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Microwave dielectric properties of scheelite (A = Ca, Sr, Ba) and wolframite (A = Mg, Zn, Mn) $AMoO_4$ compounds

Geun-Kyu Choi, Jeong-Ryeol Kim, Sung Hun Yoon, Kug Sun Hong *

School of Materials Science & Engineering, College of Engineering, Shinrim-dong san 56-1, Gwanack-ku, Seoul 151-742, Republic of Korea

Abstract

The microwave dielectric properties of scheelite (A = Ca, Sr, Ba) and wolframite (A = Mg, Mn, Zn) $AMoO_4$ compounds and their relations with structure have been examined using a network analyzer and X-ray powder diffraction. The Mo ion polarizability has been also investigated from $AMoO_4$ compounds using a least square refinement technique in conjunction with the Clausius–Mosotti equation. It was found that dielectric properties such as dielectric constant, temperature coefficient of resonant frequency, and quality factor were found to be correlated with the size of A-cations and the structure of compounds. The well sintered $AMoO_4$ samples (>95% of theoretical density) exhibited dielectric constant of 7–11, quality factor of 37,000–90,000 GHz and temperature coefficient of resonant frequency of −57 to −87 ppm/°C, respectively. These investigations showed that $AMoO_4$ ceramic could be selected as a possible candidate for microwave dielectric ceramics because of its low dielectric constant and high quality factor.

Keywords: Sintering; X-ray methods; Dielectric properties; Polarizability

1. Introduction

According to the rapid development of mobile telecommunication system, such as mobile phones, high quality microwave dielectric ceramics are required. In the case of microwave substrate application, dielectric ceramic substrate with low permittivity and high-Q is required to minimize cross-coupling with conductors and to maintain overall high-Q circuits by lowering power dissipation. Alumina and rare-earth aluminates (such as $LaAlO_3$)[1,2] are the standard materials for the manufacturing of hybrid circuits via thick or thin film technology and for high integrated multilayer circuits produced via co-firing of metallized green tapes. Although these compounds have good dielectric properties, they have some demerits such as high sintering temperature. So, the search for new materials with much better sintering and microwave dielectric properties is surely required.

Molybdenum (Mo) containing mixed oxides have been of practical interest because of their attractive luminescence property[3] and possibility of negative electrode (anode) materials.[4] The scheelite compound has been investigated as a host crystal for laser applications. Also, the dielectric constant and the anisotropy of the dielectric constant (ε') of single crystals (grown by the Czochralski method) were firstly reported by Brower et al.[5] The dielectric constant (ε') parallel to a-axis of $CaMoO_4$ single crystal was 24.0 ± 0.2; parallel to c-axis, 20.0 ± 0.2 at 1.59 kHz. The dielectric loss ($\tan \delta$) for both orientations of $CaMoO_4$ specimen was 10^{-3} or less. Unfortunately, not many works have been done on the dielectric properties for microwave application. For investigation of possibility of microwave application, we researched the divalent metal molybdate compounds. The Mo ion polarizability has been also investigated from $AMoO_4$ compounds using a least square refinement technique in conjunction with Clausius–Mosotti equation.

2. Experimental procedure

The powders were prepared by conventional mixed oxide method. ACO_3 [A = Ca (99.99%), Sr (99.5%), Ba (99.9%)], MgO (99.9%), Mn_3O_4 (98%), ZnO (99.9%) and MoO_3 (99.9% high purity) purity powders were weighed and mixed for 24 h with stabilized zirconia media and ethanol. The mixed slurry was dried and then powders were calcined at 700–1000 °C for 2 h in air and then the calcined powder was granulated with an organic binder after ball milling for 24 h. The milled powders

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* Corresponding author. Tel.: +82 2 880 8024; fax: +82 2 886 4156.
E-mail address: kshongss@plaza.snu.ac.kr (K.S. Hong).

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were uniaxially pressed into disks 8 mm in diameter and 2–4 mm thick under a pressure of 1000 kg/cm^2. Pellets were sintered at 700–1150 °C for 2 h in air with a heating rate of 5 °C/min. The bulk density of the sintered specimens was determined by the Archimedes' method.

