Inorganic and Mineral Compounds


Crystal structure of the perovskite type CeNbO₅ was characterized by X-ray powder diffraction. Crystal structure of LaNbO₅ was already reported but it was synthesized and characterized in the same conditions as the cerium compound in order to compare the data obtained, with regards to crystal structure.

Perovskite structure double oxides with formula LnNbO₅ have the Ln ions located in high symmetry sites which is important when studying spectroscopic properties. On the other hand, in this perovskite structure there are vacant Ln sites. It is interesting to provide information on the influence of defects on the stability of the crystal lattice and to look for the relationship between crystal structure and dielectric properties in those distorted perovskite structure.

The compounds were synthesized by solid state reaction and characterized by X-ray powder diffraction. CeNbO₅ is orthorhombic, space group Pnnm, a=3.898(4) Å, b=9.317(2) Å, c=7.876(6) Å, V=120.50(1) Å³, z=2/3. LaNbO₅ is also orthorhombic, space group Pnmm, a=3.912(2) Å, b=9.312(3) Å, c=7.912(1) Å, V=121.344(3) Å³, z=2/3. Crystal data were determined using the TREOR program. For crystal structures refinement the DBWS-9006PC program was used.

**PS08.00.44 HYDROTHERMAL SYNTHESIS AND STRUCTURAL STUDY OF BARIUM ZINC ARSENATES.** Sue-Lein Wang* and Fen-Ling Liao, Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043

In comparison with the rich structural chemistry of transition metal phosphates, reports on the arsenates are rare. Recently we have investigated the structural chemistry of transition metal arsenates and have synthesized a number of new compounds in the A-M-AsV₅-O system (A = alkali or alkaline-earth metals and M = V, Fe, Co, Ni, Cu, and Mo) by using hydrothermal methods. Most of these arsenates adopt new structural types and have stoichiometries not found in the phosphates. To explore novel frameworks built up from various polyhedra, we have extended our work to zinc-based arsenate systems. With respect to various coordination geometries adopted by ZnO₄ (x = 4, 5, 6), the structural chemistry of zinc-based oxy compounds is considered unique. This has been shown by a great number of ternary and quaternary zinc phosphates. This presentation reports the hydrothermal synthesis and characterization of two barium zinc arsenates, Ba₃Zn₂(AsO₄)₂ and BaZn₂(AsO₄)₂AsO₄. They are the first examples in the B₃-Zn-AsV₅-O system. Ba₂Zn₂(AsO₄)₂ is isostructural with the Ba₂Zn₂(PO₄)₂ analog and reveals new features concerning the layered framework. BaZn₂(AsO₄)₂ contains the unusual Zn₄O₆ cluster units in which four ZnO₆ square pyramids linked together via common vertices and edges. It is the first experimental evidence that the hydrogen-diarsenate anion, H₂AsO₄⁻ exists in metal arsenates.

**PS08.00.45 OCTAHEDRAL TILTING DISTORTIONS IN THE PEROVSKITE STRUCTURE.** Patrick M. Woodward, Arthur W. Sleight, Department of Chemistry and Center for Advanced Materials Research. Gilbert Hall 153, Oregon State University, Corvallis, OR 97331-003

Distortions of the AMO₃ perovskite structure that can be described by tilting of essentially rigid octahedra have been investigated. Earlier work by Glazer, which showed that such distortions can be classified into 23 different tilt systems, has been revisited. It can be shown that in six of these tilt systems (a+a+, a+b+b-, a+a+c-, a+b+c-, a+b+b-, a+b+b-, a+b+c-) it is not possible to link together a three dimensional network of perfectly rigid octahedra. In these tilt systems small distortions of the octahedra must occur. All 23 tilt systems are compared in terms of their A cation coordination. On this basis they can be divided into two categories, those in which all of the A cation sites remain crystallographically equivalent, and those in which the A cation sites become nonequivalent. For most perovskites the tilt systems with equivalent A cation sites are strongly favored. When the Goldschmidt tolerance factor becomes smaller than 0.975, the a+b+b- tilt system (GdBaO₃ structure) is found almost exclusively. Both empirical lattice energy calculations and extended Hückel molecular orbitals have been performed to determine which of the A-O interactions are optimized in this tilt system. The ideal cubic structure is found to be stabilized only by oversized A cations, and M-O π bonding interactions. Tilt systems with nonequivalent A site environments are favored only when there are at least two types of cations, with different sizes and/or bonding preferences, present on the A site. In these tilt systems the ratio of large to small cations will dictate the most stable tilt system. The predicted space groups for all 23 tilt systems have been extended to ordered perovskites, A₂MM'0₆. These results should be of interest not only in understanding the behavior of known perovskite compounds, but also in searching for and correctly assigning symmetry to new compounds.