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LETTER TO THE EDITOR

New perovskite dielectrics $(\text{Pb}_{1-x}\text{Ba}_x)(\text{In}_{0.5}\text{Ta}_{0.5})\text{O}_3$ and $(\text{Pb}_{1-x}\text{Ba}_x)(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$

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Abstract. New complex perovskite-type dielectric materials, $(\text{Pb}_{1-x}\text{Ba}_x)(\text{In}_{0.5}\text{Ta}_{0.5})\text{O}_3$ (PBIT) and $(\text{Pb}_{1-x}\text{Ba}_x)(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (PBIN) have been successfully synthesized using a rapid thermal sintering process. These new complex perovskite materials show relaxor-type dielectric properties, and the temperature at which the real part of the permittivity shows a broad maximum is shifted towards lower temperature by the substitution of Ba ions for A-site Pb ions.

The relaxor-type ferro- or antiferroelectric materials were investigated in view of the relation between the B-site sublattice ordering and the phase transformation (Bokov *et al* (1986), Prokopalo *et al* (1982), Setter and Cross (1980), Stenger and Burggraaf (1980)). $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (PIN) and $\text{Pb}(\text{In}_{0.5}\text{Ta}_{0.5})\text{O}_3$ (PIT) belong to this group of materials: the ferroelectricity in disordered PIN was confirmed by Yasuda and Shibuya (1989); Kania (1990) suggested that the ordered PIT single crystal showed an antiferroelectric state in the low-temperature phase. It is known to be very difficult to synthesize pure perovskite-phase specimens to PIT and PIN. Recently Yasuda *et al* (1992) successfully prepared the pure perovskite-phase polycrystal samples utilizing a rapid thermal sintering process. Their dielectric measurements showed that both PIT and PIN show strong dielectric dispersion and that the real parts of the permittivities have broad maxima at temperatures T_m ; those of PIT and PIN were reported as 278 K and 332 K at 1 kHz. We noted the dielectric properties of PIT and PIN at temperatures above their T_m s; the temperature dependence of the real part of the permittivity is not as strong and the dielectric loss tangent is small in the higher-frequency region. We tried to substitute each of Ca, Sr and Ba for the A-site Pb ion, and to shift the T_m s to lower temperature. Then we could successfully obtain the perovskite-phase $(\text{Pb}_{1-x}\text{Ba}_x)(\text{In}_{0.5}\text{Ta}_{0.5})\text{O}_3$ (PBIT) and $(\text{Pb}_{1-x}\text{Ba}_x)(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (PBIN) ceramic specimens using a rapid thermal sintering process.

In order to enhance the formation of the perovskite phase, B-site oxides were preformed by calcination and subsequently reacted with PbO and BaCO_3 (Baumgartner (1988), Landin and Schulze (1990)). Wolframite-phase oxides InTaO_4 and InNbO_4 were synthesized by firing at 1200°C for 24 hours in oxygen with starting materials Ta_2O_5 (99.9%) or Nb_2O_5 (99.9%) and In_2O_3 (99.9%). The mixtures of each calcined wolframite-phase oxide, PbO and BaCO_3 were made into pellets and rapidly reacted by insertion into the heated tube furnace after pre-firing at 350°C for 3 hours. The batches of PBIT and PBIN were sintered at 1000°C for 5 minutes and 900°C for 55 minutes. In the present work no samples were annealed after the sintering process.

X-ray diffraction patterns measured by 2θ - ω scans with Cu $K\alpha$ are shown in figure 1. X-ray diffraction confirms that the sintered samples of PBIT and PBIN have an approximately

