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Microwave dielectric properties of $ATiO_3$ (A = Ni, Mg, Co, Mn) ceramics

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Abstract

Relationships between structural characteristics and microwave dielectric properties of $ATiO_3$ (A = Ni, Mg, Co, Mn) with ilmenite structure were investigated. The oxygen octahedral distortion was dependent on the type of A-site ions which affected to the temperature coefficient of the resonant frequency (*TCF*) of $ATiO_3$ ceramics. The quality factor (*Qf*) of $ATiO_3$ (A = Mn, Ni, Co) specimens was appreciably lowered than that of $MgTiO_3$ specimens due to the degree of covalency of cation–oxygen ion bond and the ordering of A-site ions. Also, the dielectric constant (*K*) was dependent on the electronic oxide polarizabilities of $ATiO_3$ ceramics.

Keywords: Ilmenite structure; Dielectric properties; Covalency; Octahedral distortion; Electronic oxide polarizabilities

1. Introduction

$ATiO_3$ (A = Ni, Mg, Co, Mn) ceramics have the ilmenite structure, which is an ordered derivative of the corundum structure. The ilmenite structure is based on hexagonal closest packed oxygen layers with cations occupying two thirds of the octahedral sites available.[1] In contrast to the fully disordered corundum structure, the ilmenite structure results from equal amounts of divalent and tetravalent cations, which are ordered at the octahedral sites and alternate along the *c*-axis of the unit cell. The same type of octahedron in the ilmenite structure shares an edge along the *a*-axis, a pair of AO_6 and TiO_6 octahedra shares a face along the *c*-axis and a corner along the oblique direction. One pair of edge-shared TiO_6 octahedra is isolated by the cation vacancies along the *a*-axis and that is separated by the AO_6 octahedron along the oblique direction.

If the ionic radius of A-site ion is much larger than 1.0 Å, such as Ca^{2+} (1.34 Å) or Sr^{2+} (1.44 Å)[2] in $CaTiO_3$ or $SrTiO_3$, the compound turns to the perovskite structure which is formed by corner sharing of the TiO_6 octahedron, and the coordination number of A-site cations turns from 6 to 12.

For high frequency applications and stability of the resonant frequency, the low loss dielectric materials with ilmenite structure such as $MgTiO_3$ have been widely investigated for the microwave telecommunication systems.[3] With the types of A-site ions of $ATiO_3$ ceramics, the microwave dielectric properties are expected to be changed. Dependence of microwave dielectric properties on structural characteristics should be studied to control and predict the dielectric properties of $ATiO_3$ ilmenite compounds.

Therefore, the microwave dielectric properties of ilmenite titanates, $ATiO_3$ (A = Ni, Mg, Co, Mn) ceramics have been investigated in view point of the characteristics of bonds between cations and oxygen, the distortion of oxygen octahedra and ordering of cation in ilmenite structure.

2. Experimental procedure

$ATiO_3$ (A = Ni, Mg, Co, Mn) powders were separately prepared by a conventional solid-state reaction from oxide powders with purities above 99%. To obtain a single phase of each composition, $ATiO_3$ (A = Ni, Mg, Co, Mn) powders were calcined at 1100 °C for 5 h. These calcined powders were milled again with ZrO_2 balls for 24 h in ethanol and then dried. The dried powders were pressed isostatically into 10 mm-diameter disks at 1500 kg/cm^2. The resultant pellets were sintered from 1200 to 1500 °C for 3 h in air.

The apparent densities of the sintered specimens were measured by Archimedes method. The relative densities were obtained from the apparent densities and the theoretical values. Powder X-ray diffraction (XRD) analyses (D/Max-3C, Rigaku, Japan) were used to determine the phase identification. The lattice parameters, unit cell volumes and atomic positions were obtained from Rietveld refinements of XRD patterns. The

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Rietveld refinements were performed using the RIETAN-2000 program.[4] The initial structure model for ilmenite compounds was taken from the work by Wechsler and Von Dreele,[5] using neutron powder diffraction at room temperature. The ordering of crystal structure was confirmed by a Raman spectra meter (T 64000, HORIABA Jobin Yvon, France) with an Ar^+ ion laser operating at 514 nm for excitation. The microstructure of the specimens was observed using a scanning electron microscope (SEM, JSM-6500F, JEOL, Japan). The microwave dielectric properties were measured by Hakki and Coleman's method[6] with the TE_{011} mode at 10–11 GHz. The *TCF* of specimens was measured by the cavity method[7] in the temperature range from 25 to 80 °C.

