

Letter

High-temperature infrared reflectivity of yttria-stabilized hafnia single crystals

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Abstract

Infrared reflectivity spectra of cubic yttria-stabilized hafnia were measured in the frequency range 30–5000 cm^{-1} at temperatures from 300 to 1100 K. A heavily damped oscillator has been observed in the far infrared, its parameters being essentially constant in the whole temperature range. This term is attributed to vibrations of clusters of defects, in accord with previous studies on other fluorite-type ionic conductors. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Yttria-stabilized hafnia (denoted in the following as YSHf) belongs to the group of fluorite-structured oxygen superionic conductors. These materials are widely employed in various high temperature applications (solid state fuel cells, oxygen sensors, etc.) and their potential use in other ones (e.g. anticorrosion, thermal barrier or optical coatings) has been examined. Although their macroscopic characteristics are known, the underlying microscopic properties, namely the conductivity mechanism, are not well understood yet. Thus the investigations in this direction appear to be of interest.

The chemical formula of YSHf is $\text{Hf}_{1-x}\text{Y}_x\text{O}_{2-x/2}$. Doping of hafnia by yttrium creates oxygen vacancies, which play an essential role in the conductivity mechanism. At the same time, the doping ‘stabilizes’ the cubic phase that in pure HfO_2 exists at high temperatures only; thus, in YSHf, the overall cubic symmetry (space group $\text{Fm}\bar{3}\text{m}$) is conserved down to room temperature.

Earlier, room temperature infrared reflectivity spectra of cubic YSHf have been measured in the range 180–900 cm^{-1} for $x = 15\%$ [1] and 200–1300 cm^{-1} for $x = 10\%$ [2]. Our aim was to investigate the reflectivity

also in far infrared and to follow its development upon heating in order to check for presence of possible effects in far infrared related to the superionic conductivity.

2. Experimental

The sample was grown from a melt under standard atmospheric conditions [3] in the General Physics Institute, Moscow. It had the form of a polished single crystal platelet with the thickness of 1.5 mm and about 20 mm in diameter. Using the technique of electron microprobe connected to an electron microscope, the doping rate has been established as $x = 0.15 \pm 0.005$.

Near-normal incidence infrared reflectivity spectra were measured with the resolution of 6 cm^{-1} using a commercial Bruker IFS-113v Fourier-transform spectrometer with the optic path adapted for high-temperature measurements [4]. The measurements were carried out in the spectral range of 30–5000 cm^{-1} at temperatures 300–1100 K. The sample was placed in a water cooled platinum furnace and the temperature was measured by a thermocouple placed on the sample side opposite to the reflecting one; the values of T were corrected for the gradient within the sample on the base of previous calibration measurements with a

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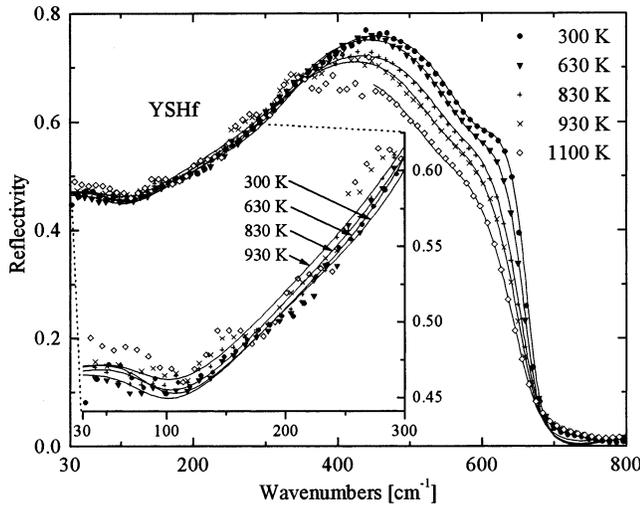


Fig. 1. Infrared reflectivity of spectra of the $(\text{HfO}_2)_{0.85}(\text{Y}_2\text{O}_3)_{0.15}$ single crystal at temperatures 300 to 1100 K: experimental data (symbols) and fits (solid lines).

quartz sample of similar dimensions. Because of the setup of the furnace and in order to ensure its thermal contact with the sample, the interferometer and the sample chamber were not evacuated but purged with a small flow of dry air. Liquid-He cooled Si bolometer was used as detector in the spectral region $30\text{--}600\text{ cm}^{-1}$.

3. Results and evaluation

The measured reflectivity spectra $R(\omega)$ for selected temperatures are shown by symbols in Fig. 1. The spectral region $800\text{--}5000\text{ cm}^{-1}$ that contains no features, is not shown. At room temperature, the main

reflectivity band maximum is located near 450 cm^{-1} , in agreement with earlier measurements [1], but its intensity is 0.76, substantially higher than the value ≈ 0.65 , reported in [1]. We observe equally a smaller band near 650 cm^{-1} . In the far infrared, where, to our knowledge, no data were published previously, a marked increase in reflectivity towards low frequencies can be seen below $\approx 100\text{ cm}^{-1}$.

