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(Tb, Ce)-L_{III} XAS High Pressure Study of Tetravalent BaTbO₃ and SrCeO₃

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Abstract: We have studied the Tb- and Ce-L_{III} XAS of distorted-perovskite type BaTbO₃ and SrCeO₃ at pressure up to 20 GPa using a diamond anvil cell. While the XANES spectra of both tetravalent systems monitor an increase of hybridization and crystal-field splitting with pressure, the EXAFS spectra indicate an approach towards an undistorted perovskite structure with pressure.

1. INTRODUCTION

Previous R-L_{III} edge studies of RO₂ and RF₄ (R = Ce, Pr, Tb) reveal important information about the hybridization of the tetravalent rare-earths ions with the ligands [1-3]. Similar information was obtained in a Pr-L_{III} XANES study of BaPrO₃ [4], where strong crystal-field splittings of the characteristic "white-line" (WL) structures were observed. We extend in the present contribution these studies to BaTbO₃ and SrCeO₃, both also of distorted-perovskite structure [5], and study also the effect of pressure on both XANES and EXAFS spectra.

2. EXPERIMENTAL

The high-pressure studies at the (Ce,Tb)-L_{III} edges were performed in diamond-anvil cells [6] at the EXAFS II beamline (HASYLAB/DESY, Hamburg) employing a Si(111) double-crystal monochromator and a focussing Au mirror; higher harmonics were suppressed by this mirror and by detuning of the monochromator. Reference spectra were taken simultaneously with TbF₃ and CeF₃.

3. Tb-L_{III} XANES OF BaTbO₃

The L_{III}-XANES spectra of both BaTbO₃ (Fig. 1) and SrCeO₃ (not shown) exhibit double-peaked WL structures similar to those observed for BaPrO₃ [4] and BaCeO₃ [7]. In the XANES data analyses of tetravalent R-systems [1-4] the normalized R-L_{III} spectra were fitted by two subspectra consisting of a superposition of an arctangens step function and one or two Lorentzians. The instrumental resolution of the monochromator is considered in the fits by a convolution of the theory function with a Gaussian. Here we applied a new approach to fit the XANES spectra: the experimental spectra were at first deconvoluted from the instrumental broadening and these deconvoluted spectra were used for the calculation of the first and second derivatives as shown in Fig. 1. The first derivative is sensitive for the edge position (showing the arctangens by a maximum), while the second derivative is sensitive for the WL positions (showing the maxima of the Lorentzians as minima). In the fit analysis, the deconvoluted spectrum as well as first and second derivatives were fitted by the corresponding functions of the edges (dashed lines) and WLs (dotted lines). The new fitprogram is named DEF (derivative-edge-fit).

In the Tb-L_{III} DEF spectra of BaTbO₃ the crystal-field (CF) splitting is monitored by the splitting A₁-A₂ of the A component (2p⁵4f⁸5d* final state). This splitting increases from 4.4(1) eV (0 GPa) to 5.0(1) eV (19 GPa). The intensity of the B component, attributed to a 2p⁵4f⁸5d*_L final state [1-4] with CF-split substructures B₁ and B₂, is less than in SrCeO₃, BaCeO₃ and BaPrO₃ [4,7]. This points to a smaller hybridization in Tb(IV) systems, similar to the observations in RF₄ (2). The intensity of B₁+B₂ with respect to A₁+A₂ increases with pressure as observed in RO₂ systems [1,3]. We observe for the present systems also typical differences in the A₁/A₂ and B₁/B₂ intensity ratios between the L_{II}- and L_{III}-edge spectra (so-called "j-effects") similar to those reported in [3,4].

4. (Tb,Ce)-L_{III} EXAFS OF BaTbO₃ AND SrCeO₃

Structural informations about the pressure dependence of the Tb-O and Ce-O distances were obtained from EXAFS studies up to 20 GPa. Details of the complex EXAFS analyses (because of the distorted perovskite structure) will be presented elsewhere. Here we show in Fig. 2 as "fingerprints" for the pressure induced changes only the Fourier transforms (FT) and compare them with a simulated FT spectrum of undistorted (cubic) BaTbO₃, obtained by the FEFF6 code [8] and being in its characteristic features very similar to the simulated FT of (cubic) SrCeO₃. Comparison of the simulated and experimental spectra in Fig. 2 (a,b,c) gives evidence that with increasing pressure a less distorted perovskite structure is approached. The pressure induced changes are more pronounced for SrCeO₃ (Fig. 2 c), which is more distorted than BaTbO₃ at ambient pressure.

