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Finite-temperature properties of disordered and ordered $Pb(Sc_{0.5}Nb_{0.5})O_3$ alloys

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A first-principles-derived approach is used to study the properties of rocksalt-ordered and disordered $Pb(Sc_{0.5}Nb_{0.5})O_3$ (PSN) alloys. The paraelectric-to-ferroelectric transition temperature T_c is strongly dependent on the atomic configuration, while the piezoelectric response versus T/T_c is nearly independent of the chemical order. Our calculations are consistent with the experimental finding of Chu *et al.* [J. Appl. Phys. **77**, 1671 (1995)] that, at $T=T_c$, ordered PSN undergoes a normal ferroelectric transition, while disordered PSN transforms from a relaxor state to a ferroelectric state. © *2000 American Institute of Physics.* [S0003-6951(00)02148-3]

The heterovalent perovskite alloys $Pb(Sc_{1/2}Nb_{1/2})O_3$ (PSN) and $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST) feature B-site cations from columns III and V of the periodic table. These alloys adopt a macroscopic rhombohedral ferroelectric ground state. They can be grown with different degrees of chemical order, from a completely ordered rocksalt-type structure to a completely disordered one.[1–5] While the interactions responsible for the existence of compositional long-range atomic ordering (LRO) in PSN and PST are now better understood,[6–8] the precise effect of atomic arrangement on their properties is not very clear. First, on one hand, Ref. 1 indicates that the paraelectric-to-ferroelectric transition temperature T_c is independent of the atomic ordering in PST. On the other hand, Chu *et al.*[2] reported an *increase* of this temperature by more than 30 K, when going from the disordered to the rocksalt-ordered PST alloy, while Malibert *et al.*[4] found that the rocksalt long-range order in PSN leads to a significant *decrease* of T_c by 50 K with respect to the random case. Second, the relaxor (dielectric) behavior was first linked to B-site atomic disorder,[1,9] while recent measurements in PSN and PST suggest that positional disorder alone is not sufficient for the relaxor behavior to persist.[2,3] Finally, we are not aware of any study pointing out the effect of LRO on the piezoelectric response in PSN or PST.

The thrust of this letter is to investigate theoretically the effect of LRO on structural, dielectric, and piezoelectric properties of PSN. For this purpose, we choose to compare the finite-temperature properties of the completely long-range rocksalt-ordered alloy with those of the fully disordered material. Our findings are as follows: (1) Rocksalt ordering in PSN does lead to a significant increase of T_c with respect to the random case; (2) the dielectric response strongly suggests that the ordered material exhibits a normal ferroelectric transition at T_c, while the disordered material shows signs of a relaxor behavior above T_c and a normal ferroelectric behavior below T_c; (3) the piezoelectric responses versus T/T_c of disordered and ordered materials are nearly identical. Items (1) and (2) are consistent with the experimental observations in Refs. 2 and 3. Item (3) calls for experimental confirmation.

Here, we use the numerical scheme proposed in Ref. 10, which consists of constructing an alloy effective Hamiltonian from first-principles calculations. The total energy E is thus written as a sum of two energies:

$$E(\{\mathbf{u}_i\},\{\mathbf{v}_i\},\eta_H,\{\sigma_j\})=E_{\rm ave}(\{\mathbf{u}_i\},\{\mathbf{v}_i\},\eta_H)+E_{\rm loc}(\{\mathbf{u}_i\},\{\mathbf{v}_i\},\{\sigma_j\}), \qquad (1)$$

