

# 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  $Pb_{1-x}Bi_{4+x}Ti_{4-x}Mn_xO_{15}$  ( $x = 0, 0.2, 0.4$ ) 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  $\text{cm}^{-1}$  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  $BaBi_4Ti_4O_{15}$ , 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  $\text{cm}^{-1}$  in  $Pb_{1-x}Bi_{4+x}Ti_{4-x}Mn_xO_{15}$  with  $x = 0, 0.2, \text{ and } 0.4$  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 ( $A_{n-1}Bi_2B_nO_{3n+3}$  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  $\text{Mo}^{6+}$ ) 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  $PbBi_4Ti_4O_{15}$  with  $Mn^{3+}$



and  $\text{Bi}^{3+}$  substituting for B-site  $\text{Ti}^{4+}$  and A-site  $\text{Pb}^{2+}$ , respectively, has been synthesized, aiming to introduce magnetic properties via partial B-site substitution of  $\text{Ti}^{4+}$  by  $\text{Mn}^{3+}$  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  $\text{Ti}^{4+}$  by  $\text{Mn}^{3+}$  also affected to local structure of  $\text{BO}_6$ . 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  $\text{Mn}^{3+}$  to B site cation changes the bond length of B-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  $\text{Pb}$ ) structure, albeit Bragg diffraction delivers information only on the long-range order, i.e. the average over  $\sim 10$  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  $\text{Pb}, \text{B}'' = \text{Mn}$ ) is studied using Raman spectroscopy. The peak positions ( $\omega$ ) of all compounds are compared to deduce the chemically induced changes in bond lengths and bond angles.

## 2. Experiment

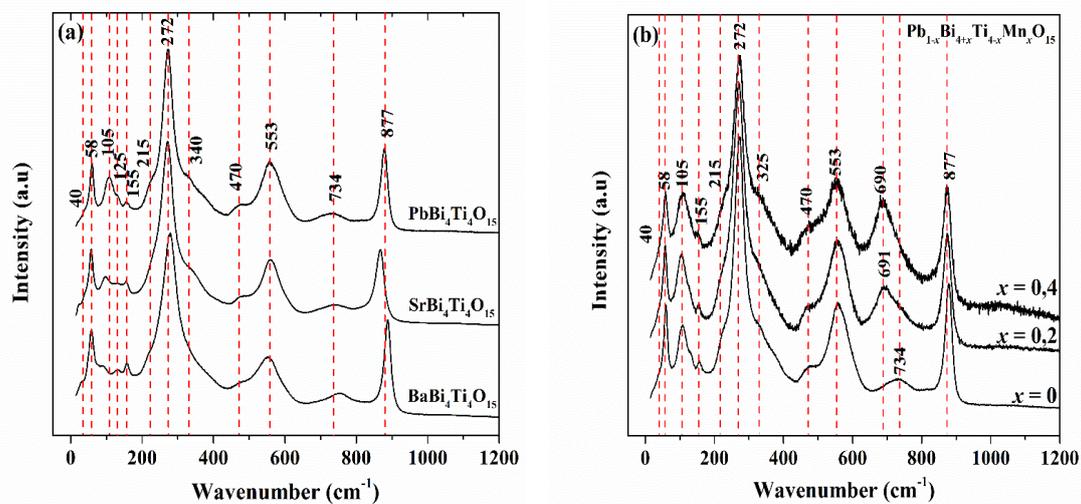
Polycrystalline  $\text{ABi}_4\text{Ti}_4\text{O}_{15}$  ( $A = \text{Ba}, \text{Sr}$ ) were synthesized via a solid state reaction of  $\text{Bi}_2\text{O}_3$ ,  $\text{ACO}_3$  ( $A = \text{Ba}, \text{Ca}$ ) and  $\text{TiO}_2$  [4]. Polycrystalline  $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$  (PBT),  $\text{Pb}_{0.8}\text{Bi}_{4.2}\text{Ti}_{3.8}\text{Mn}_{0.2}\text{O}_{15}$  (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  $0.35 \text{ cm}^{-1}$ , using the 514.5-nm line of an  $\text{Ar}^+$  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

