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Temperature-dependent polarized far-infrared optical properties of $CaNdAlO_4$ single crystal

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ABSTRACT

Polarized near-normal incident infrared reflectivity spectra of (1 0 0) $CaNdAlO_4$ single crystal along the *ab* plane and *c*-axis have been measured under different temperatures in the frequency region between 100 and 6000 cm^{-1}. All the spectra are fitted with the factorized form of the dielectric function. Assignment of different phonon modes has been done in both crystalline directions. The dielectric property and optical conductivity of the $CaNdAlO_4$ crystal are analyzed. The differences between $CaNbAlO_4$ and $SrLaAlO_4$ are discussed with respect to vibration frequency and static optical permittivities.

1. Introduction

Good substrate materials for epitaxial deposition of high-T_c superconductor (HTSC) thin films must satisfy the requirements for an ideal insulating substrate; namely, lattice matched, chemically compatible, thermal expansion matched and undergoing no structural phase transition between the film growth temperature and the device operation temperature. Several perovskite-type single crystals, such as $SrTiO_3$ [1], $KTaO_3$ [2], $LaGaO_3$ [3], and $LaAlO_3$ [4], have been demonstrated to be excellent substrates for epitaxial growth of HTSC thin films. Unfortunately, some of them have high dielectric loss and large dielectric constant, or exhibit unacceptably large absorptions at submillimeter-wave frequencies [5], which eliminate them as substrate candidates for microwave applications. In the meantime, yttrium-stabilized zirconia also exhibits high dielectric loss, and MgO, while having reasonable electric properties, is chemically unstable and easily cleaves. To solve this problem, attempts have been made by using single crystals which have improved dielectric properties such as low dielectric loss and reasonable cryogenic dielectric constants. Due to its chemical stability, low dielectric loss and small lattice mismatch with the HTSCs, the rare-earth neodymium calcium aluminate $CaNdAlO_4$ (CNAO) was found to be an excellent choice as the substrate material for the epitaxial growth of HTSC thin films suitable for microwave and far-infrared applications [6–9]. It may also be used as a laser-active material because it is chemically stable and hard.

$CaNdAlO_4$ belongs to the group of $ABCO_4$ type compounds, where A = Sr, Ca; B = La, Nd; and C = Al, Ga, or a mixture thereof. It crystallizes in a tetragonal structure of the K_2NiF_4 type (space group $I4/mmm\text{-}D_{4h}^{17}$) with lattice constants $a = b = 3.685$ Å and $c = 12.12$ Å. The elementary cell of CNAO crystal similar to $SrLaAlO_4$ (SLAO) is shown in Fig. 1 [10]. The crystal is built up along the *c*-axis. The Al ions occupy the centers of the oxygen octahedra, which form a two-dimensional net of corner-shared oxygen. The Ca and Nd ions are statistically located between the octahedrons on nine-coordinated sites of C_{4v} symmetry, forming a rock salt structure with the apex oxygen.

The structure, thermal and dielectric properties of CNAO have been investigated by different groups [11–13]. It is of great interest to explore its infrared properties and determine its dielectric function in order to facilitate its utilization as a substrate for the growth of high-temperature superconductors. Moreover, there has rarely been any report on its temperature-dependent optical responses, which is also important from the viewpoint of being a substrate for devices operating at low temperatures. In this paper, we study the polar phonons by means of infrared spectroscopy and extract the transverse and

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longitudinal phonon parameters for different orientations at different temperatures. Optical properties related to the phonon vibrations are being discussed.

2. Experiment

Single crystal of $CaNdAlO_4$ was grown by Hefei Kejing Materials Technology Co. Ltd. with the Czochralski growth method. A rectangular piece ($10 \times 10 \times 0.5\,mm^3$) of single crystal $CaNdAlO_4$ was cut and one-side polished with the surface parallel to the (1 0 0) plane. Near-normal incident measurements (with the incident angle about 8°) were performed with the electric field along and perpendicular to the crystallographic *c*-axis. All the reflectivity spectra were taken on a BOMEM DA8 FT-IR spectrometer in the range of 100–6000 cm^{-1} with a resolution of 4 cm^{-1}. The sample was mounted in an optical cryostat in vacuum and the temperature was varied from 300 down to 10 K with an accuracy of 0.02 K. A DTGS detector was utilized in the far-infrared range of 100–700 cm^{-1}, and a liquid-nitrogen cooled mercury cadmium telluride detector was employed in the mid-infrared range of 450–6000 cm^{-1}. To obtain the absolute reflectivity, an evaporated golden mirror was served as a reference.

