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Temperature-dependent dielectric functions and interband critical points of relaxor lead hafnate-modified $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ ferroelectric ceramics by spectroscopic ellipsometry

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The electronic band structures and dielectric functions of $(1-x)\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3-x\text{PbHfO}_3$ ceramics with different composition have been investigated by variable-temperature spectroscopic ellipsometry. Using the standard critical-point (SCP) model, three typical interband transitions can be observed from the second derivative of dielectric functions. The CP transitions, which are sensitive to B-site order degree, show a redshift trend with the temperature due to the electron-phonon interactions and lattice thermal expansion. The linear temperature coefficients are varied with oxygen vacancy, B-atom (Sc, Ta, Hf) arrangement, and Pb-O bonds owing to addition of PbHfO_3 .

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Relaxor ferroelectrics are extensively studied due to their excellent dielectric, electrostrictive, and pyroelectric properties and accordingly their applications in tunable capacitors, actuators, and electro-optic devices.^{1–6} In particular, Pb-based ABO_3 perovskites have attracted considerable attention, such as $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN), $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$ (PFN), $\text{PbFe}_{1/2}\text{Ta}_{1/2}\text{O}_3$ (PFT), and $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ (PST).^{1,6–8} In this kind of compounds, the Pb off shifts are essential for the occurrence of spontaneous polarization. Both Pb-O and B-O hybridizations are important in polar instabilities, indicating the complexity of physical mechanism for these materials.^{1,4} Among them, PST is of high interest due to its high permittivity with a broad maximum near room temperature. From the structural point of view, Sc^{3+} and Ta^{5+} cations may occupy B sites randomly or can develop 1:1 NaCl-type order on the {111} planes. Note that the arrangement of cations can be described by the B-site order degree.^{3,8} It is well-known that the B-site order plays an important role in the physical properties, including phase transition temperature, dielectric response, and electronic interband transitions.^{5,8,9} Correspondingly, the structural order can be controlled by the doping/mixing or growth parameters, such as thermal treatment. Thus, macroscopical physical properties derived by these factors should be thoroughly studied by means of electrical, optical, and magnetic measurements.

Especially, several interesting solid solutions of PST-based perovskites, such as $(1-x)\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3-x\text{PbTiO}_3$ and $(1-x)\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3-x\text{PbZrO}_3$, present improved dielectric and pyroelectric properties.^{10,11} Although mixing PST system with PbHfO_3 [$(1-x)\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3-x\text{PbHfO}_3$, (PSTH)] can increase Curie temperature (T_c), decrease sintering temperature, tailor the B-site order, and enhance pyroelectric properties of PST ceramics,⁹ the intrinsic mechanism and

its origin have not been presented to date. Recently, we have studied the electronic band structures and dielectric functions of PSTH ceramics by reflectance spectra at room temperature. It was found that the electronic structures, which depend closely on the BO_6 octahedron, are sensitive to the B-site atom concentration.⁸ Unfortunately, temperature effect on the electronic band structures, which can give an important insight on the pyroelectric, ferroelectric, and dielectric properties of ferroelectric oxides, is still an open issue. Therefore, physical mechanism behind the phenomena needs further investigations with aid of spectral experiments under different external fields (such as temperature and pressure), which can induce the structural and electronic state variations.

On the other hand, dielectric functions (ϵ) are crucial for the design and optimization of optoelectronic devices. The parameters ϵ exhibit numerous peak or shoulder structures, which are closely associated with electronic transitions. It was reported that the dielectric behavior of $\text{Pb}(\text{B}_1\text{B}_2)\text{O}_3$ is related to the nature of chemical distribution for B-site cations on the octahedral sublattice.² Fortunately, the dielectric functions of semiconductors and/or ferroelectric materials can be measured by spectroscopic ellipsometry (SE), which also give the information about microstructure and electronic band structure.^{12–14} In addition, it can be used to study the band and local (corrected) character in the optical spectra of solids.¹³ Moreover, temperature-dependence of interband electronic transition energies can provide important information about collective excitations and absorption characteristics. Therefore, variable-temperature SE analysis is desirable for presenting more insights on the intrinsic features for optical response behavior of PSTH ferroelectric oxides.