The X-ray powder diffraction (XRD) studies were performed with monochromatic X-ray diffractometer (XRD: Model M18XHF, Mac Science Instruments, Japan). Lattice parameters were calculated by refinement of data collected at range $20^\circ < 2\theta < 60^\circ$ with a step of 0.02, counting time of 1 s per step and Si powder was used as an internal standard. Polished and thermally etched surfaces of sintered specimens were examined using field emission scanning electron microscopy (FESEM: Model JSM6330F, Jeol, Japan). The microwave dielectric properties of sintered samples were measured at x-band frequencies (14–17 GHz) using a network analyzer (model HP8720C, Hewlett Packard, Palo Alto, CA). The quality factor ($Q \times f$) was measured by the transmission cavity method using a Cu cavity and Teflon supporter. Relative dielectric constant (ε_r) was measured using the post resonator method and temperature coefficient of resonant frequency (τ_f) was measured using an Invar cavity in the temperature at range 20–80 °C.

3. Results

Fig. 1 shows relative densities of $AMoO_4$ (A = Ca, Sr, Ba, Mg, Mn, Zn) samples as a function of sintering temperature. The maximum relative densities of $AMoO_4$ samples, which have sintered densities more than 95% of their theoretical densities were achieved over the temperature range (800–1100 °C). As shown in Fig. 1, sintering temperature of wolframite compounds was lower than that of scheelite compounds.

Fig. 2 shows the X-ray diffraction of sintered $AMoO_4$ compounds. The single phase structure of all compounds was confirmed by X-ray powder diffraction. As shown in Fig. 2, diffraction peaks shifted to lower angle in the same structure as the radius of cation increased, except $ZnMoO_4$ compound (the structure of $ZnMoO_4$ is triclinic). The structure of $AMoO_4$ changed from wolframite (A ionic radius ≤ 0.77 Å: Mg, Mn, Zn) to scheelite (A ionic radius ≥ 0.99 Å: Ca, Sr, Ba).[6] The wolframite structure (space group $C12/m$, 12, monoclinic) has hexagonally close-packed oxygens with certain octahedral sites filled by A and Mo cations in an ordered way. On the contrary, the scheelite structure (space group $I4_1/a$. 88, tetragonal) has cubic-packed array of A^{2+} and $[MoO_4]^{2-}$ units with the coordination around molybdenum is quite symmetrically tetra-hedral, like for any scheelite-type compound, while the overall coordination of A site ion is eight.

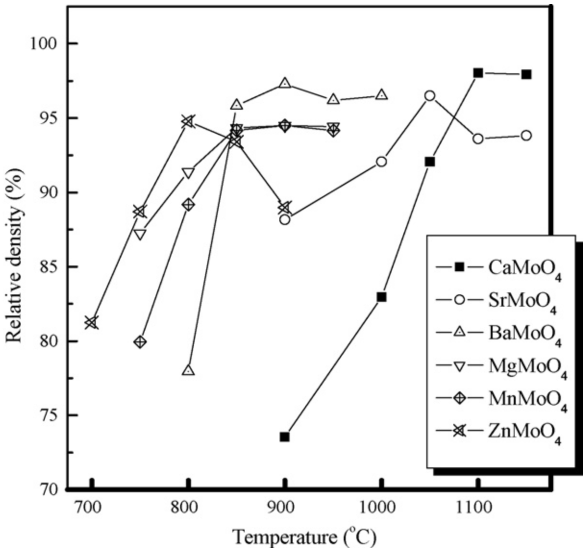

Fig. 1. The relative densities of $AMoO_4$ (A = Ca, Sr, Ba, Mg, Mn, Zn) samples as a function of sintering temperature.

