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The Formation and Properties of Solid Solutions in the $\mathrm{PbTiO_3}$-$\mathrm{Pb(Ni_{1/2}W_{1/2})O_3}$ System

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Synopsis. By usual and high-pressure techniques, a series of $\mathrm{PbTiO_3}$–$\mathrm{Pb(Ni_{1/2}W_{1/2})O_3}$ solid solution was formed with a perovskite structure. With an increase in the $\mathrm{Pb(Ni_{1/2}W_{1/2})O_3}$ content, the Curie point shifted to lower temperatures and the degree of tetragonality decreased. The thermal-expansions were also measured, showing anomalies at the Curie point.

$\mathrm{PbTiO_3}$ is a ferroelectric perovskite with a high Curie point of 490 °C.[1] However, its inability to produce dense $\mathrm{PbTiO_3}$ ceramics and the relatively high conductivity of pure $\mathrm{PbTiO_3}$ ceramics have restricted its usefulness.[2] On the other hand, $\mathrm{Pb(Ni_{1/2}W_{1/2})O_3}$ has been synthesized only by high-pressure technique, and it has been suggested that it exhibits an antiferroelectric behavior.[3] The corresponding perovskites, $\mathrm{Pb(Mg_{1/2}W_{1/2})O_3}$ and $\mathrm{Pb(Co_{1/2}W_{1/2})O_3}$, have been prepared by usual solid-state reactions, and solid-solution series were formed over the whole composition range in the $\mathrm{PbTiO_3}$–$\mathrm{Pb(Mg_{1/2}W_{1/2})O_3}$ and $\mathrm{PbTiO_3}$–$\mathrm{Pb(Co_{1/2}W_{1/2})O_3}$ systems.[4,5] Much attention has been paid, from the physical and crystallographic points of view, to how solid solutions between $\mathrm{PbTiO_3}$ and $\mathrm{Pb(Ni_{1/2}W_{1/2})O_3}$ are formed. The present paper will report on the structural, dielectric, and thermal-expansion properties of this system.

Experimental

For the sample preparations, PbO, $\mathrm{TiO_2}$, NiO, and $\mathrm{WO_3}$ of high purities were used. Prefiring was done at 800 °C for 3 h in air. When the samples were then fired at temperatures of 850—1000 °C for 2 h, dense bodies were obtained. For samples which were not obtained as a single phase, high-pressure and high-temperature experiments (850 °C, 30 kb, 1 h) were made using a tetrahedral anvil apparatus. The sample was sealed by thin platinum foil to avoid contamination of the sample during the run. The sample container also served as a heating element. The room-temperature structure and the lattice constants of the samples were determined by the X-ray diffraction technique. The dielectric properties were measured on an universal bridge at 1 kHz. The thermal expansions of the sintered 0.7 cm-diameter specimen were measured with an automatic-plotting fused-quartz dilatometer.

Results and Discussion

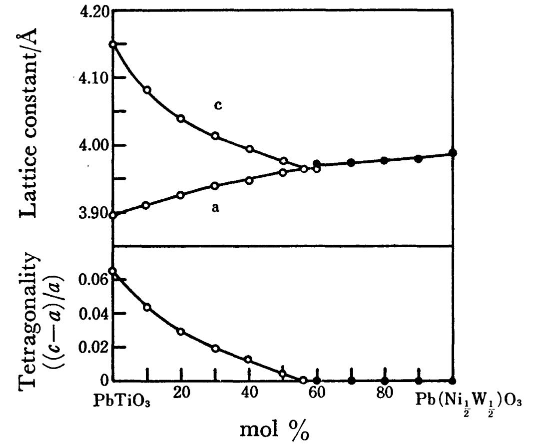

Fig. 1. Lattice constants and the tetragonality in the $\mathrm{PbTiO_3}$–$\mathrm{Pb(Ni_{1/2}W_{1/2})O_3}$ system.
○: sample obtained by usual solid state reaction.
●: sample obtained by high pressure reaction.

