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1994 J. Phys.: Condens. Matter 6 4655

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## On the Pb thermal vibrations in PbHfO<sub>3</sub> crystals

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Received 3 December 1993

**Abstract.** In PbHfO<sub>3</sub> single crystals the amplitude of the thermal vibrations for Pb ions in the high-temperature *Pm3m* phase, calculated from the Debye–Waller factor, reached unexpectedly large values. The random displacements of Pb ions were assumed and the new thermal vibration amplitude, which is more reasonable from the crystal lattice dynamics point of view, was calculated. A possible displacive-type phase transition was observed in the vicinity of 400 °C.

### 1. Introduction

Lead hafnate (PbHfO<sub>3</sub>) has the perovskite-type structure (Shirane and Pepinsky 1953). Two phase transitions were observed: the first from the paraelectric to the antiferroelectric state at 215 °C, and the second between two antiferroelectric states at 163 °C. Until now, the dielectric properties and basic structure parameters have been investigated for antiferroelectric phases only. Using the x-ray diffraction method the structure parameters of PbHfO<sub>3</sub> were determined (Forker *et al* 1973, Leontiev *et al* 1984) and the results obtained in those papers were similar. There is very little information about the paraelectric phase. The crystal lattice dynamics have not been investigated yet.

Several workers (Comes *et al* 1968, Itoh *et al* 1985, Chen Jun *et al* 1988, Bonneau *et al* 1991, Glazer and Roleder 1993) have reported the existence of ‘disorder’ in perovskites even in the paraelectric phase whose symmetry is commonly described by the *Pm3m* space group. The theoretical model describing this ‘disorder’ state was proposed by Comes *et al* (1968). This model was then applied to BaTiO<sub>3</sub> (Itoh *et al* 1985), to BaTiO<sub>3</sub> and KNbO<sub>3</sub> (Chen Jun *et al* 1988) and to PbMg<sub>x</sub>Nb<sub>1-x</sub>O<sub>3</sub> (Bonneau *et al* 1991).

In this work, the results on the structure and crystal lattice dynamics investigations of PbHfO<sub>3</sub>, especially in the paraelectric phase, are presented.

### 2. Experimental details

The PbHfO<sub>3</sub> single crystals were obtained by the flux method, similar to that used by Smotrakov and Fesenko (1975) for PbZrO<sub>3</sub> crystals. A mixture of PbHfO<sub>3</sub>, PbO and B<sub>2</sub>O<sub>3</sub> in the proportions 2.6 mol% : 77 mol% : 20.4 mol% was placed in a platinum crucible and annealed at a temperature of 1200 °C for 4 h. Then the melt was cooled at a rate of 12 °C h<sup>-1</sup> to 1050 °C and the solvent was poured off. A constant temperature gradient along the axis of the crucible of about 10 °C cm<sup>-1</sup> was maintained throughout. Transparent light-grey crystals in the form of thin plates were obtained.

X-ray measurements of crystal lattice parameters and dynamics were performed on powdered single crystals using the modified DRON-1.5 diffractometer (filtered Cu K $\alpha$

radiation). The diffraction patterns were recorded at several temperatures in the  $20^\circ < 2\theta < 120^\circ$  range in  $0.04^\circ$  steps and with a counting time of 20 s. The temperature was stabilized to within  $\pm 0.5^\circ\text{C}$  accuracy. In all measurements the sample was first heated to  $600^\circ\text{C}$  and then cooled to the required temperature. Structural refinements were performed using the Rietveld method. The weighted pattern  $R$ -factor fluctuated between 7% and 10%. The mean square thermal vibration amplitude  $\langle u^2 \rangle$  was calculated from the Debye–Waller factor  $B$  using the formula  $B = 8\pi^2\langle u^2 \rangle$ .

### 3. Results

The temperature dependences of the pseudo-perovskite cell parameters of  $\text{PbHfO}_3$  are shown in figure 1. The values of the cell parameters and their temperature dependences in the antiferroelectric phases are similar to those obtained earlier by Shirane and Pepinsky (1953) and Leontiev *et al* (1984). In those studies the measurements were, however, stopped at below  $300^\circ\text{C}$ , while in our work the temperature reaches  $600^\circ\text{C}$ . In figure 1 we can see that near  $400^\circ\text{C}$  the shape of the  $a(T)$ -dependence changes, which means a change in the thermal expansion coefficient.

