08.2-07 STRUCTURAL STUDIES ON A - CATION DEFICIENT PEROVSKITE Th $\square_3$ Nb$_4$ O$_{12}$. THORIUM VACANCY SHORT RANGE ORDERING IN SLOW-COOLED SAMPLES. By M. Labeau, M.A. Alario-Franco, H. Vincent, J.C. Joubert, Laboratoire de Cristallographie, CNRS, 166 X, 38042 Grenoble France and I.E. Grey, CSIRO, Division of Mineral Chemistry, P.O, Box 124, Port Melbourne, Victoria 3207, Australia.

The A. cation deficient perovskite, Th $_{0.25}$ NbO$_3$, i.e. ThNb$_4$O$_{12}$, when slowly cooled from the melt, presents an interesting hierarchy of ordering phenomena. We have studied the associated diffraction effects using electron microscopy/diffraction and X-ray diffraction techniques. Three main types of ordering processes occur, with different degrees of long-range order and different average periodicities. A primary-ordering of thorium atoms into alternate (001)$_p$ planes of A-cation sites (cell a_p x b_p x 2c_p, P4/mmm) exhibits well

established long-range ordering. A secondary ordering of thorium atoms within the (001)$_p$ planes (cell $3\sqrt{2}a_p$ x $\sqrt{2}b_p$ x 4c_p, Immm) is short-range in nature and gives rise to superlattice reflections in the form of diffuse rods directed along $g(110)_p$ and $g(\bar{1}10)_p$. The length of the rods corresponds to correlation lenghts of only 20-30 Å between {110}$_p$ planes of thorium atoms, and the thorium/vacancy ordering is adequately described by a sinusoïdal modulation model. Ordering of co-lumms of thorium atoms and vacancies, parallel to [110]$_p$ and [$\bar{1}$10]$_p$, occurs in microdomains, with domain boundaries parallel to (100)$_p$ and (010)$_p$ and with average separations of 6a_p, 6b_p $\cong$ 24 Å. The domains corresponding to the orientations of thorium columns form a chequerboard pattern of two interpenetrating sets of corner-shared squares. In either set the ordering of columns is propogated along diagonal rows of corner shared domains, but there is no evidence for correlation between adjacent rows. Thirdly a system of octahedral tilts is described by a cell $\sqrt{2}$ a_p x $\sqrt{2}$ b_p x 2 c_p,

Pmam. The NbO$_6$ octahedra are tilted by 15° about [110]$_p$ and [$\bar{1}$10]$_p$ axes and the domain boundaries act as mirror-twin planes for the octahedral tilt systems. This periodic change in the tilt-axis orientation gives rise to characteristic clusters of split superlattice spots in the diffraction patterns for ThNb$_4$O$_{12}$. Optical transform methods were used to check the validity of microdomain models.

In the quenched samples one observes the same primary ordering of thorium atoms into the cuboctahedral sites in alternate (001)$_p$ layers, but the secondary-ordering arrangements of thorium atoms and vacancies in the occupied (001)$_p$ layers is different. The thorium atoms and vacancies are ordered in alternate rows parallel to [100]$_p$ and [010]$_p$. Short segments (20-50 Å) of the two orientation variants are statistically distributed in a type of tweed pattern, separated by boundaries which are aligned predominantly parallel to (110)$_p$ and (110)$_p$.

08.2-08 SINGLE-CRYSTAL X-RAY STUDY OF A CaGeO$_3$ PEROVSKITE. S. Sasaki, C. T. Prewitt and R. C. Liebermann, Dept. of Earth & Space Sciences, State University of New York, Stony Brook, NY 11794, U.S.A.