3. Results and discussion

3.1. Physical properties

With the increase of sintering temperature from 1200 to 1500 °C, the sintered densities of $ATiO_3$ (A = Ni, Mg, Co, Mn) ceramics increased and showed the different sinterability with the types of A-site ions. To reduce the effects of density on the microwave dielectric properties, the optimal sintering temperatures for the higher sintered densities than 96% of theoretical values were 1300 °C for $MnTiO_3$, 1350 °C for $MgTiO_3$ and $CoTiO_3$, and 1400 °C for $NiTiO_3$, respectively.

Fig. 1 shows the XRD patterns of $ATiO_3$ (A = Ni, Mg, Co, Mn) sintered specimens. A single phase of the trigonal ilmenite structure (*R3-H*) was confirmed through the entire compositions. With the types of A-site ions (A = Ni, Mg, Co, Mn), the peak at $2\theta = 32°–34°$ in XRD patterns shifted to lower angle, which indicated that the unit cell volume increased with the ionic radius of A-site ions (A = Ni, Mg, Co, Mn). Since the ionic size of Ni^{2+} (0.69 Å) was smaller than those of Mg^{2+} (0.72 Å), Co^{2+} (0.745 Å) and Mn^{2+} (0.83 Å) at the same coordination number of 6,[2] the unit cell volume of $NiTiO_3$ specimens was smaller than those of $MgTiO_3$, $CoTiO_3$ and $MnTiO_3$ specimens. Also, the crystallographic parameters, refined atomic positions and occupancies of the sintered specimens obtained from the Rietveld refinement of XRD patterns are summarized in Table 1.

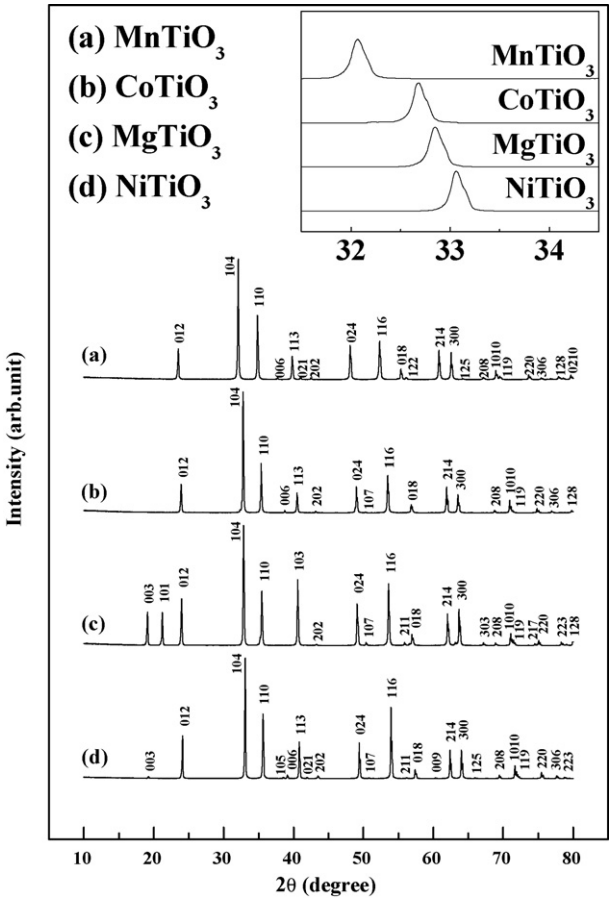

Fig. 1. X-ray diffraction patterns of $ATiO_3$ (A = Ni, Mg, Co, Mn) sintered specimens.

