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Experimental measurement of the elastic constants of $GdScO_3$ via resonant ultrasound spectroscopy utilizing *ab initio* calculations

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The complete elastic tensor of single crystal $GdScO_3$ was determined using resonant ultrasound spectroscopy (RUS) in combination with *ab initio* calculations. The experimental determination of all nine elastic constants also provides a method for probing the dynamic lattice properties for this recently developed orthorhombic material. The experimentally determined elastic constants differed from theoretical values on average by 10%, and all but three of the nine elastic constants varied by less than 10%. These results indicate that *ab initio* calculations are now sufficiently accurate for the precise determination of the elastic tensor using RUS as the sole experimental source. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2901881]

$GdScO_3$ is an orthorhombic perovskite with a relatively high bandgap ($E_g \sim 5.6$ eV)[1–3] and high dielectric constant ($K=19-29$, depending on direction).[4] These properties, coupled with its stability in direct contact with silicon,[5] make it of interest as an alternative dielectric for silicon-based metal-oxide semiconductor field-effect transistors.[6–8] Single crystals of $GdScO_3$ are being used as substrates for the growth of epitaxial perovskite thin films, particularly ferroelectric compositions such as $BaTiO_3$,[9] where the strain imparted by commensurate growth on the $GdScO_3$ substrate can greatly enhance the properties of the ferroelectric film.[10,11] It is also an appropriate substrate for the growth of strained layer superlattices consisting of perovskite layers with slightly larger and smaller lattice constants than the underlying $GdScO_3$ substrate, enabling the growth of arbitrarily thick superlattices with the highest structural perfection ever reported.[12] The high bandgap of $GdScO_3$ has enabled Raman spectroscopy to be utilized as a probe of the folded acoustic phonon peaks of strained layer perovskite superlattices using a forward scattering geometry.[13] In epitaxial form, $GdScO_3$ and other rare earth scandates ($ReScO_3$) are also being used in multilayer structures for field-effect applications[14] to customize dielectric constants,[3] or as buffer layers to control the strain of overlying layers.[15] Oxide superlattices have also shown promise over superlattices of compound semiconductors for phonon confinement structures, where a mismatch in acoustic impedance is used to make Bragg mirrors and cavities for phonons.[16] For all of these thin film uses of $GdScO_3$, it is important to know its mechanical properties as these impact its critical thickness, the strain partitioning among layers, and the acoustic impedance of the $GdScO_3$ layer. In order to obtain this knowledge, the complete elastic tensor of $GdScO_3$ was determined using resonant ultrasound spectroscopy (RUS).

Recently developed materials are often only available in small sample sizes, with the consequence that determining the elastic properties with traditional time of flight measurement is often too difficult. However, the small sample RUS technique is ideal for such measurements.[17] Using this technique, measurements can be performed on samples with dimensions as small as a few hundred microns and mass as little as a few hundred of micrograms. The RUS technique enables the complete determination of the elastic properties from the knowledge of the sample dimensions, density, and the measured natural frequencies.

The forward problem, solving for the frequencies and normal modes of vibration for a given elastic tensor and sample geometry, had been solved analytically as early as 1882 for a small set of special geometries.[18] With the advent of digital computers, numerical methods are now able to provide solutions for arbitrary geometries whose accuracy is limited only by the computational resources available. By contrast, the inverse process, recovering the elastic constants solely from the natural frequencies, is not trivial because there is no direct relation giving the elastic constants in terms of the natural frequencies. The inverse problem, however, is soluble using an iterative approach.[19–23] For a given density, geometry, and crystal symmetry, the solution is reached by assuming a set of initial values for the elastic constants and then calculating the resonant spectrum. These calculated frequencies are then compared to the experimentally measured frequencies in a least squares sense. One requirement is that there must be at least as many experimentally measured frequencies as unknown elastic constants. However, each frequency may not couple to all elastic constants, thus, additional frequencies beyond the minimum are often required.[23,24] One method to ensure the measurement of a sufficient number of frequencies is to examine the influence of the elastic constants on each frequency $\partial f_n / \partial c_{ij}$; thus, ensuring sufficient coupling between the measured frequencies and all unknown elastic constants.[22,25] The estimated elastic constants are then adjusted iteratively, minimizing the least

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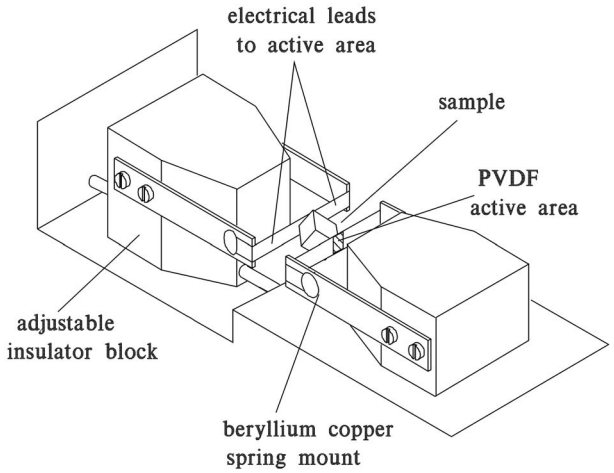