A single-crystal X-ray study of a perovskite form of CaGeO$_3$ synthesized at 100 kb and 1000° C (Liebermann, Jones & Ringwood, Phys. Earth Planet. Inter. (1977) **14**, 165-178) has been made using both precession cameras and a Picker four-circle diffractometer. Previously, Ringwood & Major (Earth Planet. Sci. Lett. (1967) **2**, 106-110) reported this form (120 kb and 900° C) to be cubic with a=3.723 Å on the basis of X-ray powder photography, while Prewitt & Sleight (Science (1969) **163**, 386-387) pointed out that it has a doubled cell parameter (a=7.448 Å) to account for weak reflections on both the Guinier and precession photographs. The present results, however, reveal that this CaGeO$_3$ perovskite is orthorhombic (pseudocubic; close to tetragonal) with space group Pbnm; the cell parameters obtained from a four-circle diffractometer are a=5.2607(6) Å, b=5.2688(10), c=7.4452(15), V=206.36(6) Å^3, Z=4, maintaining the relation of a$\cong\sqrt{2}$a$_p$, b$\cong\sqrt{2}$a$_p$ and c$\cong$2a$_p$ (a$_p$: a pseudocubic subcell parameter). It should be mentioned that a few reflections such as 5/2 1/2 0, 1/2 5/2 0 and 1/2 3/2 3, having very weak intensities close to the background level, were observed in ψ-azimuthal scans, although such reflections could not be detected on long-exposure precession photographs; if meaningful, this perovskite may have a cell of a'=2a, b'=2b and c'=c.

Intensity data from a parallelepiped-like crystal (0.14 x 0.10 x 0.07 mm) were collected up to 2θ=80° (ref.(measured)=689; ref.(used)=343) using the ω-2θ technique (graphite monochromatized Mo Kα). The final atomic parameters, and some interatomic distances, determined with least-squares calculations (R=0.035), after corrections for Lorentz-polarization, absorption, and isotropic extinction effects, are as follows:

	Ca	Ge	O(1)	O(2)
x	-0.0051(5)	0	0.0587(16)	0.7159(10)
y	0.0273(3)	1/2	0.4911(17)	0.2829(9)
z	1/4	0	1/4	0.0321(9)
B$_{equiv.}$	0.60	0.29	0.75	0.64

Ca-O(1)		2.467(9)	Ge-O(1)	x2	1.887(1)
-O(1)		2.356(9)	-O(2)	x2	1.897(5)
-O(1)		2.919(9)	-O(2)	x2	1.889(5)
-O(1)		2.845(9)	<Ge-O>		1.891 [1.861]
-O(2)	x2	2.349(6)			
-O(2)	x2	2.569(6)	O(1)-O(2)	x2	2.690(8)
-O(2)	x2	2.601(6)	-O(2)	x2	2.661(9)
-O(2)	x2	3.065(6)	-O(2)	x2	2.662(9)
<Ca-O>		2.646	-O(2)	x2	2.679(8)
		[2.632]	O(2)-O(2)	x2	2.659(7)
			-O(2)	x2	2.696(7)
[ ]: the value of the			<O-O>		2.675
ideal cubic model.					[2.632]

The most prominent distortion from the ideal cubic-perovskite structure is the tilting of the polyhedra. The polyhedra have the following characteristics: (1) The ratio of (<M-O>-<M-O>$_{cubic}$)/<M-O> shows that the oxygens around the Ge atom are more extended (0.016) from the ideal cubic-positions than those around Ca (0.005). (2) The 12-oxygen Ca-polyhedron is distorted (the bond-length distortion, Δ=9.2 = $1/n\sum_i[\{R_i-\bar{R}\}/\bar{R}]^2$ x10^3), whereas the Ge octahedron is close to a regular one (Δ=0.01). The distortions, however, are less than those of some orthorhombic perovskites such as MgSiO$_3$ (Δ=27.1, 0.26), ScAlO$_3$ (37.5, 0.04) and GdFeO$_3$ (28.7, 0.04). (3) The tolerance factor of CaGeO$_3$ (0.99) is closer to 1.0 (cubic model) than that of MgSiO$_3$ (0.98), ScAlO$_3$ (0.97), or GdFeO$_3$ (0.98).