According to Pauling,[8] the ionic character of bonds could be estimated by the electronegativity difference (Δe) between cation and oxygen by Eq. (1).

$$\Delta e = \frac{(X_{A–O} + X_{B–O})}{2} \quad (1)$$

Due to the larger electronegativity difference (Δe) than 2.0, $MgTiO_3$ (2.015) showed the larger ionic bond characteristics than $NiTiO_3$, $CoTiO_3$ and $MnTiO_3$ because those of $NiTiO_3$

Table 1
Crystallographic parameters, refined atomic positions and occupancies of $ATiO_3$ (A = Ni, Mg, Co, Mn) sintered specimens.

Compound	Atom	Wyckoff site	*x*	*y*	*z*	Occupation
	Ni	6c	0	0	0.3508	1.0
$NiTiO_3$	Ti	6c	0	0	0.1440	1.0
	O	18f	0.3115	0.0057	0.2476	1.0
	Mg	6c	0	0	0.3557	1.0
$MgTiO_3$	Ti	6c	0	0	0.1451	1.0
	O	18f	0.3159	0.0214	0.2463	1.0
	Co	6c	0	0	0.3551	1.0
$CoTiO_3$	Ti	6c	0	0	0.1456	1.0
	O	18f	0.3162	0.0209	0.2459	1.0
	Mn	6c	0	0	0.3600	1.0
$MnTiO_3$	Ti	6c	0	0	0.1476	1.0
	O	18f	0.3189	0.0310	0.2439	1.0

Table 2
Covalency of $ATiO_3$ (A = Ni, Mg, Co, Mn) sintered specimens.

Compound		R (Å)	R_1 (Å)	N	a	M	s	f_c	Covalency (%)	Average covalency (%)
$MgTiO_3$	Mg–O	2.015	1.622	4.29	0.54	1.64	0.327	0.086	26.40	31.93
	Ti–O	1.977	1.806	5.20	0.49	1.57	0.624	0.234	37.46	
$NiTiO_3$	Ni–O	2.049	1.680	5.40	0.60	1.50	0.342	0.120	35.09	35.61
	Ti–O	2.002	1.806	5.20	0.49	1.57	0.586	0.212	36.12	
$CoTiO_3$	Co–O	2.111	1.727	5.60	0.60	1.50	0.325	0.111	34.20	35.83
	Ti–O	1.977	1.806	5.20	0.49	1.57	0.624	0.234	37.45	
$MnTiO_3$	Mn–O	2.193	1.798	5.60	0.60	1.50	0.329	0.113	34.42	35.93
	Ti–O	1.978	1.806	5.20	0.49	1.57	0.624	0.233	37.44	

(1.715), $CoTiO_3$ (1.73) and $MnTiO_3$ (1.895) are smaller than 2.0. The bond characteristics between cation and oxygen of $ATiO_3$ (A = Ni, Mg, Co, Mn) could also be evaluated by the relationships between the bond strength (s) and covalency (f_c) of octahedral cation–oxygen ion bonds as shown in Eqs. (2)–(4).[9,10]

$$s = \left(\frac{R}{R_1}\right)^{-N} \tag{2}$$

$$f_c = as^M \tag{3}$$

$$\text{Covalency } (\%) = \frac{f_c}{s} \times 100 \tag{4}$$

where R, R_1 and N are the refined bond length, empirical constant which depends on the cation site, and the constant which is different for each octahedral cation–oxygen ion pair, respectively. Moreover, a and M in Eq. (3) are empirical constants which depend on the number of electrons. Table 2 summarizes the bond strength and covalency of $ATiO_3$ (A = Ni, Mg, Co, Mn) sintered specimens. Comparing to the covalency (%) of Mg–O bond of $MgTiO_3$, Ni–O, Co–O, and Mn–O bonds showed larger covalency (%) and Ti–O bonds of $ATiO_3$ did not changed much with the type of A-site ions. These results may be associated with the loss of electronic polarization of 3d electrons in Ni^{2+} ($3d^8$), Co^{2+} ($3d^7$) and Mn^{2+} ($3d^5$).