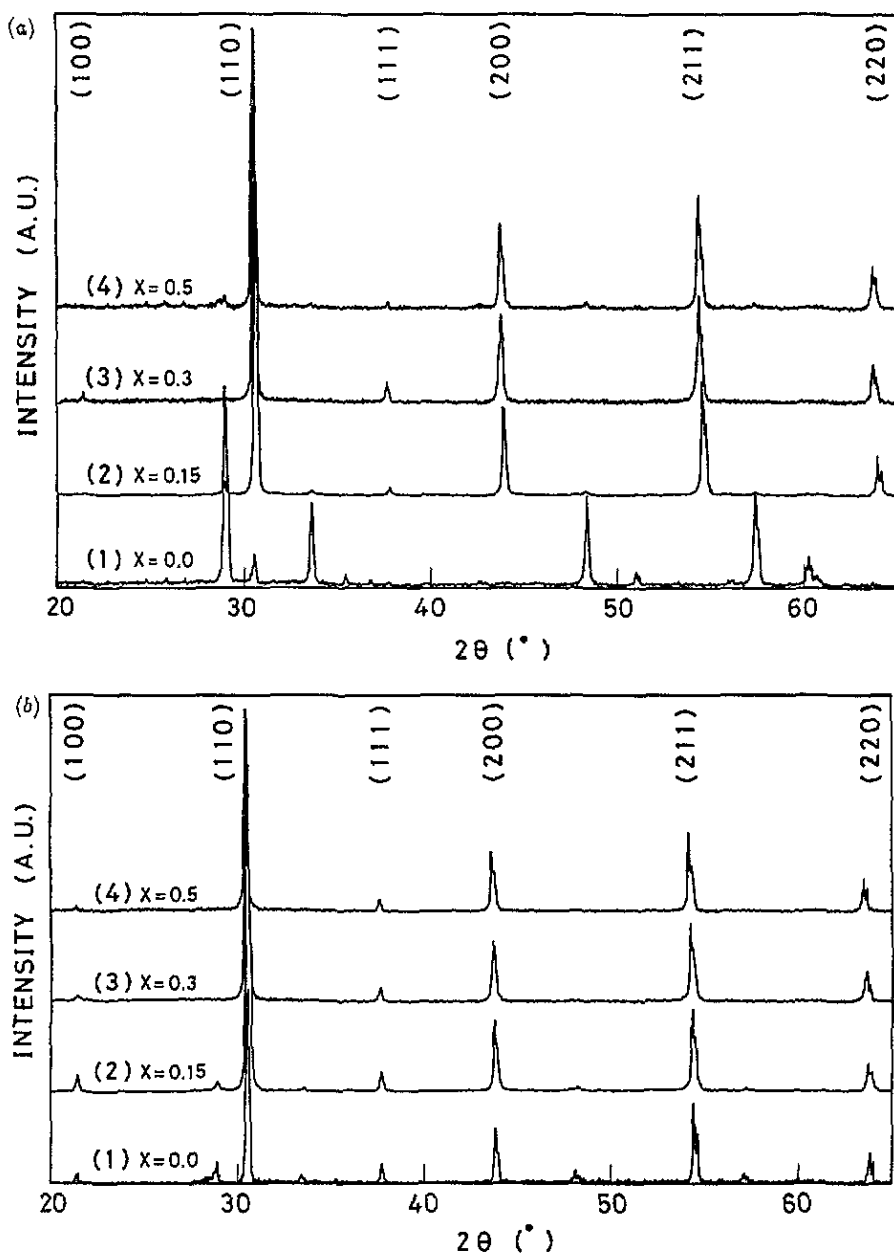


Figure 1. X-ray diffraction patterns of (a) PBIT and (b) PBIN obtained at 295 K. x corresponds to the Ba content. The indices (h, k, l) correspond to the cubic perovskite structure, and peaks with no indices show the impurity phases.

perovskite structure, and that the substitution of the Ba ion makes it easy to synthesize perovskite-phase specimens. In our PBIT and PBIN samples the satellite diffractions caused by superstructures were not observed. It is also suggested that both A- and B-site ions are in a disordered state. The lattice constants of PBIT and PBIN specimens were estimated by a least-squares method. The accuracy of the diffraction data was checked using Au diffraction data obtained under the same measurement conditions. The lattice constants obtained at

295 K are presented in table 1, which were estimated assuming the cubic unit cell. The cubic lattice constants of PBIT and PBIN increase with the nominal content of Ba in the samples.

Table 1. The lattice constants obtained by the x-ray diffraction at 295 K. x corresponds to the content of Ba ions (see text). All measurements are in Å.

x	0.00	0.15	0.30	0.50
PBIT	4.109*	4.1161(1)	4.1295(1)	4.1324(2)
PBIN	4.117*	4.1237(1)	4.1292(12)	4.1350(1)

*After Yasuda *et al* (1992).

