Far infrared properties of the rare-earth scandate DyScO₃

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Abstract
We present reflectance measurements in the infrared region on a single crystal the rare-earth scandate DyScO₃. Measurements performed between room temperature and 10 K allow us to determine the frequency of the infrared-active phonons, never investigated experimentally, and to get information on their temperature dependence. A comparison with the phonon peak frequency resulting from \textit{ab initio} computations is also provided. We finally report detailed data on the frequency dependence of the complex refractive index of DyScO₃ in the terahertz region, which is important in the analysis of terahertz measurements on thin films deposited on DyScO₃.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

DyScO₃, together with other rare-earth scandates (RScO₃), has recently received considerable attention, since it is considered to be among the best substrates for the epitaxial growth of high-quality ABO₃ perovskite-type thin films [1]. On such thin films it is possible to induce ferroelectric and multiferroic properties tailoring their lattice constants by changing R in RScO₃. For example, SrTiO₃ exhibits strain-induced ferroelectricity if grown on a RScO₃ substrate [2]. Furthermore, scandates are considered to be some of the most promising candidates to substitute SiO₂ as the gate dielectric in MOSFET, thanks to the high value of their static dielectric constant \(\varepsilon_0\) [3]. SrTiO₃/DyScO₃ heterostructures are also widely used for applications in the terahertz (THz) range [4].

We remark that scandates are increasingly used as substrates for film growth and that the optical investigation of a film often allows basic studies which can be difficult when only small size single crystals are available. In particular, the large and flat surface of a film permits accurate optical measurements in the far-IR and THz regions, which have an important role in studying superconducting films [5]. When the radiation penetration depth is larger than the film thickness the optical response of the substrate affects the measured far-IR/THz spectrum, and the complex dielectric function \(\tilde{\varepsilon}(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)\) of the film material cannot be obtained through Kramers–Kronig (KK) transformations. In this case more elaborate procedures [6, 7] must be used to extract the \(\tilde{\varepsilon}(\omega)\) of the film from the reflectance or transmittance data, which require the knowledge of the substrate complex refractive index \(\tilde{n}(\omega) = n(\omega) + ik(\omega)\). While the far-infrared properties of common perovskites-like substrates such as SrTiO₃ and LaAlO₃ are well known [8–10], no far-IR data are available in the DyScO₃ case. For this system, theoretical calculations of the phonon modes have been reported [3], which could be compared only with data from recent Raman investigations [11, 12].

Moreover, both infrared (IR) and Raman spectroscopy are of interest in investigating the structural properties of oxide materials with the perovskite structure, since the study of the optical phonons can provide direct information on even subtle structural distortions of the ideal perovskite structure.

We have performed reflectance measurements in the IR region on a DyScO₃ single crystal, at a number of temperatures in the 10–300 K range. The infrared-active phonons of DyScO₃ have been investigated for the first time, allowing a direct comparison with the results of the \textit{ab initio} calculations [3]. Moreover the frequency and temperature dependence of the
2. Experimental details and results

Reflectance measurements were performed at near-normal incidence on the 110 surface of a DyScO3 (DSO) single crystal. The sample was glued with silver paint, to ensure thermal contact, on an optically black cone [13] mounted on the end of a Helitran cryostat’s coldfinger. The cone was aligned, with the use of three tilting screws, so to have the sample surface perpendicular to the incident radiation. By employing a home-built reflectivity unit, measurements were performed over a broad energy range (50–12 000 cm\(^{-1}\)) with a Michelson interferometer at a spectral resolution of 2 cm\(^{-1}\).

To obtain the absolute value of the reflectivity \(R(\omega)\) we employed the overfilling technique [13]. A metallic film of Au is deposited in situ on the sample surface and used as reference. This allows us not only to prevent thermal misalignment but also to take into account any effect of diffraction due to the sample size or diffusion if the sample surface is not mirror-like.

The optical reflectivity \(R(\omega)\) is plotted up to 800 cm\(^{-1}\) in figure 1 at various temperatures. Several phonon lines, which show a weak temperature dependence, can be observed in this spectral region. At higher frequencies \(R(\omega)\), in agreement with the insulating properties of the DyScO3 crystal, is nearly flat and constant at a value of about 0.1 up to the highest measured frequency (see figure 2).