SEM micrographs of $ATiO_3$ (A = Ni, Mg, Co, Mn) ceramics sintered at each optimal sintering temperature are shown in Fig. 2. The grain size of $MnTiO_3$ specimens was larger than those of $ATiO_3$ (A = Co, Ni, Mg) specimens.

3.2. Dielectric properties at microwave frequencies

Fig. 3 shows the dielectric constant (K) of $ATiO_3$ (A = Ni, Mg, Co, Mn) specimens sintered from 1200 to 1500 °C for 3 h.

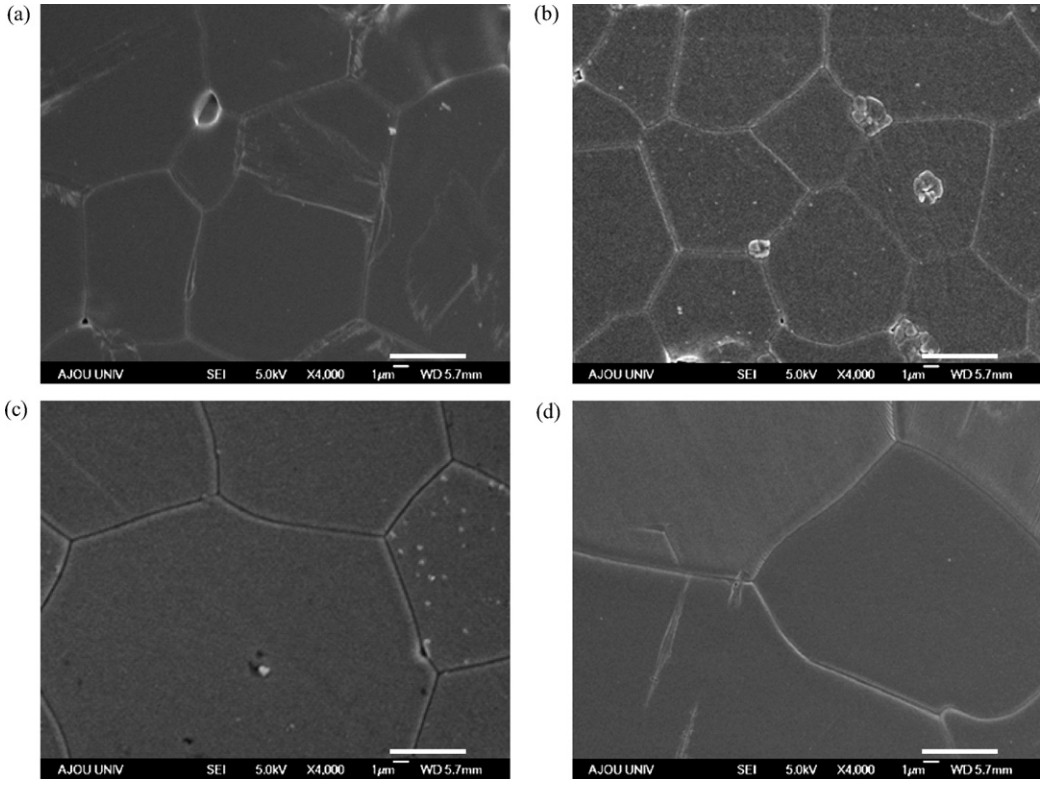

Fig. 2. SEM micrographs of $ATiO_3$ (A = Ni, Mg, Co, Mn) sintered specimens: (a) $NiTiO_3$, (b) $MgTiO_3$, (c) $CoTiO_3$, and (d) $MnTiO_3$ (bar = 5 μm).

