JOURNAL OF MATERIALS SCIENCE LETTERS 10 (1991) 210–213

Ultrasonic characterization of ceramic superconductors

M. C. BHARDWAJ
Ultran Laboratories, Inc., State College, PA 16801, USA

A. S. BHALLA
Materials Research Laboratory, Pennsylvania State University, University Park, PA 16802, USA

Concurrent with the recent advances in structural, electronic and biomedical materials, ultrasonic non-destructive characterization (NDC) has also undergone a similar revolution. The significance of time-domain (for direct correlation with test material density and porosity, defect detection and elastic properties) and frequency-domain (for direct correlation with materials' microstructure, and process and compositional parameters) analyses by ultrasound is now well established [1–6]. The advantages of ultrasonic NDC are obvious, yet it is important to use a suitable technique that will not adversely affect the composition or physical characteristics of a test material during the analytical process. Consideration of these elements can provide significant process- and applications-related parameters of materials, besides establishing the reliability of test procedures [7].

Recently, high-T_c bulk superconductors have become significantly important due to their possible applications in various industries. Although reproducible superconducting properties are obtained, the high critical current, J_c, has been always a problem. Various factors such as compositional and structural parameters, chemical phase, grain size and morphology, grain orientation, processing conditions, oxygen annealing and the ambient conditions (water, CO_2, etc.) affect the behaviour of final superconducting components. Therefore, it has become rather important to look into a suitable and non-destructive technique to characterize the high-T_c materials. Such a technique can provide useful guidelines for the processing of high-T_c materials as well as in establishing the relationship between J_c and sample quality.

In this letter we report preliminary time- and frequency-domain observations from selected YBC superconducting samples. Since these materials are susceptible to damage by moisture and conventional wet-coupling techniques, a novel dry-coupling transducer mechanism has been used for their characterization [3]. In order to enhance the accuracy and sensitivity of time- and frequency-domain analyses, the transducer coupling mechanism has been further supplemented by short-duration ultrasonic impulse and near "white" frequency spectra [3, 8]. Four YBC-based superconducting samples, two each corresponding to single phase and multiphase, were investigated by time- and frequency-domain analyses. The salient characteristics of these materials are shown in Table I, and their processing methods are described in [9].

Test samples were clamped between transmitting and receiving dry-coupling transducers in order to maintain a constant pressure. The transmitter was excited by a short-duration (about 5 ns) electrical pulse of controlled repetition frequency and the transmitted signals were received directly by the receiving transducer. Transmitted signals were amplified by a broadband (approximately 1 KHz to 50 MHz) amplifier. Fig. 1 shows the schematic representation of the ultrasonic system and tranducers configuration with respect to the test samples used in this investigation. The longitudinal and shear waves velocities were determined by measuring their respective times of flight through the known thicknes-

TABLE I Characteristics of superconducting samples investigated by time- and frequency-domain analytical techniques

Sample	Composition	Grain size	Density	Processing parameters	Superconductivity
YBC-2	High-purity phase pure orthorhombic	Fine	> 90%	Sintered at 950 °C, annealed at ~ 700 °C in O_2, slow cooling	93 K
YBC-3[a]	Commercial single phase	Fine	~ 85%	Unknown	87 K
YBC-4[b]	70% YBC and 30% low-melting glass (~ 450 °C)	Medium to coarse		O_2 annealed powder, no oxidation of composite	Superconducting composite (magnetic measurement method), 90 K
YBC-5	Green-phase (211) + YBC (123)	Coarse	High	Hot-pressed at 900 °C and 3500 p.s.i. (~ 24 MPa)	Poor

[a]Courtesy NASA Lewis Research Center, Cleveland, Ohio, USA. The rest of the samples were prepared at Materials Research Laboratory, Pennsylvania State University [9].
[b]Evidence of fractured interfaces between grains.

