Excess microwave ultrasonic attenuation in vacuum-heated rutile (TiO_2)

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It was observed by Lange that rutile (TiO_2) appropriately heated in a vacuum showed an anomalous attenuation peak for 1-GHz ultrasound. He suggested that the cause of the attenuation was some lattice defects, and not conduction electrons. By comparing the attenuations of 3-GHz ultrasound in vacuum-heated TiO_2 with that in Nb-doped TiO_2 we find strong evidence for Lange's conclusion.

The nature of the defects produced in rutile (TiO_2) by heating it in vacuum has been the subject of many investigations. There is a twofold interest; because of weight loss during the heat treatment it is believed that some O_2 is driven out of the lattice, which results in lattice defects of some kind. There have been attempts to understand the resulting lattice defects in terms of point defects,[1] but there are also observations that at high concentrations the defects are extended in character.[2] Recently, it has been pointed out that most experiments may have been performed under conditions of "dirty" vacuum[3] and that some impurity may be necessary for defect formation at temperatures below 1000 °C. The second source of interest arises because it is found that the electrical conduction can be enormously increased by the vacuum heating. There is an extensive literature on the nature of the electrical conduction in heat-treated TiO_2.[4]

The present paper relates to the observations of Lange,[5] that the heat treatment of TiO_2 produced a considerable increase of attenuation of 1-GHz ultrasound. The attenuation was found to vary with temperature with a broad peak centered around 80 °K. An important feature noted was that the only polarizations of ultrasound that had excess attenuation were those whose velocity contained the elastic constant C_{44}. To help determine the cause of the attenuation, Lange measured the attenuation in the presence of a 13-kG magnetic field perpendicular to the propagation direction of the sound. There was no effect on the attenuation. This was interpreted as showing that the attenuation was not caused by the electronic carriers, since a magnetic field would presumably have affected electronic attenuation.[6] It was, therefore, suggested that the attenuation was due to ultrasonically induced motion of a lattice defect.

Because of the obscurity of the nature of the lattice defects in TiO_2, the fact that some of them could respond to such high-frequency ultrasound at relatively low temperature seems an important observation and worth checking. On the other hand, the possibility of electronic attenuation may not be completely rejected. Because of strong electron-phonon coupling in TiO_2, it is likely that the electrons are better described as small polarons.[4] It is not clear what effect a magnetic field has on the ultrasonic attenuation due to small polarons, so that Lange's observation of the absence of a magnetic field effect may not be decisive. It would not be surprising if electrons (or polarons) could respond to microwave ultrasound.[7]

The experiments we initiated to separate the electronic (polaronic) contribution from the lattice-defect contribution to the ultrasonic attenuation were to measure the attenuation in samples which had similar electronic concentrations but had different amounts of lattice defects. One set of samples was obtained by heat treatment of pure TiO_2 and thus contained both free electrons and lattice defects. The comparison set of samples was TiO_2 doped with Nb. These samples had similar conductivity but no lattice defects comparable to those in the heat-treated samples. (The group-V element Nb replaced Ti^{+4} substitutionally[8] in the TiO_2 lattice and thus engenders little distortion. Nb^{+4} acts as a shallow donor[9] to produce electrical conductivity.)

The Nb-doped samples were produced by adding Nb_2O_5 powder to TiO_2 before the growth by the Verneuil method. This was done at the National Bureau of Standards and the samples were kindly provided to us by Dr. H. P. R. Frederikse of NBS.

The heat-treated samples were prepared from undoped single-crystal TiO_2. The vacuum was obtained by using a liquid-N_2-trapped Hg diffusion pump. The sample [100] VH was sealed in a quartz tube in a vacuum of 6×10^{-3} Torr. It was heated for 14 h at 850 °C. The sample [110] VH was sealed in a Vycor tube in a vacuum of 1.4×10^{-2} Torr and heated for about 60 h at 800 °C. In both cases the samples changed from clear to opaque because of the heat treatment.

