Acoustic Phonon Spectrum Engineering in Bulk Crystals via Incorporation of Dopant Atoms

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Abstract

We report results of Brillouin – Mandelstam spectroscopy of transparent Al2O3 crystals with Nd dopants. The ionic radius and atomic mass of Nd atoms are distinctively different from those of the host Al atoms. Our results show that even a small concentration of Nd atoms incorporated into the Al2O3 samples produces a profound change in the acoustic phonon spectrum. The velocity of the transverse acoustic phonons decreases by ~600 m/s at the Nd density of only ~0.1 %. Interestingly, the decrease in the phonon frequency and velocity with the doping concentration is non-monotonic. The obtained results, demonstrating that modification of the acoustic phonon spectrum can be achieved not only by nanostructuring but also by doping have important implications for thermal management as well as thermoelectric and optoelectronic devices.

Keywords: Brillouin spectroscopy; phonons and phonon engineering; thermal conductivity

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Acoustic phonons make a dominant contribution to thermal transport in electrical insulators and semiconductors and, at the same time, scatter electrons and holes, limiting the mobility of the charge carriers\(^1\). Recent years have witnessed a strong increase of interest to the methods of controlling acoustic phonon transport and scattering by tuning the phonon spectrum, \textit{i.e.} dispersion relation, \(\omega(q)\) (here \(\omega\) is the phonon frequency and \(q\) is the phonon wave vector)\(^2,3\). A possibility of engineering the phonon spectrum provides an additional tuning capability for changing thermal conductivity over the conventional approach, which involves phonon – boundary scattering\(^4–7\). It also allows one to affect the way phonons interact with electrons and light. Until now, the \textit{phonon engineering} approach has been associated with the nanostructured materials, where the phonon dispersion undergoes modification due to the periodic or stationary boundary conditions imposed in addition to the periodicity of the atomic crystal structure\(^4–11\). In this method, nanometer scale dimensions are essential in order to reveal the wave nature of the phonons and induce modification in their spectrum via boundaries\(^12–14\). The average “gray” phonon mean free path (MFP), \(\Lambda\), determined from the expression \(\Lambda=3K/C_p\nu\) is on the order of 10 nm – 100 nm at room temperature (RT) for many materials\(^15\) (here \(K\) is the phonon thermal conductivity, \(C_p\) is the specific heat and \(\nu\) is the phonon group velocity). The latter estimates explain the need for structuring the material and nanometer scale. A strong modification of the acoustic phonon dispersion has been demonstrated in numerous periodic phononic crystals\(^8–11\) and even in individual semiconductor nanowires\(^16\).

In this Letter, we describe a drastically different approach for changing the acoustic phonon spectrum of the materials, which does not rely on nanostructuring. Our results show that one can engineer the phonon spectrum in bulk crystals via introduction of a small concentration of dopant atoms that have a substantially different size and mass from those of the host atoms. The importance of the obtained data goes beyond the developments of the traditional phonon engineering approaches. A noticeable decrease in the phonon velocity with even extremely small concentration of foreign atoms (~0.1 %) means that the theoretical description of thermal conductivity, at least in certain cases, \textit{e.g.} large size or mass difference of dopant atoms, should be adjusted accordingly. Indeed, in the Callaway – Klemens method, and other Boltzmann transport equation approaches, the effects of doping are accounted for by introduction of the phonon – point
defect scattering term proportional to the defect density concentration, or fraction of the foreign atoms\textsuperscript{17,18}. This treatment always assumes that the velocity of acoustic phonons itself does not change with the doping. Our results demonstrate that the latter is not always the case.

Commercially available Al\textsubscript{2}O\textsubscript{3} (99.99% purity, Taimei Chemicals, Japan) was processed using current activated pressure assisted densification (CAPAD)\textsuperscript{19} using a similar method described in \textsuperscript{20}. Briefly, the as received (un-doped) and Nd\textsubscript{2}O\textsubscript{3} doped (99.99% purity, Alfa Aesar, USA) powders were mixed to achieve a doping level (Nd\textsuperscript{3+: Al\textsuperscript{3+}) of 0.1-0.5 at.\%. using water and low energy ball milling, followed by planetary ball milling before densification in CAPAD. X-ray diffraction was taken on a Phillips instrument (X'Pert Model: DY1145), operating in the point source mode, 45 kV potential and 40 mA current was taken on a with a 0.002 step size and 4 s integration time. The experimental data were fitted using Gaussian profiles, with the K-\(\alpha_2\) contribution removed numerically.