0261-8028/91 $03.00 + .12

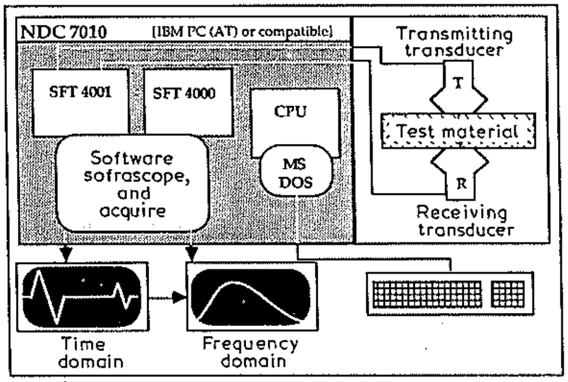

Figure 1 Schematic diagram of the computer-based pulsed ultrasonic set-up used for the measurement of time- and frequency-domain characteristics by sandwiching the test material between transmitting and receiving dry-coupling highly broadband ultrasonic transducers. SFT 4001, Ultrasonic pulser–receiver PCB; SFT 4000, analogue-to-digital converter PCB; SOFRASCOPE, software for signal display; and ACQUIRE, software for time- and frequency-domain analysis.

ses of test samples [7]. The nominal frequency of the longitudinal wave transducer was 10 MHz and that of the shear wave transducer was 5 MHz. An example of longitudinal and shear waves times-of-flight measurements is shown in Fig. 2 for the YBC-2 sample, 6.73 mm thick. Measured ultrasonic velocities were used to determine the elastic properties of superconducting samples. Table II provides a summary of these data as well as those for a commercial sample of a copper plate. Single-phase samples revealed acoustic characteristics that were very similar to those measured in copper. Their mechanical properties are in the average range of a ceramic and a ductile metal. The Poisson's ratio also represents the same features.

Frequency-domain characteristics were measured by performing fast-Fourier transformation (FFT) of the transmitted ultrasonic signals through superconducting samples. The transmitting and receiving transducers utilized for frequency-domain measurements are characterized by near "white" ultrasonic spectra, corresponding to 3.5–17.5 MHz at -6 dB level and 1.5–22.5 MHz at the -20 dB level. As a reference, the frequency domain of these transducers from 1.0 cm optically flat and clear fused quartz (CFQ) was assumed as standard. Typical frequency spectra as a function of the measured acoustic pressure/intensity of representative single- and multiphase superconducting samples are shown in Fig. 3, together with those of the reference CFQ and copper. Since the test materials varied in thickness, their frequency spectra were norrmalized to yield dB cm^{-1} units. As shown in Fig. 3, relative to the reference spectrum, the single-phase YBC superconductor exhibited less attenuation than its multiphase

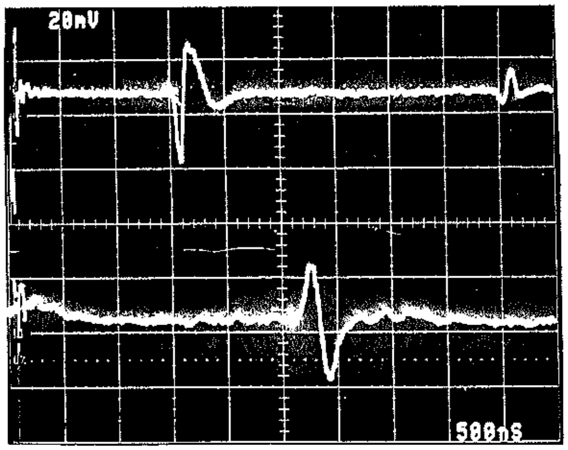

Figure 2 An example of time-domain analysis of a superconducting sample. Shown here are the r.f. A-scans of longitudinal (top trace) and shear (bottom trace) waves propagation through the YBC-2 sample, 6.73 mm thick, obtained by a dry-coupling direct transmission technique. In both traces the extreme left-hand signal respresents the incident or transmitting pulse, whereas the signal immediately following it corresponds to the transmitted ultrasound through the test specimen. The distance between these two signals yields the time of flight for ultrasound travel. Longitudinal wave time of flight = 1.466 μs, longitudinal velocity = 4590 m s^{-1}, shear wave time of flight = 2.626 μs and shear velocity = 2560 m s^{-1}.

