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Raman scattering study of the effect of *A*- and *B*-site substitution on the room-temperature structure of $ABi_4Ti_4O_{15}$

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Abstract. Aurivillius-type materials exhibit promising ferroelectric and multiferroic properties that can be tailored via chemistry variations in the perovskite block. Hence, it is important to clarify the relations composition-structure, also on a local-scale level. The aim of this contribution is to give further insights into the effect of *A*- and *B*-site cations to the room-temperature local structure of Aurivillius four-layered $ABi_4Ti_4O_{15}$ ($A = \text{Sr, Pb, Ba}$) and $\text{Pb}_{1-x}\text{Bi}_{4+x}\text{Ti}_{4-x}\text{Mn}_x\text{O}_{15}$ ($x = 0, 0.2, 0.4$) by Raman scattering. The effect of *A*-site cation to the local structure of perovskite block was identified by the phonon mode near 750 and 870 cm^{-1} arising from BO_6 stretching. *A*-site Ba^{2+} , having the largest ionic radius among the considered elements, significantly stiffens the TiO_6 octahedra, as derived from the fact that the TiO_6 stretching modes have the highest wavenumber for $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$, i.e. the Ti-O bond strength is strongest for this compound. The replacement of Ti^{4+} by Mn^{3+} cation at the *B*-site also influences the *B*-O bond. The comparison of the phonon modes near 700 and 870 cm^{-1} in $\text{Pb}_{1-x}\text{Bi}_{4+x}\text{Ti}_{4-x}\text{Mn}_x\text{O}_{15}$ with $x = 0, 0.2$, and 0.4 shows that the lowest wavenumber, which is due to the elongation of Ti-O bonds is observed for $x = 0.4$.

1. Introduction

Aurivillius oxides ($A_{n-1}\text{Bi}_2\text{B}_n\text{O}_{3n+3}$ with n = the number of BO_6 layers in the perovskite (ABO_3) block, $A = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Pb}^{2+}, \text{Bi}^{3+}, \text{Na}^{+1}, B = \text{Ti}^{4+}, \text{Nb}^{5+}, \text{Ta}^{5+}, \text{W}^{6+}$ or Mo^{6+}) have a great potential to be used in diverse technological applications, due to their ferroelectric, magnetoelectric, thermoelectric, luminescence and photocatalytic properties [1-3]. On cooling four-layered Aurivillius compounds $ABi_4Ti_4O_{15}$ ($A = \text{Ba, Sr, and Pb}$) undergo a paraelectric-ferroelectric phase transition from tetragonal $I4/mmm$ to orthorhombic $A2_1am$ symmetry [4]. The perovskite block of Aurivillius compounds exhibit structural flexibility, allowing for cationic substitution at both the *A* site and *B* site, which in turn gives opportunity to improve or tune the physical properties. Recently double-doped $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$ with Mn^{3+}



and Bi^{3+} substituting for B-site Ti^{4+} and A-site Pb^{2+} , respectively, has been synthesized, aiming to introduce magnetic properties via partial B-site substitution of Ti^{4+} by Mn^{3+} and indeed paramagnetic properties have been reported for $\text{Pb}_{1-x}\text{Bi}_{4+x}\text{Ti}_{4-x}\text{Mn}_x\text{O}_{15}$ with $x = 0.2$ and 0.4 [5]. The substitution partially of Ti^{4+} by Mn^{3+} also affected to local structure of BO_6 . The neutron diffraction of $\text{Pb}_{1-x}\text{Bi}_{4+x}\text{Ti}_{4-x}\text{Mn}_x\text{O}_{15}$ ($x = 0, 0.2$ and 0.4) showed that the introduction of Mn^{3+} to B site cation changes the bond length of $B\text{-O}$ [5].