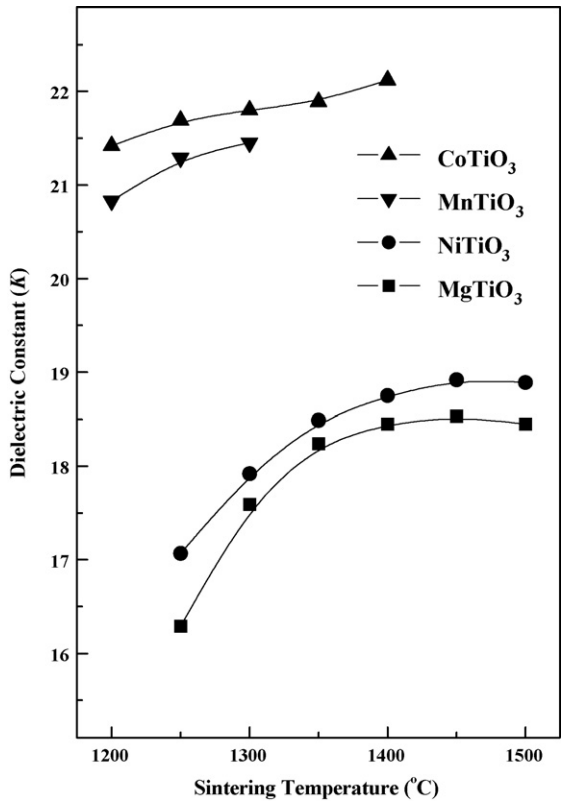

Fig. 3. Dielectric constant (K) of $ATiO_3$ (A = Ni, Mg, Co, Mn) specimens sintered from 1200 to 1500 °C for 3 h.

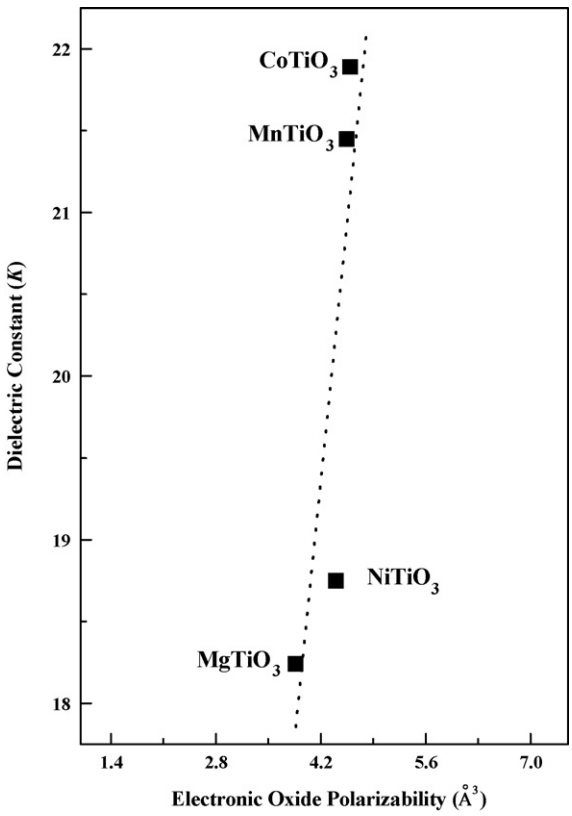

Fig. 4. Dependence of dielectric constant (K) on the electronic oxide polarizability of $ATiO_3$ (A = Ni, Mg, Co, Mn) sintered specimens.

With the increase of the sintering temperature, the K of the specimens was increased due to the increase of density. At microwave frequencies, the K is dependent on the theoretical dielectric polarizabilities ($\alpha_{theo.}$) obtained from the additive rule.[11] However, the K of $CoTiO_3$ was larger than those of $MnTiO_3$, $NiTiO_3$ and $MgTiO_3$, even though the $\alpha_{theo.}$ of $MnTiO_3$ (11.6 Å^3) was larger than those of $CoTiO_3$ (10.61 Å^3), $MgTiO_3$ (10.28 Å^3) and $NiTiO_3$ (10.19 Å^3). These results could be attributed to the bond characteristics of $ATiO_3$ (A = Ni, Mg, Co, Mn) ceramics. Due to the covalency of cation–oxygen bond and the localized 3d electrons Ni^{2+} ($3d^8$), Co^{2+} ($3d^7$) and Mn^{2+} ($3d^5$), the electronic oxide polarizabilities ($\alpha_{O^{2-}}$) should be considered. The $\alpha_{O^{2-}}$ reported by Dimitrov and Sakka[12] from the energy gap and the molar volume as well as the polarizability of cation was used. With the ionic radius of A-site ions (A = Mg, Ni, Mn, Co), the K of the sintered specimens was increased due to the increase of the $\alpha_{O^{2-}}$, as shown in Fig. 4. Therefore, the energy gap and the molar volume should also be considered as well as the dielectric polarizabilities to predict and control the K of $ATiO_3$ with ilmenite structure.