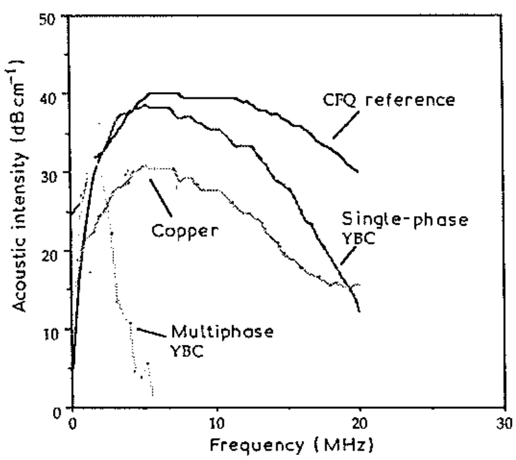

Figure 3 Frequency-domain spectra of single- and multiphase YBC-based superconductors shown with the reference clear fused quartz (CFQ) spectrum and a commercial sample of copper.

TABLE II Ultrasonically measured elastic properties of superconducting samples, with those of copper as a reference

Sample	Velocity (m s^{-1})		Density (kg m^{-3})	Young's modulus (GPa)	Shear modulus (GPa)	Bulk modulus (GPa)	Poisson's ratio
	Longitudinal	Shear					
YBC-2	4590	2540	5580	92.0	36.0	69.0	0.279
YBC-3	4490	2660	5370	93.0	38.0	58.0	0.231
YBC-4	3290	1960	4150	39.0	16.0	23.5	0.224
YBC-5	3770	2210	4980	60.0	24.0	38.0	0.237
Copper	4690	2240	8710	118.0	44.0	133.0	0.351

counterpart, indicating higher scattering (due to larger grains) of ultrasound by the latter. The relative frequency attenuation for each sample was determined by subtracting its measured acoustic intensity from that of the reference CFQ spectrum [10].

Fig. 4 shows the relative frequency attenuation for single-phase YBC-2 and YBC-3 samples, together with that of copper as a reference. The trend of attenuation for both samples is similar; however, numerically YBC-2 exhibited less frequency attenuatuion than YBC-3. Since frequency attenuation in polycrystalline materials of the same chemical composition increases with the grain size and decreases with the density, it can be concluded that either YBC-2 is a finer and compositionally homogeneous grain or it is a denser material than the YBC-3 sample. It is also interesting to note that a denser YBC-2 sample exhibited less attenuation than copper within the range of measured frequencies. Such characteristics of YBC superconductors have some practical advantages over metal components in some devices.

Assuming the constancy of composition, longitudinal wave velocity measurements can also provide significant information about test material densities [7]. Higher velocities are indicative of higher densities. In the present case the longitudinal wave velocity of YBC-2 was 4600 $m s^{-1}$, whereas for YBC-3 it was 4500 $m s^{-1}$, supporting the argument that the former is denser.

Fig. 5 shows the relative frequency attenuation of multiphase superconducting samples, indicating a higher frequency attenuation of YBC-5 than YBC-4. Assuming that texture plays the dominant role in the frequency attenuation of these samples, it is possible that YBC-4 is a finer-grained material than the YBC-5. This is expected, since YBC-5 is a typical hot-pressed sample with a grain size of the order of few micrometres, besides which there could also be some contribution to scattering by the second phase.

Besides the evaluation of sintered materials, a

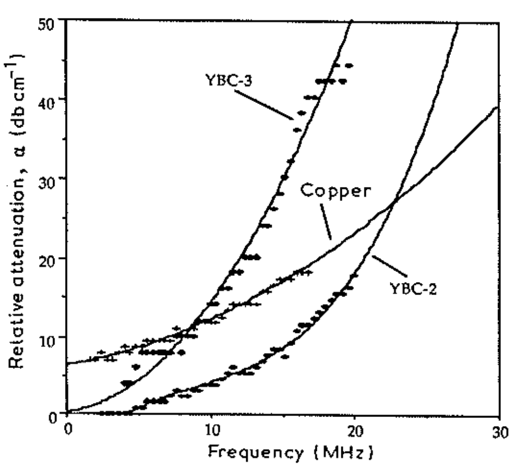

Figure 4 Relative frequency attenuation of single-phase superconducting samples, shown with that of copper for reference purposes.

