Directional Hardness of Strontium Titanate by Peripheral Grinding

by **A. A. GIARDINI** and **M. A. CONRAD**

Department of Mineralogy, University of Michigan, Ann Arbor, Michigan

A study has been made of the directional variation of grinding hardness in strontium titanate. The method used is that of peripheral (zonal) grinding on oriented thin single-crystal disks. A significant anisotropy, consistent with the *m*3*m* symmetry of the crystal structure, has been observed. Experimental data are presented in detail for the three principal zones: [100], [110], and [111].

I. Introduction

Although there is no known strontium titanate mineral,[1] relatively large single crystals recently have been grown successfully by the flame-fusion method of Verneuil. A summary of the manufacturing process, typical chemical purity, physical properties, and potential commercial uses has been given by Merker.[2] Like $BaTiO_3$, strontium titanate is a member of the perovskite class of compounds. In contrast, however, $SrTiO_3$ possesses *m*3*m* symmetry at normal temperature, and therefore represents the "ideal" cubic structure of this class.

This investigation is concerned with the directional variation of hardness in strontium titanate and represents the first such study for this material. A significant anisotropy consistent with *m*3*m* symmetry has been observed. The symmetry of the holosymmetric class of the isometric or cubic system (*m*3*m*) is displayed by a cube which has three fourfold symmetry axes parallel to the edges, [100]; six twofold axes parallel to the face diagonals, [110]; and four threefold axes parallel to the body diagonals, [111]. The method used for this work is that of peripheral (zonal) grinding on crystallographically oriented thin single-crystal disks. The technique has been found to give systematic and reproducible results. Experimental data are presented in detail for the three principal zones: [100], [110], and [111].

II. Experimental Technique

A detailed account of the experimental technique may be found in an earlier publication describing the anisotropy of grinding hardness in silicon.[3] For convenience, however, a brief description will be given here.

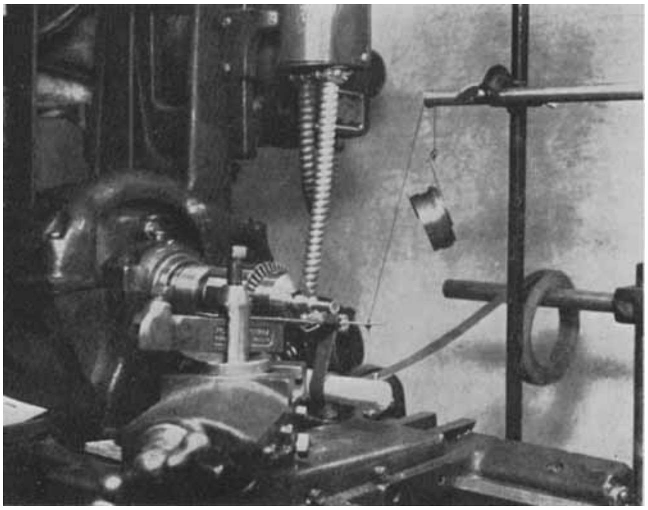

Fig. 1. View of peripheral grinding apparatus.

Crystallographically oriented thin single-crystal disks were ground peripherally with a flexible, bonded silicon carbide abrasive cloth. Each disk was coaxially mounted on the end face of a brass spindle by means of a special centering jig. Dopping wax was used as the cementing agent. The spindle, with disk, was mounted and centered on a machinist's lathe. A flat spring, equipped with a pair of parallel rollers and mounted on the lathe tool holder, served as a flexible backing for the abrasive and as a constant-pressure regulator. A compensating force was placed on the spring to counterbalance the pull of the abrasive cloth moving over the rollers. An additional force of 200 gm. was applied to the system during grinding operations. The contact surface between the disk and abrasive strip was empirically determined as 0.01 sq. cm. ±10%.

