



## Raman Scattering Study of the $\text{Pb}(\text{Hf}_x\text{Ti}_{1-x})\text{O}_3$ Ceramics

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**Abstract.** Raman spectroscopy was used to study the long wavelength vibrations of tetragonal perovskite (space group  $P4mm$ )  $\text{Pb}(\text{Hf}_x\text{Ti}_{1-x})\text{O}_3$  (PHT) ( $0.10 \leq x \leq 0.50$ ) samples at room temperature and at  $\approx 20$  K. For  $x \leq 0.40$ , Raman spectra collected from the PHT samples were very similar to the previous spectra collected from the PZT samples with the same value of  $x$ , except the mode at around  $190 \text{ cm}^{-1}$ , whose frequency was decreasing with increasing  $x$  in PHT ceramics. Correspondingly, the latter feature was taken as a sign of the 'mass effect' (Hf versus Zr) while the similarity of the remaining parts of the Raman spectra was assumed to be due to the almost identical ionic radii difference between  $\text{Ti}^{4+}$  and  $\text{Zr}^{4+}$  and between  $\text{Ti}^{4+}$  and  $\text{Hf}^{4+}$  ionic radii. The behaviour of the mode at around  $280 \text{ cm}^{-1}$  revealed that a phase transition occurred once  $x$  was changing from 0.40 to 0.50.

**Keywords:** Raman spectroscopy, peak split, tetragonal, perovskite, lead hafnate titanate

### 1. Introduction

Previous studies indicated that the (ideally twofold degenerate)  $E$ -symmetry modes of the tetragonal perovskites of type  $AA'BO_3$  and  $ABB'O_3$  were split [1, 2]. To the first category fall Nd or La modified  $\text{PbTiO}_3$  ceramics and to the second one  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  (PZT) ceramics with  $x < 0.50$ . The  $E$ -symmetry modes involve the vibrations of anions and cations in the tetragonal  $ab$  plane. High-resolution neutron powder diffraction (NPD) experiments revealed that the average symmetry of  $\text{Pb}(\text{Zr}_{0.20}\text{Ti}_{0.80})\text{O}_3$  sample remained tetragonal down to the lowest measurement temperature 4.2 K [3], and another kind of explanation than the average symmetry lowering for the mode splitting must be invoked. The phenomenon itself has been known for long (for example, see ref. [4], where a random-element-isodisplacement model was introduced to model the peak split in  $\text{GaAs}_x\text{P}_{1-x}$  single crystals). Alloying  $\text{PbTiO}_3$  by Zr or Hf leads to numerous phase transformations. By following the behaviour of the long wavelength vibrations (which first order Raman scat-

tering essentially probes) in samples with different  $x$ , one gets insight to the mechanisms which gradually lead to a phase transformation. The importance of lattice vibrations on the prediction of phase diagrams of substitutional alloys is discussed in detail in ref. [5].

To clarify the present situation, we prepared  $\text{Pb}(\text{Hf}_x\text{Ti}_{1-x})\text{O}_3$  (PHT) ceramics and characterized the average crystal structure by x-ray powder diffraction and NPD [6]. Even though the crystal structure of the  $x \leq 0.40$  single phase samples were nicely modelled by the space group  $P4mm$  with one formula unit per primitive cell (down to 4 K), Raman scattering revealed that there were significant and systematic deviations from the average symmetry. Although the peak split was apparent already at room temperature, we concentrate on the analysis of low-temperature data. This is due to the fact that the widths of the Raman peaks are considerably narrower at low temperature. Also the  $a$ -axis contracts with decreasing temperature, which should enhance the phenomenon in the case of the  $E$ -symmetry modes. In addition, the low-frequency 'background' (as is discussed in ref. [2]) is significantly weaker at low temperature. Our purpose was to study the effect of (i) the  $B$ -cation mass, (ii) the  $B$ -cation ionic radii (bond lengths) and (iii) temperature on the

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Raman spectra of PHT and PZT samples. Attention is also paid on the phase transformation as a function of  $x$  observed in PHT and PZT samples at low temperature.

