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Vibrational spectroscopy study of the lattice defects in $CaZrO_3$ ceramics

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Abstract

$CaZrO_3$ materials were prepared by a solid state reaction. The samples were pre-calcined and sintered at 1673 K for 6 h. They were then analysed using Fourier Transform-Infrared spectroscopy. Microwave dielectric function ($\varepsilon = \varepsilon' + i\varepsilon''$) were determined by Kramers–Kronig analysis. The reflectance spectra were then adjusted using the classical dispersion equations taking into account the LO/TO (longitudinal/transverse optic) mode splitting. The most unfavourable mode in terms of dissipation was found to be the first one ($\omega_T = 106.9$ cm^{-1}). A simple adjustment of this mode transverse optic damping constant was then carried out to fit the reflectance spectra of slightly non-stoichiometric $CaZrO_3$ materials. This procedure was conclusive except for excessive Zr non-stoichiometry (extrapolated to $>2.78\%$).

Keywords: $CaZrO_3$; Defects; Dielectric properties; Infrared spectroscopy

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1. Introduction

Many perovskite-type materials are of interest for capacitors or dielectric resonators microwave applications due to their low loss tangent (tanδ) and high dielectric constant (ε). $CaZrO_3$ is one such compound, having a dielectric constant around 30, quality factor (Q = 1/ tanδ) of about 3000 at about 13 GHz, and a temperature coefficient of dielectric constant (τ_ϵ) of about −30 ppm °C^{-1}. In spite of these attractive properties, it is often only used as a doping agent for other materials to adjust their properties, presumably due to the high sintering temperature (from 1800 to 2000 K depending on authors).[1–3] This compound is a perovskite-type material (ABO_3) with a *Pcmn* space group.[4] Unit cell parameters determined, by powder neutron diffraction, are $a = 5.5912$, $b = 8.0171$ and $c = 5.7616$ Å.[5] There are a few references concerning its vibrational properties : the first study of its infrared (IR) response was made in 1965 by Perry et al.[6] who examined the influence of the cations in the ABO_3 structure on the infrared modes obtained from a Kramers–Kronig analysis (A = Ca, Sr, Ba, Pb ; B = Ti, Zr); luminescence properties were studied by Merino et al.[7] in Er doped $CaZrO_3$; Peña et al. studied the unpolarised Raman spectra in CaO–ZrO_2 eutectics [8]; finally, Orera et al.[9] studied, in 1998, the Raman and infrared characteristics of $CaZrO_3$ grown by the laser floating zone method and the infrared characteristics of $CaZrO_3$ compressed pellets. In this last study, the authors derived an hybrid equation of the classic expression proposed by Gervais[10] for the dielectric response at microwave frequencies to fit their data. This equation lies on an uncoupling of the different modes.

In this work, we achieved reliable data for IR measurements which allowed us to fit them using the oscillator model by Gervais et al.[11] Moreover, we have studied the effect of a slight non-stoichiometry on the modes parameters [i.e. transverse optic (TO) and longitudinal optic (LO) frequencies and damping constants]. The extrapolated values of the loss tangent from IR measurements are comparable to the values obtained from direct measurements.

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2. Experimental procedure and theoretical background

The required reagents were mixed in the desired stoichiometric ratio (stoichiometric $CaZrO_3$, $CaZrO_3$ 1 and 3% deficient either in calcium or zirconium) and wet-ball-milled in an agate mortar with agate balls in ethanol. The slurry was dried and calcined at 1373 K for 2 h. The calcined powder was made into pellets, which were sintered at 1673 K for 6 h to increase the density and enhance the reflectance signal. The pellets were highly polished using diamond paste. The powder X-ray diffraction patterns were obtained using Cu_{K_α} radiation in the range $2\theta = 10$–$90°$ using a Philips XPERT diffractometer. The infrared reflectance spectrum was recorded using a Fourier transform spectrometer (Nicolet Magna-IR spectrometer, Series II) equipped with a fixed-angle specular reflectance accessory. The measurement was done under dried N_2. The range for measurements was 50–1200 cm^{-2} (1 cm^{-1} resolution; 128 scans). A polished aluminium mirror was used as the reference. The quality factor was measured by the reflection method of the TEMEX Society (Pessac, France). The dielectric constant at low frequency (1MHz) was measured with a FLUCKE 6306 LCR meter.