The X-ray diffraction (XRD) technique is commonly used to reveal the effect of A - and B -site cations on $\text{ABi}_4\text{Ti}_4\text{O}_{15}$ ($A = \text{Ba}, \text{Sr}$, and Pb) structure, albeit Bragg diffraction delivers information only on the long-range order, i.e. the average over ~ 10 unit cells and therefore subtle structural changes on the local level of a few unit cells can hardly be detected. Raman spectroscopy is an ideal tool for detecting local distortions in the crystal structure such as weak layer octahedron tilting, cation disorder in a fine-scale range, or local structural deviations from the global symmetry [6,7]. In this work, the local structure of $\text{A}_{1-x}\text{Bi}_{4+x}(\text{Ti}_{4-x}\text{B}''_x)\text{O}_{15}$ the different types of cations at the A and B sites ($A = \text{Ba}, \text{Sr}$, and Pb , $B'' = \text{Mn}$) is studied using Raman spectroscopy. The peak positions (ω) of all compounds are compared to deduce the chemically induced changes in bond lengths and bond angles.

2. Experiment

Polycrystalline $\text{ABi}_4\text{Ti}_4\text{O}_{15}$ ($A = \text{Ba}, \text{Sr}$) were synthesized via a solid state reaction of Bi_2O_3 , ACO_3 ($A = \text{Ba}, \text{Ca}$) and TiO_2 [4]. Polycrystalline $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$ (PBT), $\text{Pb}_{0.8}\text{Bi}_{4.2}\text{Ti}_{3.8}\text{Mn}_{0.2}\text{O}_{15}$ (PBTM0.2), and $\text{Pb}_{0.6}\text{Bi}_{4.4}\text{Ti}_{3.6}\text{Mn}_{0.4}\text{O}_{15}$ (PBTM0.4) were synthesized by the molten salt method [5]. Raman spectra were collected with a Horiba Jobin-Yvon T64000 triple-grating spectrometer with spectral resolution of $\sim 2 \text{ cm}^{-1}$ and peak-position precision of 0.35 cm^{-1} , using the 514.5-nm line of an Ar^+ laser. The spectra were temperature-reduced by the Bose-Einstein occupation factor and fitted with Lorentzians to obtain peak positions, full widths at half maximum (FWHMs), and integrated intensities.

3. Results and Discussion

According to group theory, the Raman active modes in the room-temperature phase (space group $A2_1am$) are $36A_1 + 35A_2 + 34B_1 + 36B_2$ [6]. Figure 1 shows the Raman spectra of $\text{ABi}_4\text{Ti}_4\text{O}_{15}$ ($A = \text{Pb}, \text{Ba}, \text{Sr}$) and $\text{Pb}_{1-x}\text{Bi}_{4+x}\text{Ti}_{4-x}\text{Mn}_x\text{O}_{15}$ ($x = 0.2$, and 0.4) at room temperature.

3.1 $\text{ABi}_4\text{Ti}_4\text{O}_{15}$ ($A = \text{Ba}, \text{Sr}, \text{Pb}$)

It is well known that the ionic-radius size of the A -site cation influences the BO_6 configuration in terms of internal octahedral distortion and octahedral tilts, which is mirrored by the tolerance factor $t = (r_A + r_O) / [\sqrt{2}(r_B + r_O)]$. The size of A -cation ionic radius in $\text{ABi}_4\text{Ti}_4\text{O}_{15}$ decreases in order $\text{Ba} > \text{Pb} > \text{Sr}$, which causes a decrease in t and a change in T_c [4]. Figure 2 shows the dependence of phonon wavenumbers on the type A -site cation for $\text{ABi}_4\text{Ti}_4\text{O}_{15}$ ($A = \text{Ba}, \text{Sr}, \text{Pb}$). The mode near 58 cm^{-1} , arising from displacements of the Bi_2O_2 fluorite-like planes relative to the perovskite-like blocks, shows no difference in the peak position. However, the modes near 40 and 100 cm^{-1} , involving displacements of A -site cations, shift towards higher wavenumbers. It is due to Sr^{2+} being lighter than Ba^{2+} . For these modes the Pb compound exhibits higher peak positions, although Pb^{2+} is heavier than Ba^{2+} . This indicates a considerably stronger Pb-O bond strength as compared to Ba-O and Sr-O , which is consistent with the fact Ba-O and Sr-O interactions have more ionic character than Pb-O and show no lone pairs in contrast to in Pb^{2+} . The influence of the type of A -site cation on the local structure of BO_6 can be deduced from the modes near 750 and 870 cm^{-1} , having the highest wavenumber for $A = \text{Ba}$, which means the energy of $B\text{-O}$ stretching is highest. The symmetrical stretching BO_6 mode near 870 cm^{-1} consists predominantly of O vibrations and therefore the trend of its wavenumber with chemistry is directly related with the $B\text{-O}$ bond strength. It is apparent that the $B\text{-O}$ bond strength decreases with the decrease in the A -cation ionic radius and correspondingly the tolerance factor.

