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Infrared optical properties of perovskite substrates for high-T_c superconducting films

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Perovskite-like compounds like $LaAlO_3$, $LaGaO_3$, and $NdGaO_3$ have been recently proposed as substrates for high-T_c superconducting films with optimum mechanical and dielectric properties. Measurements of room temperature and 25 K reflectance have been performed from 100 to 20 000 cm^{-1} in these compounds. The complex dielectric functions $\tilde{\epsilon}$, as well as phonon mode parameters, have been obtained by a best fitting procedure in terms of Lorentzian oscillators. The use of these compounds in the study of the optical properties of thin films is discussed.

Since the last few years, high-T_c superconducting films have been the object of an increasing number of optical investigations [1]. Indeed, the transport, structural and superconducting properties of films have become comparable with those of bulk materials [2], which only seldom are flat on a surface large enough to allow for accurate optical measurements. However, good superconducting properties are commonly achieved in thin films where the presence of an underlying substrate strongly perturbs the measured optical spectra.

In previous works it has been shown that phonon contributions from the substrate – although seldom considered in the literature – may give rise to spurious structures in the measured reflectance of high-T_c superconducting and insulating thin films [3,4]. Moreover, in these cases the complex refractive index of the film $\tilde{n}_f$ cannot be obtained by standard Kramers–Krönig transformations and special procedures have to be used in order to get reliable results [3,4].

The aim of the present paper is to extend the previous work by measuring and fitting the reflectance of $LaAlO_3$, $LaGaO_3$ and $NdGaO_3$, perovskite-like compounds which are to be used as substrates for a high-T_c superconducting film [5–12] instead of the most common $SrTiO_3$ or MgO. It has been recently pointed out that films with superior mechanical, dielectric and superconducting properties can be grown on these substrates [12]. Calculations of the substrate-film mismatch strains show indeed that these compounds, in particular $NdGaO_3$, are best suited for growing $YBa_2Cu_3O_{7-\delta}$ epitaxial films [12]. Moreover, they have a static dielectric constant ϵ_0 one order of magnitude smaller than that of $SrTiO_3$. Finally, twin-free superconducting films will become available as soon as twin-free $NdGaO_3$ will be grown, which seems likely in the near future [12].

The present study will provide an explicit expression of the dielectric function $\tilde{\epsilon}_s(\omega)$ for these perovskite-like compounds in terms of phonon and impurity contributions. It will also point out that $LaGaO_3$ and $NdGaO_3$ substrates are not suitable for studying the optical properties of thin superconducting films because of the strong perturbations they introduce in the far- and/or mid-infrared part of the spectra.

Let us consider the general case of a film f of thickness d on a semi-infinite substrate s: the measured reflectance R is related to the complex refractive index of the film $\tilde{n}_f = n_f + ik_f$, of the substrate $\tilde{n}_s$ and of the vacuum n_0 by the formula [13]

$$R = \frac{(g_f^2 + h_f^2)\exp(2\alpha_f) + (g_s^2 + h_s^2)\exp(-2\alpha_f) + A\cos(2\gamma_f) + B\sin(2\gamma_f)}{\exp(2\alpha_f) + (g_f^2 + h_f^2)(g_s^2 + h_s^2)\exp(-2\alpha_f) + C\cos(\gamma_f) + D\sin(2\gamma_f)}, \tag{1}$$

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where

$$\alpha_{\rm f}=\frac{\omega d}{c}k_{\rm f}\,,\qquad \gamma_{\rm f}=\frac{\omega d}{c}n_{\rm f}\,,$$

$$A=2(g_{\rm f}g_{\rm s}+h_{\rm f}h_{\rm s})\,,\qquad B=2(g_{\rm f}h_{\rm s}-g_{\rm s}h_{\rm f})\,,\qquad(2)$$

$$C=2(g_{\rm f}g_{\rm s}-h_{\rm f}h_{\rm s})\,,\qquad D=2(g_{\rm f}h_{\rm s}+g_{\rm s}h_{\rm f})\,,$$

and

$$g_{\rm f}=\frac{n_0^2-n_{\rm f}^2-k_{\rm k}^2}{(n_0+n_{\rm f})^2+k_{\rm f}^2}\,,\qquad h_{\rm f}=\frac{2n_0k_{\rm f}}{(n_0+n_{\rm f})^2+k_{\rm f}^2}\,,\qquad(3)$$

$$g_{\rm s}=\frac{n_{\rm f}^2-n_{\rm s}^2+k_{\rm f}^2-k_{\rm s}^2}{(n_{\rm f}+n_{\rm s})^2+(k_{\rm f}+k_{\rm s})^2}\,,\qquad h_{\rm s}=\frac{2(n_{\rm f}k_{\rm s}-n_{\rm s}k_{\rm f})}{(n_{\rm f}+n_{\rm s})^2+(k_{\rm f}+k_{\rm s})^2}\,.\qquad(4)$$