In order to record hardness data properly, the orientation of the principal crystallographic directions and the direction of rotation were directly scribed on the exposed flat surface of the disks. At regular intervals during grinding operations, maximum and minimum diametral measurements and their respective orientations were made with a micrometer gauge readable to 0.0005 in. The accuracy of this orientational procedure was found to be ±3 degrees of arc. Figure 1 is a view of the grinding apparatus.

III. Specimen Preparation

Specimen orientation was carried out by the Laue method of X-ray diffraction. The apparatus and technique have been described.[4] Orientational error of specimens was maintained within ±30 minutes of arc. Oriented flat and parallel wafers were cut from boules with a precision diamond saw. A small diamond core drill was used to cut true circular disks of constant diameter from the wafers. Two disks

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At the time this work was done, the writers were research associates, Mineralogical Laboratories, University of Michigan. A. A. Giardini is now project leader, Exploratory Research Division E, U.S. Army Signal Research and Development Laboratory, Fort Monmouth, New Jersey.

[1] Charles Palache, Harry Berman, and Clifford Frondel, Dana's System of Mineralogy, Vol. I, 7th ed. John Wiley & Sons, Inc., New York, 1944. 834 pp.; *Ceram. Abstr.*, **1953**, April, p. 74*b*.

[2] Leon Merker, "Synthesis and Properties of Large Single Crystals of Strontium Titanate," *Mining Eng.*, **7** [7] 645–48 (1955) (*Trans. Am. Inst. Mining Met. Engrs.*, **202** (1955)).

[3] A. A. Giardini, "Study of Directional Hardness in Silicon," *Am. Mineralogist*, **43** [9/10] 957–69 (1958).

[4] A. A. Giardini, "Double Arc Goniometer Head for Crystal Orientation, Sawing, and Grinding," *Am. Mineralogist*, **43** [3/4] 370–75 (1958).

Table I. Observed Radial Reduction After 15 Minutes of Grinding*

[100] disk		[110] disk		[111] disk	
Azimuth (degrees)	Radial reduction (cm.)	Azimuth (degrees)	Radial reduction (cm.)	Azimuth (degrees)	Radial reduction (cm.)
20	0.0953	10	0.0356	10	0.0318
65	.0445	70	.0254	40	.0368
110	.0953	100	.0305	70	.0318
155	.0445	130	.0279	100	.0368
200	.0953	190	.0356	130	.0316
245	.0445	250	.0254	160	.0368
290	.0953	280	.0305	190	.0316
335	.0445	310	.0279	220	.0368
				250	.0316
				280	.0368
				310	.0316
				340	.0368

* Radial measurements were made with a micrometer readable to 0.0005 in.

each were made having peripheral zones [100] and [111]. Only one disk of zone [110] could be made, however, owing to the limited supply of $SrTiO_3$. In order to eliminate small fracture irregularities which developed along the edges of the disks during core drilling, all were simultaneously ground with lapping blocks until all noticeable imperfections were removed. The dimensions of the specimens were the following: diameter = 1.05 cm. ±0.005, thickness = 0.165 cm. ±0.001.

IV. Experimental Data

Experimental data have been obtained for the three zones [100], [110], and [111]. Owing to the peripheral nature of the grinding procedure, radial reduction values are observed for all possible planes within each respective zone investigated. Numerical values are given for the principal crystallographic directions in Table I. Orientational correlation is provided by Fig. 2. Data reported for zones [100] and [111] are the averages obtained from two separate specimens each, whereas data for the [110] zone were obtained from one specimen.

All reported values were obtained under the following experimental conditions: (*a*) The average surface speed of the disks during the 15-minute grinding period was approximately 660 cm. per minute, (*b*) the average rate of feed of the abrasive cloth (240 grit) was 35 cm. per minute, and (*c*) the grinding pressure was maintained at approximately 20 kg. per sq. cm.

