

**PS11.10.06 STRUCTURAL PROPERTIES OF SILICON AT LOW TEMPERATURES.** A. Okazaki, Y. Soejima, Department of Physics, Kyushu University, Fukuoka 812-81, Japan

A review is given of recent high-precision X-ray diffraction experiments on perfect or nearly perfect crystals of silicon in a temperature range 20-300 K, having been carried out by the group in the Department. The technique applied is the high-angle double-crystal X-ray diffractometry (HADOX), the Bond method coupled with a quadruple-crystal monochromator, and the Pendellösung fringes method. It is found that  $d(440)(T)$ , the lattice spacing of (440) as a function of temperature, is reproducible and coincides with the thermal expansivity data in a higher accuracy; on the other hand,  $d(444)(T)$  is not a one-to-one function of temperature and depends on specimen and its thermal history. A variety of  $d(444)(T)$  curves can be specified by the temperature where  $d$  shows a minimum, or the minimum  $d$  value. This means that the irreproducibility of  $d(T)$  or the instability of the lattice spacing is directly related to the negative thermal expansion that is commonly observed in  $sp^3$ -bonded crystals except diamond but not theoretically explained yet. The present experiment suggests that silicon in an ideal situation shows a structural transition around 60 K accompanied with a discontinuous change in the lattice constant a smearing of the transition over a temperature range of several ten K can bring about a temperature region of apparent negative thermal expansion. Moreover, the results of  $d(444)(T)$  experiment under uniaxial external stresses show that the stress-strain response is very slow, the relaxation time being several ten minutes. This viscoelastic character may be connected with the history dependent behaviour of  $d(444)(T)$ , and with the apparent negative thermal expansion. Another feature of silicon that is observed in all the experiments mentioned above is the aging effect at the lowest temperature. As a mechanism of rearranging atoms, a phonon-mediated long-range interaction between defects in the silicon lattice is mentioned.

**PS11.10.07 AN INVESTIGATION INTO NEW NLO PHOSPHATES.** Reeve, W. F., Clarendon Laboratory, Physics Department, Oxford University, England

As interest increases in optical technology, so the need grows for new nonlinear crystals with widely varying properties. For many years scientists have used materials from the phosphate series for use as frequency converters. Indeed, two of the most well known, and commercially successful nonlinear optical (NLO) materials come from the phosphate series, namely potassium titanyl phosphate<sup>(1)</sup> (KTiOPO<sub>4</sub> or KTP) and potassium dihydrogen phosphate<sup>(2)</sup> (KH<sub>2</sub>PO<sub>4</sub> or KDP). Given the success of both these materials, it seems worthwhile to investigate the phosphate family further.

A preliminary report is given on the theoretical models used in determining structural guide-lines in a systematic search for new NLO phosphates. The screening procedure used for identifying possible materials from structural databases, such as examining structural geometry, is summarised. A description is given of the initial testing for second-harmonic generation efficiency using the Kurtz<sup>(3)</sup> test and the later more accurate single-crystal NLO analysis based on that developed by Velsko<sup>(4)</sup>. Early results are presented on the XYPO<sub>4</sub> (where X=Li, Na, Rb and Y=Pb, Ca, Sr, Ba) family, including a description of material preparation, X-ray diffraction analysis and NLO properties, including phase-matchability and average effective nonlinearity.

It is hoped that this new investigation into phosphates may produce further new NLO materials with different capabilities needed in future optical technology, and also, when analysed with accurate structure determinations, may also help in furthering our

knowledge of NLO structure-property relationships. This would not only enable more accurate structural guidelines for further searches to be established, but also increase the probability of improving already commercially used materials.

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**PS11.10.08 METALLIC ZINTL PHASES IN RARE-EARTH-METAL TRELIDES.** Jing-Tai Zhao<sup>1</sup> and John D. Corbett, Ames Laboratory and Iowa State University, Ames, IA50011, USA

The development of new solid state materials demands more and more understanding of properties as they related to structure. The Zintl-Klemm concepts[1] proved to be useful when dealing with the structure-bonding-property relationships of the so-called Zintl Phases. The breath of the applicability of these rules were explored to rare-earth-metal trelides with more polar character.

La<sub>3</sub>In<sub>5</sub>, Pu<sub>3</sub>Pd<sub>5</sub>-type, contains well-defined indium square pyramids In<sub>5</sub><sup>9-</sup> (C<sub>2v</sub>, d(In-In)~3.0-3.2Å) (the denoted charges here and thereafter have only formal meanings) with minimum intercluster separation of 3.43 and 3.58Å, which can be readily described as a close shell nidodeltahedron.

Y<sub>3</sub>Ga<sub>2</sub>, Gd<sub>3</sub>Ga<sub>2</sub>-type, contains isolated Ga<sup>5-</sup> and single bounded dumbbell Ga<sub>2</sub><sup>8-</sup> units.

YGa, CrB-type, contains single-bounded infinite zigzag chains ∞<sup>1</sup>[Ga<sup>3-</sup>](d(Ga-Ga)~2.56Å) with minimum interchain separation of >4.0Å.

All the above three compounds can be readily described structurally as Zintl phases and they are poorly metallic and Pauli-paramagnetic-like character[2].

The term "metallic Zintl phase" seems appropriate to describe compounds with structures containing tightly bound anion arrays in the classical limit, while with the weak metallic conduction resulted from the presence of some slightly delocalized electrons at the Fermi level.

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**PS11.10.09 STRUCTURAL PECULIARITIES OF MUSCOVITE AND PHLOGOPITE CRYSTALS AT LOW TEMPERATURES.** T. E. Moskovskaya, J. G. Timirgaleeva, O. V. Roskin, Irkutsk State University, Irkutsk, Russia

In mica crystals one can come across great number of water layers and gas-water lenses, in which water films are in special boundary store. A rare possibility of studying the influence of crystals inner active surfaces, bordering on the films on its volume properties, first of all on the electroconductivity and absorption of electric charges is given.

After the voltage had been supplied to the crystal current of conductivity decreased in time very quickly. It should be mentioned that volume charges were being accumulated electrodes in crystal, forming antifields close on the value to the external field. Having taken out the external field and after sample short circuit depolarization current of reverse direction had been appeared, but the charge absorbed in sample had been flown down for a long time. It gives the reason to state that mica is inhomogeneous greatly. For absorption process division and defining their nature, we used depolarization method at low temperature.

Mica samples were preliminary polarized at room temperature and than were cooled by liquid nitrogen under tensivity till 180 K. Having taken out the intensity and making short of electrodes, crystals had been heated till 290 K. One can see on the polarization curve the series of maximum 205, 250, 280 K.

Thus the charge accumulated in crystals in the polarization process is being kept for a long lime cooling as 240 - 230 K, because of the crystallization of water films crystals become electrets.