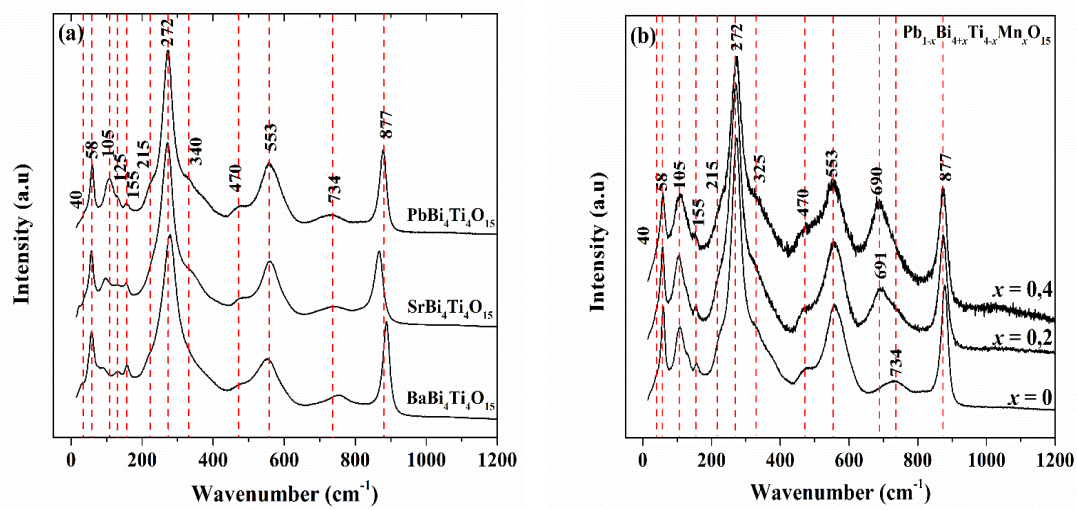


Figure 1. Raman scattering of (a) $ABi_4Ti_4O_{15}$ ($A = Ba, Sr, Pb$), and (b) $Pb_{1-x}Bi_{4+x}Ti_{4-x}Mn_xO_{15}$ ($x = 0, 0.2$, and 0.4) at room temperature.

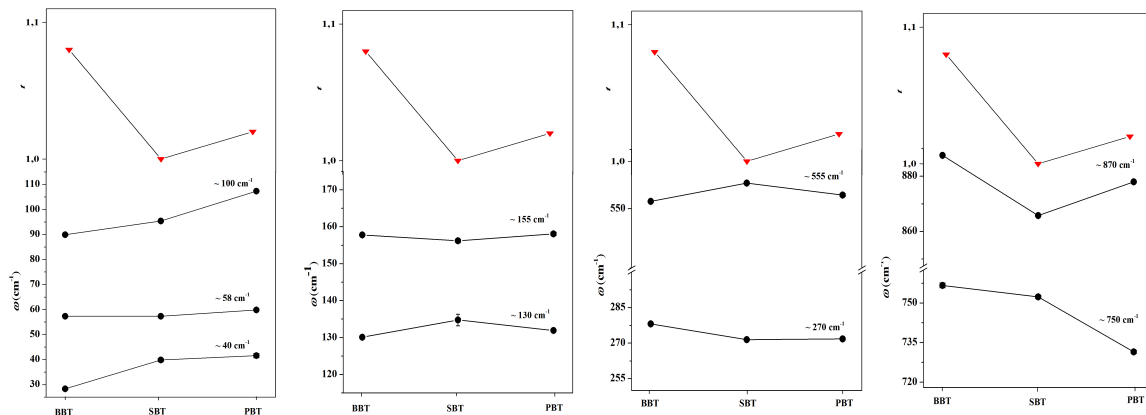


Figure 2. Peak position of phonon modes in $ABi_4Ti_4O_{15}$ ($A = Ba, Sr, Pb$). The red triangles in the upper part of the corresponding plot represent the trend of the tolerance factor t . (The data tolerance factor from Kennedy, *et al.* (2008)).