## 2. Experimental

Ceramic PHT samples, with  $0.10 \leq x \leq 0.50$ , were prepared from high purity oxides (PbO, HfO<sub>2</sub> and TiO<sub>2</sub>) through solid state reaction technique. First, oxides were weighed in desired Hf/Ti ratios, ball-milled, annealed at 800°C, ground, ball-milled again and then pressed into a pellet form and sintered at 1100°C under inverted, sealed alumina crucible. Pellets were covered with the same PHT powder in order to prevent composition alteration during sintering (particularly PbO is very volatile). For the diffraction experiments, pellets were ground. According to the X-ray diffraction and high resolution NPD experiments, all powders contained only tetragonal phase [6].

Visible laser light (wavelength 514.532 nm) and Jobin Yvon T64000 spectrometer were used for Raman measurements. Slits were adjusted so that the resolution was about 1 cm<sup>-1</sup>. Prior to each measurement, spectrometer was calibrated using a Ne lamp. The spectra between -800 cm<sup>-1</sup> and 1421 cm<sup>-1</sup> (anti-Stokes and Stokes) were measured using a triple monochromator with a grating of 1800 grooves per mm. All measurements were carried out under the microscope (laser spot diameter was estimated to be between 1 and 2 μm). Low temperature measurements were carried out using liquid helium cryostat (allowing cooling down to 4.2 K). During low temperature measurements, laser beam power was adjusted to be 50 μW in order to prevent local heating. At 4.2 K (temperature at coldfinger), only noise was observed in the anti-Stokes spectra, and correspondingly the local temperature was estimated to be below 20 K. In order to have higher resolution, CCD detector pixels were not binned.

Raman spectra were analyzed using Jandel-Scientific Peak Fit 4.0 software. Typically, a second order polynomial was used to model the background, while peaks were modelled by a sum of Lorentzian and Gaussian functions (so called pseudo-Voigt function).

## 3. Results and Discussion

Figure 1 shows the Raman spectra collected from the PHT and PZT samples with  $x = 0.10, 0.20, 0.30, 0.40$  and 0.50 at 4 K (estimated local temperature was less

than 20 K), while Fig. 2 gives the peak positions obtained from the peak fit. Due to the overlapping of numerous peaks we could not obtain reliable curve fit for the  $x = 0.50$  sample in the case of the high frequency regime. In the case of the perovskites with  $P4mm$  symmetry with one formula unit per primitive cell, the Brillouin zone centre modes transform as the representation  $3A_1 \oplus B_1 \oplus 4E$ , i.e., there are 12 optical modes corresponding to eight different frequencies ( $E$ -symmetry modes are twofold degenerate). The number of observed peaks was roughly double due to the fact that transversal and longitudinal modes have different frequencies, and in addition there were several subpeaks in the case of the  $A_1(1TO)$  mode. Although the  $A_1(1TO)$  symmetry mode is consisted of a series of subpeaks, their intensity and frequency dependence as a function of temperature were well explained by the anharmonic effects (for details, see refs. [7, 8]). Comparison of the present and previous Raman data allowed to make a mode assignment proposal. In addition, each longitudinal mode has much weaker intensity and higher frequency than the corresponding transversal mode. Due to the lack of translational symmetry, the total number of peaks is further increased in solid solutions, such as in PZT and PHT. Although solid solutions lack a well-defined symmetry (so that classification of vibrations into optical and acoustical ones is not strictly valid), we classified the peaks of the tetragonal phase either being  $E$ -type (vibration in a tetragonal  $ab$ -plane) or  $A_1$ -type (vibration along the  $c$ -axis) for those modes for which a comparison with the single crystal data [7, 9] was possible. Basically, in the case of the  $E$ -symmetry modes with infinite wavelength (which the first order Raman scattering essentially probes) all  $B$  cations move in phase. This is not anymore true in the case of solid solutions: both the phase and amplitude of the  $B$  cation displacement may differ. Thus, one must increase the number of basis functions by specifying separate displacement vectors for both types of  $B$  cations, although a more accurate description necessitates that one also allows oxygen positions to be correspondingly changed. In addition, there were modes whose origin is not clear, such as the modes at around 50, 580 and 830 cm<sup>-1</sup>.