Table II. Sources of Error and Some Observed Limiting Values

	Sources	Limits (%)
(*a*)	Surface speed of $SrTiO_3$ disks	±1.0
(*b*)	Rate of feed of abrasive cloth	±0.05
(*c*)	Grinding contact area	±10.0
(*d*)	Micrometer measurements	±0.15
(*e*)	Disk orientational error	±0.5
(*f*)	Orientational error in hardness vectors	±3.33
(*g*)	Weight measurements	±0.2
(*h*)	Grinding period time	±0.15
(*i*)	Nonuniformity of grinding force	(?)

V. Sources of Error

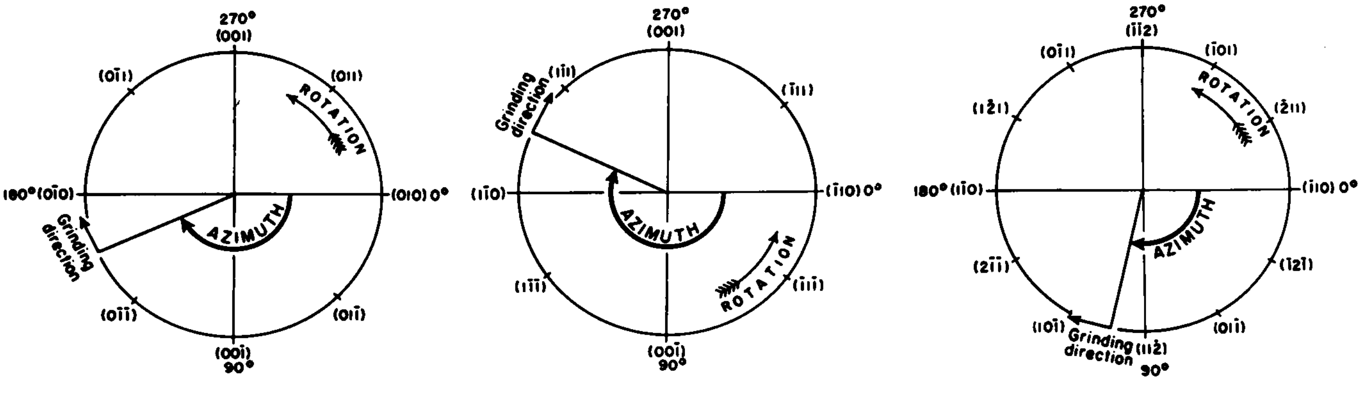
Sources of error in hardness research are numerous, difficult to control, and difficult to correct. No theoretical corrections have been derived in this present study; however, most of the recognized sources of error have been minimized by careful and repeated measurements. A listing of the various sources of error and their approximate limits is given in Table II.

The total accountable error amounts to ±15.4%. This value represents the sum of the limits of error. Actual experimental agreement between individual disks of zonal pairs, both with respect to radial reduction and weight-loss measurements, amounted to ±5%.

VI. Discussion of Results

Relative grinding hardness, H, has been defined by Denning[5] as $H = K_2/K_1$, in which K_2 is the constant for the chosen reference vector and K_1 is the constant being considered. The constant, K, is defined by $K = v/tF$, in which v is the volume of the material removed, t is the time of grinding, and F is the force on the contact area of the grinding. The foregoing definition is used in this study.

As the force on the grinding surface, the grinding contact area, and the time of grinding were held constant or as nearly constant as possible, the constants, K, are directly proportional to the radial reductions. The relative grinding hardness may then be computed by dividing the radial reduction of the reference vector by the radial reduction of the vector in question.



[100] Disk [110] Disk [111] Disk

Fig. 2. Disk orientation.

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[5] R. M. Denning, "Directional Grinding Hardness in Diamond," *Am. Mineralogist*, **38**, 108–17 (1953).