In order to get the film complex dielectric function $\tilde{\epsilon}_{\rm f}(\omega)$, it is modeled as a sum of contributions from a Drude term with plasma frequency $\omega_{\rm p}$ and linewidth $\Gamma_{\rm D}$ and from Lorentzian oscillators with energies $\omega_{{\rm f}i}$, linewidths $\Gamma_{{\rm f}i}$ and strengths $S_{{\rm f}i}$

$$\tilde{\epsilon}_{\rm f}(\omega)=\tilde{n}_{\rm f}^2=\epsilon_{{\rm f}\infty}-\frac{\omega_{\rm p}^2}{\omega^2+{\rm i}\omega\Gamma_{\rm D}}+\sum_i\frac{S_{{\rm f}i}^2}{(\omega_{{\rm f}i}^2-\omega^2)-{\rm i}\omega\Gamma_{{\rm f}i}}\,,\qquad(5)$$

where $\epsilon_{{\rm f}\infty}$ takes into account the contributions from higher energy optical transitions [14]. The above param-

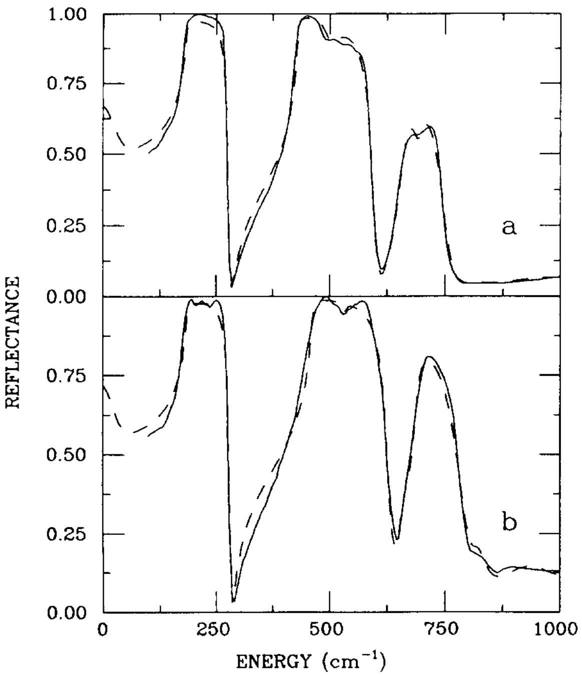

Fig. 1. Room temperature (a) and 25 K (b) reflectances $R(\omega)$ of a $LaAlO_3$ sample are plotted for $100<\omega<1000$ cm^{-1}. Experimental data are given by solid lines, fits to eq. (8) by dashed lines.

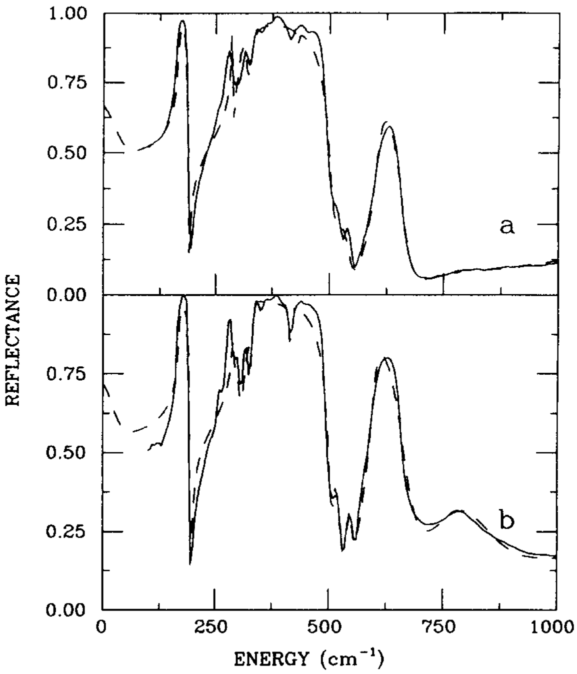

Fig. 2. Room temperature (a) and 25 K (b) reflectances $R(\omega)$ of a $LaGaO_3$ sample are plotted for $100<\omega<1000$ cm^{-1}. Experimental data are given by solid lines, fits to eq. (8) by dashed lines.

eters are then determined by best-fitting the measured reflectance R to eq. (1) once the substrate dielectric function

$$\tilde{\epsilon}_s(\omega)=\tilde{n}_s^2=\epsilon_{s\infty}+\sum_i \frac{S_{si}^2}{(\omega_{si}^2-\omega^2)-i\omega\Gamma_{si}} \tag{6}$$

is known [3,4].