In this letter, temperature dependence of dielectric functions and interband critical-point parameters of PSTH ceramics have been investigated by spectroscopic ellipsometry. Influences from the temperature and PbHfO_3 composition on electronic band structure have been discussed in detail.

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The PSTH powders ($x = 0, 0.05, 0.1, 0.15,$ and 0.2) were synthesized by the two-stage calcination route and the ceramics were fabricated by hot-pressing sintering method. Note that 5 wt. % excess PbO was added to compensate for the PbO loss during sintering.^{8,9} All PSTH ceramic wafers were double-side polished with a mechanical polishing process to smooth the surface. This process consists of three procedures: coarse grinding, fine grinding, and polishing. Then, the ceramics were rigorously cleaned in pure ethanol with an ultrasonic bath and rinsed several times by deionized water for spectral measurements. The X-ray diffraction (XRD) pattern shows that the ceramics are well crystallized in perovskite structure without the impurity phases.⁹ From the XRD and infrared reflectance spectra, the degree of structure ordering on B-site was calculated. A variable structural ordering was found in PSTH solid solutions where the B-site order decreases by increasing PbHfO₃ composition ($0 \leq x \leq 0.1$) and becomes completely disordered ($x = 0.1, 0.15,$ and 0.2).^{8,9} Temperature-dependent SE experiments were carried out in the photon energy range of 1.24–6.4 eV (193–1000 nm) by a vertical variable-angle near-infrared-ultraviolet SE (V-VASE by J.A. Woollam Co., Inc.). It was measured with the zone average polarizer at an incident angle of 70° and the spectral interval is set to 2 nm. For the variable-temperature measurements, the samples are mounted into a Instec cell and the temperature can be controlled from –60 to 400 °C with a precision of about ± 1 °C. Note that the surface roughness can be neglected in extracting the dielectric function because the root-mean-square roughness is about 2 nm, which can be derived from atomic force microscopy (AFM) experiment (Bruker Dimension Icon). It indicates that the present ceramics are free from surface oxidation due to the fact that the severely polishing treatment is taken.

Figures 1(a)–1(e) show the real and imaginary parts of dielectric functions ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) for PSTH ($0 \leq x \leq 0.2$) ceramics between 1.24 and 6.4 eV at –60, 100, 200, 400 °C, respectively. The ε of all PSTH ceramics shows the similar behaviors with increasing the temperature, which has an obvious effect on the dielectric functions. From the change of ε_2 , it is evident that the intensity of peak located around 3.75 eV decreases with increasing the temperature, while the peak around 5.35 eV shows an opposite trend. Especially, the amplitude variation of the transition peak around 5.35 eV is distinct, as shown in Figure 1(f). The peaks and shoulder structures in the ε_2 spectra correspond to p - d and d - d charge-transfer transitions or the electronic band-band transitions.¹⁵ Note that the intensity of peaks is also sensitive to the inter-band transitions. As the temperature increases, the ε_{2max} decreases slightly first and then increases gradually. Note that the value keeps almost unchanged in the high temperature (> 200 °C) region. The parameter ε_{2max} has the minimal value around T_c and it may be due to the structure transformation from cubic (paraelectric) to rhombohedral (ferroelectric) at T_c , which was confirmed by temperature-dependent Raman scattering experiments.⁵ The conversion from increment to near constant appears around 200 °C, which can be ascribed to the stabilization by the tetragonal strain and enhanced correlations between polar nanoregions or associated with the occurrence of polar-cluster coupling.^{4,5} Note