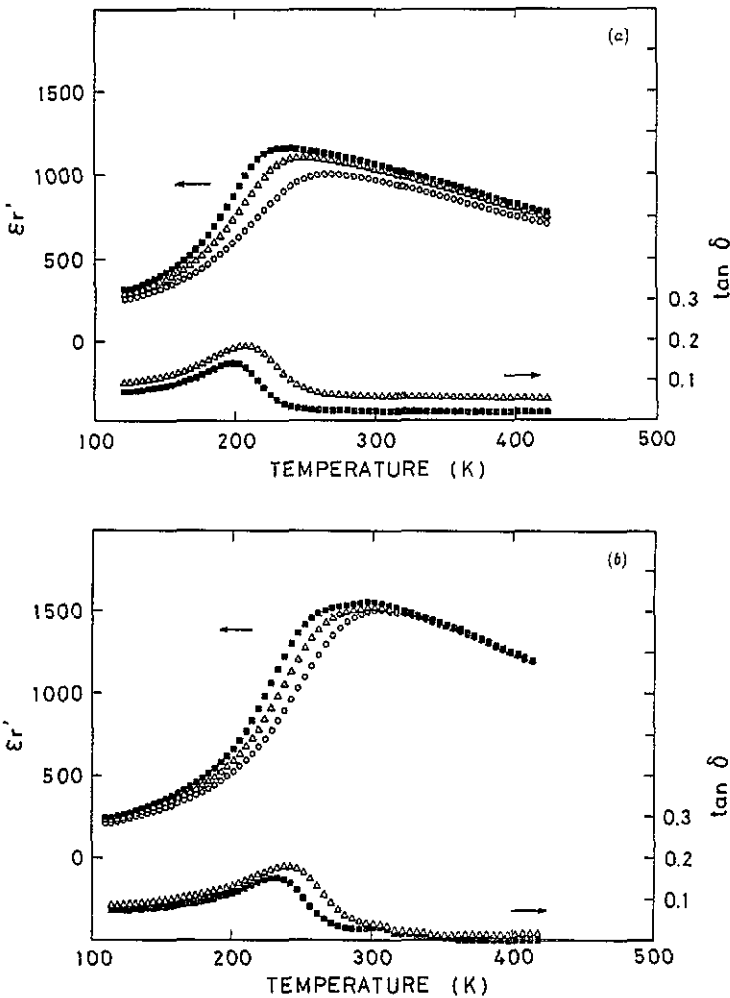


Figure 2. The temperature dependence of the dielectric constants of (a) PBIT ($x = 0.15$) and (b) PBIN ($x = 0.15$). The data points \blacksquare , \triangle and \circ correspond to the measurement frequencies of 10 kHz and 1 MHz. The dielectric loss data at 1 MHz could not be measured accurately because of the large electrical resistance of each sample ($R > 10 \text{ M}\Omega$).

The lattice constants expected from the typical ionic radii of oxygen and B-site ions are 4.24 Å (PIT) and 4.34 Å (PIN); otherwise, that expected from oxygen and Pb ions is 3.74 Å. The ionic radii used are $r(\text{In}^{3+}) = 0.92$ Å, $r(\text{Ta}^{5+}) = 0.68$ Å, $r(\text{Nb}^{5+}) = 0.69$ Å, $r(\text{Pb}^{2+}) = 1.32$ Å, $r(\text{Ba}^{2+}) = 1.35$ Å and $r(\text{O}^{2-}) = 1.32$ Å (Inoue *et al* (1990)). The crystal lattice constants obtained in real samples are 4.109 Å (PIT) and 4.117 Å (PIN) (Yasuda *et al* (1992)), so it is suggested that the lattice lengths of real crystals of PIT and PIN are a result of a kind of trade off on the crystal lattice formation energy. Further, the real atomic distances between oxygen and B-site ions (In, Ta or Nb) are less than typical ones. So, the real spacing for B-site ions is much closer than that expected of regular ionic radii, which are clearly much smaller than those of Pb and Ba ions. We did not succeed in substituting Ca or Sr ions, whose ionic radii are much smaller than that of the Ba ion, and are much larger than those of In, Ta and Nb ions. Therefore, it seems that the A-site Pb ion is substituted by the Ba ion having a larger ionic radius than Pb. The substitution of the Ba ion for the Pb ion results in a longer lattice constant than that expected merely from the difference between the typical ionic radii of Pb and Ba.

The dielectric constants of PBIT and PBIN were measured in nitrogen (or air) from about 100 K to 450 K at 10, 100 and 1000 kHz with a field weaker than 2 V cm^{-1} using an impedance analyser. Figure 2 shows the temperature dependence of the dielectric constants for the PBIT and PBIN specimens. The typical densities of PBIT ($x = 0.15$) and PBIN ($x = 0.15$) used in these measurements were obtained as 8.3 g cm^{-3} and 6.6 g cm^{-3} and are about 91% and 91% respectively of the theoretical densities. The absolute values of dielectric constants are seriously affected by the sample quality, but the tendency of temperature dependence is not seriously influenced by that. The real part of the complex relative permittivity ϵ_r' has a broad maximum at a temperature T_m and those values strongly depend on the measurement frequency, which are the characteristics of relaxor antiferro- or ferroelectrics (Smolenskii (1970), Cross (1987)). The T_m s are also affected by Ba substitution: the T_m s of PIT and PIN were obtained as 303 K and 351 K by Yasuda *et al* (1992) at 100 kHz; otherwise, those for PBIT ($x = 0.15$) and PBIN ($x = 0.15$) samples are 249 K and 300 K.

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