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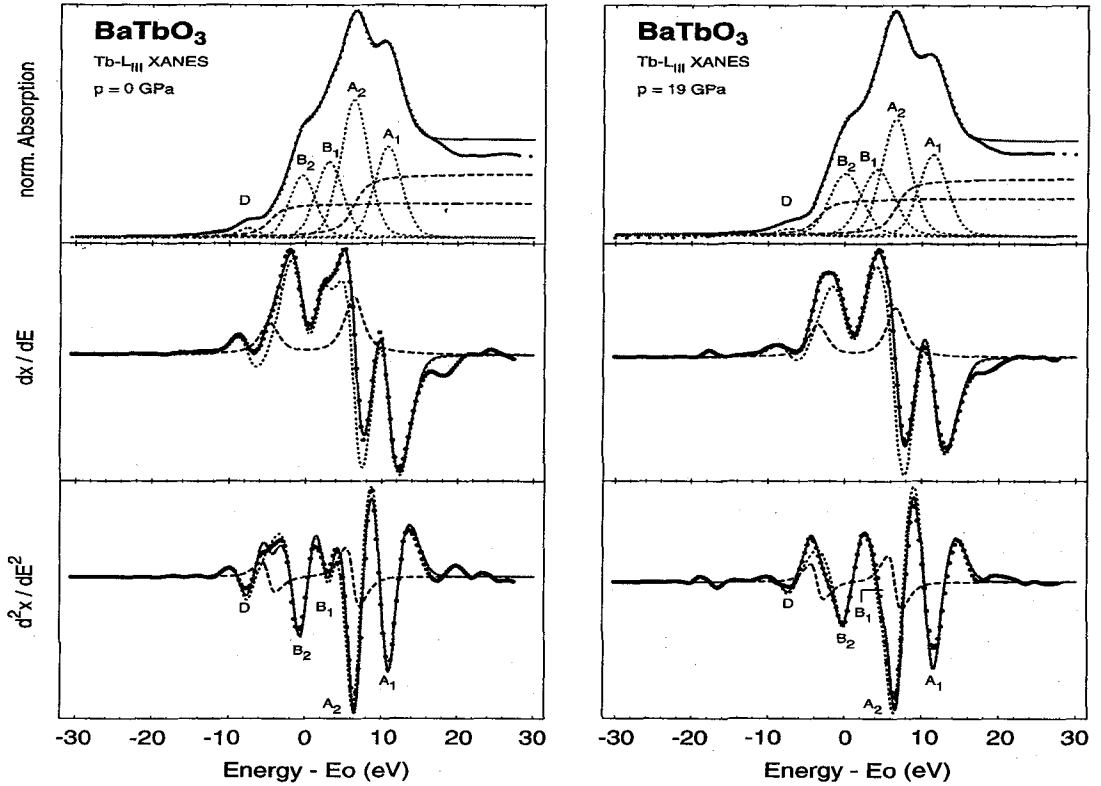


Fig.1: DEF spectra of Tb-L_{III} XANES of BaTbO₃ at p = 0 GPa (left) and p = 19(2) GPa (right). The spectra were deconvoluted with 2.8 eV FWHM (Tb-L_{III} at E = 7514 eV, Si(111)). The zero position is identical with the WL position of the TbF₃ reference.

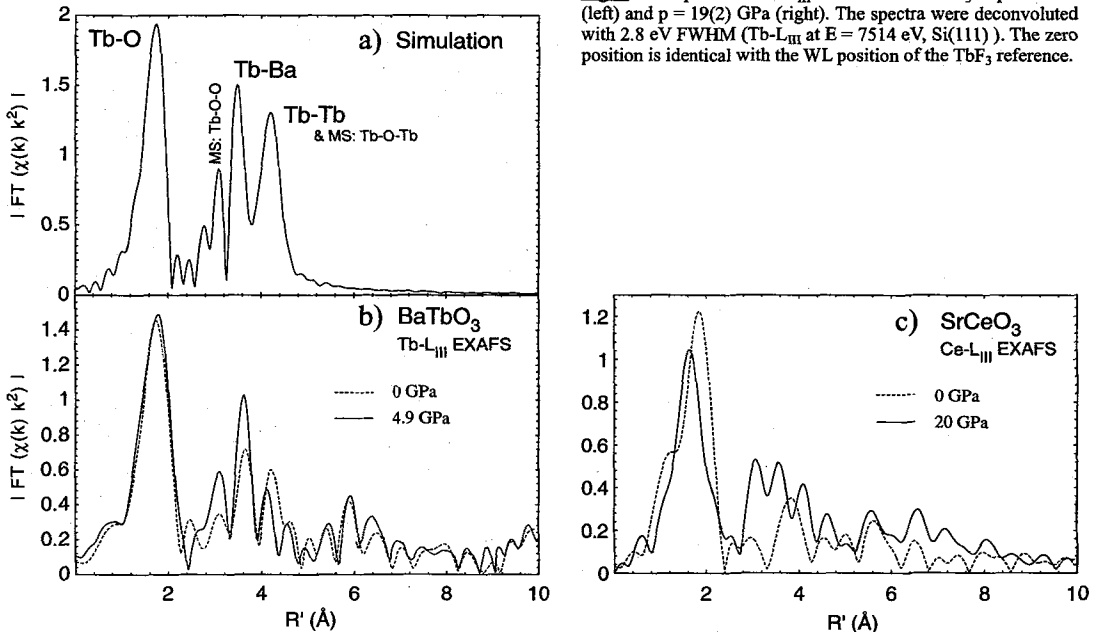


Fig. 2: a) Fourier Transforms of a cubic perovskite-structured simulation of BaTbO₃ with multiple scattering paths (MS) and (Tb,Ce)-L_{III} FT of b) BaTbO₃ and c) SrCeO₃, respectively.