Figure 1 shows that the Raman spectra of PHT and PZT samples with  $x \leq 0.40$  were similar to each other (despite the large mass difference between Hf and Zr, which one could expect to be important for the low frequency modes), except the mode at around 190 cm<sup>-1</sup> (indicated by an arrow in Fig. 1), whose frequency was

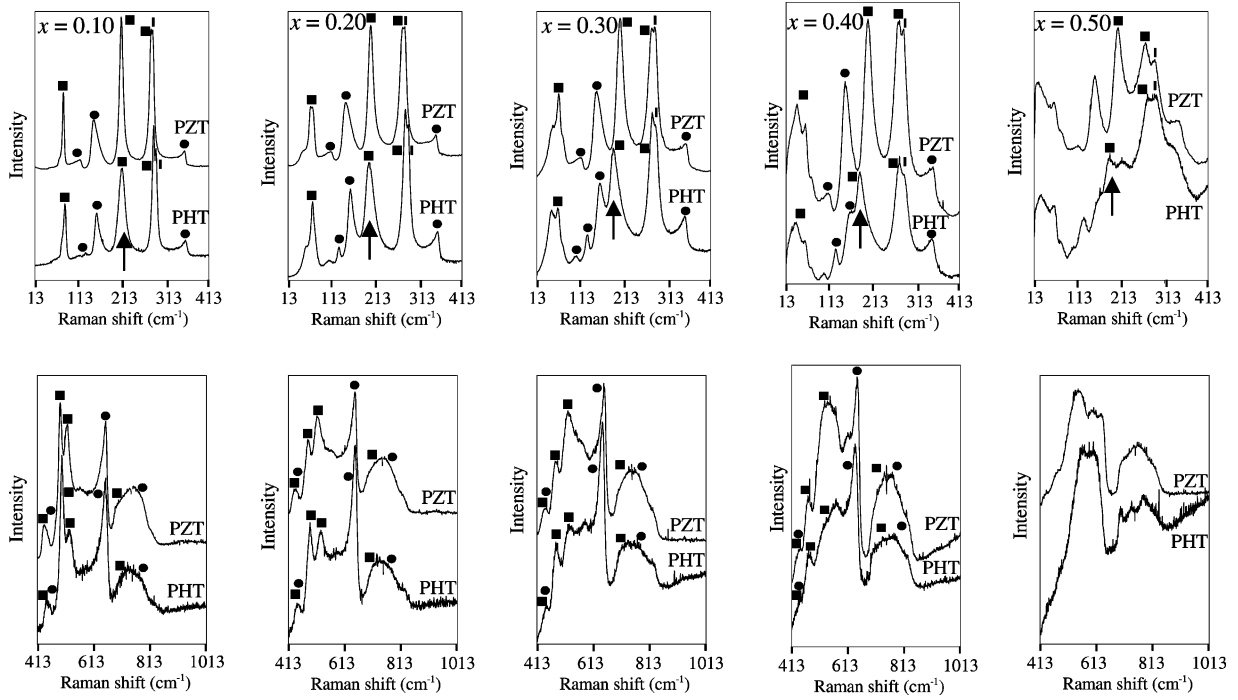


Fig. 1. Raman spectra collected from the PHT and PZT samples at  $\approx 20$  K. Upper row shows the low frequency regime and the lower row shows the high frequency regime of the spectra. The mode at around  $190\text{ cm}^{-1}$  in PHT ceramics is indicated by an arrow. In the case of the  $x \leq 0.40$  samples, tick mark, square and circle label the  $B_1$ ,  $E$  and  $A_1$  type modes, respectively. In the case of the  $x = 0.50$  sample square and tick marks label the peaks carrying the most relevant information concerning the phase transition.