3. Analysis and discussion

DyScO3 has an orthorhombically distorted perovskite structure with space group \(Pnma\) with a 20-atom primitive cell. Therefore, one expects, as in the isostructural LaMnO3 manganite [14–17], 60 phonons, among which 24 are Raman active (corresponding to the irreducible representations 7\(A_g\), 5\(B_{1g}\), 7\(B_{2g}\), 5\(B_{3g}\)), 25 are infrared-active (9\(B_{1u}\), 7\(B_{2u}\), 9\(B_{3u}\)), eight silent (8\(A_u\)), and three acoustic (\(B_{1u}\), \(B_{2u}\), \(B_{3u}\)). By measuring the reflectance on the 110 surface, we should detect all the \(B_{1u}\) modes [11, 14–16] corresponding to the dipole moment oscillating along \(z\), where the orthorhombic axis \(z\) is defined as \(z = [001]\) (see [11] for more details), and a linear combination of the \(B_{2u}\) and \(B_{3u}\) corresponding to the dipole oscillating along \(y\) and \(x\), respectively [15].

In order to perform the KK analysis [6], we first performed a Lorentz fit on \(R(\omega)\) so to extrapolate its behavior as \(\omega \to 0\). We have fitted the low-frequency part of \(R(\omega)\) (i.e. below 400 cm\(^{-1}\)) in order to obtain a careful description in the terahertz region. This procedure resulted in a convincing extrapolation of the experimental data down to zero frequency and in reliable results in the far-IR once the KK transformations are performed. We remark that data have been collected up to 12 000 cm\(^{-1}\), so to avoid problems in the KK procedure due to the high-frequency extrapolation of the spectra. The resulting \(\epsilon_2(\omega)\) are reported in figure 3 for frequencies below 600 cm\(^{-1}\) at selected temperatures.

At 10 K, 19 of the expected 25 IR-active modes are clearly visible in the spectrum. As in the case of the isostructural LaMnO3 system, the three phonon modes (external, bending, and stretching modes) proper of the cubic perovskite structure [18] are split in several phonons because of the orthorhombic distortion. The low-frequency phonon modes originate from the external mode, i.e. are due to vibrations of the Dy-cation sublattice with respect to the network of ScO\(_6\) octahedra. The high-frequency phonons originate from the stretching mode of oxygens in the ScO\(_6\) octahedra, the phonons at intermediate frequencies from the bending mode. However, due to the strong orthorhombic lattice distortions, none of the modes can be classified as purely bending or as purely
stretches as these modes imply considerable changes of both the bond angles and bond lengths in the ScO 6 octahedra [15]. In the vibrational spectra we distinguish one phonon mode around 100 cm$^{-1}$ and one around 115 cm$^{-1}$. These frequencies are close to those predicted by ab initio calculations for B$_3u$ and B$_1u$ modes, respectively. Their dipole moment is due to vibrations of the -cation sublattice with respect to the ScO$_6$ octahedral network, are those with higher intensity. This finding supports the theoretical prediction [3] that in DyScO$_3$ the high value of the static dielectric constant $\epsilon_0$, i.e. $\epsilon(\omega \rightarrow 0)$, is associated with low-frequency ionic vibrations. On the basis of the employed procedure, $\epsilon_0$ is given by $\epsilon_0 = \sum J_j$ (see equation (1)). Since the fitting procedure provides the $A_j$ value for each mode (as reported in table 1), we find that the phononic contribution to $\epsilon_0$, i.e. $\sum J_j A_j$ is large, of about 21, mainly due to the phonon mode at 135 cm$^{-1}$. Moreover we expected and in good agreement with the behavior found in [12] at higher temperatures. A closer inspection of data shows that the broad peak, visible at 300 K just below 200 cm$^{-1}$ is due to two different phonon modes at 190 and at 199 cm$^{-1}$ (see table 1). The apparent splitting of this peak is due to the softening of the more intense mode (at 190 cm$^{-1}$) to 185 cm$^{-1}$ and the simultaneous hardening of the second mode. Some other weak modes also show a light softening by decreasing $T$ as reported in table 1. This softening might correspond to subtle lattice modifications (still within the Pnma crystal structure) as $T$ decreases. To the best of our knowledge, the $T$-behavior of the DyScO$_3$ lattice parameters has been investigated between 298 and 1273 K, that is the temperature range of interest for perovskite thin film growth [19], while no data exist at lower temperatures. Therefore one cannot link unambiguously the modifications in the IR-active phonon response to a structural rearrangement.