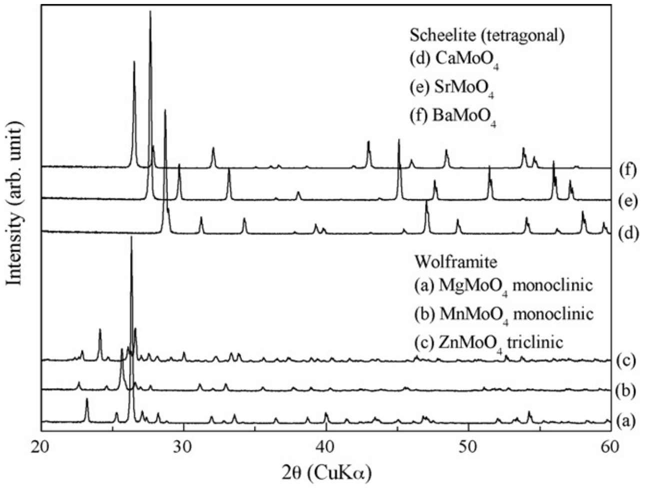

Fig. 2. XRD patterns of sintered $AMoO_4$ powders: (a) $MgMoO_4$ sintered at 900 °C for 2 h, (b) $MnMoO_4$ sintered at 900 °C for 2 h, (c) $ZnMoO_4$ sintered at 800 °C for 2 h, (d) $CaMoO_4$ sintered at 1100 °C for 2 h, (e) $SrMoO_4$ sintered at 1050 °C for 2 h, and (f) $BaMoO_4$ sintered at 900 °C for 2 h.

The SEM micrographs of the surfaces of sintered $AMoO_4$ samples are shown in Fig. 3. Grain size was in range of 2–7 μm and the dense microstructures were confirmed by a SEM analysis. The dielectric properties of $AMoO_4$ compounds were summarized in Table 1. The samples of scheelite structure had good microwave dielectric properties. In the case of $CaMoO_4$, $Q \times f$ was ~90,000 and $\varepsilon_r \approx 10.8$, and τ_f about −57 ppm/°C.

4. Discussion

Table 1 shows the dielectric properties of $AMoO_4$ specimens. The well sintered $AMoO_4$ samples (>95%) exhibited dielectric constant of 7–11, quality factor of 37,000–90,000 GHz and temperature coefficient of resonant frequency of −57 to −87 ppm/°C, respectively. As the size of A-site cation increased, the dielectric constant and quality factor of scheelite $AMoO_4$ (A = Ca, Sr, Ba) samples were decrease, while those of wolframite samples were increased. For investigating relationship between A-site cation and dielectric constant, we used the Shannon's suggestion[7] and Clausius–Mosotti equation.

Shannon reported a set of 61 ion polarizabilities, which has been derived from the dielectric constants of 129 oxides and 25 fluorides using a least squares refinement technique in conjunction with the Clausius–Mosotti equation. In the case of $AMoO_4$