Fig. 5 shows the quality factor (Qf) of $ATiO_3$ (A = Ni, Mg, Co, Mn) specimens sintered from 1200 to 1500 °C for 3 h. The Qf value of $MgTiO_3$ specimens was much larger than those of (A = Co, Ni, Mn) specimens. It has been reported[11] that the Qf value was dependent on density, secondary phase and grain size. In these systems, the effects of the density, secondary phase and grain size could be neglected, because the relative density was higher than 96%, and there was no secondary phase and no

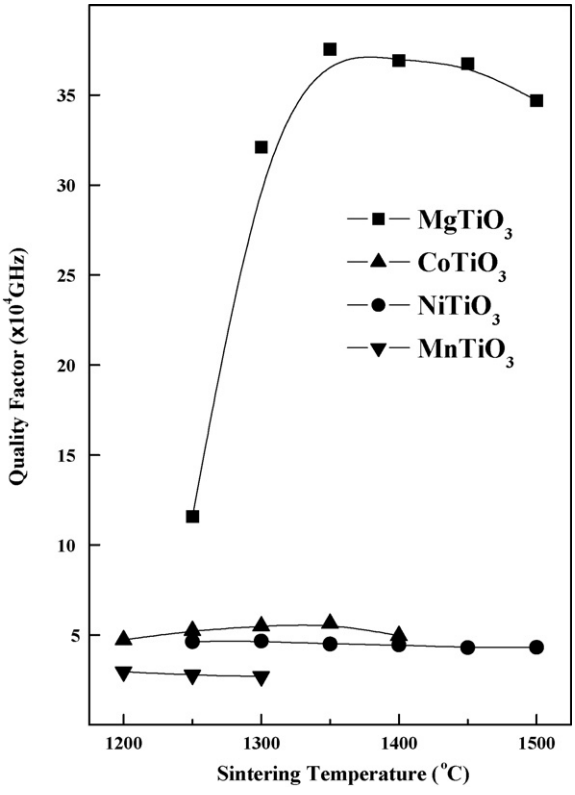

Fig. 5. Quality factor (Qf) value of $ATiO_3$ (A = Ni, Mg, Co, Mn) specimens sintered from 1200 to 1500 °C for 3 h.

Table 3
Average octahedral distortion and *TCF* of $ATiO_3$ (A = Ni, Mg, Co, Mn) sintered specimens.

	$NiTiO_3$	$CoTiO_3$	$MgTiO_3$	$MnTiO_3$
$R1_{A-O}$ (Å) ×3	2.103	2.170	2.165	2.278
$R2_{A-O}$ (Å) ×3	1.995	2.052	2.045	2.107
Average R_{A-O} (Å)	2.049	2.111	2.105	2.193
$R1_{Ti-O}$ (Å) ×3	2.107	2.085	2.089	2.082
$R2_{Ti-O}$ (Å) ×3	1.896	1.870	1.866	1.874
Average R_{Ti-O} (Å)	2.002	1.977	1.977	1.978
A-site octahedral distortion ($\Delta_A \times 10^3$)	0.698	0.785	0.821	1.520
Ti-site octahedral distortion ($\Delta_{Ti} \times 10^3$)	2.767	2.978	3.186	2.758
Average octahedral distortion ($\Delta \times 10^3$)	1.733	1.881	2.003	2.139
TCF (ppm/°C)	−48.48	−52.57	−54.48	−63.92

agreement with the change of grain size. Shon et al.[13] reported that the *Qf* value of $MgTiO_3$ specimens was larger than those of the other ilmenite titanates due to the absence of 3d electrons which induce the conductivity.