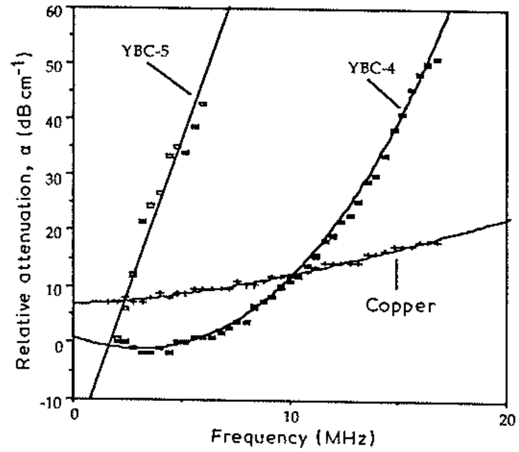

Figure 5 Relative frequency attenuation of multiphase YBC superconducting samples, shown with that of copper for reference purposes.

dry-coupling ultrasonic mechanism has also been successfully applied for the characterization of velocity–density relationships for green ceramics [11]. Our initial observations on green superconducting tapes, about 50 μm to 6 mm, appear promising. Green-stage NDC is considered vital for establishing the desired microstructure and optimum process and compositional parameters of ceramic superconducting materials. Green-stage NDC also offers advantages such as the early detection of defects and discrete point heterogeneity analysis, and materials, energy and time savings. The results of these studies will be reported in the near future.

In conclusion, we have shown that time- and frequency-domain ultrasonic techniques are useful for the non-destructive characterization of materials. We have also established the feasibility of the dry-coupling ultrasonic technique for reliable characterization of environment-sensitive materials such as ceramic superconductors. This technique can thus be exploited for quality control of large production of bulk YBC superconductors in green as well as final sintered bodies.

Our preliminary ultrasonic observations from single- and multiphase superconducting samples indicate definite relationships that apparently describe the frequency dependence of ultrasonic attenuation as a function of the test material microstructure. Since, for a given composition, the microstructure of the final product plays the dominant role in defining the practical uses of superconductors, we understand that modern ultrasonics offers exciting opportunities for practical advancement of these materials. However, in order to gain more knowledge about the bulk characteristics and microstructure, it is imperative for selectively varying compositions and processing conditions of superconducting materials to be examined. Besides the obvious advantages of ultrasonic NDC of green and sintered materials, it is believed that systematically determined time- and frequency-domain data from superconductors might be significant in defining their device-oriented properties.

Acknowledgements

The authors gratefully acknowledge the contributions of C. J. Valenza for the preparation of special dry-coupling and broadband ultrasonic transducers used in this investigation.

References

1. A. B. BHATIA, "Ultrasonic absorption, an introduction to the theory of sound absorption and dispersion in gases, liquids, and solids" (Oxford University Press, New York, 1967).
2. J. W. McCAULEY, in "Nondestrive testing of high-performance ceramics", edited by A. Vary (American Ceramic Society, Westerville, Ohio, 1987) p. 1.
3. M. C. BHARDWAJ, *ibid.* p. 472.
4. S. SERBIAN, *Brit. J. Non-destruct. Testing* **22** (1980) 69.
5. E. R. GENERAZIO, *Mater. Evaluation* **43** (1985) 995.
6. P. K. LIAW, R. E. SHANNON and W. G. CLARK, in "Fundamental relationships between microstructures and mechanical properties of metal matrix composites", edited by M. N. Gugnar and P. K. Liaw (Minerals, Metals, and Materials Society, Warrendale, Pennsylvania, 1989) p. 581.
7. M. C. BHARDWAJ, in "Metal and ceramic matrix composites: processing, modelling and mechanical behaviour", edited by R. B. Bhagat, A. H. Clauer, P. Kumar and A. M. Ritter (Minerals, Metals, and Materials Society, Warrendale, Pennsylvania, 1990) p. 509.
8. M. C. BHARDWAJ, *Ceram. Bull.* **69** (1990) 1490.
9. A. S. BHALLA, R. ROY and L. E. CROSS, in "Chemistry of oxide superconductors", edited by C. N. R. Rao (International Union of Pure and Applied Chemistry/Blackwell Scientific, London, 1988) p. 71.
10. M. C. BHARDWAJ, K. TRIPPETT and A. S. BHALLA, in "Superconductivity and ceramic superconductors", edited by K. M. Nair (American Ceramic Society, Westerville, Ohio, 1990).
11. M. C. BHARDWAJ and K. TRIPPETT, Presented at the 92nd Annual Meeting of the American Ceramic Society, Dallas, Texas, 1990.

Received 5 June
and accepted 13 July 1990