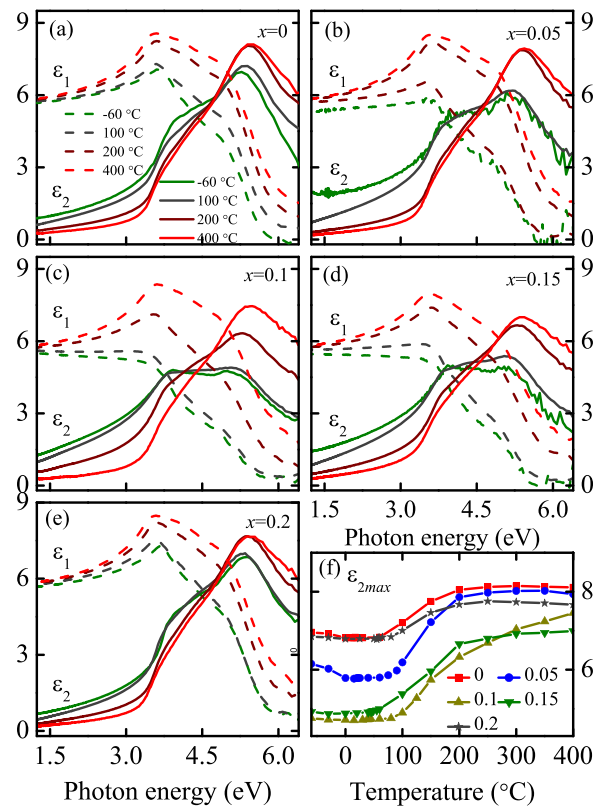


FIG. 1. (a)–(e) Real (ε_1) and imaginary (ε_2) parts of dielectric functions for $(1-x)\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3-x\text{PbHfO}_3$ ceramics measured at –60, 100, 200, and 400 °C, respectively. (f) The maximum value of ε_2 as a function of the temperature from –60 to 400 °C for PSTH ceramics.

that the PST ceramic (i.e., $x = 0$) has the maximal value of dielectric function in the entire temperature range. The ε_{2max} decreases with increasing x ($x = 0, 0.05,$ and 0.1). For the disordered PSTH ($x = 0.1, 0.15,$ and 0.2) ceramics, however, the ε_{2max} becomes larger with increased PbHfO₃ composition. It was found that the B-site order decreases with addition of PbHfO₃ ($x = 0, 0.05, 0.1$) from XRD and infrared reflectance.^{8,9} The B-site atom arrangement can be related to the electronic band structures and then influence the ε_{2max} .^{16,17} When x is larger than 0.05, however, the PSTH ceramics become completely disordered and the lattice expands with increasing x .⁹ The lattice expansion and oxygen vacancies mostly affect the formation of band structures and induce the increment of ε_{2max} .¹⁸ The results agree well with the previous reports derived by ultraviolet-near-infrared reflectance spectra at room temperature.⁸

In order to further analyze the fine band structures of ε , which correspond to the interband transitions (critical points, CPs), the second derivative of dielectric functions ($d^2\varepsilon/dE^2$) is calculated. A line-shape analysis with standard critical-point (SCP) model was performed, which has been applied to semiconductors and ferroelectric materials.^{19,20} The SCP expression can be written as the following:¹³

$$\frac{d^2\varepsilon}{dE^2} = \begin{cases} n(n-1)A_m e^{i\phi_m} (E - E_m + i\Gamma_m)^{n-2}, & n \neq 0 \\ A_m e^{i\phi_m} (E - E_m + i\Gamma_m)^{-2}, & n = 0. \end{cases} \quad (1)$$

Here, A_m , E_m , Γ_m , and ϕ_m in order are the m th amplitude, threshold energy, broadening, and excitonic phase angle,