In the $\mathrm{PbTiO_3}$–$\mathrm{Pb(Ni_{1/2}W_{1/2})O_3}$ system, tetragonal perovskite solid solutions were formed as a single phase up to the composition containing 50 mol% $\mathrm{Pb(Ni_{1/2}W_{1/2})O_3}$, although $\mathrm{Pb(Ni_{1/2}W_{1/2})O_3}$ was not synthesized by usual solid-state reaction. Superstructural lines were not observed in powder X-ray patterns. The lattice constants and the tetragonality ($c/a-1$) are shown in Fig. 1. The tetragonality is continuously decreased by the substitution of the 1/2Ni+1/2W ions for the Ti ions. In a 60 mol% $\mathrm{Pb(Ni_{1/2}W_{1/2})O_3}$ sample, other phases were observed to be formed in small amounts besides a cubic perovskite phase. The substitutional limitation of $\mathrm{Pb(Ni_{1/2}W_{1/2})O_3}$ for $\mathrm{PbTiO_3}$, as estimated from the dependence of the tetragonality on the composition, was *ca.* 56 mol%. In fact, a sample with this composition showed a single-phase pattern with the cubic perovskite structure, and its lattice constant was in good agreement with that in the sample with 60 mol% $\mathrm{Pb(Ni_{1/2}W_{1/2})O_3}$. For samples contain-

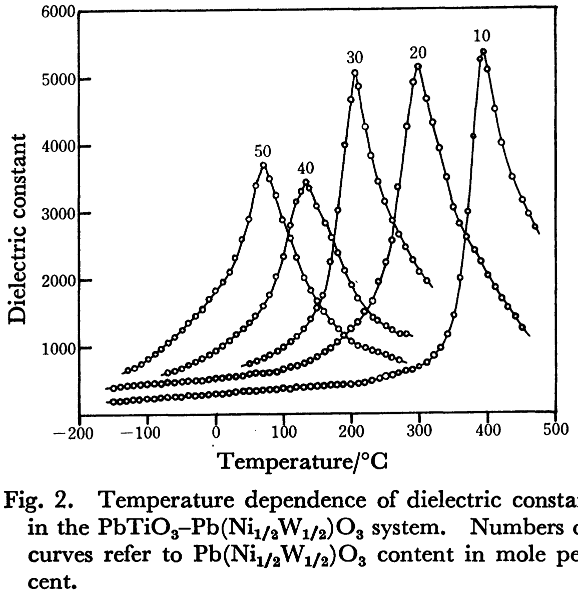

Fig. 2. Temperature dependence of dielectric constant in the $\mathrm{PbTiO_3}$–$\mathrm{Pb(Ni_{1/2}W_{1/2})O_3}$ system. Numbers on curves refer to $\mathrm{Pb(Ni_{1/2}W_{1/2})O_3}$ content in mole percent.

ing more than 60 mol% $Pb(Ni_{1/2}W_{1/2})O_3$, a high-pressure technique was applied. Consequently, all the samples showed single-phase patterns of cubic perovskite. The lattice constant gradually increases with the increase in $Pb(Ni_{1/2}W_{1/2})O_3$, as is shown in Fig. 1. Superstructural lines indicating the NaCl-type ordering were observed for samples containing 70 mol% $Pb(Ni_{1/2}W_{1/2})O_3$.

Figure 2 shows the temperature dependence of the dielectric constant from −190 to 500 °C. High values of the dielectric constant are noticeable in these samples. A dielectric-constant peak characteristic of the ferroelectric substance was observed for each sample. With the increase in $Pb(Ni_{1/2}W_{1/2})O_3$, the sharp peak shifted to lower temperatures. This is attributed to the decrease in tetragonal distortion. The loss tangent for these samples was less than 0.05 below 200 °C and then rapidly increased with the temperature.

