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Measurement of the elastic tensor of $SmScO_3$ and $NdScO_3$ using resonant ultrasound spectroscopy with ab initio calculations

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The complete elastic tensors of $SmScO_3$ and $NdScO_3$ were measured using resonant ultrasound spectroscopy (RUS) in combination with *ab-initio* calculations. Measurement of the elastic tensor of these recently synthesized single crystal RE scandates is essential for understanding dynamic lattice applications including phonon confinement, strain induced thin film growth and superlattice construction. On average, the experimental elastic constants differed by less than 5% of the theoretical values, further validating the accuracy of modern *ab-initio* calculations as a means of estimating the initial elastic constants used in RUS measurements. [doi:10.1063/1.3641248]

Rare-earth (RE) scandates possess high band gaps ($E_g \approx$ 5.75 eV),[1–4] high dielectric constants (K=20-40, depending on direction)[5] and thermal stability in contact with silicon.[6] Thus, these materials are suited for electronic applications including gate dielectrics and as an alternative to SiO_2 in silicon-based metal-oxide semiconductor field-effect transistors (MOSFETs).[4,7–9] RE scandates have been exploited as substrates to produce strain induced growth effects such as dramatically modified ferroelectric transitions in $BaTiO_3$ thin films[10,11] and thin film superlattices with unprecedented structural uniformity.[12] In similar oxide superlattices, phonon confinement has been demonstrated[13] with potential applications in acoustic lasers.[14] In all of these instances knowledge of elastic constants is essential. Thus, the complete elastic tensors of $SmScO_3$ and $NdScO_3$, which both exhibit orthorhombic crystal symmetry, were found using resonant ultrasound spectroscopy (RUS) with *ab-initio* calculations.

The material sample's elastic constants are determined using RUS by minimizing the least squares difference between the experimentally measured natural frequencies of a sample and a set of theoretically calculated frequencies.[15–21] The theoretical frequencies are calculated using the sample geometry, density and an assumed set of elastic constants. The assumed elastic constants are then iteratively adjusted in a computer program until the minimum between the two spectra is found thus recovering the true elastic constants. The RUS method requires at least as many experimentally measured frequencies as unknown elastic constants. Typically more than the minimum number of frequencies are used because not every frequency necessarily couples to all the unknown elastic constants. In order to ensure that adequate coupling exists between the measured frequencies, f_n, and the elastic constants, c_{ij}, the derivative, $\partial f_n / \partial c_{ij}$, are also calculated.

An essential component of the RUS method is reasonable starting values for the initial estimates of the elastic constant. Relatively recent improvements in *ab-initio* calculations used to produce theoretical elastic constants have enabled RUS to be utilized as the sole experimental source for determination of elastic constants.[22] For ab-initio calculations, the cell parameters of $NdScO_3$[23] and $SmScO_3$[24] were taken from corresponding crystal structure reports.[23,24] Accepting Nigglis a<b<c ranking of cell edges placed all five isostructural materials in a same Pbnm setting of space group Pnma (#62). The XYZ axes of the Cartesian reference system were then selected respectively along the xyz crystallographic axes of this Pbnm setting.

TABLE I. A comparison of the theoretical and RUS experimental elastic constants of $SmScO_3$ and $NdScO_3$.

$SmScO_3$	c_{11}	c_{22}	c_{33}	c_{44}	c_{55}	c_{66}	c_{23}	c_{12}	c_{13}
Experimental (GPa)	287.0	302.1	266.1	117.2	80.2	85.6	122.0	128.7	116.3
Theoretical (GPa)	284.7	299.5	248.1	100.9	81.5	83.7	122.7	133.3	115.4
% difference	0.81	0.87	7.00	14.93	1.59	2.29	0.54	3.45	0.78
$NdScO_3$	c_{11}	c_{22}	c_{33}	c_{44}	c_{55}	c_{66}	c_{23}	c_{12}	c_{13}
Experimental (GPa)	307.9	307	281.5	107.8	89.5	81.2	130.3	146.7	129.7
Theoretical (GPa)	297.9	296.9	282.5	102.1	85.8	86.6	128.7	148.9	128.2
% difference	3.31	3.34	0.34	5.38	4.23	6.41	1.24	1.52	1.16

