found to change with the cooling cycle. When samples are quenched, the striations appear in straight lines, when they are cooled at moderate rates the striations appear in wavy lines and when they are slow cooled the striations disappear completely. In addition to the phase studies, the mechanism of formation of striations is being studied and a proposed explanation will be given.

### 10:30 a.m.

26-B-63.  Sub-Solidus Equilibria in the CaO–ZrO₂ System

S. I. FERNANDES and L. J. BEAUDIN,* Norton Co., Chippawa, Ontario, Canada

The cubic phase which occurs at the $ZrO_2$ end of the binary $CaO-ZrO_2$ diagram has always been interpreted as a solid solution of CaO in $ZrO_2$. The present investigation, carried out by solid phase reactions at controlled temperatures between 900° and 1500°C, indicates that a revision of this concept is necessary. Careful measurements of phase composition and lattice constant of quenched samples has allowed the accurate location of boundary lines in the region 0–20 wt% CaO. The existence of a new cubic binary compound, $CaO \cdot 4ZrO_2$, is shown. It is demonstrated that the cubic "stabilized zirconia" phase is actually a solid solution of $ZrO_2$ in $CaO \cdot 4ZrO_2$. Some of the implications of this new concept are discussed in detail.

### 10:45 a.m.

27-B-63.  An X-Ray Diffraction Study of the High Temperature Phase Transitions in NaNbO₃

VICTOR J. TENNERY, University of Illinois, Urbana

A diffractometer study was made of the two strongest superlattice lines and the N = 12 and N = 16 groups of diffraction lines of $NaNbO_3$ as a function of temperature. An analysis was made of the line groups and the parameters of the small perovskite pseudo cell were determined. Five phase transitions were observed in $NaNbO_3$ between 25° and 640°C. They occur at approximately 365°, 425°, 470°, 530°, and 640°C.

The structure changes from pseudomonoclinic to pseudotetragonal at about 365°C with $c_0/a_0 \simeq 1.0022$. This ratio decreases to essentially unity at 425°C. The structure remains pseudocubic to 470°C whereupon it becomes pseudotetragonal with $c_0/a_0 \simeq 0.999$. This ratio decreases slightly and then increases until at 530°C the ratio is $\simeq 0.9993$. The axial ratio then starts to change more rapidly with temperature and becomes $\simeq 0.9980$ at 586°C whereupon it starts to increase with increasing temperature and becomes unity at 645°C.

The superlattice lines are split in the pseudomonoclinic phase but are unsplit in any of the other phases. They vanish abruptly at the 645°C transition.

See also the programs for Society Symposiums 1, 2, and 3, for Tuesday morning.

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## Tuesday Afternoon • April 30

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Terrace Room, Lobby Floor

Session Chairman: THOMAS R. CLEVENGER

Massachusetts Institute of Technology, Cambridge

### Electrical Conductivity and Transport Phenomena

### 2:00 p.m.

28-B-63.  A Thermodynamic Study of Nonstoichiometric Rutile (TiO₂)

R. N. BLUMENTHAL, J. B. MOSER, and D. H. WHITMORE,* Department of Materials Science, Northwestern University, Evanston, Ill.

Oxygen partial pressure-temperature-composition relations for nonstoichiometric rutile ($TiO_{2-x}$) have been determined with the aid of both thermogravimetric and solid-electrolyte, galvanic cell

measurements. Cell measurements were conducted over the temperature range 900° to 1070°C, whereas the thermogravimetric experiments were carried out from 1000° to 1350°C. Both sets of observations were confined to the compositional range over which the homogeneous $TiO_{2-x}$ phase ($x \gtrsim 0.008$) was stable, the composition of nonstoichiometric rutile being approximately dependent upon $p_{O_2}^{-1/5}$ within this range. Although the observed compositional dependence on oxygen pressure may be rationalized satisfactorily on the basis of a defect structure involving titanium interstitials, this interpretation is not completely unambiguous and the possibility of a defect structure involving oxygen vacancies could not be ruled out entirely. Calculated values of the relative partial molar enthalpies and entropies for non-stoichiometric rutile are presented as a function of temperature and composition.

### 2:15 p.m.

29-B-63.  Electrical Conductivity of Rutile (TiO₂) as a Function of Oxygen Partial Pressure

E. H. GREENER,* F. J. BARONE, and W. M. HIRTHE, Materials Science, Marquette University, Milwaukee, Wis.

A detailed study has been made of the electrical conductivity of $TiO_2$ as a function of oxygen pressure in the range of 1.0 to 0.005 atm and at temperatures between 700° and 1425°C. Above 1150°C the conductivity varied as a function of the oxygen partial pressure according to the relation $\sigma \alpha P_{O_2}^{-1/4}$ which can be interpreted on the basis of the excitation of a single trapped electron from an oxygen ion vacancy. The conductivity was independent of oxygen pressure below 1150°C. The isobaric conductivity exhibited an exponential temperature dependence with an activation energy of 1.8 ev in the range where conductivity is defect controlled (T > 1150°C); and an activation energy of 1.5 ev in the low temperature range (T < 1150°C) where the conductivity is independent of oxygen pressure. It is felt that the low temperature activation energy is not associated with the defect structure but can be possibly interpreted in terms of ionic or impurity controlled conduction. Results of single crystal rutile with conduction parallel to "a" and "c" directions will also be presented.

### 2:30 p.m.

30-B-63.  Dielectric Measurements on Glass Systems at Very High Pressures

L. E. CROSS* and D. CHAKRAVORTY, Materials Research Lab., College of Mineral Industries, Pennsylvania State University, University Park

A technique has been developed for making dielectric measurements on glass samples under pressures of up to 50 Kbars over a temperature range from 25° to 600°C. This technique has been used to examine the dielectric properties of glass compositions in the systems $Na_2O-Al_2O_3-SiO_2$. Reproducible dielectric data have been obtained, but it is shown that in the temperature range from 25° to 180°C electrode polarization phenomena make unequivocal interpretation of the data impossible.

Above 180°C conduction loss dominates the element impedance and the ac method has been used to measure resistivity. It is shown that though the resistivity is changed by more than one order of magnitude under a pressure of 40 Kbars, the activation energy for conduction remains unchanged, in agreement with the work of Charles at lower pressures. The changes in resistivity of the glass samples are currently being used to examine the kinetics of the densification process in the glass under high pressures.

### 2:45 p.m.

31-B-63.  Cation Movements in the Corundum Structure

N. M. TALLAN* and H. C. GRAHAM, Aeronautical Research Lab., Wright-Patterson Air Force Base, Ohio

A dissipation factor maximum, attributed to dipolar relaxation involving a mobile cation, has been observed in undoped sapphire. The activation energy for the charge movement, calculated from the temperature and frequency dependencies of the maximum, is $16.5 \pm 0.5$ kcal/mol. and is independent of orientation. If the relaxation time is assumed to be of the form $\tau_0 \exp \Delta H/kT$, the intrinsic relaxation time $\tau_0$ decreases slightly from about $3.6 \times 10^{-11}$ sec with the applied field perpendicular to the optic axis to about $5.6 \times 10^{-12}$ sec with the applied field parallel to the optic axis. A model, involving cation movements from octahedral to tetrahedral to octahedral sites, is proposed to account for the absence of pronounced anisotropy in the observed activation energies. The observed activation energy is compared to the value deduced from available diffusion measurements.