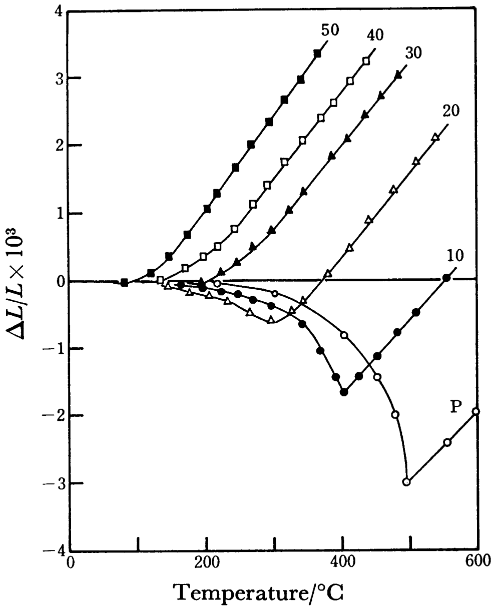

Fig. 3. Linear thermal-expansion curves in the $PbTiO_3$–$Pb(Ni_{1/2}W_{1/2})O_3$ system. Numbers on curves refer to $Pb(Ni_{1/2}W_{1/2})O_3$ content in mole percent and the symbol P means a sample of $PbTiO_3$ with 0.1 mol % CaF_2.

The thermal-expansion curves are shown in Fig. 3. Tien and Carlson have reported that $PbTiO_3$ with a 0.1 mol% addition of CaF_2 shows a net length expansion through a net length contraction at the Curie point.6) Such a tendency appeared in these samples. With an increase in the $Pb(Ni_{1/2}W_{1/2})O_3$ content, the dilatometric anomaly also shifted to lower temperatures and the total quantity of contraction at the transition temperature became significantly lower. The phase-transition temperature obtained by dielectric and dilatometric measurements agree well. The linear thermal-expansion coefficients above the transition temperature were of the same order of magnitude, 10^{-5} per °C, for all the samples.

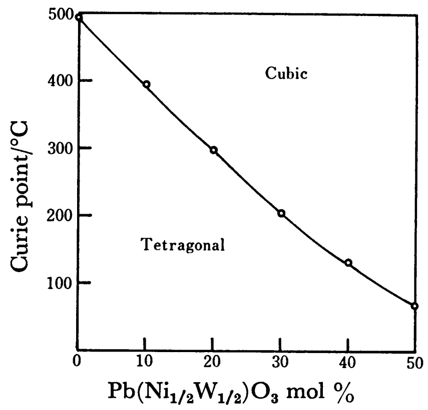

Fig. 4. Dependence of the Curie point on composition of $PbTiO_3$–$Pb(Ni_{1/2}W_{1/2})O_3$ solid solutions.

It may be concluded from these results that solid solutions containing less than 50 mol% $Pb(Ni_{1/2}W_{1/2})O_3$ are transformed from a tetragonal(ferroelectric) to a cubic(paraelectric) structure at the transition temperature. In this range of compositions, the arrangements of the cations in the octahedrally coordinated positions are at random, and the combination of Ni^{2+} and W^{6+} ions lowers the Curie point as is shown in Fig. 4. In samples containing more than 70 mol% $Pb(Ni_{1/2}W_{1/2})O_3$, the Ni^{2+} and W^{6+} ions show a partial ordering of the same type as in $Pb(Ni_{1/2}W_{1/2})O_3$.3) With the increase in $Pb(Ni_{1/2}W_{1/2})O_3$, the intensities of the superstructural lines increase and the lattice expands. This expansion is probably due to an increase in the mean size of the cations occupying oxygen octahedra (according to Shannon *et al.*,7,8) the ionic sizes of Ti^{4+}, Ni^{2+}, and W^{6+} ions being 0.605 Å, 0.69 Å, and 0.60 Å respectively). The dielectric anomaly would exist below room temperature, since perovskite solid solutions obtained by high-pressure technique are cubic at room temperature.

The structural and dielectric properties of this system have a tendency similar to those of the $PbTiO_3$–$Pb(Mg_{1/2}W_{1/2})O_3$ and $PbTiO_3$–$Pb(Co_{1/2}W_{1/2})O_3$ systems.4,5)

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