The spectra were fitted using the formulas which relate the normal-incidence reflectivity with the complex refraction index \tilde{N} and the complex dielectric function ε : $R(\omega) = |(\tilde{N} - 1)/(\tilde{N} + 1)|^2$ and $\tilde{N}^2 = \varepsilon$. We used the factorized form of the dielectric function [5],

$$\varepsilon(\omega) = \varepsilon_\infty \prod_{j=1}^J \frac{\omega_{j\text{LO}}^2 - \omega^2 + i\omega\Gamma_{j\text{LO}}}{\omega_{j\text{TO}}^2 - \omega^2 + i\omega\Gamma_{j\text{TO}}} \quad (1)$$

where ε_∞ is the high-frequency limit of ε , $\omega_{j\text{LO}}$, $\omega_{j\text{TO}}$ are the longitudinal and transverse oscillator frequencies. Finally, $\Gamma_{j\text{LO}}$ and $\Gamma_{j\text{TO}}$ denote longitudinal and transverse damping, respectively. The transverse oscillator strength of any of J terms is defined in this model as

$$\Delta\varepsilon_j = \frac{\varepsilon_\infty}{\omega_{j\text{TO}}^2} \frac{\prod_{k \neq j} (\omega_{k\text{LO}}^2 - \omega_{j\text{TO}}^2)}{\prod_{k \neq j} (\omega_{k\text{TO}}^2 - \omega_{j\text{TO}}^2)} \quad (2)$$

We have fitted the spectra using a model with $J=4$ terms (see Table 1), the terms No. 1, 3 and 4 describing the features mentioned above. The term No. 2 appears necessary in order to reach a good agreement of the fit with the experimental data in the region between 100 and 600 cm^{-1} .

The spectra obtained above room temperature have been fitted also with four terms, their parameters changing in a monotonous way with T . The set of

Table 1

Fit parameters used to describe the dielectric function $\varepsilon(\omega)$ of YSHf at room temperature

j	$\omega_{j\text{TO}} [\text{cm}^{-1}]$	$\Gamma_{j\text{TO}} [\text{cm}^{-1}]$	$\omega_{j\text{LO}} [\text{cm}^{-1}]$	$\Gamma_{j\text{LO}} [\text{cm}^{-1}]$	$\Delta\varepsilon_j$
1	90.0	100.0	100.0	100.0	6.1
2	240.0	224.0	298.3	350.5	13.1
3	346.0	152.0	599.0	126.0	15.2
4	610.5	107.0	666.0	30.0	3.9×10^{-2}

$\varepsilon_\infty = 4.20$

Table 2

Fit parameters used to describe the dielectric function $\varepsilon(\omega)$ of YSHf at $T=930\text{ K}$

j	$\omega_{j\text{TO}} [\text{cm}^{-1}]$	$\Gamma_{j\text{TO}} [\text{cm}^{-1}]$	$\omega_{j\text{LO}} [\text{cm}^{-1}]$	$\Gamma_{j\text{LO}} [\text{cm}^{-1}]$	$\Delta\varepsilon_j$
1	90.0	110.1	100.0	113.9	6.1
2	238.0	224.0	285.2	350.5	12.2
3	329.5	180.7	548.9	140.4	6.1
4	561.5	140.4	661.1	57.2	9.9×10^{-2}

$\varepsilon_\infty = 4.20$

parameters for $T=930$ K is listed in Table 2. At $T=1100$ K, there is an increased noise level below $\omega=450$ cm^{-1} ; therefore, below this frequency, we retained the eigenfrequencies and corresponding damping constants used for $T=930$ K and we adjusted only the remaining ones. The resulting calculated spectrum in Fig. 1 is shown only for $\omega \geq 450$ cm^{-1} .

With increasing temperature, the reflectivity level between 350 and 700 cm^{-1} decreases and the maximum shifts to lower frequencies: accordingly, the parameters of terms No. 3 and 4 change in a way usual for ordered crystals: the damping constants increase and the eigenfrequencies decrease. In the frequency region from 30 to about 350 cm^{-1} , the reflectivity increases slightly on heating (see inset in Fig. 1). This effect appears to be mainly due to the increase of $\Gamma_{\text{ILO}} - \Gamma_{\text{ITO}}$ with T .

4. Discussion

We have shown that Eq. (1) approximates sufficiently well the spectra using only four terms; by contrast, the classical oscillator model of $\varepsilon(\omega)$ applied previously [2] fits worse the experimental data even using seven terms above $\omega=200$ cm^{-1} . We consider that the lower number of terms makes it possible to analyse the spectra in a more efficient way.

The fact that the frequencies of the lowest-frequency term and its oscillator strength are virtually temperature independent indicates that this term is not directly related to the superionic conductivity. As its damping constants exceed somewhat its eigenfrequencies, it represents an oscillator that is heavily damped, although not overdamped. Such a feature is also known from the cubic phase of ZrO_2 at high temperatures [6], as well as from other fluorite-structured non-stoichiometric superionic conductors: yttria-stabilized zirconia [7] and various kinds of rare-earth doped barium fluoride [8,9]. In the latter, it is assumed that it originates in localized vibrations which include clusters of defects, the size of clusters being of the order of the lattice constant, as shown by diffuse neutron scattering experiments [10,11]. The same could apply to YSHf, where clusters of vacancies are known to exist [12], with dimensions also close to the lattice constant. Another possible explanation of the origin of the low-frequency term is

that it is due to relaxation of selection rules connected to the broken translational periodicity.

5. Conclusions

The experiment has shown that the IR reflectivity spectra of YSHf do not display anomalies related to the oxygen conductivity in the far infrared. The direct effect of ionic conductivity will occur only at lower frequencies. In this spectral region a heavily damped oscillator has been observed to our knowledge for the first time. Its parameters, obtained by modelling the dielectric function, are essentially temperature independent.

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