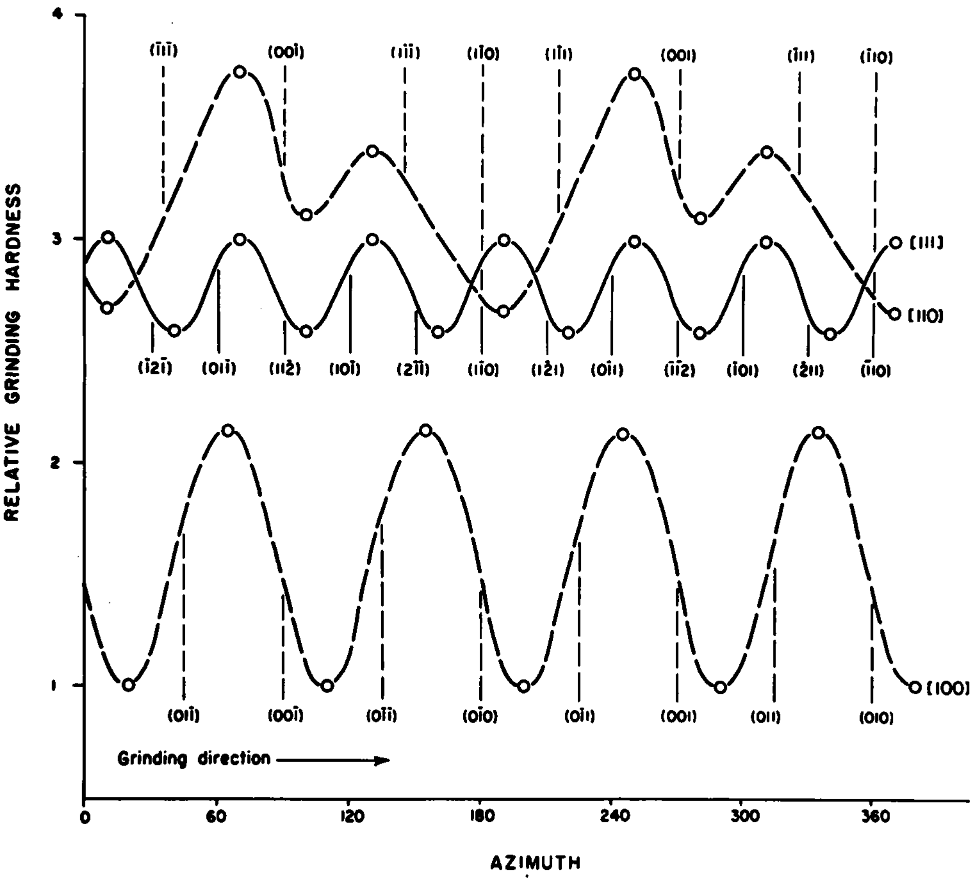

Fig. 3. Curves of relative grinding hardness.

Figure 2 illustrates the orientation of the disks and shows the direction of rotation, direction of grinding, and the starting orientation and traverse of the azimuth. It should be emphasized that there are an infinite number of possible grinding directions on any plane. The peripheral grinding method permits the observation of only one vector on each of the planes in the zone of the disk. Figure 3 is a plot of the relative grinding hardness for the three principal zones investigated. Azimuths are those illustrated in Fig. 2, and the principal planes in each zone also are indicated.

The magnitude of the relative hardness differential within zones [100] and [110] is approximately twice that of the differential within zone [111]. Furthermore, it is seen that the average relative hardness of zone [100] is only approximately one-half as great as the average of zones [110] and [111]. The marked directional hardness in the [100] zone of $SrTiO_3$ is clearly illustrated by Fig. 4, which is a photograph of the [100] disk before and after grinding for 15 minutes.

A summary of the observed relative directional grinding hardness for the principal planes and azimuths is given in Table III. The hardness of strontium titanate on the Mohs scale, as reported by Merker,[2] is 6.0 to 6.5. This range of hardness was confirmed during the course of this investigation by extensive scratch tests along essentially all azimuths on the planes (100), (110), and (111). The flat surfaces of the grinding disks were used for this purpose. In correlation with these two methods of relative hardness description, grinding data for zones [110] and [111] represent approximately the upper limit of the Mohs value, and zone [100] contains the lower Mohs value. A review of the hardness curves of Fig. 3 illustrates the wide range of relative hardness encompassed within the Mohs values of 6.0 to 6.5.