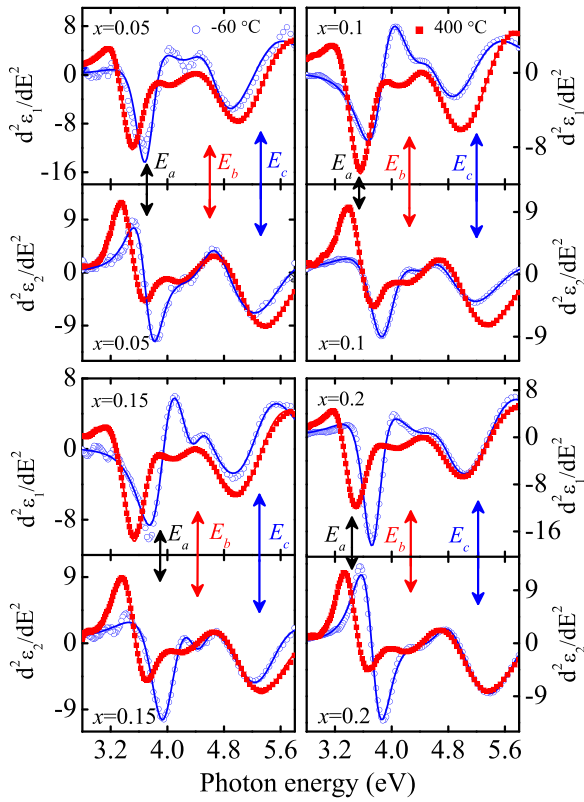


FIG. 2. Experimental (dots) and the best-fit (solid lines) second derivatives of ϵ_1 and ϵ_2 at -60 and 400 °C for PSTH ($x=0.05, 0.1, 0.15,$ and 0.2) ceramics, respectively. Note that the arrows indicate three typical interband electronic transitions.

respectively. The exponent n has the value of $-\frac{1}{2}, 0, \frac{1}{2}$, and -1 , which corresponds to the one-dimensional (1D), 2D, 3D, and excitonic CPs, respectively. For example, Figure 2 displays the experimental and best-fit second derivatives of dielectric functions at -60 and 400 °C for PSTH ($x=0.05, 0.1, 0.15,$ and 0.2) ceramics. Three interband transitions can be observed clearly and the CPs are labeled as $E_a, E_b,$ and E_c in the order of increasing the photon energy. Based on the

simulation, the parameter values of SCP model are listed in Table I. The error bars are less than 0.02 eV for the parameter A_0 (A_1) and 0.15 eV for A_2 . As for the phase angle ϕ_m ($m=0, 1, 2$) and broadening Γ_m ($m=0, 1, 2$), the error bars are less than 0.9° and 0.01 eV, respectively. According to the fitting values, the CP energies are estimated to be $3.72 \pm 0.08, 4.81 \pm 0.11,$ and 5.39 ± 0.12 eV for PST ($x=0$) ceramic at -60 °C. The phase angle ϕ of three CPs is located between 0° and 90° , which describes the excitonic metamorphism of critical-point line shapes.¹³

The interband transitions of perovskite oxides play a crucial role in studying the electronic band structures.^{12,17} The key step will find the relationship between the band-to-band transition and microscopic electronic structure. It can be well fulfilled by assigning the interband transition origins. For ABO_3 perovskite, the BO_6 octahedron governs the low-lying conduction band (CB) and the valence band (VB) maximum. However, when A-site is occupied by Pb atoms, the Pb $6s^2p^2$ plays an important role in the band structures (i.e., PMN and PFT).^{1,6} As an example, Lampis *et al.* calculated the electronic structure of PFT theoretically and it was found that the VB mainly consists of O $2p$ states and Pb $6s$ states while CB is dominated by Fe $3d$, Ta $5d$, and Pb $6p$ states.⁶ Base on the theoretical electronic band structures of PZT, PMN, PFT, and Ba_2ScTaO_6 oxides,^{1,6,12,21,22} it was concluded that the O $2p$ states mainly dominate the VBM and the CB consists of Sc(Ta) d states and Pb $6p$ states for the PST ceramics. Similar to the $PbHfO_3$, Pb-O bonding can also make contributions to the band structures of PSTH ceramics.^{8,22} Note that the CP E_b cannot be distinguished from reflectance spectra due to the weak intensity.⁸ However, it can be clearly observed from the second derivatives of dielectric functions determined by SE spectra, as shown in Figure 2. The transition energy E_a corresponds to the transitions from O $2p$ to the B-site d states [Sc $3d$ and Ta (Hf) $5d$] states. The transition energy E_c may be attributed to transitions from the O $2p$ to Pb $6p$ states and/or the hybridized states with B-site d states. The assignment of transition