Figure 1a is an SEM (Zeiss Sigma 500) micrograph of a fracture surface of the polycrystalline 0.25 Nd: Al\textsubscript{2}O\textsubscript{3} revealing \textasciitilde300 nm equiaxed grain structure. The inset in Figure 1a shows a picture of a representative sample on top of printed text. Our samples are transparent because samples with <0.4 at\% Nd do not have second phases and they have low Nd segregation to grain boundaries and grain triple points. Other phases and segregation or both would scatter light because of refractive index mismatch, significantly reducing transparency. Figure 1b are XRD patterns near the (113) plane of the Al\textsubscript{2}O\textsubscript{3} and Nd: Al\textsubscript{2}O\textsubscript{3} samples. Also plotted is an ICSD standard (#63647) for comparison. The pure Al\textsubscript{2}O\textsubscript{3} shows a peak at the same 2\(\theta\) location as the standard confirming the crystal structure, while the doped samples show a clear peak shift to lower angles, indicating an expansion of the lattice which is expected from the Nd doping since the radius of Nd atoms is significantly larger than Al.

[Figure 1: Samples]
The structure of the samples was also confirmed by Raman spectroscopy (Renishaw InVia). The measurements have been conducted in the backscattering configuration under 488 nm excitation. Figure 2 shows the Raman spectra of pristine Al₂O₃ and samples with 0.1 % and 0.25% of Nd dopants. We resolved seven distinct optical phonon peaks at 379.0, 418.6, 430.7, 447.1, 576.9, 645.8 and 751.0 cm⁻¹. The Raman spectrum is in excellent agreement with the previously reported studies²¹–²³. The peaks at 418.6 cm⁻¹ and 645.8 cm⁻¹ belong to A₁g vibrational modes while the others are associated with E_g vibrational bands. The relative intensity of these phonon modes varies in accordance with the crystallographic directions. It is important to note that all optical phonon modes, with exception of one at 430.7 cm⁻¹, show some softening with introduction of Nd doping atoms. This is in line with the XRD measurements, which indicated the shift of the ~43.4° peak to smaller angles, suggesting some distortion in the lattice due to Nd incorporation. The implications of this observation from the Raman and XRD studies will be discussed below.

![Figure 2: Raman](image)

The Brillouin-Mandelstam light scattering spectroscopy (BMS) allows one to directly probe the acoustic phonon frequencies close to the Brillouin zone (BZ) center²⁴–²⁶. We conducted BMS studies in the backscattering configuration. In this geometry, the p-polarized (the electric field direction of the light parallel to the scattering plane) laser light is focused on the sample by a lens with a numerical aperture of 1.4. The scattered light was collected using the same lens and directed to the high contrast six pass tandem Fabry-Perot interferometer. The spectra were excited with the solid-state diode-pumped laser (Coherent) operating at λ=532 nm²⁷,²⁸. In all experiments, the power on the sample was adjusted to be 70 mW in order to avoid self-heating effects. The incident angle of the laser light with respect to the normal to the sample was fixed at 30°. The in-plane rotation did not affect the BMS results due to the polycrystalline structure of the samples. For each sample, the BMS measurements were repeated several times (>5) by focusing light on different spots, in order to exclude a possibility of material parameters variations over the sample volume. In transparent bulk Al₂O₃ samples the volumetric elasto-optic effect is the dominant light scattering mechanism by acoustic phonons²⁴–²⁶. For this reason, interpretation of BMS data requires a
knowledge of the refractive index, $n$, of the material. The refractive index was measured by the “prism coupling” method (Metricon)\textsuperscript{29}. The measurements revealed $n=1.767$ (at $\lambda=532$ nm) in all directions confirming the optically isotropic nature of all the samples. Since the concentration of the $Nd$ dopants is very low (<0.5 wt%), the Maxwell – Garnett approximation, $n = (1 - \phi) n_m^2 + \phi n_o^2 \left( \frac{1}{n_m} + \frac{1}{n_o} \right)$ ($n_m$ and $n_o$ are the refractive indices of Al₂O₃ and $Nd$, respectively) described the trivial variation in $n$ with high accuracy. The probe phonon wave vector, $q = \frac{\pi}{\lambda}$, for the elasto-optic scattering mechanism was determined to be $q=0.0417$ nm\textsuperscript{-1} in our samples.