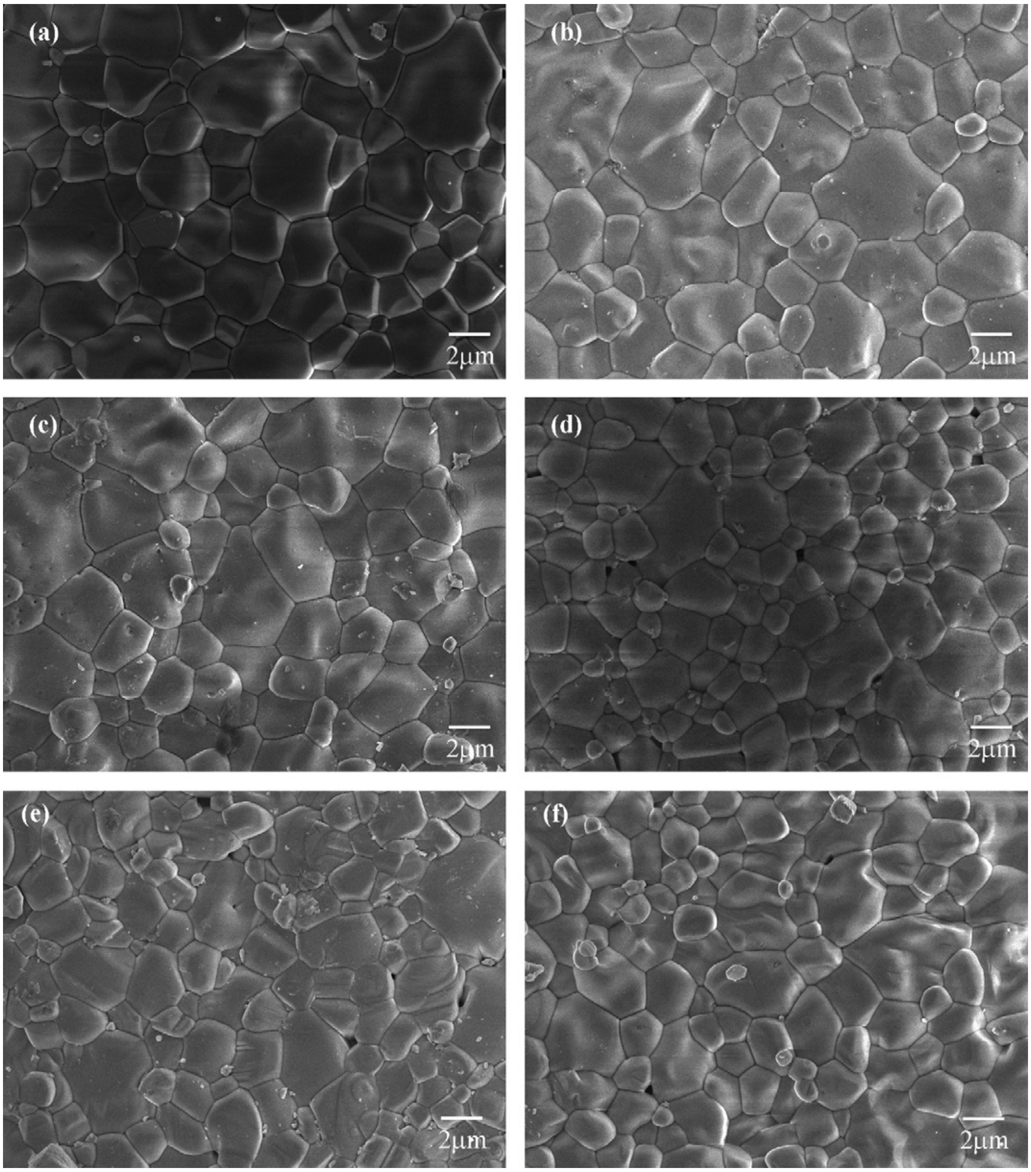

Fig. 3. SEM micrograph of the $AMoO_4$ specimens: (a) $CaMoO_4$ sintered at 1100 °C for 2 h, (b) $SrMoO_4$ sintered at 1050 °C for 2 h, (c) $BaMoO_4$ sintered at 900 °C for 2 h, (d) $MgMoO_4$ sintered at 900 °C for 2 h, (e) $MnMoO_4$ sintered at 900 °C for 2 h, and (f) $ZnMoO_4$ sintered at 800 °C for 2 h.

system, molecular polarizability can estimate from following equation.

$$\alpha(AMoO_4) = \alpha(A^{2+}) + \alpha(Mo^{6+}) + 4\alpha(O^{2-}) \quad (1)$$

where α is polarizability. The dielectric constants of $AMoO_4$ compounds could be calculated with polarizability from Shannon's suggestion and Clausius–Mosotti relation:

$$\varepsilon_{\mathrm{cal}} = \frac{3V_{\mathrm{m}} + 8\pi\alpha D}{3V_{\mathrm{m}} - 4\pi\alpha D} \quad (2)$$

where V_{m} is molar volume. Molar volume of $AMoO_4$ can be calculated with the unit cell parameters determined from the diffraction pattern, and the values of molar volume are shown in

Table 1
Microwave dielectric properties of $AMoO_4$ compounds

Compound	Sintering temperature (°C)	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)	Porosity
$CaMoO_4$	1100	10.79	89700	−57	0.0195
$SrMoO_4$	1050	9.49	61000	−67.17	0.0350
$BaMoO_4$	900	9.3	37200	−79.24	0.0270
$MgMoO_4$	900	7.07	79100	−46.02	0.0551
$MnMoO_4$	900	8.55	54100	−73.91	0.0550
$ZnMoO_4$	800	8.67	49900	−87.49	0.0523

Table 2
Molar volume, observed and calculated permittivity of $AMoO_4$ compounds

Compound	V_m	ε_{obs}	ε_{cal}	Δ (%)
$CaMoO_4$	78.064	11.11	11.45	−3.113
$SrMoO_4$	87.575	9.99	9.73	2.584
$BaMoO_4$	99.9	9.68	9.67	0.038
$MgMoO_4$	80.363	7.65	6.79	11.245
$MnMoO_4$	85.913	9.26	7.39	20.113
$ZnMoO_4$	86.667	9.35	6.47	30.827

