Formation of Oxygen Deficient Pyrochlore Solid Solutions $Pb_2Ta_{2-2x}M_{2x}O_{7-x}$(M=Ti, Sn and Zr) and Their Optical and Dielectric Properties

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It was found that oxygen deficient pyrochlore solid solutions $Pb_2Ta_{2-2x}M_{2x}O_{7-x}$ with M=Ti, Sn, and Zr exist over wide ranges. The formation of oxygen deficient pyrochlore structure results from the occupancy of Pb^{2+} ions in the A position, which have a high polarizability. Their reflectance and infrared absorption spectra, and dielectric constants were measured. With the increase of M^{4+} ions, the color turned lemon yellow to reddish yellow, and the dielectric constants increased. The infrared absorption spectra in their pyrochlore solid solutions were similar to those in $PbTiO_3$ and $PbZrO_3$. The infrared properties of two strong absorption bands observed were discussed in comparison with those in the perovskites.

Pyrochlore type compounds are represented by the general formula $A_2B_2O_7$ and exhibit interesting physical properties such as ferroelectricity in $Cd_2Nb_2O_7$[1,2] and electrooptic effect in $Ca_2Nb_2O_7$.[3] Compounds of this type have a face-centered cubic structure with a unit cell of *ca.* 10 Å. The structural framework is a three-dimensional array of BO_6 octahedra, all sharing corners, and the framework thus has the composition $(B_2O_6)_\infty$. The seventh set of oxygen ions and the A ions occupy open spaces in the framework as the large ions do in the perovskite structure. The mixed oxides consisting only of oxygen octahedra can generally yield a large internal field for ferroelectricity to occur. Both perovskite and pyrochlore are furnished with such a structural condition. There are, however, essential differences between the two structure types. In the ABO_3 perovskite, the O–B–O chains lie on straight lines parallel to the cubic axis. In the pyrochlore structure the configuration of the BO_6 octahedra is much more complicated, the O–B–O chains lying on zig-zag lines along the $\langle 110 \rangle$ directions. The zig-zag structure of O–B–O chains seems to be unfavorable for the occurrence of ferroelectricity since few[4,5] have been found to be ferroelectric among pyrochlores. Nikiforov *et al.*[6,7] concluded that oxygen deficient pyrochlores with more loose structure than pyrochlores of the type $A_2B_2O_7$ are favorable for its occurrence from a crystallochemical analysis of the conditions for a spontaneously polarized state in pyrochlores. Among perovskites, a number of ferroelectric substances have been found.[8] $PbTiO_3$ is ferroelectric with a Curie point of 490 °C and $PbZrO_3$ is antiferroelectric below 230 °C. It is of interest to see if a binary system consisting of pyrochlore and perovskite as end members exists in the form of oxygen deficient pyrochlore. In the present study, the formation of solid solutions $Pb_2Ta_{2-2x}M_{2x}O_{7-x}$ with M=Ti, Sn and Zr was examined and their optical and dielectric properties were investigated.

Experimental

Specimens were prepared from PbO, Ta_2O_5, TiO_2, SnO_2, and ZrO_2 of high purity. In particular, an electronic grade sample (>99.99%) was used for SnO_2. Mixtures of various compositions were ground together in an agated mortar, pressed into a disk and then ignited on platinum foil in the air at *ca.* 1050 °C. The resulting materials were reground, repressed and re-ignited at 1100—1200 °C for 3 h. They were then left to cool in the furnace.

Phase identification was carried out by X-ray diffraction technique using a X-ray diffractometer with nickel filtered Cu $K\alpha$ radiation. Calibration of goniometer was made using high purity silicon as a standard. Their lattice constants were determined from the reflection line of (662). The spectral reflectance between 400—760 nm was recorded with a spectrophotometer to pursue the displacement of absorption. Infrared absorption measurements between 4000—250 cm^{-1} were made for powder specimens dispersed in a pressed KBr disk, using a Perkin-Elmer infrared spectrophotometer model 457. The dielectric constants were measured on a capacitance bridge employing a frequency of 1000 cps. Fired-on silver electrodes were used for the measurements. No correction was made as regards the porosity of specimen.

Results and Discussion

Formation of Oxygen Deficient Pyrochlore Solid Solutions.