At room temperature, the $CaZrO_3$ structure is *Pcmn* (space group). The orthorhombic cell contains four formulas with Zr^{4+} in the 4b site, Ca^{2+} and four O_1^{2-} in the 4c site and eight O_2^{2-} in the 8d site. A group theory analysis gives the following optical activities for this space group: $\gamma = 7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g} + 8A_u + 10$- $+ 10B_{1u} + 8B_{2u} + 10B_{3u}$, which yields to $9B_{1u}$, $7B_{2u}$ and $9B_{3u}$ (=25) IR possible modes which are polarised parallel to the orthorhombic *x*, *y*, *z* axes (respectively B_{3u}, B_{2u} and B_{1u} modes). The equations of interest are the following :

$$R = \left| \frac{\sqrt{\varepsilon} - 1}{\sqrt{\varepsilon} + 1} \right|^2 \tag{1}$$

$$\varepsilon = \varepsilon_\infty \cdot \prod_{k=1}^{N} \frac{\omega_{Lk}^2 - \omega^2 + i\gamma_{Lk}\omega}{\omega_{Tk}^2 - \omega^2 + i\gamma_{Tk}\omega} \tag{2}$$

$$R_f = \frac{\sum (R_{\text{observed}} - R_{\text{calculated}})^2}{\sum R_{\text{observed}}^2} \tag{3}$$

$$dP = \left(J^T J\right)^{-1} \cdot J^T \text{RES}. \tag{4}$$

The reflectance spectra were fitted using the Fresnel relation [Eq. (1)] which gives the relationship between the reflectance *R* and the dielectric constant ϵ $(= \epsilon' + i\epsilon'')$ together with the frequency dependant dielectric function proposed by Gervais[11] [Eq. (2)]. Firstly, the position of the LO and TO modes were initialised to the values obtained from a Kramers–Krönig analysis (formula from10) respectively as the maxima of $(1/\varepsilon)''$ curve and the maxima of ε'' curves; all the damping constants were arbitrary initialised at 10 cm^{-1}. Then, a trial and adjustment process was performed to fit the theory to the reflectance data; the parameter to minimize was chosen to be the un-weighted *R*-factor (R_f) [Eq. (3)]. A last adjustment of the parameters was then performed through a least square refinement method [Eq. (4)], d*P* being the error vector, i.e. the vector composed of the error values on each parameter, *J* the Jacobian matrix for the system and RES the vector containing the reflectance residuals ($R_{\text{calculated}} - R_{\text{experimental}}$) for each point in the spectrum.

$$\Delta\varepsilon_j = \varepsilon_\infty \cdot \left(\frac{\omega_{Lj}^2 - \omega_{Tj}^2}{\omega_{Tj}^2} \right) \cdot \prod_{k=1, k \neq j}^{N} \left(\frac{\omega_{Lk}^2 - \omega_{Tj}^2}{\omega_{Tk}^2 - \omega_{Tj}^2} \right) \tag{5}$$

$$Q = \frac{1}{\sum_{k=1}^{N} \tan(\delta_k)} \tag{6}$$

$$\tan(\delta_j) = \frac{\Delta\varepsilon_j \cdot \dfrac{\omega\gamma_{Tj}}{\omega_{Tj}^2}}{\varepsilon_\infty + \sum_{k=1}^{N} \Delta\varepsilon_j} \tag{7}$$

The oscillator strength is given by Eq. (5)[12] and the contribution to the quality factor of the different modes [Eq. (6)] are given by Eq. (7).[13] The errors for adjusted parameters were calculated through Eq. (4) and approximated to d*P*.

3. Results and discussion

All the patterns in the diffractograms were indexed with respect to the orthorhombic phase of space group *Pcmn*. The diffractograms confirm the formation of a single phase (Fig. 1).

Fig. 2b shows the measured and calculated reflectance spectra of $CaZrO_3$. The calculated reflectance was shown independent of the 26.5° incident beam angle and Eq. (1) could then be used to speed up the computation. The solid line is the fitted reflectance, which is in good agreement [$R_f = 0.08\%$ with Eq. (1) and 0.1% using the full definition of *R* taking into account the incidence angle] with the experimentally observed values (circles). Fifteen distinct modes were used to fit the experimental spectrum. Although these modes are clearly defined on the spectrum, the possibility of lowering this number was investigated but these attempts were unsuccessful (it was neither necessary nor successful to increase this number). The values of the TO and LO mode frequencies, their corresponding damping constants, the mode strength, and the contribution to the dielectric loss factor of each modes are given in Table 1. These are

