OF DI- AND TRIOCTAHEDRAL MICA. By M.S.Metsik, V.M.Kalichman, G.A.Kuznetsova, Department of Solid State Physics, Irkutsk State University, Irkutsk, USSR.

The thermal expansion of muscovite and phlogopite crystals in the $[001]$ crystallographic direction has been studied by the low-temperature X-ray diffraction method. The investigation has been made in the interval of 80 - 300 degrees K. The significant difference of thermal expansion for the crystals studied is observed. The dependence of thermal expansion coefficient on the temperature is nonlinear and may be described as follows:

$$\alpha = A + BT + CT^2,$$

where the coefficients A , B , C have the values for muscovite $7.3 \cdot 10^{-6} T^{-1}$; $3.4 \cdot 10^{-8} T^{-2}$; $-2.1 \cdot 10^{-11} T^{-3}$ and for phlogopite $3.8 \cdot 10^{-6}$; $4.6 \cdot 10^{-8}$; $-3.6 \cdot 10^{-11}$ respectively.

The thermal expansion coefficient for muscovite is about twice that for phlogopite in the temperature interval concerned. It may be explained by a loosely packed octahedral layer for muscovite and by a closely hophrized tetrahedral nets. This genetic defect of the crystal structure gives rise to weakening bond forces and increasing the value of the coefficient α in the $[001]$ direction for muscovite as compared with the coefficient of much more perfect trioctahedral phlogopite crystal. At the same time α of phlogopites considerably increases with temperature due to the higher interlayer water content.

05.2-15 HIGH TEMPERATURE CRYSTAL CHEMISTRY OF NORMAL PARAFFINS. By S.K.Filatov¹, E.N.Kotelnikova¹, E.A.Aleksandrova². ¹Department of Crystallography, Leningrad University, Universitetskaya nab., 7/9, Leningrad, 199164, USSR, ²Grozny Petroleum Institute, Ordzhonikidze sq., 100, Grozny, 264902, USSR. Investigations of polymorphic transformations and structural deformations of paraffins with changing temperature can be considered as model experiments with respect to similar investigations of high molecular compounds and natural paraffins. Thermal deformations, polymorphic transformations and melting of normal paraffins $\text{C}_n\text{H}_{2n+2}$ with odd numbers $n=17, 19, 21$ and 23 have been studied by the powder thermooptogenography method. Common features corresponding to the four stages whose temperatures of proceeding and melting rise with the increase of number n are distinguished in the thermal deformations of all studied paraffins. Quantitative structural justification of the deformation nature is given using the principle of the aliphatic chains rotation around their axes. Orthorhombic-hexagon transformation (type II) is recorded only for paraffin with $n=23$ at 39.5 C. This is not inconsistent with the data of A.Muller (1932) obtained by thermooptogenographical method and is at variance with the results of investigations of A.A.Sherer et al. (1956) in which, on the basis of the high temperature mass-spectrometry, the existence of polymorphic transformation for all paraffins with $n > 8$ has been reported. The data on the temperatures of polymorphic transformations of paraffins and their structural conditions are useful for creating paraffins of preset plasticity.

05.2-16 CRYSTAL STRUCTURES AND CHARGE CARRIER LOCALIZATION IN BINARY OXIDES. By B. Güttler and E. Salje, Institut für Kristallographie und Petrographie, Universität Hannover, Welfengarten 1, 3000 Hannover 1, Federal Republic of Germany.

The crystal structures of binary tungsten oxides WO_{3-x} are closely related to the ReO_3 type with additional corner-sharing octahedra in a network of edge-sharing octahedra (S.G. = Pc , $P2/n$, $P\bar{1}$, $P2/m$).

Conductivity measurements and optical experiments show that two electrons are released for each block of four corner-sharing octahedra. These carriers induce semiconducting behaviour for compounds $\text{WO}_3 - \text{WO}_{2.90}$ and metallic conductivity for $\text{WO}_{2.90} - \text{WO}_{2.72}$. At $\text{WO}_{2.90}$ an Anderson transition takes place. In the semiconducting phase, local structural deformations couple with the electrons under the formation of polarons. For the first time, the simultaneous appearance of polarons and electrons was found in the metallic phase. In compounds with smaller electron concentration than at the Anderson transition ($\text{WO}_{2.90}$) all carriers are found to form polarons. Structurally, the Anderson transition takes place at the borderline between phases containing chains of corner-sharing octahedra along $\{102\}$ and $\{103\}$.