PS08.00.43 CRYSTAL STRUCTURE OF CeNb$_3$O$_9$ AND LaNb$_3$O$_9$ BY X-RAY POWDER DIFFRACTION. M. E. Villafuerte-Castrejón, L. Carrillo-Avilés, A. Ibarra-Palos, Instituto de Investigaciones en Materiales Universidad Nacional Autónoma de México. A.P. 70-360, Ciudad Universitaria, México D.F. 04500 México, J. Duque, R. Pomés, Centro Nacional de Investigaciones Científicas. Apdo. 6990, Ciudad de la Habana, Cuba

Crystal structure of the perovskite type CeNb$_3$O$_9$ was characterized by X-Ray powder diffraction. Crystal structure of LaNbO$_3$O$_9$ 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 LnNb$_3$O$_9$ 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. CeNb$_3$O$_9$ is orthorhombic, space group Pmmm, a= 3.898(4) Å, b= 3.917(2) Å, c= 7.876(6) Å, V=120.50(1) Å^3, z = 2/3. LaNbO$_3$O$_9$ is also orthorhombic, space group Pmmm, a= 3.912(2) Å, b= 3.921(3) Å, c= 7.912(3) Å, V = 121.34(4) Å^3, 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-As^V-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 ZnO$_x$ (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, BaZnAs$_2$O$_7$ and BaZn$_2$(HAs$_2$O$_7$) AsO$_4$. They are the first examples in the Ba-Zn-As^V-O system. BaZnAs$_2$O$_7$ is isostructural with the BaZnP$_2$O$_7$ analogs and reveals new features concerning the layered framework. BaZn$_2$(HAs$_2$O$_7$) AsO$_4$ contains the unusual Zn$_4$O$_{16}$ cluster units in which four ZnO$_5$ square pyramids linked together via common vertices and edges. It is the first experimental evidence that the hydrogen-diarsenate anion, HAs$_2$O$_7^{2-}$ 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 AMO$_3$ 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-, a+b+b-, a+a+c-, a+b+c-, a0b+b-, a0b+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 Goldshmidt tolerance factor becomes smaller than 0.975, the a+b-b- tilt system (GdFeO$_3$ structure) is found almost exclusively. Both empirical lattice energy calculations and extended Hückel calculations have been performed, both calculations show that 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 pi 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, A$_2$MM'O$_6$. 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.

PS08.00.46 X-RAY DIFFRACTION ON (KCN)$_X$(KBr)$_{1-X}$ MIXED CRYSTALS. Y. Yoshimura, T. Tsuruta, T. Okazaki, N. Tsuda and H. Iwasaki, Department of Physics, Ritsumeikan University, Kusatsu, Shiga 525-77, Japan

The phase transitions in the title compound (X=0.95, 0.90, 0.80, 0.70) were studied by X-ray precession method using single crystals at the temperature range between 85K and 300K. At 300K all the mixed crystals have the NaCl type cubic structure, with a disorder of linear CN- ion orientation. As the temperature is decreased, the crystals undergo an order-disorder transition associated with the change in the orientation of the CN- ions. The observed transition temperature for each crystal was 148.5K for x=0.95, 137.0K for x=0.90 and 108.5K for x=0.80. For x=0.70, no transition was observed till down to the 85K. A variety of diffraction photos indicating a coexistence of various forms were obtained in the low temperature phase. Paying attention to the presence of new reflections and splitting reflections, a coexistence of monoclinic, triclinic I and triclinic II forms was found in this phase. The lattice constants of each form for x=0.95 at 135.5K were shown in the following table.

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
monocli.	4.56(1)	4.57(1)	7.54(1)		121.9(1)	
tricli. I	9.37(1)	4.41(1)	4.55(1)	120.0(1)	119.2(1)	90.0(1)
tricli. II	4.65(1)	4.75(1)	6.40(1)	136.6(1)	136.0(1)	59.9(1)

Crystallographic relationships between each form and those and between each form and the cubic form are presented. The results are compared with the findings in the related compounds KCN and RbCN.