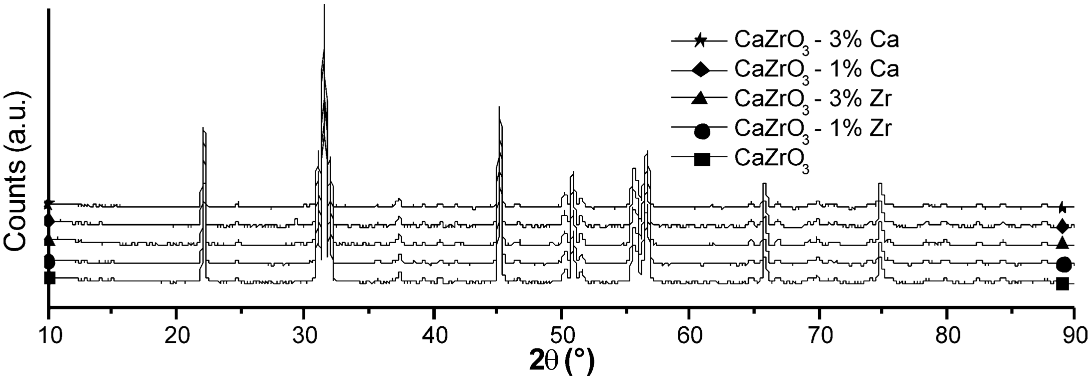

Fig. 1. X-Ray diffractograms of stoichiometric and non stoichiometric $CaZrO_3$ material.

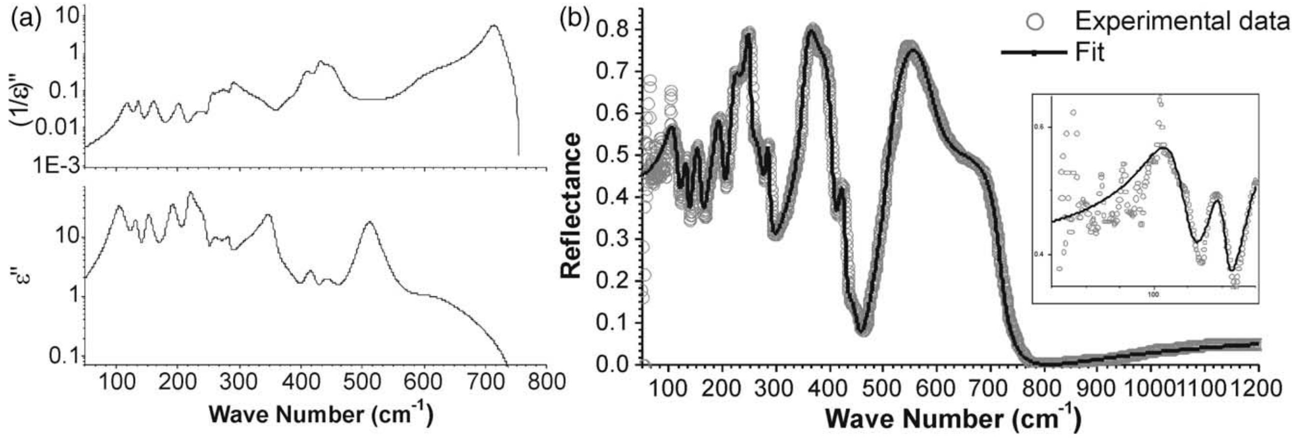

Fig. 2. Results for $CaZrO_3$ material: (a) Calculated imaginary parts of the dielectric constant and its inverse versus frequency; (b) Experimental and fitted reflectance curve. The inset is a zoom over the range 50–150 cm^{-1}.

Table 1
Modes adjusted parameters obtained from the fit, their strength, contribution to the quality factor and assignement for $CaZrO_3$ stoichiometric material[a]

