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## Nonstoichiometry In BaTiO<sub>3</sub>

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This technique might be especially appropriate to the structural study of such crystallizable glasses as those of glass-ceramic compositions or to the study of phase separation. Seward *et al.*,<sup>8</sup> for example, used vapor deposition to avoid phase separation of BaO-SiO<sub>2</sub> melts during quenching. However, the likely differences in structure between glasses prepared by quenching liquids and noncrystalline solids made by vapor deposition can be avoided by using the splat method.

<sup>1</sup> R. C. Ruhl, "Cooling Rates in Splat Cooling," Tech. Rept. 12-DSR 7618, Department of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass., 1966.

<sup>2</sup> P. T. Sarjeant and Rustum Roy, "New Glassy and Polymorphic Oxide Phases Using Rapid Quenching Techniques," *J. Amer. Ceram. Soc.*, **50** [10] 500-503 (1967).

<sup>3</sup> R. H. Willens; Paper EE-6 in Proceedings of 5th International Congress for Electron Microscopy. Edited by S. S. Breese. Academic Press, New York, 1962.

<sup>4</sup> J. Zarzycki and R. Mezard, "Direct Electron Microscope Study of the Structure of Glass," *Phys. Chem. Glasses*, **3** [5] 163-66 (1962).

<sup>5</sup> A. M. Turkalo, "Technique for Obtaining Thin Glass Sections for Transmission Electron Microscopy," *J. Amer. Ceram. Soc.*, **51** [8] 470-71 (1968).

<sup>6</sup> T. P. Seward III, D. R. Uhlmann, David Turnbull, and G. R. Pierce, "Transmission Electron Microscopy of Thin Glass Samples," *ibid.*, **50** [1] 25-29 (1967).

<sup>7</sup> I. M. Stewart and L. Green, "Preparation of Thin Glass Films for Electron Microscopic Examination by Direct Transmission," *J. Sci. Instrum.*, **44** [3] 216 (1967).

<sup>8</sup> T. P. Seward III, D. R. Uhlmann, and David Turnbull, "Development of Two-Phase Structure in Glasses, with Special Reference to the System BaO-SiO<sub>2</sub>," *J. Amer. Ceram. Soc.*, **51** [11] 634-43 (1968).

## Nonstoichiometry in BaTiO<sub>3</sub>

G. J. CONGER and H. U. ANDERSON

THE nonstoichiometry occurring in BaTiO<sub>3</sub> at 900°C at 10<sup>-6</sup> to 1 atm O<sub>2</sub> pressure was measured using a tensiometric apparatus described in detail elsewhere.<sup>1</sup> The apparatus makes use of the fact that a nonstoichiometric oxide compound at thermodynamic equilibrium with atmospheric O<sub>2</sub> will adjust its oxygen content as the O<sub>2</sub> activity in the atmosphere is changed. Thus, as the O<sub>2</sub> activity is changed, oxygen will either be evolved from or absorbed into the oxide as the stoichiometry changes. At constant temperature, the pressure change occurring as a result of the change in oxygen content is related directly to the degree of nonstoichiometry occurring in the compound. By using a sensitive capacitance manometer, pressure changes on the order of 10<sup>-7</sup> atm, which correspond to evolution or absorption of 10<sup>-7</sup> g of O<sub>2</sub>, could be determined reliably.

Specific procedures and analyses similar to those used with TG measurements were developed for use with the apparatus, so that the pressure dependence, absolute concentration, and diffusion coefficient for the particular defect involved could be determined.

The specimen was 13.85 g of 99.95%-pure BaTiO<sub>3</sub> powder with an average grain size of ≈800 Å whose cation ratio was fixed at 1 by the technique described by Eror and Smyth.<sup>2</sup> Preliminary results at 900°C indicated a *p-n* transition at 4 × 10<sup>-3</sup> atm O<sub>2</sub> partial pressure. A plot of the data according to the treatment of Duenwald and Wagner<sup>3</sup> is shown in Fig. 1. At atmospheric pressure (0.98 atm O<sub>2</sub>), the amount of nonstoichiometry measured represents 10<sup>-4</sup> mol of excess oxygen. Since it is very unlikely that excess oxygen can be present in the BaTiO<sub>3</sub> structure, this nonstoichiometry represents cation vacancies.

At the *p-n* transition, the amount of excess oxygen present relative to the *p* side is 10<sup>-5</sup> mol. From a least-squares fit, the pressure dependencies of the defect concentrations determined on the *p* and *n* sides were +0.6 ± 0.3 and -0.6 ± 0.1, respectively. The spread in the data points is a result of a systematic problem in measuring total oxygen pressure which is being remedied. At present, the uncertainty of the pressure dependence makes it impossible to assign defect structures to the two sides of the transition. However, the predominant defects on the *n* side must be oxygen vacancies and those on the *p* side cation vacancies whose identity and state of ionization have yet to be resolved.

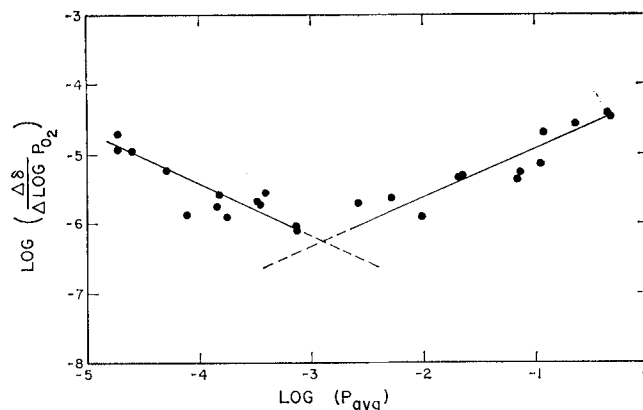


Fig. 1. Plot showing pressure dependence of oxygen stoichiometry,  $\delta$  in BaTiO<sub>3.6</sub>, at 900°C;  $\Delta\delta$  refers to change in oxygen concentration occurring in specimen for known change in total oxygen pressure,  $\Delta P_{O_2}$ , and  $P_{avg}$  refers to average total oxygen pressure over specimen during duration of experiment.

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<sup>1</sup> G. J. Conger, "A Tensiometric Apparatus: Theory, Calibration, and Use in Investigation of Oxygen Nonstoichiometry of Pure BaTiO<sub>3</sub>," M. S. Thesis, University of Missouri—Rolla, Rolla, Mo., June 1972.

<sup>2</sup> N. G. Eror and D. M. Smyth; pp. 62-74 in *The Chemistry of Extended Defects in Non-Metallic Solids*. Edited by L. Eyring and M. O'Keefe. North-Holland Publishing Co., Amsterdam, 1970.

<sup>3</sup> H. Duenwald and C. Wagner, "Investigation of Disorder Phenomena in Cuprous Oxide and Its Influence on the Electrical Properties," *Z. Phys. Chem., Abt. B*, **22**, 212-25 (1933).