It is important to notice that the low-frequency modes, due to vibrations of the R-cation sublattice with respect to the ScO$_6$ octahedral network, are those with higher intensity. This finding supports the theoretical prediction [3] that in DyScO$_3$ the high value of the static dielectric constant $\epsilon_0$, i.e. $\epsilon(\omega \rightarrow 0)$, is associated with low-frequency ionic vibrations. On the basis of the employed procedure, $\epsilon_0$ is given by $\epsilon_0 = \sum J_j A_j$ (see equation (1)). Since the fitting procedure provides the $A_j$ value for each mode (as reported in table 1), we find that the phononic contribution to $\epsilon_0$, i.e. $\sum J_j A_j$ is large, of about 21, mainly due to the phonon mode at 135 cm$^{-1}$. Moreover we

![Figure 3. Imaginary part $\epsilon_2(\omega)$ of the complex dielectric function of DyScO$_3$. Data are shown at a number of temperatures and shifted for sake of clarity. At 10 and 300 K both data and Lorentz fitting are reported.](image)

| $\omega$ (cm$^{-1}$) | $\omega$ (cm$^{-1}$) | $A_j$ | $\omega$ (cm$^{-1}$) |
|-------------------|-------------------|------|-------------------|
| 300 K             | 10 K              | 10 K | Ref. [3]          |
| 101               | 104               | 0.52 | 97.9              |
| 113               | 117               | 0.96 | 111.0             |
| 131               | 135               | 15.35| 129.4             |
| 160               | 159               | 1.12 | 173.7             |
| 190               | 185               | 0.37 | 193.3             |
| 199               | 205               | 1.14 | 197.0             |
| 256               | 257               | 0.85 | 278.8             |
| 295               | 298               | 2.53 | 293.9             |
| 306               | 309               | 0.69 | 328.8             |
| 344               | 332               | 0.04 | 334.4             |
| 346               | 344               | 0.14 | 336.4             |
| 354               | 358               | 0.23 | 356.7             |
| 371               | 367               | 0.44 | 368.6             |
| 381               | 385               | 1.51 | 369.5             |
| 434               | 436               | 0.35 | 435.5             |
| 434               | 436               | 0.35 | 445.3             |
| 484               | 482               | 0.03 | 484.8             |
| 501               | 503               | 0.12 | 509.7             |
| 539               | 544               | 0.07 | 532.6             |
| 570               | 570               | 0.01 | —                 |
find a total static dielectric constant $\varepsilon_0 \approx 25$, as the sum of $\varepsilon_\infty \approx 4$ and the phononic contribution, in excellent agreement with theory [3] and experiments on single crystals [2].

Finally we report in figure 4 the frequency dependence of the complex refractive index $\tilde{n} = n + ik$ in the terahertz region as directly obtained from $\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2$. Below 100 cm$^{-1}$ $n$ is nearly flat reaching a value of about 5 for $\omega \to 0$, while the vanishingly small $k$ value indicates the absence of an appreciable absorption in the same spectral region.

The $n$ and $k$ data at 10 K have been recently employed in the analysis of the terahertz measurements performed on a film [20], grown on a DSO substrate [21], of the BaFe$_{1.84}$Co$_{0.16}$As$_2$ compound, that belongs to the class of the new Fe-based superconductors which attracted strong attention since their recent discovery [22].

4. Conclusions

We have presented here the first experimental data on the IR phonon spectrum of the rare-earth scandate DyScO$_3$. In the temperature range between 10 and 300 K no dramatic changes occur in the phonon response indicating that the $Pnma$ structure is stable down to the lowest measured temperature. The overall agreement with the recent $ab$ initio calculations is to be considered satisfactory. We finally note that the present work can provide reference data and extrinsic peak selection for future infrared investigations of thin films grown on DyScO$_3$ substrates.

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