where $\mathbf{u}_i$ is the local soft mode in unit cell i; $\{\mathbf{v}_i\}$ are the dimensionless local displacements which are related to the inhomogeneous strain variables inside each cell;[11] η_H is the homogeneous strain tensor; and the $\{\sigma_j\}$ characterize the atomic configuration of the alloy. That is, $\sigma_j=+1$ or -1 corresponds to the presence of a Nb or Sc atom, respectively, at lattice site j of the $Pb(Sc_{1/2}Nb_{1/2})O_3$ alloy. The $\{\sigma_j\}$ parameters are incorporated into the second energy term $E_{\rm loc}$, which thus accounts for the charge and size differences between Sc and Nb atoms. For $E_{\rm ave}$, we generalize the analytical expression of Ref. 11—proposed for simple compounds—to the study of the $Pb(Sc_{1/2}Nb_{1/2})O_3$ alloy. This generalization consists in using the virtual crystal approximation (VCA), i.e., in creating a $Pb\langle B\rangle O_3$ simple system in which the $\langle B\rangle$ atom is a virtual atom involving a kind of potential average between Sc and Nb atoms.[12] We then derived $E_{\rm loc}$ by treating the alloy configuration $\{\sigma_j\}$ as a perturbation of the VCA system. Here, unlike in $Pb(Zr_{1-x}Ti_x)O_3$ (Ref. 10)—we adopted an expression that only includes *intersite* contributions, since the *onsite* alloy parameters were found to be negligible in PSN. As a result, we have

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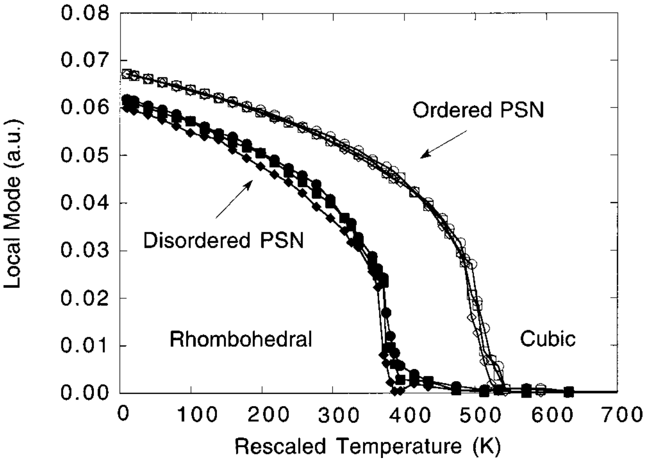

FIG. 1. Largest, middle, and smallest average Cartesian coordinates u_1, u_2, and u_3 of the local-mode vector and as a function of temperature in single crystals of $Pb(Sc_{0.5}Nb_{0.5})O_3$. Filled symbols refer to disordered PSN, while open symbols refer to rocksalt-ordered PSN. The temperature has been rescaled to fit the experimental value of T_c in disordered PSN.

$$E_{\mathrm{loc}}(\{\mathbf{u}_i\},\{\mathbf{v}_i\},\{\sigma_j\})=\sum_{ij}\left[Q_{j,i}(\sigma_j)\mathbf{e}_{ji}\cdot\mathbf{u}_i+R_{j,i}(\sigma_j)\mathbf{f}_{ji}\cdot\mathbf{v}_i\right)], \tag{2}$$

where the sum over i runs over all the unit cells, while the sum over j runs over the mixed sublattice sites. $\mathbf{e}_{ji}$ is a unit vector joining the site j to the center of the soft mode $\mathbf{u}_i$, and $\mathbf{f}_{ji}$ is a unit vector joining the site j to the origin of $\mathbf{v}_i$. All the parameters entering the analytical expressions of Eqs. (1) and (2) are derived by performing local-density approximation[13] plane-wave ultrasoft-pseudopotentials calculations[14] on small cells.

Once our effective Hamiltonian is fully specified, the total energy of Eq. (1) is used in Monte Carlo simulations to compute finite-temperature properties of PSN alloys. We use $12\times12\times12$ supercells to obtain converged results.[15] Two different atomic configurations are generated. First of all, the $\{\sigma_j\}$ variables are chosen randomly in order to mimic maximal compositional disorder. Second, Sc and Nb atoms successively alternate along the pseudocubic directions in order to reproduce the fully rocksalt-ordered structure. For each configuration, the $\{\sigma_j\}$ variables are kept fixed during the Monte Carlo simulations. We also use the correlation-function approach of Ref. 16 to derive the piezoelectric and dielectric responses from these Monte Carlo simulations.