Information obtained from the [111]-zone disk describes the relative hardness of the $(11\bar{2})$ plane along an azimuth parallel to the twofold symmetry axis, $[1\bar{1}0]$, of the crystal, and the $(1\bar{1}0)$ plane along $[11\bar{2}]$. It is shown that the latter vector possesses a slightly greater hardness than the former, the "numerical" value of the $[11\bar{2}]$ vector on the plane $(1\bar{1}0)$ being approximately 2.9, whereas the vector $[1\bar{1}0]$ on the plane $(11\bar{2})$ shows a value of 2.7.

The symmetrical displacement of the maximum and minimum hardness vectors with respect to the crystallographic directions, as a function of peripheral grinding direction, has been confirmed during the course of this investigation. This displacement, inherent to the mechanics of

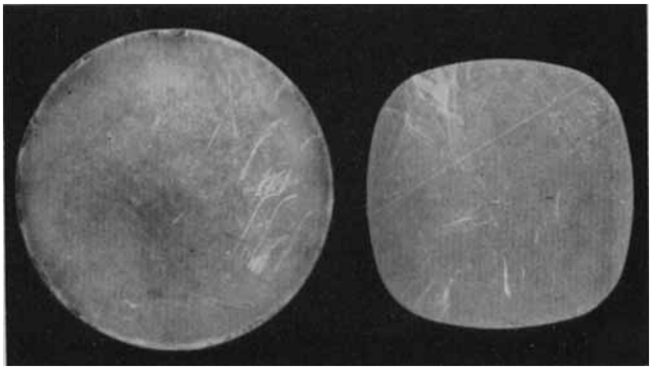

Fig. 4. A [100] disk before and after grinding for 15 minutes. (*Left*) before grinding and (*right*) after grinding.

Table III. Observed Relative Grinding Hardness of Principal Planes for Specified Grinding Azimuths

	Grinding on plane	In the direction toward	Descriptive relative hardness	Comparative numerical hardness*
(*a*)	(001)	$(\bar{1}11)$	Hardest principal vector	3.25
(*b*)	$(\bar{1}11)$	$(\bar{1}10)$	Approximately same as (*a*)†	3.25
(*c*)	$(1\bar{1}1)$	(001)	Second hardest vector	3.05
(*d*)	$(\bar{1}10)$	$(\bar{1}2\bar{1})$	Third hardest vector	2.90
(*e*)	$(\bar{1}10)$	$(\bar{1}1\bar{1})$	Fourth hardest vector	2.75
(*f*)	(011)	(010)	Fifth hardest vector	1.65
(*g*)	(001)	(011)	Softest principal vector	1.50

* The numerical scale is based on the softest vector having the arbitrary value of unity, and a zero reduction in disk radius having a hardness value of "infinity."

† The hardness of (*b*) appears to be slightly less than that for (*a*); however, the observed difference approaches the limit of experimental error.

the grinding procedure, is considered of no serious consequence with respect to evaluations of relative hardness.

The data presented in Figs. 3 and 4 clearly illustrate the symmetrical nature of grinding hardness as observed in $SrTiO_3$ by the peripheral method of hardness evaluation. If a point on a curve (hardness vector) is repeated, in the same environment, *n* times in 360 degrees, the disk displays *n*-fold symmetry. As anticipated, zone [100] displays fourfold symmetry, zone [110] twofold symmetry, and zone [111] apparent sixfold symmetry which is compatible with threefold symmetry. Agreement is observed, therefore, between structural symmetry and hardness symmetry.

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Phase Equilibria in the Ferrite Region of the System Fe–Ni–O

by A. E. PALADINO, JR.