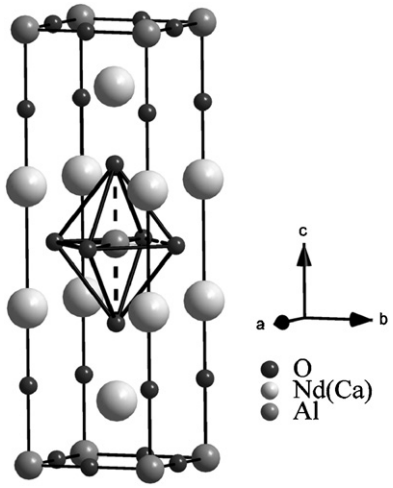

Fig. 1. The elementary cell of $CaNdAlO_4$ single crystal. Al atoms sit at the center of the octahedral.

3. Results and discussion

Shown in Fig. 2(a) and (b) are the reflectivity spectra of $CaNdAlO_4$ single crystals with the electric field along and perpendicular to the crystallographic *c*-axis at temperatures from 300 down to 10 K, respectively. The reflectivity of the $CaNdAlO_4$ single crystal is typical of an insulator. The sharp features in the reflectivity at low frequency are due to the unscreened infrared-active optical phonon modes, while above the highest observed lattice vibration frequency the reflectance is flat and featureless up to the highest measured frequency. In the spectra with polarization $E \| a$, three modes located at about 233, 512 and 765 cm^{-1} can be easily identified at all temperatures. The two lowest frequency modes show splitting into doublets, probably due to a slight orthorhombic distortion of the lattice. The doublets become more evident upon decreasing the temperature. In the $E \| c$ spectra, which are quite different from those of $E \| a$, four phonon modes are always observed at all temperatures. In both $E \| a$ and $E \| c$ spectra, it can be seen that the reflectivity within the reststrahlen bands at low frequency is almost unchanged. Only the highest frequency mode increases slightly with decreasing temperature. It is probably due to the fact that anharmonic thermal motion would weaken with decreasing T so that the oscillation strength of the modes increases. In the following, detailed discussion on the assignment for these vibrational modes will be made.

The mode frequencies are obtained from a damped harmonic oscillator fit of reflectivity spectra with a complex dielectric function $\varepsilon(\omega)$ in the factorized form (generalized Lyddane–Sachs–Teller relation) [14–18]:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = \varepsilon_\infty \prod_j^N \frac{\omega_{jLO}^2 - \omega^2 + i\omega\gamma_{jLO}}{\omega_{jTO}^2 - \omega^2 + i\omega\gamma_{jTO}}, \quad (1)$$

where ε_∞ denotes high-frequency dielectric constant, ω_{jTO} and ω_{jLO} are the transverse and longitudinal eigenfrequencies of the *j*th optical phonon mode, and γ_{jTO} and γ_{jLO} their transverse and longitudinal damping constants. Using this dielectric function, all the reflectivity spectra in our measurements are fitted with the well-known Fresnel formula,

$$R(\omega) = \left| \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \right|^2. \quad (2)$$

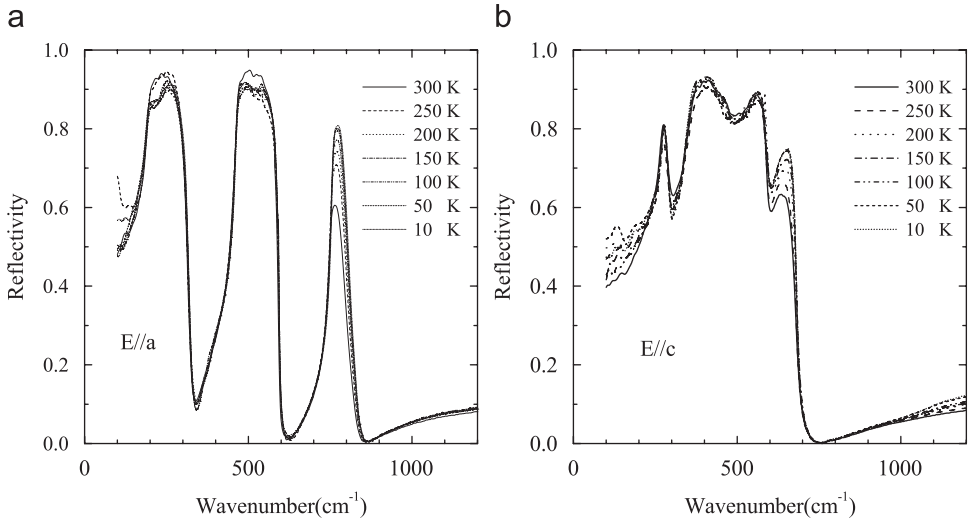

Fig. 2. Experimental FIR reflectivity spectra of $CaNdAlO_4$ crystal at various temperatures for the two polarized orientations. (a) $E \| ab$ plane; (b) $E \| c$.