Figure 1 shows the predicted largest, middle, and smallest Cartesian coordinates (u_1, u_2, and u_3) of the supercell average of the local mode vectors in disordered and ordered PSN as a function of the temperature. Each coordinate is close to zero at high temperature. As each of the two systems is cooled down, u_1, u_2, and u_3 increase and remain nearly equal to each other. This characterizes a transition from a paraelectric cubic phase to a ferroelectric rhombohedral structure, consistent with experiments.[3,4] The *theoretical* value of the paraelectric-to-ferroelectric transition temperature T_c is determined with good precision by identifying the temperature yielding a maximum of the piezoelectric coefficients; we find $T_c=944$ and 1265 K in disordered and ordered PSN, respectively. A comparison of the theoretical T_c of disordered PSN with the experimental value of 373 K (Ref. 3) may appear disappointing. However, we have found in previous work with effective Hamiltonians[10,16] that a linear rescaling of the simulation temperature often leads to surprisingly good agreement with experiment. Adopting this approach again here, we rescale the temperature in Fig. 1 so that the theoretical T_c in disordered PSN is forced to match the experimental value. We then predict a T_c of 500 K for ordered PSN. Thus, the atomic ordering is found to enhance T_c strongly, in qualitative agreement with Ref. 2. The predicted room-temperature value for the angle between the primitive lattice vectors of the rhombohedral phase in *disordered* PSN is 89.49°, in very good agreement with the experimental result of 89.46°.[3] This confirms the high accuracy of our scheme once the temperature is rescaled. (We also compared direct first-principles calculations with the low-temperature predictions of our effective Hamiltonian approach for the internal ferroelectric atomic displacements in *ordered* PSN, further confirming this high accuracy.)

We now use our effective Hamiltonian approach to investigate the effects of LRO on the piezoelectric and dielectric response of PSN. At room temperature and when representing the piezoelectric tensor in the orthonormal basis formed by $\mathbf{a}_1=[1\bar{1}0]/\sqrt{2}$, $\mathbf{a}_2=[11\bar{2}]\sqrt{6}$, and $\mathbf{a}_3=[111]/\sqrt{3}$, we find that the four independent piezoelectric coefficients d_{31}, d_{33}, d_{22}, and d_{15} are, respectively, -80, 310, 145, and 1160 pC/N for disordered PSN, and -30, 150, 110, and 941 pC/N for ordered PSN. These values yield a d_{33} along the pseudocubic [001] direction of 554 pC/N for the disordered alloy and of 439 pC/N for the ordered solid solution. An enhancement of piezoelectricity is thus predicted to occur when going from the [111] polar direction to the [001] direction for both PSN materials. This enhancement is consistent with the findings of Refs. 17 and 18, and is mainly due to the huge value of d_{15}.

Interestingly, Fig. 2(a) demonstrates that the piezoelectric coefficients of disordered PSN are very similar to those of ordered PSN when plotting them as a function of the ratio between the rescaled temperature T and their own rescaled T_c. This is consistent with the fact that the piezoelectric coefficients of ordered PSN are smaller than those in disordered PSN at room temperature, since T_c is larger and further away from 300 K in ordered PSN than in the disordered sample.