Platelets like those measured in the present work can be considered as thick films between two semi-infinite layers of air. Their reflectivities should then be fitted using eqs. (1)–(5), with $\tilde{n}_s$ and n_0 replacing $\tilde{n}_f$ and $\tilde{n}_s$, respectively, and d being the substrate thickness. However, these equations have been derived in the case of an ideal Fabry–Perot, i.e. a film with perfectly parallel faces on the λ scale, which can hardly be the case for commercial substrates in the near-infrared and visible range. Moreover, in the far-infrared the sample transmittance is very low, so that interference effects are usually negligible over the full energy range. In this case, the intensity I_r of the reflected beam is given by the sum of the squared amplitudes rather than by the square of the sum of amplitudes and one has

$$I_r/I_0=R\left[1+\frac{(1-R)^2\exp(-2\alpha d)}{1-R^2\exp(-2\alpha d)}\right], \tag{7}$$

where I_0 is the incident beam intensity. Equations (6–7), together with the relation

$$R=\frac{(n_s-1)^2+k_s^2}{(n_s+1)^2+k_s^2} \tag{8}$$

can therefore be used to get the substrate dielectric constant $\tilde{\epsilon}_s(\omega)$. In the present work the number of oscillators of eq. (6) has been kept to the minimum value which can satisfactorily reproduce the overall experimental $R(\omega)$. This procedure, as well as the neglect of phonon–phonen interactions, may sometimes give rise to minor misfits.

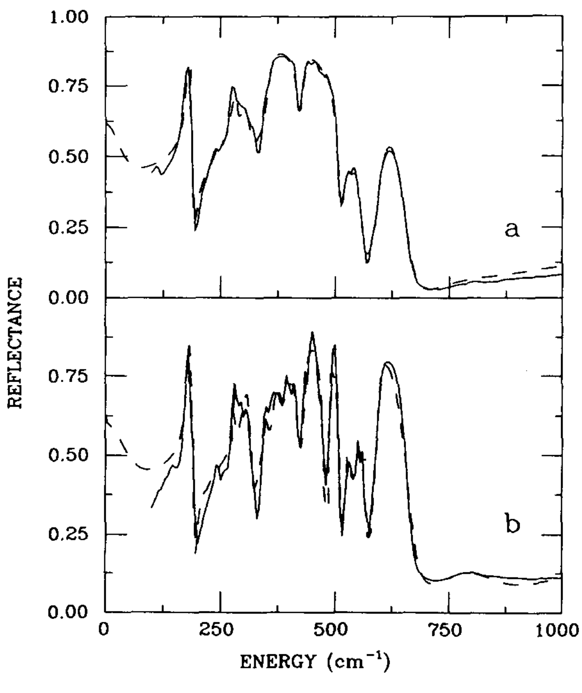

Fig. 3. Room temperature (a) and 25 K (b) reflectances $R(\omega)$ of a $NdGaO_3$ sample are plotted for $100<\omega<1000$ cm^{-1}. Experimental data are given by solid lines, fits to eq. (8) by dashed lines.

Reflectances at 300 and 25 K have been measured under vacuum and at normal incidence, with an RIIC chopped Michelson interferometer from 100 to 500 cm^{-1}, with a Bomem DA3 rapid scanning interferometer from 400 to 20 000 cm^{-1}. An uncertainty of 1–2% in $R(\omega)$ applies to all data. In the mid- and far-infrared spectral region, the reference was a Au-film evaporated onto a sapphire optical window. In the visible, the reference was a polished Pt foil. A wide variety of sources, beam-splitters and detectors have been used to cover the investigated energy range. The good match between spectra obtained in different optical configurations attests of data accuracy and reliability.