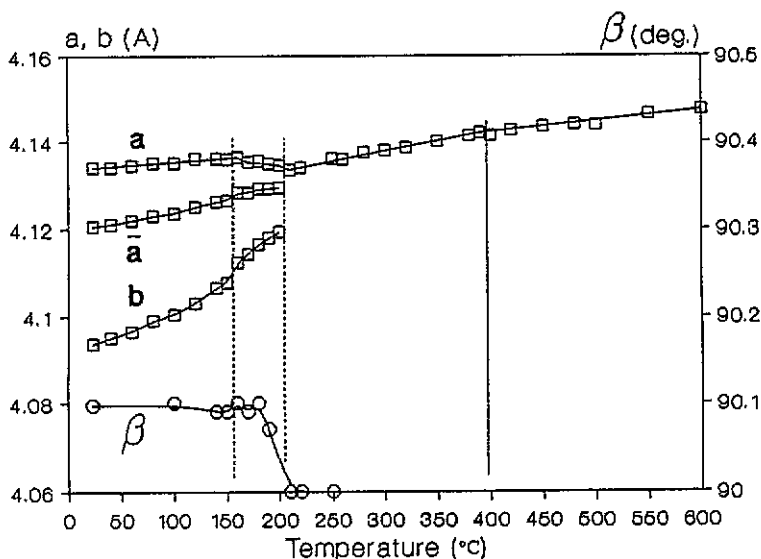


Figure 1. Pseudo-perovskite lattice parameters versus temperature.

Considering the mean ion positions given by the  $Pm3m$  space group and using the Rietveld method of data analysis we obtained the isotropic Debye–Waller factor  $B$  for each ion, i.e.  $B(\text{Pb})$ ,  $B(\text{Hf})$  and  $B(\text{O})$ . These factors  $B$  and the related mean square thermal vibration amplitudes  $\langle u^2 \rangle$  are shown in figure 2. Up to  $300^\circ\text{C}$ , we can see that  $B(\text{Pb}) > B(\text{Hf}) = B(\text{O})$  and at higher temperatures,  $B(\text{Pb}) > B(\text{O}) > B(\text{Hf})$ . In the whole temperature range the value of  $B(\text{Pb})$  is significantly higher than  $B(\text{Hf})$ . A similar relation was observed for other lead-containing perovskites:  $\text{PbTiO}_3$  and  $\text{PbZrO}_3$  (Glazer and Mabud 1978, Kuprianov and Kogan 1991). It is surprising that the heaviest atoms in the structure

have the largest  $\langle u^2 \rangle$ -values. The masses of the Pb and Hf ions are comparable and the Pb ion is one order of magnitude heavier than the O ion. From the crystal dynamics point of view and considering the relations between the ion masses, there is a small probability for Pb ions to have a  $\langle u^2 \rangle$ -value almost twice the  $\langle u^2 \rangle$ -value for Hf ions and about 30% greater than for O ions.

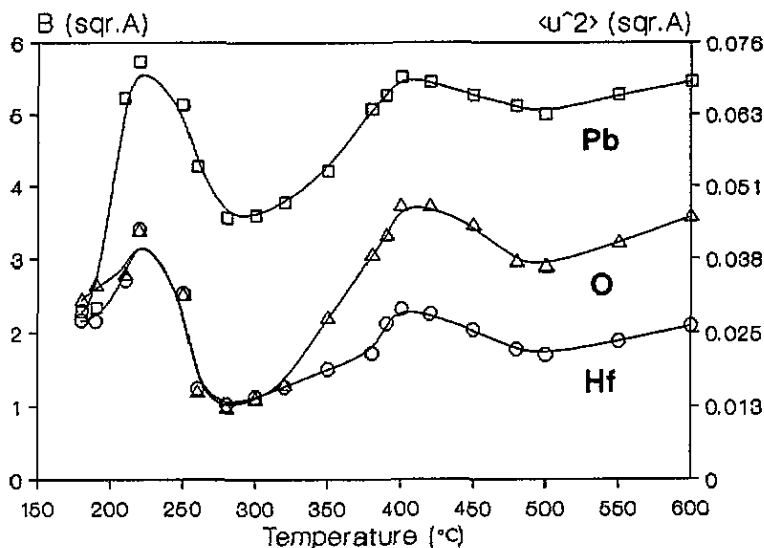
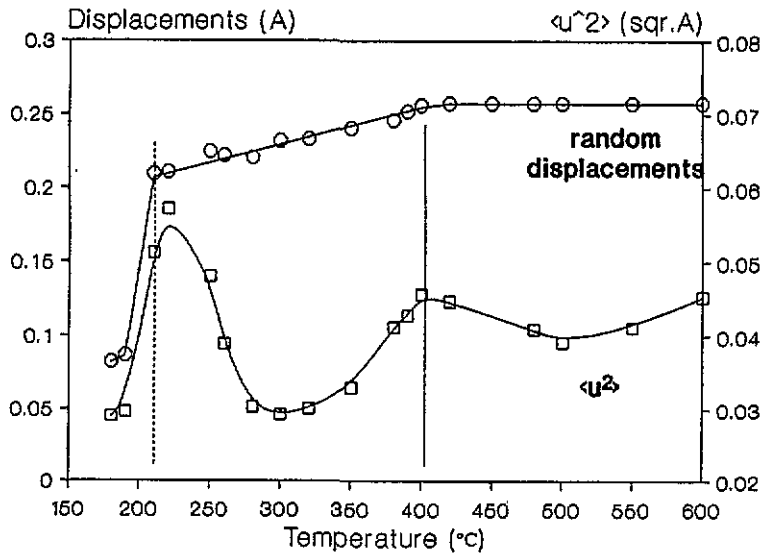


Figure 2. Isotropic temperature factors  $B$  and connected mean thermal vibration amplitudes  $\langle u^2 \rangle$  versus temperature for ions in positions given by the  $Pm3m$  space group.