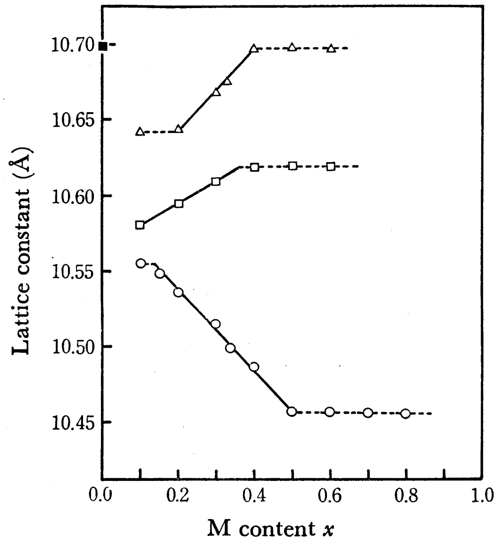

Fig. 1. Lattice constants for the solid solutions of pyrochlore $Pb_2Ta_{2-2x}M_{2x}O_{7-x}$ (M=Ti, Sn, and Zr).
○: Ti-containing system, □: Sn-containing system, △: Zr-containing system, ■: rhombohedral $Pb_2Ta_2O_7(\sqrt[3]{\overline{V}})$.

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Powder X-ray diffraction analyses show that cubic pyrochlore solid solutions exist in wide ranges. The variation of lattice constants for the solid solutions $Pb_2Ta_{2-2x}M_{2x}O_{7-x}$ with M=Ti, Sn and Zr are shown in Fig. 1. The part drawn by solid line represents the compositional range in which a single phase of cubic pyrochlore is observed in the powder X-ray patterns. $Pb_2Ta_2O_7$ is known to be rhombohedrally distorted pyrochlore with the unit cell with dimensions, $a=10.700$ Å and $\alpha=88°25'$. Partial substitution of M^{4+} ions for Ta^{5+} ions makes it possible for the cubic pyrochlore to form. In the case of Ti-containing system, the crystal distortion disappears when $x=0.15$. The unit cell dimension of cubic pyrochlore phase becomes smaller with a further increase in x, but remains much the same when the value of x, exceeds *ca.* 0.50. From the result, the substitutional limitation of Ti^{4+} ions to form the cubic pyrochlore phase is *ca.* $x=0.50$. According to Ahrens's radii,9) the ionic size of Ti^{4+} ion is 0.68 Å and is the same as that of Ta^{5+} ion. The unit cell dimension in this system, however, decreases with the increase of x in the substitutional range of Ti^{4+} ions. This affords an experimental proof for the formation of pyrochlore structure with oxygen deficiencies.

In the case of Sn- and Zr-containing systems, similar series of solid solutions exist in the form of cubic oxygen deficient pyrochlore. Their unit cell dimensions, however, increased with the increase of x in the compositional ranges in which cubic oxygen deficient pyrochlore is formed as a single phase. The regions of their solid solutions were narrower than that in the Ti-containing system. This is because the ionic sizes of Sn^{4+} ion (0.71 Å) and Zr^{4+} ion (0.79 Å) are larger than that of Ta^{5+} ion.

When Ta^{5+} ions were substituted partially with Ti^{4+} ions in cubic pyrochlore $Ca_2Ta_2O_7$, a series of oxygen deficient pyrochlore solid solution was not formed as in the case of the pyrochlore with Pb^{2+} ions in the A position. The partial substitution of Y^{3+} ions plus Ti^{4+} ions for Ca^{2+} ions plus Ta^{5+} ions gave a pyrochlore. The formation of the oxygen deficient pyrochlore structure seems to be related with the occupancy of Pb^{2+} ions in the A position. The structure with oxygen deficiency is derived from the pyrochlore structure by the removal of oxygen ions located in the tetrahedral interstices of the cationic array of Pb ions.10) The oxygen ions removed do not contribute to the framework structure even though they are necessary in the structure. Pb^{2+} ion has an eigthfold coordination (nearly an hexagonal bipyramid) in the pyrochlore structure. However, Pb^{2+} ion has a coordination less than eightfold in the oxygen dificient pyrochlore structure. The removal of oxygen ions located in the tetrahedral interstices results in an increase in the oxygen polarization. Since Pb^{2+} ion has a high polarizability due to its electronic configuration ($6s^2$), the occupancy of Pb^{2+} ions in the A position is favorable for the formation of oxygen deficient pyrochlore structure. It is understandable that oxygen deficient pyrochlores have often been formed, as in the examples of $Pb_2Ti_{1.5}W_{0.5}O_{6.5}$11) and $Bi_2Zn_{4/3}Ta_{2/3}O_6$,6) when Pb^{2+} or Bi^{3+} ion occupies the A position. Consequently the occupancy of Ca^{2+} ions in the A position seems unfavorable for the formation of oxygen deficient pyrochlore structure.