Table 2. The dielectric constant in Table 1 was polycrystalline data, even though well sintered $AMoO_4$ samples have densities more than 95% of theoretical density. So, the dielectric constant in Table 2 (ε_{obs}) was corrected by following equation.

$$\varepsilon_{obs} = \varepsilon_{exp}(1 + 1.5P) \tag{3}$$

where P is porosity and ε_{exp} is measured dielectric constant.[8] Unfortunately, Mo ion polarizability was not reported by Shannon. We investigated Mo ion polarizability from $AMoO_4$ compounds using a least square refinement technique in conjunction with the Clausius–Mosotti equation. Ion polarizabilities, α_D (ion), can be used as a set of refinable parameters in a least squares procedure which minimizes the function.

$$\sum_{i=1}^{M} \omega_i (\alpha_{obs} - \alpha_{cal})^2 \tag{4}$$

where i varies over the number of measurements of α_{obs} for variety of compounds and $\omega_i = \sigma_i$, and σ_i is the estimated % error in the experimental dielectric constant. The results of least squares refinement were evaluated by examining the weighted variance of fit (F):

$$F = \frac{\left(\sum_i \varpi_i [(\alpha_{obs})_i - (\alpha_{cal})_i]^2\right)}{\sum_i \omega_i} \tag{5}$$

The first results from refinements of α_D(Mo) made using experimental dielectric constant data from six $AMoO_4$ compound were $\alpha_D(Mo) = 4$ in $F = 0.748\%$. This results in a poor agreement between observed and calculated dielectric constant. But second results from three scheelite compound, $\alpha_D(Mo) = 3.28$ in $F = 0.013\%$, shows good agreement with deviations in observed and calculated dielectric constant in scheelite system ($\Delta\% < 3.1\%$), as shown in Table 2. This phenomenon was explained by following structural consideration. In wolframite structure system, the overall coordination around molybdenum is six, giving rise to ribbons of edge-sharing distorted octahedral, which form a polymeric anionic structure with composition $[(Mo_2O_8)^{4-}]_n$. Similarly, the coordination at A site ion is also six and gives rise to parallel ribbons of sharing distorted octahedral. In fact, the wolframite structure can be taken as a slightly distorted superstructure of the α-PbO_2-type structure, where the octahedral are occupied alternatively by the two different cations.[9] In wolframite $MgMoO_4$ structure system, Mo ions have two site positions. The one Mo position has two molybdenum–oxygen distances being definitely longer (3.088 Å 2×) than the other four (1.731 Å 2×, 1.801 Å 2×) around Mo atom, the other Mo position has longer (3.425 Å 2×) distance and four shorter (1.730 Å 2×, 1.752 Å, 1.845 Å) distance.[10] So that it seems reasonable to interpret this structure on the basis of a distorted tetrahedral coordination around molybdenum, as well as $MnMoO_4$ structure system.[6] On the contrary, the coordination around molybdenum in scheelite structure system is quite symmetrically tetrahedral (Mo–O: 1.755 Å 4× in $CaMoO_4$ system). Shannon explained the deviations of ε_{cal} from ε_{obs} generally reflect one or more of the following: inaccurate dielectric constants, ionic or electronic conductivity, the presence of H_2O or CO_2 in channels, the presence of "rattling" or "compressed" cations having unusually large or small cation polarizabilities, respectively, or the presence of dipolar impurities. The presence of rattling cations group, shorted by Shannon, shows dielectric deviation ($\Delta\% = 13$–34%), similarly in our wolframite system, in Table 2. This effect was described by Dunitz and Orgel[11] as a progressive, loosening of the central cation at the center of its surrounding octahedron to off-center displacements characteristic of ferroelectric and antiferroelectric substances, as the size of the central cation in an octahedron decreased. The polydedron can adjust its configuration to adapt to the small cation by movement of the cation and or anions resulting in polyhedral distortion.