On the other hand, Fig. 2(b) indicates that the dielectric response versus T/T_c is quite different in disordered and ordered PSN. The rocksalt-ordered PSN sample exhibits a normal ferroelectric transition, as demonstrated by the peak in the dielectric susceptibility χ_{33} near T_c, and as experimentally observed in ordered PST[1,2] and PSN.[4] In disordered PSN, (i) the curve of χ_{33} vs T/T_c is much broader than in the ordered material, and (ii) the maximum of the dielectric susceptibility occurs at a temperature higher than T_c. These two features are consistent with the relaxor behavior (see Fig. 1 in Ref. 19) that has been observed in disordered PSN for temperature above T_c.[3] Furthermore, disordered PSN exhibits a sharp decrease of χ_{33} upon cooling just below T_c, which is consistent with a first-order transition from a relaxor state to a normal ferroelectric state observed in disordered PSN at $T=T_c$.[3] These results provide tantalizing evidence that at least some features of the relaxor behavior are cor-

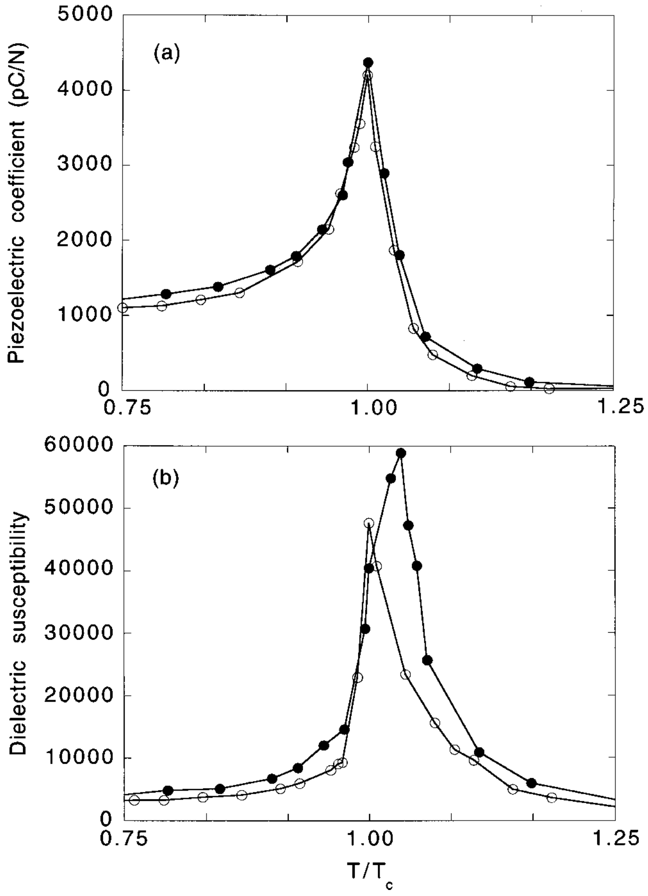

FIG. 2. Piezoelectric coefficient d_{15} (a) and dielectric susceptibility χ_{33} (b) as a function of the ratio between the rescaled temperature T and the rescaled T_c in single-crystals of $Pb(Sc_{0.5}Nb_{0.5})O_3$ solid solutions. The rescaled T_c is 373 and 500 K in disordered and ordered PSN, respectively. Filled symbols refers to disordered PSN, while open symbols refers to rocksalt-ordered PSN. Statistical errors are estimated to be ~15% of the values displayed.

rectly captured by our effective-Hamiltonian technique. Further intensive investigations, which are beyond the scope of this letter, will be needed to determine the microscopic effects responsible for the relaxor behavior occurring in disordered PSN.

In summary, we have used the first-principles derived computational scheme of Ref. 10 to study finite-temperature properties of rocksalt-ordered and disordered $Pb(Sc_{0.5}Nb_{0.5})O_3$ solid solutions. We find that (i) the paraelectric-to-ferroelectric transition temperature T_c is strongly dependent on the atomic ordering; (ii) the piezoelectric responses versus T/T_c of disordered and ordered materials are nearly identical; (iii) the dielectric response strongly suggests that the ordered material exhibits a normal ferroelectric transition at T_c, while the disordered material transforms at $T = T_c$ from a relaxor state to a normal ferroelectric state. Furthermore, both PSN alloys have a large value of the d_{15} piezoelectric coefficient. This large value leads to an effective d_{33} coefficient along the pseudocubic [001] direction that is significantly larger than along the polar [111] direction.

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