Reflectance Spectra. Samples of cubic oxygen deficient pyrochlore prepared were yellowish powder, a slight difference in the tone of color being found. Figure 2 shows the reflectance spectra in the range 400—760 nm for the Ti-containing system. The curves show strong absorption extending over violet and blue parts of visible light. The strong absorption is responsible for the yellowish color development. $Pb_2Ta_2O_7$ is white powder. With the increase in the amount of substituted Ti^{4+} ions, the reflectance curve shifts towards higher wavelength side, the color changing from lemon yellow to reddish yellow. Similar results were obtained for Sn- and Zr-containing systems. Each reflectance in the vicinity of the blue part increased in the order of Sn-, Ti-, and Zr-containing oxygen deficient pyrochlores under the condition of equimolecular substitution of M^{4+} ions. It seems that the color development can be ascribed to a significant contribution of covalent character in the Pb-O bond of these oxygen deficient pyrochlores. The Pb-O distances in $Pb_2Ta_{1.4}Ti_{0.6}O_{6.7}$ were calculated as an example, using its lattice constant ($a=10.518$ Å) and atomic coordinate parameters of cubic pyrochlore structure12) (oxygen parameter $u=5/16$). It was found that each Pb atom has two close oxygen neighbors at 2.28 Å and six close oxygen neighbors at 2.69 Å. Of the two kinds of Pb-O distance, the former is a little smaller than that in tetragonal PbO, which is a reddish color. The latter distance is nearly the same as that (2.70 Å) in $Pb(NO_3)_2$ with a typical ionic character. Pb^{2+}, Ta^{5+}, Ti^{4+}, or O^{2-} alone causes no visible absorption, but the combination gave a yellowish color. In the shorter Pb-O distance, consideration must be given to the fact that the outer electron orbits and energy levels are affected by the neighboring ions of oxygen. This is the electron band in which color-producing transition occurs as known in Cu_2O (red) and tetragonal PbO (reddish).13) The development of yellowish color is attributed to visible absorption in the vicinity of the violet part, by which the nonbonding electrons of O^{2-} ions are transferred to the outer orbits of Pb^{2+} ions. The volume of rhombohedral $Pb_2Ta_2O_7$ was larger by 2.8% than that of cubic $Pb_2Ta_2O_7$ (actually not existing at room temperature) estimated from the curve of lattice constant *vs.* composition in the solid solution $Pb_2Ta_{2-2x}Ti_{2x}O_{7-x}$. The atomic coordinates of each atom in rhombohedral $Pb_2Ta_2O_7$ have not been determined yet. The crystal distortion would cause the shorter Pb-O distance to enlarge, since rhombohedral $Pb_2Ta_2O_7$ is colorless.

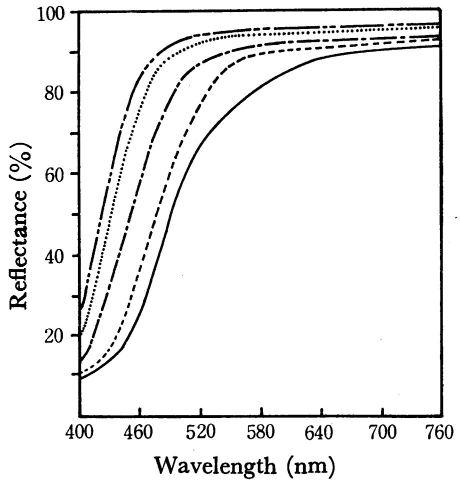

Fig. 2. Reflectance spectra of pyrochlore solid solution $Pb_2Ta_{2-2x}Ti_{2x}O_{7-x}$.
—··—: $x=0.1$, ······: $x=0.2$, —·—; $x=0.3$, -----: $x=0.4$, ——: $x=0.5$.

