

[o.m2.p1] Syntheses and Characterization of BaTiO₃ ceramic powders and delineation of methodologies for the fine control of stoichiometry in the synthesis of mixed oxides. A.E. Marteel, J.A. Davies, *Department of Chemistry, University of Toledo, Toledo, Ohio 43606.*
Keywords: green chemistry, doped perovskites, stoichiometry.

Barium titanate is the major raw material for the production of multilayer ceramic capacitors used in decoupling, filtering, timing and other applications.

The properties of perovskites such as BaTiO₃ are sensitive to stoichiometry and precise control of composition is required in synthesis. The development of a synthetic method from simple titanium and barium precursors that utilizes only aqueous media, inexpensive starting materials and moderate temperatures has already been reported¹. It is also known that replacement of Ba by Sr decreases the Curie temperature of BaTiO₃ and so generates materials with interesting properties for the electroceramics industry. As a consequence, control of the stoichiometry of (Ba, Sr)TiO₃ materials is important. The preparation of ceramics with different Ba: Sr ratios reported here only involves the selection of a strontium source, SrX, where the ratio of the solubility products of SrX:BaX has the appropriate value. All experiments have been performed using strontium carbonate as the strontium source.

In order to determine the conditions for each system to come to equilibrium, reactions have been performed for varying lengths of time with and without reflux of the aqueous reaction medium. Ceramics products have been generated and the stoichiometries determined by X-ray powder diffraction analysis.

[o.m2.p2] Structural Control of Perovskite-type BaXO₃ by Selection of X ions. H. Horiuchi, *Faculty of Education, Hirosaki University, Hirosaki 036-8560, Japan*, T. Shishido, *Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*, and M. Tanaka, *Photon Factory, Institute of Materials Structure Science, Tsukuba, 305-0801, Japan.*
Keywords: perovskite, phase change, powder X-ray diffraction.

Structural characteristics of BaXO₃ were investigated by powder X-ray diffraction, where X is given by four kind combinations of (Ce, Tb), (Pr, Tb), (Pr, Zr) and (Tb, Zr) with charges of 4+. That is, four kind solid solutions were examined. Six phases with $p = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0 for $X = (X1_{1-p}, X2_p)$ in each solid solution were prepared by solid-solid reaction of 20 hours at 1500°C and 1600°C in O₂ gas flow.

All of the phases obtained were confirmed to be single phases with perovskite-type structures by means of powder X-ray diffraction. Furthermore, the changes from orthorhombic to rhombohedral structures were observed in the phases for $X = (\text{Ce, Tb})$ and (Pr, Tb) , on the other hand, the change from rhombohedral to cubic structures was observed in those with $X = (\text{Tb, Zr})$. It is of interests to note that the changes from orthorhombic to cubic through rhombohedral structures were observed in the phases for $X = (\text{Pr, Zr})$.

As a result of the careful analyses of crystal lattices based on their powder diffraction patterns, average ionic radii of X at the phase boundaries between orthorhombic and rhombohedral structures and those between rhombohedral and cubic structures are nearly fixed to be 0.745Å and 0.825Å, respectively, over all of the phases BaXO₃ examined in this investigation.

In our previous studies¹⁻³ on the solid solution of perovskite-type (Nd_xSm_{1-x})AlO₃, we found that the phase transition temperature T_c from orthorhombic to rhombohedral structures decreases about 10°C by the increase of only 1% amount of substitution of Nd for Sm. This suggests that the T_c decreases about 35°C due to the 10⁻³Å increase of average ionic radius of R³⁺ in the structure of RAlO₃. In the same manner, the structural changes of BaXO₃ are also considered to be sensitive to the average ionic radii of X. In particular, the structural behavior of Ba(Pr, Zr)O₃ under temperature change are interested to note because three different structural phases exist in this solid solution at room temperature.

[1] Davies, J.A.; Dutremez, S. "Electroceramics from Source Materials via Molecular Intermediates: BaTiO₃ from TiO₂ via [Ti {catecholate}₃]²⁻" *J. Am.Chem.Soc.*, (1990), 73: 1429-1430.

[1] Syntheses of the solid solution of (Nd_xSm_{1-x})AlO₃ and its structure relation to a series of rare earth orthoaluminates RAlO₃. A.Yoshikawa, *et al.*, *J.Solid State Chem.*, **126**(1996), 221-226.

[2] Orthorhombic to trigonal phase transition of perovskite-type (Nd_xSm_{1-x})AlO₃. A.Yoshikawa, *et al.*, *J. Alloys & Compounds*, **266**, (1998)104-110.

[3] Structural change caused by substitution of Nd for Sm in (Nd, Sm)AlO₃: Application of synchrotron high-resolution powder X-ray diffraction. A.Saitow, *et al.*, *J. Applied Crystallogr.*, **31**,(1998) 663-671.