

PS11.05.51 THERMO-OPTIC STUDIES OF STRUCTURAL PHASE TRANSITIONS IN CRYSTALS OF THE KTiOPO_4 FAMILY. M. N. Womersley, P. A. Thomas, Department of Physics, University of Warwick, Coventry, CV4 7AL, England

A uniquely-modified Kösters prism interferometer is used for simultaneous and separate measurement of the change in refractive index, δn , and the thermal expansion coefficient with temperature, with a resolution of 4×10^{-7} , on 1mm^3 biaxial crystals, is described. The application of this technique to new nonlinear optical materials of the KTiOPO_4 (KTP) family is made with the aim of elucidating and modelling the onset and increase of the alkali-metal mobility in the temperature range from 300°C to 900°C and studying the high-temperature ferroelectric to paraelectric phase transition.

The evolution of the refractive index as a function of temperature, $n(T)$, is plotted for a number of materials, with the high-temperature high-symmetry component above the phase transition deduced from the low-temperature data and is fitted to a model describing both the extrinsic (structure-dependent) and intrinsic (polarizability-dependent) contributions to the thermo-optic effect. The results are reviewed within the context of structure-property relationships and the high-temperature phase transitions in the KTP family.

PS11.05.52 DISORDER AND THE MECHANISM OF PHASE TRANSITION OF $[(\text{CH}_3)_2\text{CHNH}_3]_2\text{BiCl}_5$. Jacek Zaleski and Adam Pietraszko[#], Institute of Chemistry, University of Opole, 45-951 Opole, Oleska 48, Poland, [#]Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50-950 Wrocław, Okólna 2, Poland

The alkylammonium halogenoantimonates (III) and bismuthates (III) are ionic-molecular salts. Recently the physical properties of the family attracted considerable attention. Many compounds of this group show interesting ferroic properties. They possess complicated sequences of phase transitions, some of them to polar phases.

$[(\text{CH}_3)_2\text{CHNH}_3]_2\text{BiCl}_5$ crystallises at 298 K in $P2_1/c$ space group. Its anionic sublattice is composed of isolated $\text{Bi}_2\text{Cl}_{10}^{4-}$ units, composed of two BiCl_6^{3-} octahedra sharing an edge. There are two crystallographically non-equivalent cations in crystal structure. One ordered and one disordered by splitting the position of tertiary carbon atom between two sites with occupancy factors 0.5.

The analysis of orientation and eigenvalues of tensor of moment of inertia of isopropylammonium cation with relation to the observed disorder is discussed. Results lead to the conclusion that disorder is associated with the overall rotation of the cation between two positions. We may thus expect freezing of rotation of the cation on decreasing temperature.

The temperature dependence of lattice parameters, DSC and dielectric dispersion studies indicate that $[(\text{CH}_3)_2\text{CHNH}_3]_2\text{BiCl}_5$ undergoes an order-disorder phase transition at 164 K. Dielectric dispersion studies reveal low frequency relaxation process described by the Cole-Cole formula with $\alpha \approx 0.15-0.20$ in the phase transition temperature region. Results of these studies confirm the postulated mechanism of freezing of reorientation motion of the disordered isopropylammonium cation at the phase transition temperature.

PR11.05.53 STRUCTURAL TRANSITIONS IN NICKEL PERCHLORATE HEXAHYDRATE. Soma Ghosh, Monika Mukherjee, Siddhartha Ray, Department of Solid State Physics, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India

X-ray studies of the phase transitions in $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (at $\sim 361\text{K}$, $\sim 311\text{K}$ & $\sim 245\text{K}$) were undertaken to find out the possible mechanisms of phase transitions. The complex crystallizes in space group $P6_3mc$, however, the true symmetry is orthorhombic (space group $\text{Pmn}2_1$) due to the distribution of metal atoms in twice their number of available sites. This orthorhombic cell occurs in three orientations giving rise to a three-component twinning. Moreover, due to antiphase formation, diffuse streaks along odd layer lines in oscillation photograph about c-axis and some diffuse spots in corresponding Weissenberg photographs are observed. At $\sim 323\text{K}$, these streaks disappeared, with no change in cell dimensions, but all spots in first layer Weissenberg photographs were elongated along ω -direction. On cooling, elongation of spots vanished and the diffuse streaks originally present, did not reappear. Above $\sim 363\text{K}$, each spot splitted into two/three components along ω -direction which coalesced into single sharp spots on cooling to room temperature. The overall hexagonal symmetry remained unchanged throughout. This indicated that the perchlorate-water arrangement was continuous throughout the crystal and the peculiar three-component twinning existed even in the transformed phase. Experiments conducted at low temperature ($\sim 223\text{K}$) indicated no structural changes.

The splitting of the spots at high temperature in the crystal is probably due to slight deviation of the ratio of b/a of the three orthorhombic cells from $\sqrt{3}$ so that interplanar spacings of each of the three orthorhombic cells become different. The decrease in the probability of mistakes in repetition along b-axis of orthorhombic cells with increase in temperature accounts for the disappearance of diffuse streakings.

Phase Transition I

MS11.05a.01 MARTENSITIC TRANSFORMATION IN Au-49.5at% Cd ALLOY Takuya Ohba, Department of Materials Science and Engineering, Teikyo University, Toyosatodai, Utsunomiya 320, Tochigi, Japan

Martensitic transformation is the typical first order and diffusionless (displacive) transformation. In general, structure phase transformation may be divided into two, order-disorder and displacive type transformation. For the displacive type of the second order transformation, displacements are small comparing with the interatomic distances. In case of martensitic transformation, on the other hand, displacements are larger than that of the second order displacive type transformation. The mechanism of the martensitic transformation is the central issue in recent research. AuCd is the typical alloy which shows martensitic transformation. Near equiatomic composition the high temperature phase is well known to be CsCl type. The martensitic phase is called ζ_2' phase. Although the crystal structure of the ζ_2' phase was not solved for long time, recently it was successfully determined using a stress induced single crystal martensite. From the results of the structure determination of ζ_2' martensite, a transformation mechanism was proposed. Phonon softening, which was expected from the proposed mechanism, was also observed using an isotope of Cd. The static approach was also made to reveal the characteristics of the martensitic transformation. Structure factors in the parent phase were measured at various temperature. The measurements reveal that they decrease with approaching transformation temperature. These characteristics of the martensitic transformation in AuCd alloy will be discussed.