The pyrochlores were stable without dissolution in the lead glaze and the yellowish color remained unchanged when about 5% of them by weight were well dispersed in the lead glaze and their mixtures were ignited at 900 °C. These pyrochlore solid solutions might be used as a pigment in ceramics.

Infrared Absorption Spectra. Figure 3 shows infrared spectra of the solid solution $Pb_2Ta_{2-2x}Ti_{2x}O_{7-x}$. Two strong absorption bands were observed in all the specimens. Their

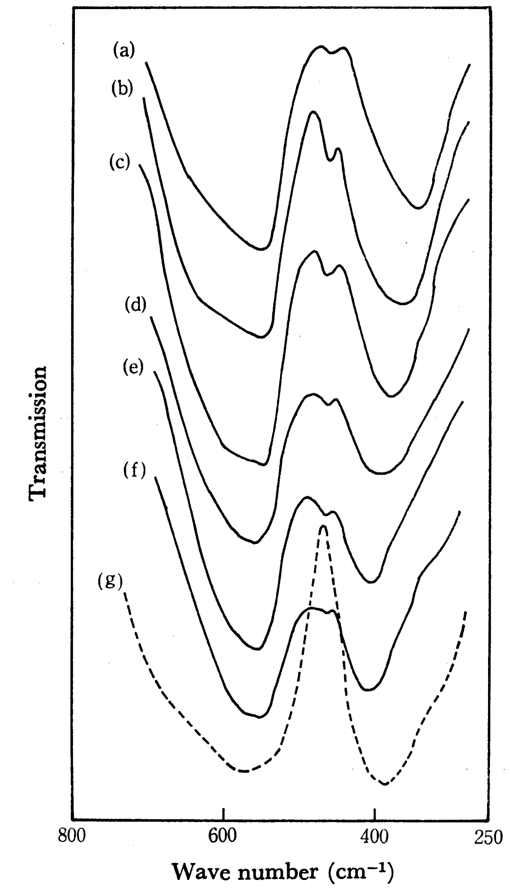

Fig. 3. Infrared absorption spectra of pyrochlore solid solution $Pb_2Ta_{2-x}Ti_{2x}O_{7-x}$ and $PbTiO_2$.
(a): x=0.0, (b): x=0.1, (c): x=0.2, (d): x=0.3, (e); x=0.4, (f): x=0.5, (g): $PbTiO_3$ (x=1.0).

spectra were all similar in general features. The higher frequency bands, ν_1, extend from *ca.* 800 to 490 cm^{-1}, with a peak of *ca.* 550 cm^{-1}. They are asymmetric, with a high-frequency tail. The lower frequency bands, ν_2, extend from *ca.* 490 cm^{-1} to the limit of the experimental range at 250 cm^{-1}, with a peak of 350—400 cm^{-1}. With the increse of Ti^{4+} ions, band locations of ν_1 remained nearly unchanged, these bands becoming slightly sharper. The band locations of ν_2 shifted towards high frequency side. Except two strong absorption bands, a weak absorption band was observed at *ca.* 460 cm^{-1}. The infrared spectra of pyrochlore solid solution were similar to that of $PbTiO_3$ except for the band locations (Fig. 3). The two absorption band peaks ν_1 and ν_2 observed in $PbTiO_3$ are 585 and 390 cm^{-1}. These values are in good agreement with Last's data.[14)] Similar absorption spectra were obtained for two series of Sn- and Zr-containing systems. Assignment of infrared spectrum has been done on perovskite,[15–17)], but not on pyrochlore. It should be noted that the infrared absorption spectra observed in these pyrochlore solid solutions were similar to those of the perovskites. The infrared absorption spectra between metastable pyrochlore $K_{1.5}(Ta_{0.65}Nb_{0.35})_2O_{5.75}$ and perovskite $K(Ta, Nb)O_3$ are similar.[18)] Thus it is of significance to compare the infrared absorption spectra of pyrochlore with those of perovskite, since they have analogous structural frameworks. According to the study by Perry *et al.*,[15,16)] the vibrations ν_1 and ν_2 observed in the ABO_3 perovskite are assigned to the B–O stretching mode and the B–O_3 torsional mode, respectively. Figures 4 and 5 show the compositional dependence of ν_1 and ν_2 for three series of oxygen deficient pyrochlore solid solutions.