A thorough *ab-initio* optimization of the atom coordinates in fixed cell parameters was then performed, followed by *ab-initio* calculation of elastic coefficients according to the symmetry-general scheme.[25]

Vienna *ab-initio* simulation package (VASP)[26,27] was used for all computations. All VASP input files were generated and interpreted by Materials Toolkit.[28] GGA PAW (Generalized gradient approximation, projector augmented wave) potentials[29] were used for all calculations. Wave functions were iteratively optimized with the Davidson blocked scheme[30] combined with reciprocal space projectors down to an electronic convergence of 1×10^{-7} eV. Reciprocal space integration was performed using a $5\times5\times5$ k-mesh and a Monkhorst-Pack scheme.[31] Energy corrections were implemented as Methfessel-Paxton smearing of order 1 and width 0.2 eV.[32] The convergence criterion for forces was 1×10^{-4} eV/Å. Spin polarization corrections were performed according to the scheme of Vosko, Wilk and Nusair 36 as implemented in VASP. The results for NdScO3 and SmScO3 are summarized in Table I.

The experimental resonant frequencies were determined using a Quasar RUSpec 4000. Polished rectangular parallelepiped samples were placed between two transducers while contact was maintained at body diagonal corners. One transducer received a signal from the function generator, which swept through a range of ultrasonic frequencies, and the sample's response was measured at the other transducer.

The samples used in this experiment were single crystals of $SmScO_3$ and $NdScO_3$, grown by the Czochralski method, which are available commercially via CrysTec GmbH.[33] The samples were cut and polished into rectangular parallelepipeds with the X, Y, and Z sample axes oriented perpendicular to the $(1\bar{1}0)$, (110), and (001) crystal planes, respectively. The standard RUS algorithm[18] uses the measured frequencies to determine the elastic tensor (c'_{ijkl}) defined relative to the sample coordinate system (X,Y,Z). Whereas the crystal elastic tensor (c_{ijkl}), which in this case is not aligned with the sample coordinate system, is defined with respect to the crystal axes (x,y,z). In order to recover the crystal elastic tensor using the standard RUS algorithm, the crystal coordinates were rotated into the sample coordinates via

$$c'_{ijkl} = R_{ip}R_{jq}R_{kr}R_{ls}c_{pqrs} \tag{1}$$

where $R_{ij}(\alpha, \beta, \gamma)$, is the rotation matrix and α, β and γ are the Euler angles.[21] For this experiment α=45°, β=0°, and γ=0°.

The experimentally measured sample dimensions and densities are shown in Table II. The number of frequencies used in the resonant spectrum fits were 17 and 18 for $SmScO_3$ and $NdScO_3$ respectively and ranged from 280 kHz to 1.6 MHz. A complete list of the experimental frequencies and the relative strength of their associated derivatives, which were used to ensure adequate coupling between the measured frequencies and the unknown elastic properties, can be found in the supplemental document.[34] The complete elastic tensors (all nine experimentally determined elastic constants for each sample) are given in Table I.

In summary, the results shown in Table I illustrate the robust nature of the RUS method in combination with modern *ab-initio* calculations. On average, the experimental elastic constants differed by less than 5% of the theoretical values. These findings further confirm the accuracy of

TABLE II. Sample dimensions and density.

Sample dimensions (mm)	X	Y	Z
$SmScO_3$ ($\rho = 6325 kg/m^3$)	0.508 mm	2.651 mm	2.179 mm
$NdScO_3$ ($\rho = 5987 kg/m^3$)	0.517 mm	2.716 mm	2.448 mm

Materials Toolkit as a means of determining elastic constants,[28] and the capability of the RUS method for accurately determining elastic constants without prior external experimental information.

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[34] See supplementary material at http://dx.doi.org/10.1063/1.3641248 for Resonant Spectral Fits of SmScO3, NdScO3 and Associated Derivative Tables.