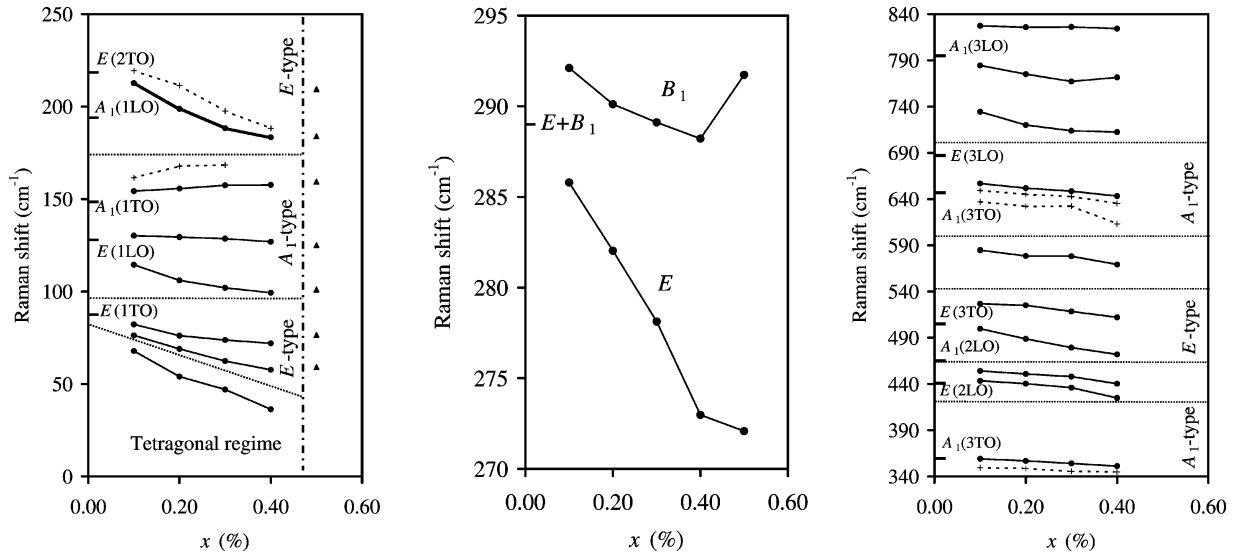


Fig. 2. Peak positions in the PHT ceramics, as obtained from the peak fit. Dotted lines tentatively divide the modes into the  $E$  and  $A_1$  types. Solid lines indicate peak position which were unambiguously revealed (as a separate peak or as a clear shoulder). Dashed lines indicate ‘modes’ which were ambiguous and were revealed during a fitting procedure as large residuals. Correspondingly, they were used to fit the unambiguous peaks more reliably. Also the room temperature values of the modes in  $\text{PbTiO}_3$  single crystals are indicated (data adapted from ref. [7] and notation from ref. [9]).

decreasing faster in the case of PHT ceramics than in the case of PZT ceramics with increasing  $x$ . The behaviour of the higher frequency mode of the peak doublet at around  $280\text{ cm}^{-1}$  as a function of  $x$  indicated that a phase transition occurred once  $x$  changed from 0.40 to 0.50 (see the middle panel in Fig. 2). This is very similar to the previous observations in the case of PZT ceramics [2, 10]. Symmetry analysis shows that the  $B_1$  symmetry mode breaks the fourfold symmetry, and thus an abrupt change in its vibration frequency probably corresponded to the symmetry lowering. Even in the case of the Raman spectra of the  $x = 0.50$  sample the most apparent change (when compared to the  $x = 0.40$  sample) was seen in this frequency range (around  $190\text{ cm}^{-1}$ ) and additionally in the range between  $500$  and  $650\text{ cm}^{-1}$ , while the spectra below  $110\text{ cm}^{-1}$  and between  $650$  and  $850\text{ cm}^{-1}$  were essentially unchanged (compare the spectra shown in Fig. 1). Thus, it seems natural to expect that the possible differences in the crystal symmetries of the PHT and PZT ceramics with  $x = 0.50$  are related to this mode (indicated by an arrow in Fig. 1). Previous NPD work indicated that the PZT sample with  $x = 0.50$  had a monoclinic symmetry at 10 K (space group  $Cm$ ) [11]. We do not yet have low-temperature NPD data for the PHT sample with  $x = 0.50$ , but work is under a way to clarify the situation. However, the Raman spectra of the PHT sample with  $x = 0.50$  was reminiscent of rhombohedral distortion (similarly to the PZT ceramics with  $x \geq 0.52$ ).