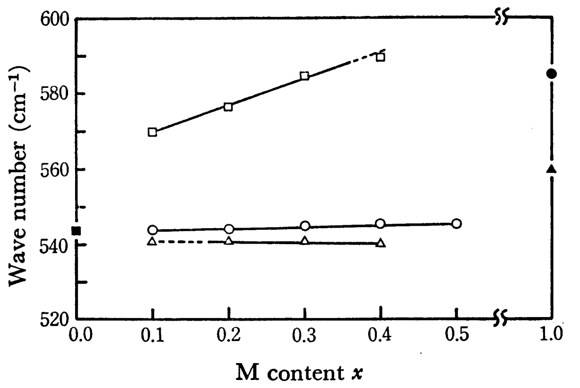

Fig. 4. Compositional dependence of ν_1 for the solid solutions of pyrochlore $Pb_2Ta_{2-2x}M_{2x}O_{7-x}$ (M=Ti, Sn, and Zr).
○: Ti-containing system, □: Sn-containing system, △: Zr-containing system, ■: rhombohedral $Pb_2Ta_2O_7$, ●: perovskite $PbTiO_3$, ▲: perovskite $PbZrO_3$.

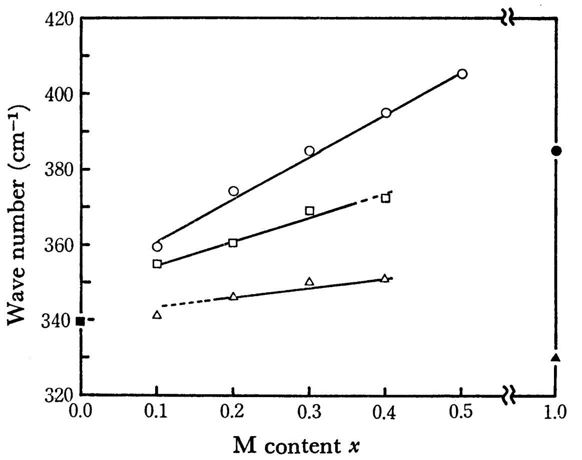

Fig. 5. Compositional dependence of ν_2 for the solid solutions of pyrochlore $Pb_2Ta_{2-2x}M_{2x}O_{7-x}$ (M=Ti, Sn, and Zr).
○: Ti-containing system, □: Sn-containing system, △: Zr-containing system, ■: rhombohedral $Pb_2Ta_2O_7$, ●: perovskite $PbTiO_3$, ▲: perovskite $PbZrO_3$.

The band locations of ν_1 remain nearly unchanged, except for Sn-containing system. On the other hand, all the band locations of ν_2 for three systems shift linearly towards high frequency side with the increase of M^{4+} ions. The values and slopes for ν_2 increase in the order of Ti-, Sn-, and Zr-containing systems. The observed band locations of ν_2 seem to have an inverse relationship between atomic masses and vibrational frequencies. Such a tendency appeared in the perovskites with the same cation in the A position. For example, the band locations of ν_1 for $BaTiO_3$, $BaSnO_3$, and $BaZrO_3$ are 578, 635, and 573 cm^{-1}, respectively, and the band locations of ν_2 for $BaTiO_3$, $BaSnO_3$, and $BaZrO_3$ are 410, 400, and 420 cm^{-1}, respectively.[19)] Similar results were obtained for $PbTiO_3$ and $PbZrO_3$ (Figs. 4 and 5). That the vibrational frequencies of ν_1 for Ti- and Zr-containing systems remain nearly unchanged is probably because both effects of reduced mass and force constant on them are cancelled out. The band locations of ν_1 for Sn-containing system, however, shift towards high frequency side, the values being larger than those observed in Ti- and Zr-containing systems. It will be attributed to larger force constants of ν_1 in Sn-containing