Generally, Raman spectroscopy was used as an ideal tool for probing the degree of ordering. Raman modes move to higher frequencies for the well-ordered structures.[14] Ten Raman active vibrational modes ($5A_g + 5E_g$) are predicted for the ilmenite structure.[15] A_{1g}, E_{1g} and E_{2g} modes of $ATiO_3$ (A = Ni, Mg, Co, Mn) sintered specimens are shown in Fig. 6. With the types of A-site ions (A = Mn, Ni, Co, Mg), all of the modes move to higher frequencies due to the increase of the A-site ordering. Therefore, the increase of *Qf* value with the A-site ions (A = Mn, Ni, Co, Mg) could be attributed to the increase of A-site ordering in $ATiO_3$ ilmenite structure.

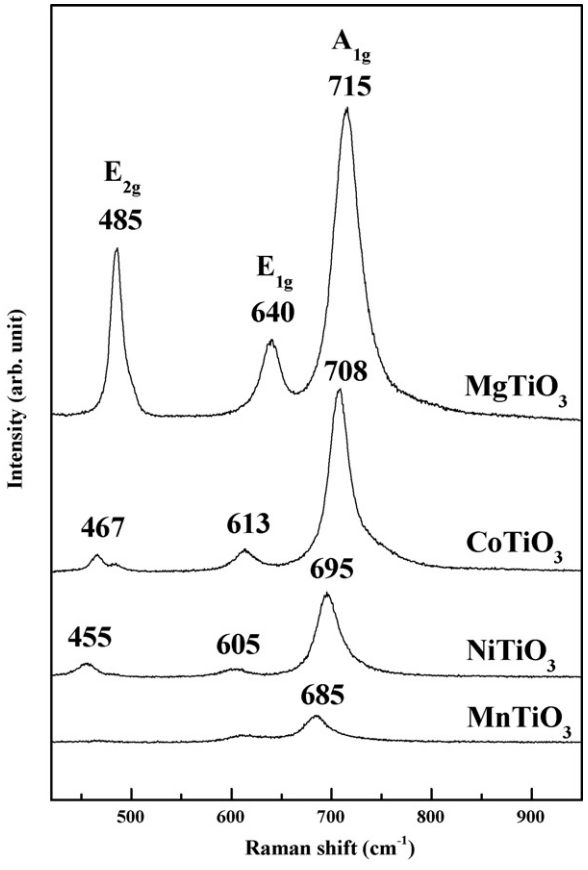

Fig. 6. Raman spectra of $ATiO_3$ (A = Ni, Mg, Co, Mn) sintered specimens.

Table 3 summarizes the average octahedral distortion and the temperature coefficient of resonant frequency (*TCF*) of $ATiO_3$ (A = Ni, Mg, Co, Mn) sintered specimens. The individual bond lengths of oxygen octahedra were obtained from the lattice parameters and atomic positions, as confirmed in Table 1. From the individual bond length of oxygen octahedra, the octahedral distortion was calculated by the equation reported by Shannon.[2] The octahedral distortion of A-site was smaller than that of Ti-site in entire compositions. With the increase of ionic radius of A-site ions (A = Ni, Co, Mg, Mn), the *TCF* of the specimens was decreased due to the increase of average octahedral distortion. These results that *TCF* of $ATiO_3$ ilmenite titanate depended on the octahedral distortion are also agreed with the reports of perovskite titanate.[16]

4. Conclusions

For the sintered specimens of $ATiO_3$ (A = Ni, Mg, Co, Mn), a single phase of ilmenite structure was confirmed through the entire composition. The dielectric constant (*K*) of $ATiO_3$ (A = Ni, Mg, Co, Mn) specimens was depended on the electronic oxide polarizabilities resulted from the energy gap and the molar volume as well as the polarizability of cation. The quality factor (*Qf*) of $ATiO_3$ (A = Co, Ni, Mn) specimens was appreciably lowered than that of $MgTiO_3$ specimens. These results could be attributed to the degree of average covalency of A–O and Ti–O bond, and the degree of A-site ordering confirmed by the shift of Raman mode. With the increase of ionic radius of A-site ions (A = Ni, Co, Mg, Mn), the *TCF* of the specimens was decreased due to the increase of average octahedral distortion.

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