The 300 K (a) and 25 K (b) reflectances (solid lines) for $LaAlO_3$, $LaGaO_3$ and $NdGaO_3$ crystals are reported in figs. 1 to 3, respectively, in the energy range 100 to 1000 cm^{-1}, where phonons are expected to dom-

Table 1
Parameters of the oscillators related to phonon modes, which have been used to fit the reflectance curves given in figs. 1–4. The thicknesses of the $LaAlO_3$, $LaGaO_3$ and $NdGaO_3$ samples are 0.1, 0.1 and 0.05 cm, respectively

Sample	$LaAlO_3$ 25 K	$LaAlO_3$ 300 K	$LaGaO_3$ 25 K	$LaGaO_3$ 300 K	$NdGaO_3$ 25 K	$NdGaO_3$ 300 K
ϵ_∞	4.2	4.2	4.3	4.3	3.5	3.5
ω_1	183	182	170	166	177	176
Γ_1	4	4	2	2	4	6
S_1	1000	854	630	500	365	390
ω_2	461	429	290	284	240	240
Γ_2	3	2	5	1	1	2
S_2	1390	1040	690	470	70	70
ω_3	531	501	301	304	280	281
Γ_3	11	39	4	11	1	10
S_3	105	200	390	930	150	490
ω_4	667	657	324	329	303	299
Γ_4	33	29	11	13	15	20
S_4	400	460	980	640	550	490
ω_5	685	695	335		352	340
Γ_5	18	26	1		5	60
S_5	415	146	780		270	650
ω_6					371	356
Γ_6					15	16
S_6					595	680
ω_7					393	
Γ_7					29	
S_7					657	
ω_8			419	431	435	427
Γ_8			1	4	13	16
S_8			205	45	485	260
ω_9					488	479
Γ_9			2		7	1
S_9					280	50
ω_{10}			419		526	520
Γ_{10}			14		9	12
S_{10}			140		205	115
ω_{11}			545	526	546	534
Γ_{11}			12	36	27	26
S_{11}			170	170	340	170
ω_{12}			597	604	593	598
Γ_{12}			15	22	12	29
S_{12}			655	435	430	335

inate the spectra. In the same figures, the dashed lines give the result of a best fit to the measured spectra. This has been performed over the whole measured energy range – 100 to 20 000 cm^{-1} – except for the $NdGaO_3$ sample which has been fitted only up to 6000 cm^{-1}. Table 1 gives the fitting parameters referring to oscillators with typical phonons energies and widths, while the ones related to higher energy oscillators are reported in table 2. The latter have been introduced to reproduce the behavior of $R(\omega)$ for $\omega \geqslant 1000$ cm^{-1} and include possible contributions from defects, impurities and band to band transitions.

$LaAlO_3$. The sample has been provided by the University of Munich (Germany). Under the D_{3d}^6 space group, the infrared active modes for this rhombohedral perovskite are eight, five E_u twofold modes and three A_{2u} single modes [15]. The room temperature energy values of the three strongest phonon modes, 182, 429 and 657 cm^{-1}, very well agree with the ones reported in ref. [16] for three out of the five E_u modes. Two weak modes at 501 and 695 cm^{-1} correspond to shoulders in the transmission data of refs. [15,16] and may be due to a lift of degeneracy of E_u modes. The oscillators detected at 815 and 930 cm^{-1} in the 25 K spectrum are possibly related to an impurity or a defect, as suggested by their widths (see table 2).

$LaGaO_3$. The sample has been supplied by Applied Technologies Enterprises (USA). This compound has the structure of an orthorhombic perovskite with space group C_{2v}^9. Forty-two single modes are infrared active, of which fourteen are A_1, fourteen B_1, and fourteen B_2 [17]. Within the resolution of the present reflectivity spectra (5 cm^{-1}), nine phonon modes are needed at low temperature (seven at room temperature) in order to obtain the fit shown in fig. 2. Phonon mode energies well agree with those of ref. [17]. A structure related to impurities or defects is visible at low temperature at 775 cm^{-1}.

$NdGaO_3$. The sample has also been supplied by Applied Technologies Enterprises (USA). Its space group and infrared active modes are the same as those of $LaGaO_3$ [17]. At least twelve (eleven) phonon modes are needed at low (room) temperature to get a good fit to data (see fig. 3). The number and the energy of the phonons agree quite well with those experimentally measured and theoretically predicted in ref. [17]. A struc-

Table 2
Parameters of the oscillators related to defects or to inter-band transitions, which have been used to fit the reflectance curves shown in figs. 1–4. The band to band transition ω_7 is not given for $NdGaO_3$ whose fit is limited at 6000 cm^{-1}