To explain the behaviour described above, according to the suggestions of Kuprianov and Kogan (1991), Itoh *et al* (1985) and Comes *et al* (1968), we assume that the mean position of the Pb ion is displaced from that given by the  $Pm3m$  space group. The movement of Pb ions can be described as the result of two mechanisms simultaneously:

- (1) the random (independent in various cells) displacements from the (0, 0, 0) position to one of the 12 equivalent  $(x, x, 0)$  positions, where chaotic jumps between these positions may take place;
- (2) thermal vibration with the mean square amplitude  $\langle u^2 \rangle$  around the new off-centre position.

The Rietveld computing procedure was repeated with  $x$  and  $\langle u^2 \rangle$  as parameters. The fitting for  $x$  and  $\langle u^2 \rangle$  was performed alternatively because of the very strong correlation between them. The  $R$ -factor did not change significantly. The data obtained are shown in figure 3. The  $\langle u^2 \rangle$ -values for Pb ions are lower than those obtained earlier (see figure 2). Now  $\langle u^2 \rangle$  for Pb ions agrees better with  $\langle u^2 \rangle$  for Hf and O ions. The random displacements of Pb ions from the central (0, 0, 0) position to one of the non-central  $(x, x, 0)$  positions between O ions could be connected with the electron structure of the Pb atoms. Cohen and Krakauer (1992) reported non-spherical symmetry of Pb electron shells. Moreover the Pb–O bond is 50% covalent (Thomann 1984), which means that it is strongly anisotropic and Pb ions do not have a spherical symmetry. The non-spherical symmetry of Pb ions results in its off-centre position between neighbouring ions.



**Figure 3.** Displacement from position given by the  $Pm3m$  space group and mean square amplitude  $\langle u^2 \rangle$  of thermal vibrations versus temperature for Pb ions (positions of the other ions without displacements from those given by the  $Pm3m$  space group).

In figure 3 we can see that during the transition from the antiferroelectric to the paraelectric phase (200–210 °C) a jump-like increase in Pb ion random displacements takes place. Moreover the  $\langle u^2 \rangle$ -value reaches a maximum, which could be connected with the displacive-type phase transition (Itoh and Fujihara 1991). This is in good agreement with the results of investigations on the crystal structure parameters shown in figure 1.

In discussing the temperature dependence of the crystal structure parameters (figure 1) we have paid attention to the change in the slope of the  $a(T)$  data at about 400 °C. This temperature is indicated in the temperature dependences of  $\langle u^2 \rangle$  and the random displacements of Pb ions (figure 3) as a vertical full line. The changes in the thermal expansion coefficient, the changes in temperature dependence of the Pb ion displacement and the presence of a maximum in  $\langle u^2 \rangle$  are symptomatic of a phase transition. According to Itoh and Fujihara (1991) the maximum thermal vibration amplitude suggests a displacive-type phase transition. Displacements of Pb ions (figure 3) were calculated as random and independent in various cells. The mean crystallographic position of Pb ions throughout the crystal is still (0, 0, 0) and that is why the displacements mentioned above do not lower the crystal symmetry. Because there is no abrupt change in ion displacement and no change in the crystal symmetry, the presence of the phase transition in the vicinity of 400 °C is not fully determined.

#### 4. Conclusions

The thermal vibration amplitude for Pb ions in the high-temperature  $Pm3m$  phase, calculated from the Debye–Waller factor  $B$ , reaches unexpectedly large values (see figure 2). To obtain a smaller thermal vibration amplitude (more reasonable from the crystal lattice dynamics point of view), the Pb ions were randomly displaced; the Pb ion can occupy one of the 12 equivalent  $(x, x, 0)$  positions, instead of the (0, 0, 0) position. A new, significantly lower

thermal vibration amplitude for Pb ions has been found (see figure 3). The new amplitude for the thermal vibration of Pb ions, lower than that for O ions and comparable with that for Hf ions, seems to be more reasonable.

Some evidence of a displacive-type phase transition was observed at about 400°C, i.e. a change in the thermal expansion coefficient, maximum thermal vibration amplitudes for all ions, and a change in the slope of the Pb ion random displacement.

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