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Thermal Evolution of BaZrO₃ and SrZrO₃ Perovskites from 4 K to 773 K: an EXAFS Study at Zr-K Edge

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Abstract. In order to better understand the lattice dynamics of perovskites, we have performed temperature-dependent XAS measurements at Zr-K edge on BaZrO₃ and SrZrO₃. At ambient temperature, BaZrO₃ is cubic, and SrZrO₃ orthorhombic. For both compounds, using the FEFF6 code, we modeled the EXAFS and extracted photo-electron-wave phase-shift and scattering-amplitude. This procedure allowed us to extract distances and Debye-Waller factors, taking into account photo-electron multiple scattering effects. For several atom shells, we fitted the evolution of the Debye-Waller factors as a function of temperature with Einstein or Debye models. The characteristic temperatures obtained show that differences in dynamic behaviour between the two compounds are mainly due to Ba-Sr substitution and that differences in symmetry play a minor role.

1. INTRODUCTION

The perovskite structure has attracted much interest in the Earth sciences because it is adopted, at very high pressure, by two important minerals: CaSiO₃, a cubic perovskite (Pm3m), and (Mg,Fe)SiO₃, a centrosymmetric orthorhombic perovskite (Pbnm), which is likely the major mineral on Earth. The main question is to know whether symmetry changes between orthorhombic and cubic perovskite have important implications for the vibrational properties of these compounds. Temperature dependent XAS studies are a powerful tool to investigate vibrational characteristics (e.g., [1]); since the silicate perovskites are unstable upon heating at ambient pressure, we have studied analog perovskites, BaZrO₃ and SrZrO₃, respectively cubic (Pm3m) and orthorhombic (Pbnm), at Zr-K edge. The photo-electron multiple scattering (MS) effects are important in perovskite compounds (e.g., [2]), in particular in BaZrO₃ and SrZrO₃ [3,4]. For this reason, we used FEFF6 [5] to calculate the EXAFS for both compounds and extract photo-electron-wave phase-shift and amplitude, and to retrieve dynamical information such as Einstein or Debye temperatures of oscillators.

2. EXPERIMENTAL PROCEDURE AND DATA ANALYSIS

XAS data were collected on powders of BaZrO₃ and SrZrO₃ between 4 K and 773 K at the D44 station of the DCI storage ring at LURE (Orsay, France), using a helium cryostat or a furnace. Energy resolution is estimated to be ≈ 4 eV with the monochromator used (two Si (311) single crystals). As an example, an experimental XAS spectrum of BaZrO₃ obtained at 4 K is represented in Fig 1. EXAFS data reduction was performed with standard methods using Fourier transform (FT) filtering [6] except for the last step of the data processing (i.e., the modeling of the FT-filtered EXAFS oscillations). The EXAFS signal $\chi(k)$ was extracted using Victoreen and spline functions, and assuming an edge energy arbitrarily chosen at the midpoint of the absorption edge. The FT of $k^n \chi(k)$ ($n=2$ or 3) was performed with a Kaiser window. FT-filtered EXAFS spectra were modeled with an inversion program [7] adapted from [8], assuming a harmonic approximation. For the first shell (6 oxygen atoms), photoelectron-wave phase-shift and amplitude were extracted from experimental spectra of BaZrO₃ at 4 K. For the other shells, for which MS may become important, EXAFS spectra were calculated with FEFF6; then phase-shift and amplitude of single scattering (SS) and MS paths were extracted from those calculated spectra, with the same procedure used for the experimental spectra. This procedure overcomes amplitude reduction effects due to FT-filtering.