Sample	$LaAlO_3$ 25 K	$LaAlO_3$ 300 K	$LaGaO_3$ 25 K	$LaGaO_3$ 300 K	$NdGaO_3$ 25 K	$NdGaO_3$ 300 K
ω_1	815	815	775	790	800	805
Γ_1	36	69	144	200	210	230
S_1	130	165	665	365	575	310
ω_2	930	950				
Γ_2	143	228				
S_2	435	380				
ω_3	1170	1270	1215	1495		
Γ_3	315	340	865	815		
S_3	700	315	1520	740		
ω_4	1840	1890			1800	1700
Γ_4	1300	1140			600	380
S_4	1880	1040			1770	1060
ω_5	3510	3790	4120	3560	3590	3400
Γ_5	4980	3740	8000	5000	930	1000
S_5	2500	2630	5500	3800	3200	3100
ω_6					5400	5260
Γ_6					1340	1340
S_6					5850	5730
ω_7	20400	21000	23600	23600		
Γ_7	2130	2790	5000	8000		
S_7	8950	9950	15500	23100		

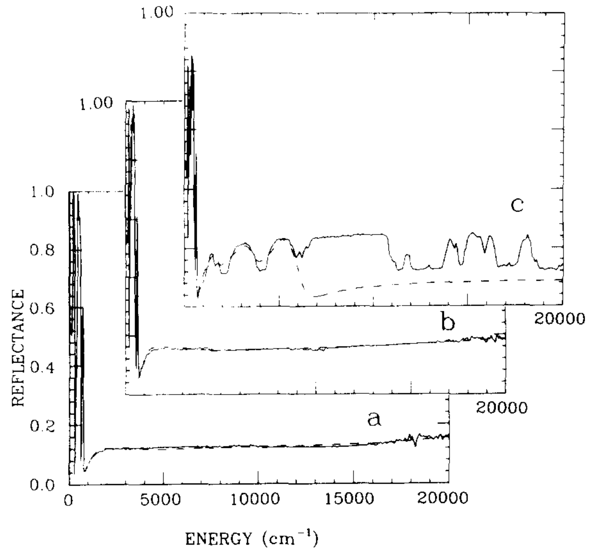

Fig. 4. Room temperature reflectances $R(\omega)$ of $LaAlO_3$ (a), $LaGaO_3$ (b) and $NdGaO_3$ (c) samples are plotted for $100<\omega<20000\ cm^{-1}$. Experimental data are given by solid lines, fits to eq. (8) by dashed lines. $NdGaO_3$ data are fitted only up to $6000\ cm^{-1}$.

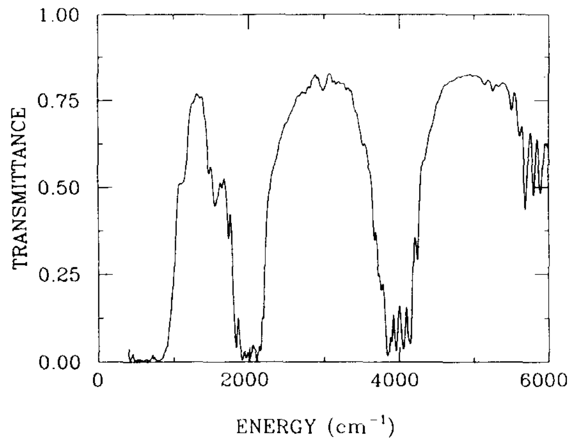

Fig. 5. The room temperature transmittance of a $NdGaO_3$ sample is plotted for $100<\omega<6000\ cm^{-1}$.

ture shows up at 800 cm^{-1} in the 25 K spectrum, similar to the previous cases.

The room temperature reflectances of the three compounds are reported in fig. 4 over the whole measured energy range, 100 to 20 000 cm^{-1}. The bands in table 2 are common to a number of other oxides and are probably due to transitions starting from defect states, as will be discussed elsewhere [18]. In the case of $NdGaO_3$, if one uses a number of oscillators comparable to that employed for $LaAlO_3$ and $LaGaO_3$, one gets a poor fit, even in the range 100–6000 cm^{-1}. In order to get a further check, we have taken the transmission spectrum of $NdGaO_3$ shown in fig. 5. It is possible to notice a very rich fine structure, likely due to transitions in atomic Nd, whose analysis is beyond the scope of this work. It is, however, out of the question that, due to its complex optical function, $NdGaO_3$ is not a substrate well-suited for high-T_c superconducting thin films, when their infrared optical properties have to be studied. The same would apply to $LaGaO_3$ too, limited to the far-infrared region of the spectrum.

In conclusion, the reflectivity of three perovskite-like substrates, best suited for epitaxial growth of high-T_c superconducting films, has been measured. Moreover, the complex dielectric function $\tilde{\epsilon}_s$ of these compounds, which is needed to extract $\tilde{\epsilon}_f$ from the experimental reflectivity of thin films whenever standard Kramers–Krönig transformations do not hold, has been determined in terms of contributions from phonon modes and defects.

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