TABLE I. The SCP model parameters for $(1-x)PbSc_{1/2}Ta_{1/2}O_3-xPbHfO_3$ ceramics are extracted from the best fitting second derivatives of dielectric functions (Fig. 2) at $-60, 200,$ and 400 °C, respectively.

Samples x	Temperature (°C)	E_a				E_b				E_c			
		A_0 (eV)	ϕ_0 (deg)	E_0 (eV)	Γ_0 (eV)	A_1 (eV)	ϕ_1 (deg)	E_1 (eV)	Γ_1 (eV)	A_2 (eV)	ϕ_2 (deg)	E_2 (eV)	Γ_2 (eV)
0	-60	1.32	45.0	3.72	0.34	1.41	49.5	4.81	0.51	10.3	40.4	5.39	0.92
	200	0.97	44.6	3.56	0.29	0.59	46.9	4.43	0.40	7.62	39.8	5.34	0.73
	400	0.87	44.5	3.49	0.28	0.94	46.1	4.21	0.49	7.67	39.6	5.29	0.77
0.05	-60	0.88	45.2	3.72	0.30	1.13	48.9	4.62	0.47	6.48	40.6	5.33	0.88
	200	1.08	44.5	3.56	0.32	0.60	46.9	4.44	0.45	7.37	39.8	5.32	0.76
	400	1.04	44.3	3.46	0.33	0.96	46.4	4.27	0.53	8.10	39.6	5.25	0.82
0.1	-60	1.27	46.3	3.86	0.40	0.31	48.0	4.55	0.40	4.49	40.3	5.21	0.88
	200	1.26	45.3	3.66	0.37	0.66	46.0	4.31	0.51	4.42	39.9	5.28	0.76
	400	1.10	44.6	3.54	0.36	0.99	46.1	4.25	0.55	6.74	39.4	5.20	0.82
0.15	-60	1.52	46.3	3.93	0.40	0.23	46.3	4.43	0.31	3.38	40.5	5.31	0.70
	200	1.14	45.0	3.64	0.36	0.34	46.1	4.33	0.40	4.98	39.9	5.29	0.77
	400	1.10	44.6	3.52	0.36	0.52	46.0	4.23	0.47	5.03	39.7	5.26	0.77
0.2	-60	1.19	45.0	3.74	0.30	0.61	48.6	4.73	0.45	7.15	40.2	5.41	0.82
	200	1.00	44.5	3.54	0.31	0.76	46.7	4.40	0.49	7.01	39.8	5.31	0.77
	400	0.97	44.3	3.44	0.32	1.30	46.3	4.27	0.60	7.10	39.5	5.22	0.80

energy E_b located between E_a and E_c is complicated because it may be related to both B-site d states and Pb $6p$ states. For the $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ($x = 0.2, 0.56, \text{ and } 0.82$) films, there also exists three CPs (3.9, 4.5, and 6.5 eV) at room temperature.¹² The discrepancy between the transition energy can be attributed to the effective electronegativity of B-site atoms and CB width influenced by B-O-B bonds.²¹ It should be emphasized that the distinct variation appears between the spectra recorded at -60 and 400°C , especially near the CP E_a (~ 3.7 eV), which indicates that the temperature has a remarkable influence on electronic band structures of PSTH ceramics.