3. RESULTS

3.1 FEFF6 calculations

In cubic BaZrO₃, we have modeled the EXAFS at Zr K-edge with FEFF6 using a cluster including the six first shells (Table 1), with ambient-temperature atomic positions (structural data: [9]). Default options of FEFF6 were used, except that we introduced an energy shift (-4 eV) with the CORRECTIONS card. We have progressively increased the half-path length, up to

6.3 Å. Taking into account MS paths (the number of legs is up to 5 in this calculation), we have obtained a good agreement between calculated and experimental spectra collected at 4 K, the Debye-Waller factor being calculated from a correlated Debye model [10]. Fig 2 shows that MS paths play a significant role, in addition to the SS paths for shells Ba₂ and Zr₃ (refer to Table 1 for the meaning of these symbols). The number of legs of these intense MS contributions to EXAFS is 3 and 4, and they imply only Zr and O atoms. The contributions to the fourth FT-peak, however, are mainly due to SS paths.

In orthorhombic SrZrO₃, similar calculations were performed (structural data: [11]) with half-path length extended up to 10 Å, taking into account MS paths with up to 7 legs. For this calculation, in addition to the options mentioned above, the NOGEOM card was used. We have obtained a good agreement between modeled and experimental spectra (Fig 3). For the six first shells, relative contributions of MS and SS paths to FT-modulus are similar in both perovskites.

Table 1 Distances around Zr in BaZrO₃ (structural data: [9]). Numbers in parentheses mean the error on the last digit.

Shell	Atom	Multiplicity	Distance (Å)
O ₁	O	[6]	2.0950 (2)
Ba ₂	Ba	[8]	3.6286 (3)
Zr ₃	Zr	[6]	4.1900 (4)
O ₄	O	[24]	4.6846 (4)
Zr ₅	Zr	[12]	5.9256 (6)
O ₆	O	[30]	6.2850 (6)

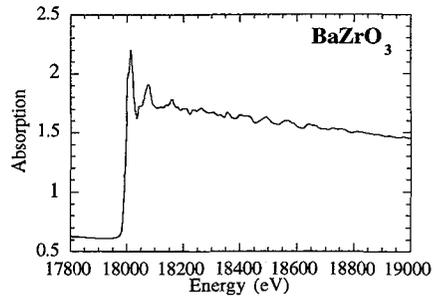


Figure 1 Zr K-edge XAS spectrum of BaZrO₃ collected at 4 K

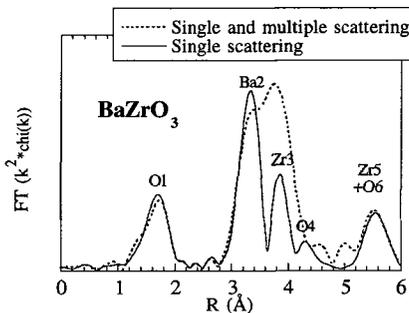


Figure 2 Modeling using FEFF6 of EXAFS oscillations in BaZrO₃. The FT-moduli show the difference between the spectra if MS contributions are taken into account (dashed line) or not (full line).

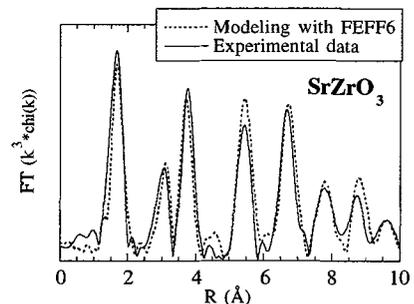


Figure 3 FT-moduli of EXAFS oscillations in SrZrO₃. Experimental data collected at 4 K (full line), and EXAFS spectrum calculated with FEFF6 (dashed line), the MS paths being taken into account.

3.1 Inversion of EXAFS data

For modeling the experimental EXAFS spectra of BaZrO₃ we have used: (i) one shell with SS of O₁ (Table 1) for the first FT-peak; (ii) three contributions inverted simultaneously, with SS of Ba₂ and Zr₃, and one contribution with 3- and 4-legs MS paths at 4.19 Å for the second and third FT-peaks; (iii) two shells with SS of Zr₅ and O₆ for the fourth FT-peak. With this procedure, we have obtained, as a function of temperature, the Debye-Waller factors of Zr-O₁, Zr-Ba₂, Zr-Zr₃ and Zr-O₆. As an example, we present the evolution with temperature of the Debye-Waller factor of O₁ (Fig 4). For SrZrO₃, a similar procedure was used, and we have obtained the Debye-Waller factor of Zr-O₁, Zr-Sr₂, Zr-Zr₃ and Zr-O₆ (we used a nomenclature of the shells similar to that of BaZrO₃).