k	ω_{Lk} (cm^{-1})	γ_{Lk} (cm^{-1})	ω_{Tk} (cm^{-1})	γ_{Tk} (cm^{-1})	$\delta\epsilon_k$	$\tan(\delta_k)/\omega$ (cm)	Assignment
1	118.37 [0.37]	17.03 [2.04]	106.86 [1.59]	22.61 [4.53]	6.37	5.39×10^{-4}	(B_{2u})
2	136.11 [0.35]	08.62 [0.15]	132.06 [0.18]	10.20 [1.01]	1.16	2.89×10^{-5}	B_{3u}
3	160.43 [0.13]	15.21 [0.01]	152.13 [0.01]	13.29 [2.43]	1.91	4.69×10^{-5}	B_{1u}, B_{2u}, B_{3u}
4	202.91 [0.36]	15.29 [0.80]	191.07 [0.06]	16.56 [2.15]	2.69	5.21×10^{-5}	B_{1u}, B_{2u}, B_{3u}
5	231.19 [2.90]	45.83 [7.52]	219.00 [0.05]	12.26 [1.09]	1.67	1.82×10^{-5}	B_{1u}
6	252.79 [0.88]	09.49 [1.43]	247.01 [5.02]	18.88 [0.63]	1.44	1.90×10^{-5}	B_{1u}
7	276.79 [2.02]	34.24 [5.36]	254.19 [8.91]	28.98 [12.27]	0.33	6.31×10^{-6}	B_{3u}
8	286.78 [0.26]	11.14 [2.43]	283.51 [0.99]	08.49 [0.50]	0.07	3.05×10^{-7}	B_{3u}
9	348.18 [19.84]	82.59 [130.20]	334.46 [29.30]	94.39 [64.14]	1.70	6.13×10^{-5}	B_{1u}
10	366.82 [22.56]	50.95 [13.23]	351.20 [0.54]	20.02 [1.11]	0.25	1.75×10^{-6}	B_{3u}
11	406.68 [1.18]	18.67 [5.00]	383.62 [16.92]	79.28 [106.50]	0.69	1.58×10^{-5}	B_{1u}, B_{2u}, B_{3u}
12	430.01 [1.53]	12.03 [5.13]	419.60 [16.94]	29.88 [37.30]	0.35	2.55×10^{-6}	B_{1u}, B_{3u}
13	452.92 [7.37]	27.28 [2.16]	431.63 [10.20]	37.42 [84.59]	0.06	5.05×10^{-7}	(B_{2u}, B_{3u})
14	589.61 [9.59]	88.30 [18.80]	511.20 [1.59]	31.31 [3.24]	1.29	6.59×10^{-6}	(B_{1u}, B_{2u}, B_{3u})
15	716.56 [2.24]	25.04 [2.02]	593.47 [11.90]	144.53 [47.19]	0.05	8.57×10^{-7}	(B_{1u}, B_{2u}, B_{3u})
$\varepsilon_\infty = 3.39 \pm 0.10$				$\Sigma\tan(\delta_k)/\omega = 8.00\times10^{-4}$ cm ($=2.67\times10^{-14}$ Hz^{-1}, ω in Hz)			

[a] Values in square brackets are the errors on parameters.

in good agreement with previous results.[9] The only differences (except the expression used for the refinement as already discussed) are the presence in our spectrum of two more modes (indexed 1 and 13) and the more pronounced presence of the 15th mode which only appeared as a shoulder in work by Orera et al.[9] Owing to the assignment of the Brillouin zone centre $CaZrO_3$ phonon modes[9] from an ab initio calculation on the structure, the first mode could be assigned to a B_{2u} vibration. The highest energy mode found by these authors is here split in two, the 14th one whose TO frequency coincides with that of their highest energy's mode and the 15th one explaining the long tail. Based on their mode assignment and their results in polarized reflectance, both modes could be assigned to B_{1u}, B_{2u} and B_{3u} vibrations. The 13th one, only considering their calculated values, could be assigned either to B_{2u} or B_{3u} vibrations (or both).

The measured value of the quality factor at microwave frequencies (12.7 GHz) is 2992. A calculation using the generalised oscillator model and the refined parameters leads to a quality factor equal to 2954 evidencing an excellent agreement (this is surprising, considering that the equations used are normally only valid near mode frequencies[14]). The measured permittivity is 25 compared to 23.4 for the calculated value. The intrinsic dielectric loss contribution at the IR frequencies is due to the damping of the ionic vibrations, which results from the anharmonic interactions. Fig. 2 a represents the calculated imaginary parts of ε and $(1/\varepsilon)$ as a function of the frequency. From this Fig. and Table 1, it can be seen that the low frequency modes present the most important strength combined with a high TO damping constant making them the most incident modes to the quality factor increase. These low energy modes are the Ca–(ZrO_2) lattice modes,[1–3] the O-Zr-O bending modes (4–5) and the Zr-O_3 torsion modes (9–11).[6] The most incident mode is the first one. Taking into account this observation, non-stoichiometric $CaZrO_3$ materials IR reflectance spectra were fitted by only adjusting the TO damping constant of the first mode. Except for the 3% Zr deficient $CaZrO_3$ IR spectrum, all the spectra could be well fitted in this way. The inset in Fig. 3 shows the TO damping constant dependence against the Ca/Zr ratio. This representation is supported by the fact that the damping constant may depend on the oscillator weight and also on the stoichiometry. A linear dependence was chosen to fit their tendency [Eq. (8)]. Eq. (8) was then introduced into Eqs. (5)–(7) to calculate the quality factor against the Ca/Zr ratio [Eq. (9)].