In order to make further investigation about the interband transition, the temperature dependence of the interband critical point energies of PSTH ceramics is presented in Figures 3(a)–3(e). Correspondingly, Figure 3(f) shows the amplitude variation of E_a and E_c with the temperature for PSTH ceramic ($x = 0.1$). It indicates that the amplitude of E_a decreases with the temperature while the intensity of E_c is enhanced, which is consistent with the experimental results as shown in Figure 1(f). As for the variation of excitonic phase angle, it was found that the deviation of ϕ between -60 and 400°C is less than 2° for the CPs from Table I. Actually, the angle almost keeps constancy with increasing the temperature, which confirms the correctness of the line-shape chosen for those CPs. The three interband transition energies show a red-shift trend with increasing the

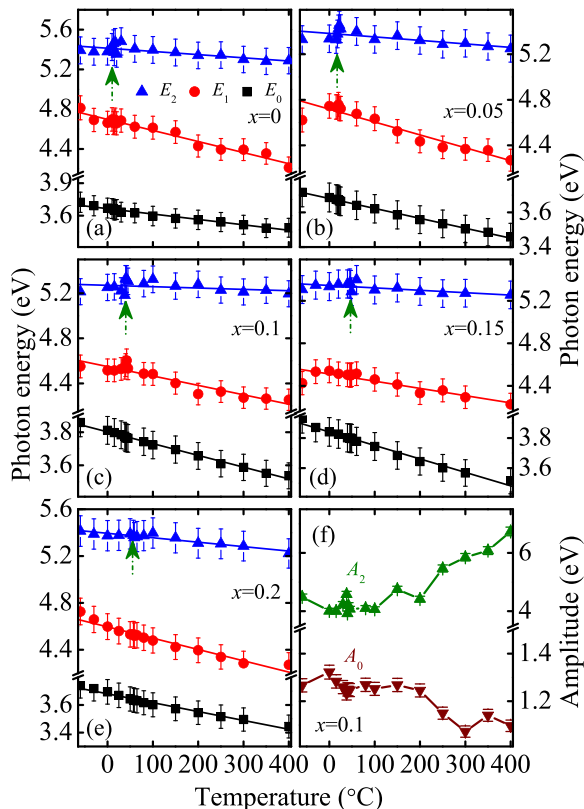


FIG. 3. (a)–(e) Temperature dependence of the interband critical point energies for PSTH ceramics. The solid lines represent the linear fitting results to guide the eyes. (f) The amplitude of CPs E_a and E_c variation with the temperature for $(1-x)\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3-x\text{PbHfO}_3$ ($x = 0.1$) ceramics. Note that the arrows indicate the small jump in the CP E_c , which corresponds to Curie temperature.

temperature, which is similar to that of silicon, GaAs, and $0.76\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.24\text{PbTiO}_3$ single crystal.^{13,23} The negative temperature dependence of the transition energy can be explained by the renormalization of the band structures caused by electron-phonon interaction and lattice thermal expansion. To investigate the behaviors of the CPs with the temperature, the transition energies can be fitted by the linear function: $E(T) = E_0 - \lambda_i T$ (i means the i th CP), which is shown by the solid lines in Figures 3(a)–3(e). For PSTH ($x = 0.1$) ceramic, the linear temperature coefficients λ_1, λ_2 , and λ_3 are 7.1×10^{-4} , 8.4×10^{-4} , and 1.2×10^{-4} eV/ $^\circ\text{C}$, respectively. The parameters can be comparable with the data from semiconductor silicon (4.1×10^{-4} eV/K).¹³ The highest electronic transition shows the minimal variation for PSTH ceramic, which indicates that the temperature has minimal influence on the CP E_c . For the first CP, the λ_1 is estimated to be $(5.0 \pm 0.2) \times 10^{-4}$, $(5.7 \pm 0.1) \times 10^{-4}$, $(7.1 \pm 0.2) \times 10^{-4}$, $(8.9 \pm 0.4) \times 10^{-4}$, and $(6.4 \pm 0.3) \times 10^{-4}$ eV/ $^\circ\text{C}$ with increasing PbHfO_3 composition, suggesting that the coefficient of E_a becomes larger with addition of PbHfO_3 . However, when the x is larger than 0.15, the coefficient λ_1 decreases. For the second CP E_b , the linear coefficient λ_2 is estimated to be 1×10^{-3} , 1×10^{-3} , 8.4×10^{-4} , 6.8×10^{-4} , 9.8×10^{-4} eV/ $^\circ\text{C}$. Correspondingly, the parameter λ_3 is 3.2×10^{-4} , 2.7×10^{-4} , 1.2×10^{-4} , 2.3×10^{-4} , and 3.6×10^{-4} eV/ $^\circ\text{C}$. Both λ_2 and λ_3 values become smaller first and then increase with increasing PbHfO_3 composition. It should be noted that the standard errors of these coefficients are much less than 5×10^{-5} eV/ $^\circ\text{C}$, which indicates that the linear analysis can be acceptable and reasonably describe the variation trends.