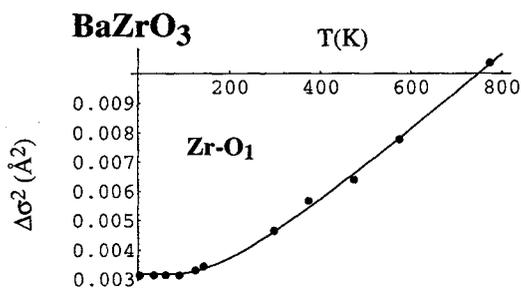


Figure 4 Square of the Debye-Waller factor of the O₁ shell vs temperature in BaZrO₃, and fit with an Einstein model ($\theta_E=520\pm 10$ K)

Table 2 Oscillators Einstein and Debye temperatures (non-correlated (nc) and correlated (c) Debye model). $\Delta\sigma_0^2$ is the same for all models, and was obtained with a least-square regression using the Einstein model.

	θ_E (K)	θ_D (nc) (K)	θ_D (c) (K)	$\Delta\sigma_0^2$ (10^{-3}Å^2)
BaZrO₃				
Zr-O ₁	520±10	910±20		-0.3±0.5
Zr-Ba ₂	180±7	315±10	260±9	-1.8±0.8
Zr-Zr ₅	254±5	438±8	400±7	-0.6±0.6
Zr-O ₆	287±15	495±25	455±25	-0.3±2
SrZrO₃				
Zr-O ₁	517±15	905±30		0.5±0.5
Zr-Sr ₂	258±10	450±15	390±14	0.0±0.8
Zr-Zr ₃	270±25	468±40	417±36	1.3±1.3
Zr-Zr ₅	239±9	415±15	375±14	1.4±1

4. EINSTEIN AND DEBYE TEMPERATURES

For each shell, the square of the DWF σ^2 vs temperature has been fitted using either Einstein or Debye model. For the Einstein model [6], we have used the equation

$$\Delta\sigma^2(T) = \frac{A_E}{\theta_E} \coth\left(\frac{\theta_E}{2T}\right) + \Delta\sigma_0^2 \quad (1)$$

where $A_E = \hbar^2/2\mu k_B$, μ being the reduced mass, θ_E the Einstein temperature, and the other symbols having their usual meaning. The two parameters of the least-square fit, θ_E and $\Delta\sigma_0^2$, are reported in Table 2. The equation used for the Debye model [12] is

$$\Delta\sigma^2(T) = \frac{A_D}{\theta_D} \left[\frac{1}{4} + \left(\frac{T}{\theta_D}\right)^2 \int_0^{\theta_D/T} \frac{xdx}{e^x - 1} \right] + \Delta\sigma_0^2 \quad (2)$$

with $A_D = 3\hbar^2/\mu k_B = 6A_E$, θ_D , the Debye temperature, being the parameter of the fit. $\Delta\sigma_0^2$ has the same value as that obtained with the Einstein model). This "non correlated" Debye model may be improved [1,10,12] if we take into account the correlation of atom motions. We observe that characteristic temperatures of Zr-O₁ are similar in both compounds, whereas Zr-Sr₂ and Zr-Ba₂ are different. It is also interesting to note that Debye temperatures obtained for Zr-Zr₅ oscillators are very similar in both compounds. Thus, changing from orthorhombic to cubic symmetry does not seem to induce important changes in the vibrational characteristics of perovskites, at least in the cases investigated here, the major changes being due to the substitution of cations.

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