3.2 $Pb_{1-x}Bi_{4+x}Ti_{4-x}Mn_xO_{15}$ ($x = 0, 0.2$, and 0.4)

Figure 3 showed the dependence of phonon modes position on the Mn^{3+} concentration for $Pb_{1-x}Bi_{4+x}Ti_{4-x}Mn_xO_{15}$ ($x = 0, 0.2$, and 0.4). The peak positions of the modes near 40 and 100 cm^{-1} , which are related to Pb^{2+}/Bi^{3+} the displacements, are only subtly affected by the double doping. It is due to the fact that both the ionic radii and mass of 12-coordinated Pb^{2+} and Bi^{3+} are almost the same. The mode near 58 cm^{-1} has the same position and indicated that there is no Pb^{2+} occupied to Bi_2O_2 layer, similar to the case of $ABi_4Ti_4O_{15}$. The mode near 150 cm^{-1} , which is related to A -cation and BO_3 translation vibrations, shifts to the lower wavenumbers with the increase of doping. It is due to the Mn^{3+} with heavier mass replaced to Ti^{4+} at the B site. The results of neutron diffraction analysis of $Pb_{1-x}Bi_{4+x}Ti_{4-x}Mn_xO_{15}$ ($x = 0, 0.2$, and 0.4) showed that Mn^{3+} influenced mainly the local structure of BO_6 especially in the changes of bond length of $B-O$ but there is no clear trend established for the Mn^{3+} concentration to $B-O$ length [5]. The change in the local structure of BO_6 octahedral was best mirrored by the BO_6 stretching modes near 740 and 870 cm^{-1} . Both modes shift towards lower wavenumbers, indicating a decrease in the $B-O$

bond strength and consequent elongation of B -O bond length as a result of Jahn-Teller effect in MnO_6 octahedra.

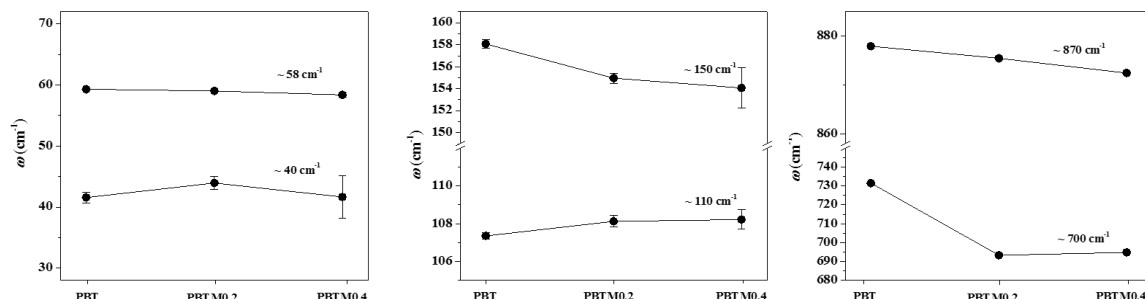


Figure 3. The peak position of external modes BO_6 on $Pb_{1-x}Bi_{4+x}Ti_{4-x}Mn_xO_{15}$ ($x = 0, 0.2, \text{ and } 0.4$): (a) modes below 100 cm^{-1} , (b) modes at $100\text{--}200 \text{ cm}^{-1}$, and (c) modes at $\sim 750, \sim 870 \text{ cm}^{-1}$.

4. Conclusion

For $ABi_4Ti_4O_{15}$ ($A = \text{Ba, Sr, and Pb}$), the size of ionic radius of the A cation influences strongly the BO_6 stretching modes near 750 and 870 cm^{-1} . The A -site cation with a largest ionic radius (Ba^{2+}) stiffens the BO_6 octahedra. For $Pb_{1-x}Bi_{4+x}Ti_{4-x}Mn_xO_{15}$ ($x = 0, 0.2, \text{ and } 0.4$), the partial of Ti^{4+} by Mn^{3+} at the B site results in elongation of B -O bond.

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