Figure 3 shows BMS data for Al₂O₃ with and without $Nd$ dopants. One can see in Figure 3 (a) that three peaks corresponding to one longitudinal (LA) and two transverse (TA\textsubscript{1} and TA\textsubscript{2}) acoustic phonon polarization branches are resolved. The peaks have been fitted and deconvoluted, when required, with individual Lorentzian functions (green curves). The red curve in Figure 3 (a) is the cumulative fitting to the experimental data. For alumina, the LA and two TA peaks were found at 73.0, 45.6 and 41.3 GHz, respectively. Adding the $Nd$ dopants resulted in an unexpected large decrease in the frequency of all three acoustic phonon peaks. Figure 3 (b) shows the evolution of the LA and TA phonon polarization branches in Al₂O₃ as the concentration of $Nd$ dopants increases from 0 to 0.50 %. Incorporation of $Nd$ dopants results in pronounced decrease of the intensity of the phonon peaks and reduction in their frequency. The decrease in the intensity, which was also observed in Raman spectra (see Figure 2) was attributed to the increase in the light absorption (especially at $Nd$ concentration ≥0.4), and corresponding decrease in the interaction volume for BMS. While the intense LA peak was persistent at all $Nd$ concentrations, the TA peaks could not be resolved in the sample with 0.50% of $Nd$ atoms.

Figure 4 (a-c) shows the variation of the peak position of LA and TA phonons with $Nd$ concentration. The frequency mean value and standard deviation have been determined from measurements on different spots of each samples. The results show a surprising sharp decrease in
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Elasticity theory relates the phonon velocity to material properties as 
\[ v = \left( \frac{E}{\rho} \right)^{1/2} \]
where \( E \) is the Young’s modulus and \( \rho \) is the mass density. Since the concentration of \( Nd \) is extremely small one would expect equally small changes due to the mass density variation. The probable scenario is that the introduction of \( Nd \) dopants changes the elastic properties of the lattice. The atomic mass difference, although large between \( Al \) and \( Nd \) (factor of \( \times 5 \)) is unlikely to change the frequency of vibrations, again due to the small concentration of dopants. A possible mechanism can be related to the lattice distortion created by larger \( Nd \) atoms (factor of \( \times 2 \) bigger than \( Al \)), which is accompanied by increased atomic plane separation, in line with Raman and XRD data. This can also account for the observed abrupt decrease at the smallest concentration of \( Nd \) (0.1%) followed by a weaker dependence at higher \( Nd \) concentrations. The smaller further reduction, as the concentration continues to increase, could be due to various effects, e.g., dopant clustering in the crystal volume or at grain boundaries. At substantially higher densities of the dopant atoms one can expect the modification in the phonon spectrum due to the changes in the atomic mass and interaction constants between the atoms. Complete understanding of the mechanism of the phonon
frequency change requires detailed microscopic studies and ab initio theory, which goes beyond the scope of this work.

It is interesting to assess implications of the phonon velocity reduction for thermal transport and phonon interaction with other elemental excitations. The phonon thermal conductivity can be written as $K = (1/3)Cu\Lambda = (1/3)Cu^2\tau$, where the phonon life-time, $\tau$, can be expressed through the phonon scattering rates in two main relaxation mechanisms: anharmonic phonon Umklapp scattering and phonon – point defect scattering so that $1/\tau = \tau_U^{-1} + \tau_p^{-1}$, where $\tau_U^{-1}$ and $\tau_p^{-1}$ are scattering rates in the Umklapp and point defect processes, respectively. The phonon scattering rate on point defects, $1/\tau_p \propto V_0(\omega/\nu)^{3}\Gamma$, where $V_0$ is the volume per one atom in the crystal lattice, $\omega$ is the phonon frequency and $\Gamma$ is the strength of the phonon - point defect scattering, which depends on the fraction of the foreign atoms. In the perturbation theory $\Gamma$ is written as\textsuperscript{17,18}

$$\Gamma = \sum_i f_i \left[ (1 - M_i / \bar{M})^2 + \varepsilon (1 - R_i / \bar{R})^2 \right]$$