A discussion of the method used to measure ultrasonic attenuation and some problems with TiO_2 are given in a recent paper.[10] Our method employs a magnetic transducer which requires that a 6-kG field be applied parallel to the ultrasound prop-

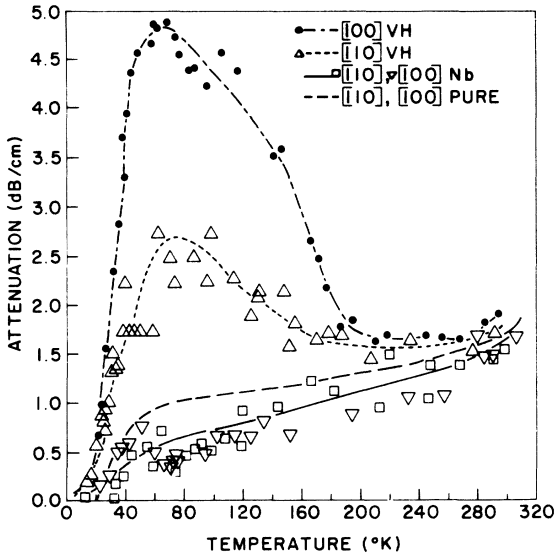

FIG. 1. Attenuation vs temperature of 3-GHz shear waves polarized parallel to the [001] direction in several rutile samples. The propagation direction is indicated for the vacuum-heated (VH) samples because they differ in the amount of heat treatment, as measured by their electrical conductivities. The Nb-doped TiO_2 curve is an average of runs with samples from the same boule but cut with [100] and [110] propagation directions. The data for different directions differ from each by less than the experimental error ($\simeq \pm 0.2$ dB/cm). The pure TiO_2 attenuation is the average of data on propagation in [100] and [110] directions (Ref. 10), which also differ from each other less than ± 0.2 dB/cm at any temperature.

agation direction. According to Lange's observation, however, this should have no effect on the measurements. Moreover, the same field is used for all the samples and should not affect their relative behavior.

Since we are interested in the comparative behavior of the vacuum-heated samples and the Nb-doped TiO_2, it is sufficient to know the relative electrical conduction of the samples, in order to distinguish electrical from lattice ultrasonic attenuation. We measured the resistance of each of the ultrasonic samples with the same four-probe resistivity instrument. The resistivities were in the ratio Nb-doped: [100] VH : [110] VH = 1 : 1.5 : 2.4 at room temperature. At 77 °K we found a ratio of resistivities Nb-doped : [100] VH ≈ 3. Thus, the Nb-doped sample was more conducting than the vacuum-heated samples. The absolute resistivity at room temperature of the Nb-doped material was measured on a [100] "spider" to be $\rho \simeq 1.4\ \Omega$ cm and the Hall mobility was $\mu_H \approx 0.3\ \mathrm{cm^2/V\,sec}$. The accuracy of the Hall measurement was poor; a [001] spider gave $\mu_H \approx 3.5\ \mathrm{cm^2/V\,sec}$, but the same resistivity as the [100] spider. This indicates a carrier density of between $1\times10^{19}/\mathrm{cm^3}$ and $1\times10^{18}/\mathrm{cm^3}$. From the data of Thurber and Mante[11] it can be deduced that the mobilities of vacuum-heated samples are about the same as that of Nb-doped samples at the same temperature. We found that at 77 °K, ρ(Nb-doped) ≈ 0.6 Ω cm and ρ([110] VH) ≈ 2 Ω cm, so that the ratio is approximately the same as at room temperature, as the Thurber-Mante's data indicate.

In Fig. 1 we show our measurements of the attenuation of the shear waves polarized parallel to [001] in these samples and pure[10] TiO_2. The velocity of these waves is $(C_{44}/\rho)^{1/2}$. One sees that the attenuation in the vacuum-heated samples has a distinct peak with maximum at about 80 °K, as first reported by Lange.[5] The more highly conducting vacuum-heated sample [100] VH has the higher peak. But the most conducting sample of all, the Nb-doped sample, has no excess attenuation. From this we conclude that the attenuation in the vacuum-heated samples is not caused by electrical carriers but rather by lattice defects. In the vacuum-heated samples, the electrical conduction is proportional to the number of defects, but it is the defects, not the electrons, that cause the attenuation. We tried an even more highly conducting Nb-doped sample having a resistivity 30% as great as the one in Fig. 1. The data were rather poor but no attenuation peak was discernible.

We agree, therefore, with Lange's[5] suggestion that it is some lattice defects that produce ultrasonic attenuation in vacuum-heated TiO_2, and not electrons. The nature of these defects, including their remarkable ability to respond on a time scale of 10^{-10} sec at temperatures near 80 °K, will require further elucidation. It should be noted that attenuation peaks of this character have been observed in some other complex oxides when they are nonstoichiometric, e.g., $LiTaO_3$[12] and the $Bi_{12}GeO_{20}$–$B_{12}SiO_{20}$ system.[13]

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