Research Division, Raytheon Manufacturing Company, Waltham, Massachusetts

Phase equilibria in the system Fe–Ni–O have been investigated near $NiFe_2O_4$ up to a temperature of 1300°C. A vacuum technique has been used for determining the equilibria relations and is described in detail. The stability of spinel solid solutions up to 1300°C. in oxygen pressures of from 1 to 10^{-2} atmospheres has been determined.

I. Introduction

FUNDAMENTAL research on the magnetic and electrical properties of ferrites requires well-defined polycrystalline samples of these materials. Past research on these materials required certain assumptions concerning the compositions because of the lack of phase equilibria data of the systems in which ferrite compounds, or solid solutions, are contained.

The present program was initiated to determine the phase equilibria relations over a limited range within certain systems containing structurally characterized ferromagnetic oxides such as nickel ferrite spinel. A number of investigations have been concerned with the properties of nickel ferrite as a function of composition,[1] from which some general conclusions about the extent of solid solubility in these systems can be made. This information, along with the excellent diagram for the system Fe–O as determined by Darken and Gurry,[2] has aided in anticipating in a general way the behavior of the ternary extension by nickel of the binary system iron–oxygen. It also was expected that the phase equilibria in the system Fe–Ni–O would be very similar to the system Fe–Co–O determined recently by Smiltens,[3] inasmuch as nickel and cobalt are chemically similar.

II. General Considerations

Figure 1 represents the framework of the ternary diagram Fe–Ni–O drawn in terms of atomic fractions. From the geometrical properties of the triaxial diagram, lines drawn from the oxygen apex to the Fe-Ni line represent all compositions with a constant ratio, $f_{Fe}:f_{Ni}$, where f_{Fe} and f_{Ni} are the atomic fractions of iron and nickel, respectively. The one drawn is for a ratio of 2.000 which passes through the composition point corresponding to $NiFe_2O_4$. Compositions considered in the present investigation are located primarily in the area bounded by Fe_3O_4-Fe_2O_3-$NiFe_2O_4$, which is drawn enlarged in Fig. 2 with the oxygen fraction lines perpendicular. A further restriction limits the compositions to those realizable in oxygen pressures from 10^0 to 10^{-2} atmospheres in the temperature range 1000° to 1300°C., which includes some compositions slightly to the right of the Fe_3O_4-$NiFe_2O_4$ line near nickel ferrite.

It has been pointed out in a number of investigations[1] that the properties of nickel ferrite depend on the composition expressed in terms of the iron content. X-ray analysis in this laboratory on a number of such compositions prepared at various temperatures indicates the existence of continuous solid solutions. From the fact that spinel solid solutions exist, and with the known properties of the system iron–oxygen, certain very general relations in the system Fe–Ni–O can be anticipated. The spinel field is indicated in Fig. 2 by the isothermal field-boundary line drawn in arbitrarily, and the area of two solid phases is labeled "spinel solid solution plus hematite." Within each area, an oxygen isobar follows a very definite path indicated by the broken line. In the area of two solid phases the system is bivariant and the isobars are tie lines for the equilibrium between hematite and a spinel solid solution. The point of intersection of the isobar and

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[1] (*a*) L. G. Van Uitert, "D.-C. Resistivity in the Nickel and Nickel-Zinc Ferrite Systems," *J. Chem. Phys.*, **23** [10] 1883–87 (1955).
(*b*) S. L. Blum and J. E. Zneimer, "Physical and Electrical Properties of a Nickel Ferrite as Affected by Compositional Changes," *J. Am. Ceram. Soc.*, **40** [6] 208–11 (1957).

[2] L. S. Darken and R. W. Gurry, "The System Iron–Oxygen: II, Equilibrium and Thermodynamics of Liquid Oxide and Other Phases," *J. Am. Chem. Soc.*, **68** [5] 798–816 (1946); *Ceram. Abstr.*, **1947**, February, p. 50g.

[3] J. Smiltens, "Investigation of the Ferrite Region of the Phase Diagram Fe–Co–O," *J. Am. Chem. Soc.*, **79** [18] 4881–84 (1957).