Here $f_i$ is the fractional concentration of the substitutional foreign atoms, $M_i$ is the mass of the $i$th substitutional atom, $\bar{M} = \sum_i f_i M_i$ is the average atomic mass, $R_i$ is the Pauling ionic radius of the $i$th foreign atom, $\bar{R} = \sum_i f_i R_i$ is the average radius, $\gamma$ is the Grüneisen parameter, and $\varepsilon$ is a phenomenological parameter. One can see from these formulas that the effect of dopants on thermal conductivity is accounted via $\tau_p^{-1}$ term: it is proportional to the concentration, and it grows with the increasing difference in the atomic radius and mass between the host the foreign atoms. Conventional theory does not consider any variation in the phonon velocity and assumes that $\nu$ remains unchanged after the doping\textsuperscript{17,18,30,31}. Our results show that in alumina, and presumably in other rather common materials, and at very small concentration of dopants the assumption of the constant phonon velocity is not strictly valid. The effect of dopant introduction can be amplified via the velocity change and affect the thermal conductivity values, particularly at low temperature where Umklapp scattering is minimal. The effects of the phonon velocity reduction are not limited
heat conduction. They can also reveal themselves in electron – acoustic phonon scattering, electron – photon interaction, which involve phonons, and electron – hole non-radiative recombination. Examples of the latter include phonon-assisted non-radiative recombination in the Auger processes, where electron – acoustic phonon coupling is inversely proportional to the phonon group velocity\(^3\),\(^3\). We should emphasize again that the observed effect is different from the phonon spectrum modification in materials with the large concentration of defects, or isotope engineered bulk crystals or two-dimensional materials, where the entire vibrational spectrum changes due to the replacement of atoms with different masses\(^3\)\(^4\)\(^5\). It is also different from the lattice softening observed in some alloys\(^4\). In our case, the changes are related to the host lattice distortion induced by introduction of a small concentration of dopants with substantially different size or mass.

In summary, we observed that the velocity of acoustic phonons can be changed by even a small concentration of dopants with distinctively different atomic size and mass. The obtained results, demonstrating a possibility of phonon engineering in bulk crystals have important implications for thermal management as well as thermoelectric and optoelectronic devices.

**Acknowledgements**

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FIGURE CAPTIONS

**Figure 1:** (a) SEM micrograph of a fracture surface of the polycrystalline 0.25 at% Nd: Al₂O₃ revealing ~300 nm equiaxed grain structure. The scale bar is 200 nm. The inset shows a picture of a representative sample on top of printed text, revealing optical transparency (b) XRD patterns near the (113) plane of the Al₂O₃ and Nd: Al₂O₃ samples. Also plotted is an ICSD standard (#63647) for comparison.

**Figure 2:** Raman spectrum of the Al₂O₃, 0.10 at% Nd: Al₂O₃ and 0.25 at% Nd: Al₂O₃. As the amount of Nd density increases, the Raman peaks except the one at ~430 cm⁻¹ shift to the lower wave numbers. The relative intensity as well as peak position of the Raman peaks confirm the composition, quality and polycrystalline structure of the samples.

**Figure 3:** (a) Brillouin-Mandelstam scattering spectra for the pure Al₂O₃ and 0.35 at% Nd: Al₂O₃. The experimental data (black curve) has been fitted using individual (green curve) and cumulative (red curve) Lorentzian fittings. The regular longitudinal (LA) and transverse (TA) acoustic phonons are present in both spectra (b) Evolution of the spectrum with increasing the Nd doping level. Note the decrease in frequency of LA and TA phonons of pure Al₂O₃ with increasing the Nd density to 0.1% and more.

**Figure 4:** Peak position of LA and TA phonon polarization branches in Brillouin spectra versus Nd density. The frequency of LA and both TA phonon branches decreases with increasing Nd concentration non-monotonically. Note that even the smallest 0.1 at% concentration of Nd results in a noticeable decrease of the phonon frequency, and, correspondingly, group velocity.
### Table I: Phonon group velocity in Al₂O₃ for different Nd doping concentration

<table>
<thead>
<tr>
<th>Sample</th>
<th>TA Group Velocity (m/s)</th>
<th>TA Group Velocity (m/s)</th>
<th>LA Group Velocity (m/s)</th>
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<tr>
<td>Al₂O₃</td>
<td>6269.0</td>
<td>6864.8</td>
<td>11012.7</td>
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<td>5670.0</td>
<td>6311.7</td>
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<tr>
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<td>0.50 at% Nd:Al₂O₃</td>
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<td>-</td>
<td>10802.6</td>
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