$$\gamma_{T1} = -791.13\text{Ca/Zr} + 813.74 \tag{8}$$

$$Q\omega_{[\text{GHz}]} \approx \frac{10^6}{654.90 - 628.25\dfrac{\text{Ca}}{\text{Zr}}}. \tag{9}$$

Fig. 3 shows the directly measured and calculated values at 10 GHz ($Q \times$ Frequency constant) for the tested non-stoichiometric compounds. It is easily seen

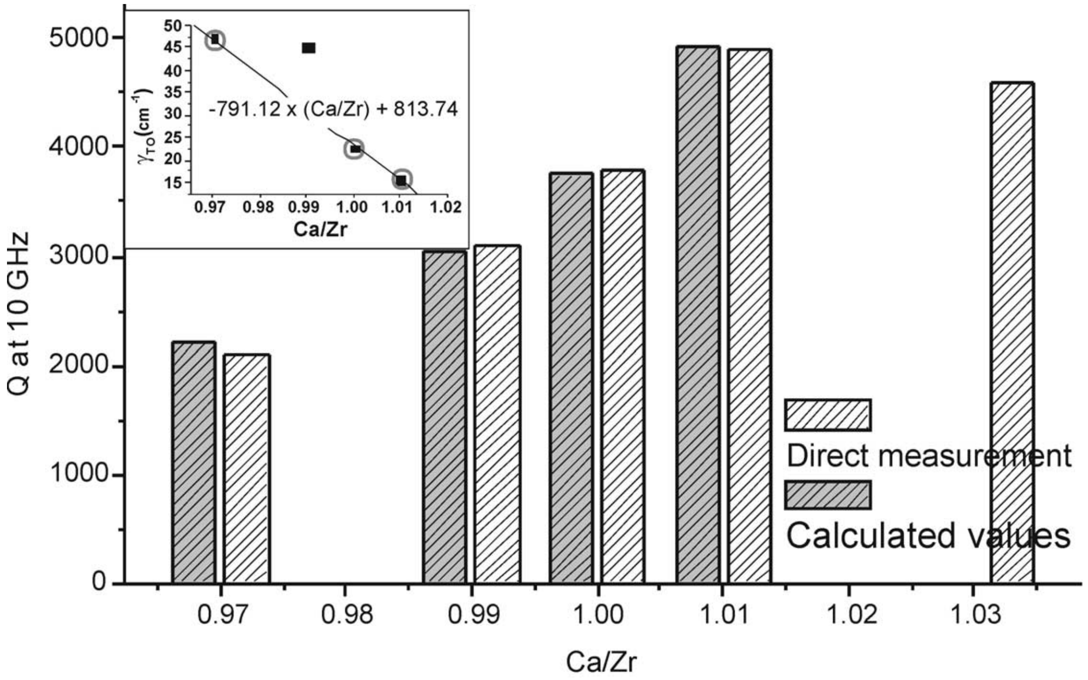

Fig. 3. Directly measured and calculated Q factor at 10 GHz against Ca/Zr ratio. Slope in the inset describes the adjusted first mode TO damping constant evolution against the Ca/Zr ratio.

that these values agree very well. The upper limit for the Ca/Zr ratio can be obtained by zeroing Eq. (8) (otherwise γ_{TO} would be negative). This upper-limit for the Ca/Zr ratio is 1.0286, i.e. an approximated 2.78% Zr deficient $CaZrO_3$ material. This value could explain why we did not succeed in fitting the 3% Zr deficient $CaZrO_3$ material IR spectrum by only adjusting the first mode TO damping constant although this mode is still observable. It should be noted that this last compound's *Q* factor slightly decreases compared to the 1% Zr deficient $CaZrO_3$ material. Two hypotheses can then be envisaged: either the *Q* factor is nearly asymptotic from a 1% Zr deficiency, or it continues to increase until the upper limit determined as above, is obtained and then decreases. Further investigations are needed to clarify this point.

4. Conclusion

$CaZrO_3$ material was analysed using Fourier Transform-Infrared spectroscopy. Applying the generalised oscillator model, its vibration modes were determined with a sufficient accuracy to accounts for the directly measured dielectric parameters. It was evidenced that the most dispersive mode is the first one attributed to the Ca-(ZrO_2) lattice mode. The effect of slight non-stoichiometry was also investigated. Considering only a shift of this first mode TO damping constant, a model is proposed that accounts for the directly measured dielectric parameters. A limit to this model is imposed by a physical constraint ($\gamma_{TO} > 0$) corresponding an upper limit to Zr deficiency at 2.78%. Studies will be made to further understand this limit and in this way improve the dielectric properties of $CaZrO_3$ based materials.

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