Fig. 4 shows relation between the temperature coefficient of resonant frequency ($-\tau_f$) and unit-cell volume of $AMoO_4$. Generally temperature coefficient of resonant frequency (τ_f) is represented by the thermal expansion coefficient (α_l) and the temperature coefficient of permittivity (τ_ε), as follows:

$$\tau_f = -\alpha_l - \frac{1}{2}\tau_\varepsilon \tag{6}$$

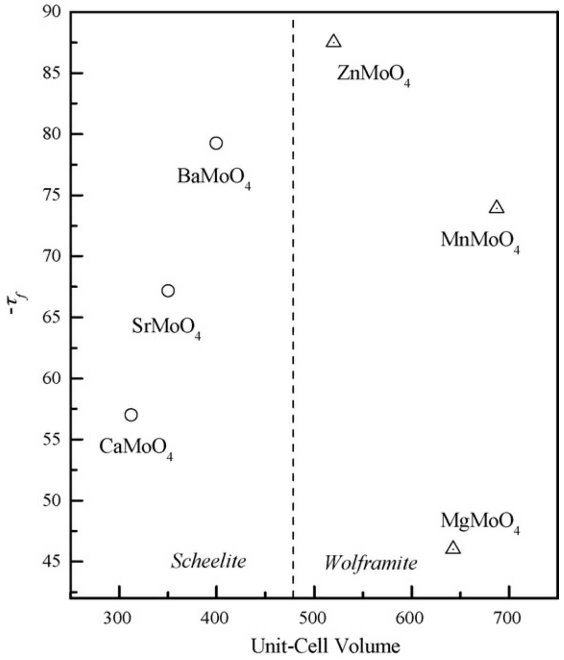

Fig. 4. Temperature coefficient of resonant frequency of $AMoO_4$ compounds as a function of unit-cell volume.

The thermal expansion coefficient of ceramic is generally in the range of 10 ppm/°C, therefore the sign and magnitude of τ_f depends on τ_ε. From Clausius–Mosotti equation, τ_ε can be derived a following expression.

$$\tau_\varepsilon = \frac{1}{\varepsilon}\left(\frac{\partial\varepsilon}{\partial T}\right) = \frac{(\varepsilon-1)(\varepsilon+2)}{\varepsilon}(A+B+C)$$

$$\left(A = -\frac{1}{3V}\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}}, \quad B = \frac{1}{3\alpha_{\mathrm{m}}}\left(\frac{\partial \alpha_{\mathrm{m}}}{\partial V}\right)_{\mathrm{T}}\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}}, \quad C = \frac{1}{3\alpha_{\mathrm{m}}}\left(\frac{\partial \alpha_{\mathrm{m}}}{\partial T}\right)_{\mathrm{V}}\right) \tag{7}$$

Bosman and Havinga suggested that the terms A and B, which correlate to volume expansion, have very similar in magnitude but opposite in sign, therefore the resulting effect on τ_ε of terms A and B is generally ignored.[12–14] Lee et al. suggested that the term C represents the restoring force acting on the ions and restoring force depends on the shape of potential well, therefore this term correlated with structure and lattice parameter.[13] Since the unit-cell volume has strong correlation with lattice energy, τ_ε is proportional to the relative magnitude of unit-cell volume. As can be shown in Fig. 4, the magnitude of $-\tau_f$ increased as the unit-cell volume increased in the same structure of $AMoO_4$.

5. Conclusion

In our study, well sintered $AMoO_4$ samples (>95% of theoretical densities) exhibited dielectric constant of 7–11, quality factor of 37,000–90,000 GHz and temperature coefficient of resonant frequency of −57 to −87 ppm/°C, respectively. $CaMoO_4$ sample exhibited $Q \times f$ value of ~90,000 GHz, dielectric constant (ε_r) = 10.79 and $\tau_f = -57$ ppm/°C. This results show that $AMoO_4$ can be selected as a suitable candidate for microwave dielectric material because of its low dielectric constant and high-Q, such as alumina.

The results from refinement of α_D(Mo) made using experimental dielectric constant data of $AMoO_4$ compounds show good agreement with deviations in observed and calculated dielectric constant in scheelite system ($\Delta\% < 3.1\%$, $F = 0.013\%$, $\alpha_D(\mathrm{Mo}) = 3.28$). Otherwise, poor agreement in wolframite system ($\Delta\% \approx 8$–30%) is well interpreted by rattling cation in oxygen octahedron.

It was found that temperature coefficient of resonant frequency was correlated with structure and unit-cell volume. The magnitude of τ_f was increased as the unit-cell volume increased in the same structure of $AMoO_4$. In scheelite $AMoO_4$ system, $-\tau_f$ shows linearity for unit-cell volume.

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