To summarize, the  $B_1$  mode indicated a phase transition to occur both in the case of PZT and PHT samples, while the different behaviour of the mode at around  $190\text{ cm}^{-1}$  might be an indication of the different phase transformation mechanism in PHT and PZT ceramics. We note that there are different ways to break the tetragonal symmetry, as is discussed in detail in ref. [12] in the case of tetragonal  $\text{PbTiO}_3$  (this study covers the high symmetry points of the Brillouin zone). Although in the case of solid solutions one cannot obtain as far reaching conclusions as in the case of crystals truly having translational symmetry, we note that the coupling of the atomic displacements and strain could result in orthorhombic and monoclinic distortions in the case of the Brillouin zone centre  $B_1$  and  $E$  modes, respectively.

Generally, the magnitude of the peak split observed in PHT ceramics was almost the same as in the case of the PZT ceramics. The ionic radii (for octahedral coordination) and masses of  $\text{Ti}^{4+}$ ,  $\text{Zr}^{4+}$  and  $\text{Hf}^{4+}$  ions were

0.61, 0.72, and 0.71 Å and 47.88, 91.22, and 178.5 u, respectively. This is hinting that the ionic radii difference between  $\text{Ti}^{4+}$  and  $\text{Zr}^{4+}$  (PZT) and between  $\text{Ti}^{4+}$  and  $\text{Hf}^{4+}$  (PHT) is the most significant factor for the understanding of the phenomenon. Within a rigid ion model [13], this means that the effect of larger mass of Hf (when compared to Zr) on vibration frequencies must largely be compensated by the short range interactions and/or effective charges. This should be the case if one wishes to explain the significant similarity between the Raman spectra measured from the PHT and PZT ceramics with  $x \leq 0.40$ . Somewhat surprisingly, no mode frequency followed simple  $m_B^{-1/2}$  ( $m_B$  is the average  $B$ -cation mass) dependency. This is further contrasted by the fact that both the Hf and Zr substitution for Ti increase the  $a$ -axis length, while the  $c$ -axis remains almost constant, and thus one could expect strong decrease in the  $E$  symmetry mode frequencies.

#### 4. Conclusions

The role of the  $B$ -cation ionic radii and mass on the long wavelength vibrations and average structure of PZT and PHT ceramics with  $0.10 \leq x \leq 0.50$  were studied by Raman spectroscopy and x-ray and neutron powder diffraction techniques. Particular emphasis was put on the study of the low-temperature properties. Except the peak at around  $190\text{ cm}^{-1}$ , the Raman spectra collected from the tetragonal ( $x \leq 0.40$ ) PHT and PZT samples with the same value of  $x$  were similar to each other. The magnitude of the peak split of the PHT ceramics was only slightly larger than that of the PZT ceramics. In addition, the  $A_1(\text{TO})$  modes of the PHT ceramics had slightly higher frequency than the corresponding modes in PZT ceramics. Although the mass difference between Hf and Zr ions is large, the role of the ionic radii was found to be dominating (the effect of mass difference between Hf and Zr on vibration frequencies was compensated by short range forces and/or effective charges of ions). At low-temperature, a phase transformation occurred in PHT ceramics once  $x$  changed from 0.40 to 0.50, as was revealed by Raman scattering.

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