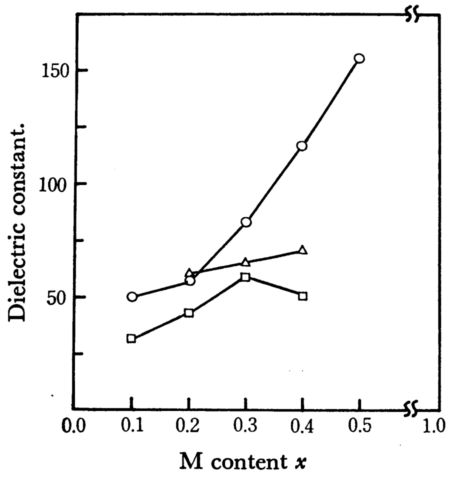

Fig. 6. Compositional dependence of dielectric constant for the solid solutions of pyrochlore $Pb_2Ta_{2-2x}M_{2x}O_{7-x}$ (M=Ti, Sn, and Zr).
○: Ti-containing system, □: Sn-containing system, △: Zr-containing system.

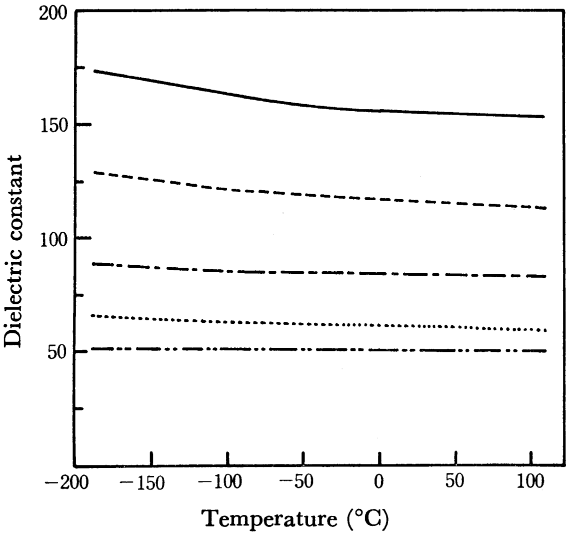

Fig. 7. Temperature dependence of dielectric constant for the pyrochlore solid solution $Pb_2Ta_{2-2x}Ti_{2x}O_{7-x}$.
—‥—: $x=0.1$, ······: $x=0.2$, —·—: $x=0.3$, ------: $x=0.4$, ——: $x=0.5$.

system than in Ti- and Zr-containing ones. The band locations of ν_1 for pyrochlores of compositions $PbTiO_3$ and $PbZrO_3$ (actually not existing), estimated from the compositional dependence of frequency (Fig. 4), are larger than those observed in the perovskites of $PbTiO_3$ and $PbZrO_3$. This is because force constants of ν_1 in these pyrochlores are larger than those in the perovskites, assuming that the higher frequency ν_1 observed in these pyrochlore solid solutions corresponds to the perovskite B–O stretching mode. The weak absorption band located at 460 cm^{-1} would result from the splitting of degeneracy in the vibrational mode of ν_2. The qualitative similarity of infrared absorption spectra between pyrochlore and perovskite can be expected in view of the assignment based on the vibrations of oxygen octahedron, since they have an analogous structural framework. Further investigation is necessary to confirm whether two absorption bands ν_1 and ν_2 observed in pyrochlores correspond to the B–O stretching mode and the B–O_3 torsional mode, respectively, or not.

Dielectric Constant. The compositional dependence of dielectric constant for the solid solutions at room temperature is shown in Fig. 6. The dielectric constants are relatively high, but small as compared with those of titanates or zirconates of typical perovskite. They increase with the increase of M^{4+} ions. In particular, a marked increase of dielectric constant was observed in the Ti-containing system. The temperature dependence of dielectric constant for the Ti-containing system from −190 to 110 °C is shown in Fig. 7. The dielectric constants tend to increase slightly with the decrease in temperature. Such a tendency also appeared in Sn- and Zr-containing systems. If ferroelectric phases occur among these oxygen deficient pyrochlores, the dielectric anomalies would be below liquid nitrogen temperature.

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