FIG. 1. Schematic diagram of a sample placed between the PVDF transducers with the sample corners maintaining contact with the "active" region.

squares difference between the calculated frequencies and the experimentally measured frequencies, thus, recovering the complete elastic tensor responsible for the spectrum. In order for the RUS measurement to precisely converge to the unique elastic tensor of the material sample, the knowledge of reasonable initial values for the elastic constants is required. The necessary accuracy required in the initial estimates is an experimentally determined parameter evaluated on a case to case basis. Details of the robust nature of the convergence procedure may be found in the literature.[20,21,23,24] The initial values, however, can often differ from the true values by 30% or more and still yield accurate final results.[25]

Because little experimental information is available for many recently developed materials, alternate methods for determining reasonable starting values for the RUS inverse calculation may be required. With the advance of computational techniques, *ab initio* calculations of the elastic properties of a material based on crystal structure, thermomechanical behavior, and atomic constituents are now possible.[26–30] The results of these calculations with MATERIALS TOOLKIT[30] are sufficient as initial starting values for the elastic constants, enabling accurate RUS measurements.

The experimental setup is illustrated in Fig. 1.[21] Polished rectangular parallelepiped samples are placed between the two piezoelectric film transducers with contact maintained at the sample corners. The transducers are composed of 0.5 mm wide and 9 μm thick strips of piezoelectric polyvinylidene fluoride (PVDF) film. The transducers are formed by the PVDF film strips which have been partially metalized on each side with the overlapping section forming an active capacitive region. The PVDF transducers are positioned on adjustable mounts which support the sample weight through the film tension, thus, avoiding any need for bonding agents. The drive transducer receives a signal, whose frequency is swept, and the sample response is measured at the other transducer.[17]

TABLE II. The pure shear (transverse) and longitudinal sound velocities of $GdScO_3$.

Wave type	Formula	Sound velocity single crystal (RUS) (m/s)	Polycrystalline[a] (m/s)
Longitudinal	$v=\sqrt{c_{11}/\rho}$	6653	6567
Transverse	$v=\sqrt{c_{55}/\rho}$	3880	3554

[a]Reference 35.

The sample for this experiment was obtained from a $GdScO_3$ single crystal which was grown via the Czochralski technique.[31] These crystals are now commercially available.[32] The sample was cut and polished as a rectangular solid whose shape corresponds to the unit cell, i.e., its faces are parallel to the crystallographic (100), (010), and (001) faces. The sample dimensions for this parallelepiped was $0.465\times0.531\times1.337$ mm parallel to the *a*, *b*, and *c* axis, respectively.[33] The resonant spectrum was then measured resulting in 11 frequencies in the range from 1 to 4 MHz. The sample density of 6.642 g/cm^3 was determined from the sample geometry and the sample mass of 2.193 mg, as measured by precision electrobalance. The experimental results for the complete elastic tensor of single crystal $GdScO_3$, utilizing the theoretically calculated elastic constants as the initial values for the inverse calculation, are shown in Table I. Six of the nine experimentally determined elastic constants differed from the theoretical values by 10% or less and if one takes into account all nine elastic constants, the average percent difference is about 10%.

In order to further characterize dynamic material properties, the knowledge of the acoustic wave propagation is required. This information can be extracted from the knowledge of the elastic constants and material density. The specific solution for orthorhombic crystal symmetry, which can have complicated wave propagation directions, can be found in the literature.[34] As an example of utilizing this information, the formulae for the longitudinal and transverse velocities, computed using the experimental elastic constants determined from the RUS measurement, are shown in Table II, along with experimental polycrystalline longitudinal and transverse sound speeds for comparison.[35]

In summary, the results in Table I are the experimental measurements of the complete elastic tensor of single crystal $GdScO_3$. The experimental results typically differ from theoretical values by less 10% for all but three of the nine elastic constants, thus, demonstrating the power of the RUS technique in combination with computational methods. Historically, the RUS technique for determination of the elastic tensor required external experimental information in order to guarantee the correct convergence to the unique elastic ten-

TABLE I. RUS experimental values for the orthorhombic elastic tensor of $GdScO_3$ along with theoretical calculated values.

	c_{11}	c_{22}	c_{33}	c_{44}	c_{55}	c_{66}	c_{23}	c_{12}	c_{13}
RUS (GPa)	294	297	248	103	100	75	123	163	91
Theory[a] (GPa)	296	318	238	103	79	82	126	130	113
Difference (%)	0.7	6.8	4.1	0.0	23	8.9	2.4	23	22

[a]Reference 30.

sor for a given material. With the evolution of *ab initio* computer algorithms and their ability to produce accurate initial values for the elastic constants, we have now approached the point where RUS calculations are sufficient as the sole experimental source for determination of the elastic tensor.

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