It was found that PSTH ($x = 0.15$) ceramic shows the largest value of λ_1 , which could be explained by the largest lattice expansion resulted from the Hf^{4+} occupation into the B-site. For PSTH ceramics ($0 < x \leq 0.15$), the B-site average radius and lattice constants increase. Due to addition of PbHfO_3 , the oxygen vacancy forms to make balance of charge and the concentration increases with increasing x .⁹ Nevertheless, the Hf^{4+} ions prefer to replace the Sc^{3+} ions and subsequently produces Pb vacancy for $x = 0.2$.⁹ In addition, the incorporation of PbHfO_3 reduces the B-site ordering and forms the Hf-O-Hf and Ta-O-Hf chains, which can also affect the variation of electronic transition energy. Moreover, the oxygen vacancy located between B-cations and the B-cation arrangement plays an important role in band-structure engineering for perovskite $\text{ABB}'\text{O}_3$ solid solutions.¹⁸ Especially, for the Pb-based compounds, the formation of short Pb-O bonds and electrostatic interaction among B-site atoms will also influence the dielectric properties.²⁴ For PSTH ($x = 0.2$) ceramic, the existence of Pb vacancy has an effect on the Pb-O bonds and repulsive interaction between B-atoms d states. From high-temperature Raman scattering, it was also concluded that the length of coherence within the Pb-O system can affect the strength of coupling between spatial polar regions comprising off-centered B cations.⁴ For the second CP, the λ_2 shows the similar variation to λ_3 and a completely reverse trend of λ_1 . It has the minimal value at $x = 0.15$, which can be also related to the oxygen vacancy and lattice expansion. It indicates that the composition has a remarkable influence on interband transitions. This

phenomenon also reflects the complexity of interband transition E_b and multiple transitions will happen at the same peak position.¹⁷ As for the last critical point E_c , the variation trend of λ_3 is correlated with the B-site order degree and has the minimal value at $x = 0.1$. As shown in Figure 1(f), the interband transition located around 5.3 eV is sensitive to the structural order parameters induced by mixing with PbHfO₃. It should be noted that the transition energy E_c shows a little jump around the T_c (marked by the arrows) due to the structural variation. Since the CP E_c corresponds to the transition between O $2p$ and Pb $6p$ states (hybridization with B-site d), it is concluded that the structural transformation is sensitive to the Pb atoms. In addition, the polarizable long pair in the $6s$ state of Pb²⁺ is related to the ferroelectric behavior.²⁵ Therefore, the Pb²⁺ ions and BO₆ (B = Sc, Ta, and Hf) octahedron dominate the electronic band structures (i.e., the interband transitions) of PSTH ceramics. Thus, the different temperature coefficients of CPs can be related to lattice expansion, existence of oxygen vacancy, and B-site order degree induced by addition of PbHfO₃.

In summary, the temperature and composition dependence of the dielectric functions and electronic band transitions of PSTH ceramics have been investigated using spectroscopy ellipsometry. The three interband transitions show a red-shift pattern with increasing the temperature due to the lattice thermal expansion and electron-phonon interaction in the temperature range of -60 – 400 °C. The addition of PbHfO₃ results in the occurrence of oxygen vacancy, lattice expansion, and degradedness of B-site order, which can contribute to the variation of electronic band structures.

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