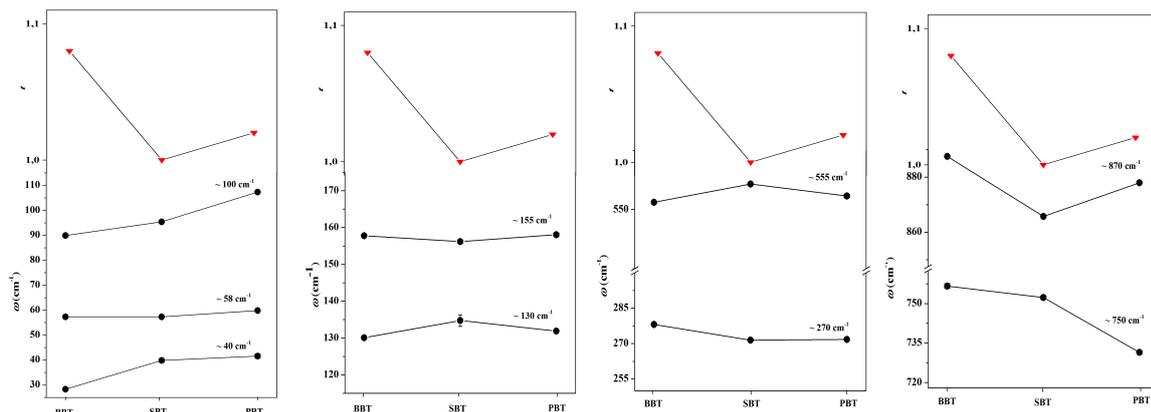
According to group theory, the Raman active modes in the room-temperature phase (space group  $A2_1am$ ) are  $36A_1 + 35A_2 + 34B_1 + 36B_2$  [6]. Figure 1 shows the Raman spectra of  $\text{ABi}_4\text{Ti}_4\text{O}_{15}$  ( $A = \text{Pb}, \text{Ba}, \text{Sr}$ ) and  $\text{Pb}_{1-x}\text{Bi}_{4+x}\text{Ti}_{4-x}\text{Mn}_x\text{O}_{15}$  ( $x = 0.2,$  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  $\text{BO}_6$  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  $58 \text{ cm}^{-1}$ , arising from displacements of the  $\text{Bi}_2\text{O}_2$  fluorite-like planes relative to the perovskite-like blocks, shows no difference in the peak position. However, the modes near  $40$  and  $100 \text{ cm}^{-1}$ , involving displacements of A-site cations, shift towards higher wavenumbers. It is due to  $\text{Sr}^{2+}$  being lighter than  $\text{Ba}^{2+}$ . For these modes the Pb compound exhibits higher peak positions, although  $\text{Pb}^{2+}$  is heavier than  $\text{Ba}^{2+}$ . 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  $\text{Pb}^{2+}$ . The influence of the type of A-site cation on the local structure of  $\text{BO}_6$  can be deduced from the modes near  $750$  and  $870 \text{ cm}^{-1}$ , having the highest wavenumber for  $A = \text{Ba}$ , which means the energy of B-O stretching is highest. The symmetrical stretching  $\text{BO}_6$  mode near  $870 \text{ cm}^{-1}$  consists predominantly of O vibrations and therefore the trend of its wavenumber with chemistry is directly related with the B-O bond strength. It is apparent that the B-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)  $Pb_{1-x}Bi_{4+x}Ti_{4-x}Mn_xO_{15}$  ( $x = 0, 0.2, \text{ and } 0.4$ ) at room temperature.

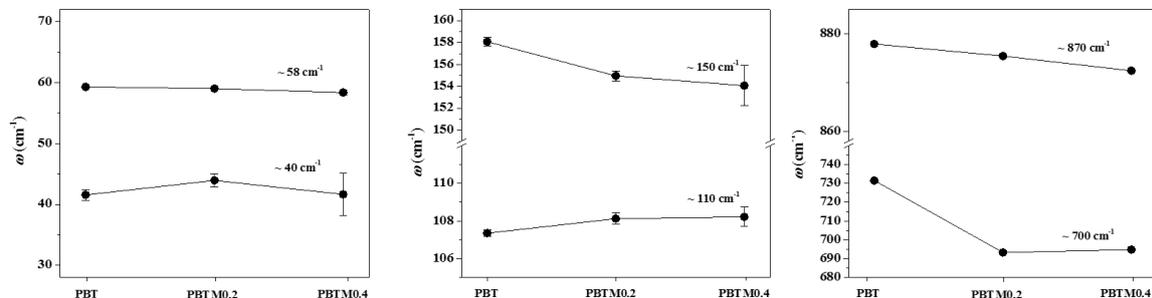


**Figure 2.** Peak position of phonon modes in  $ABi_4Ti_4O_{15}$  ( $A = Ba, Sr, Pb$ ). The red triangles in the upper part of the corresponding plot represent the trend of the tolerance factor  $t$ . (The data tolerance factor from Kennedy, *et al.* (2008)).

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

Figure 3 showed the dependence of phonon modes position on the  $Mn^{3+}$  concentration for  $Pb_{1-x}Bi_{4+x}Ti_{4-x}Mn_xO_{15}$  ( $x = 0, 0.2, \text{ and } 0.4$ ). 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  $Pb_{1-x}Bi_{4+x}Ti_{4-x}Mn_xO_{15}$  ( $x = 0, 0.2, \text{ and } 0.4$ ) 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  $100\text{ cm}^{-1}$ , (b) modes at  $100\text{--}200\text{ cm}^{-1}$ , and (c) modes at  $\sim 750, \sim 870\text{ cm}^{-1}$ .

#### 4. Conclusion

For  $ABi_4Ti_4O_{15}$  ( $A = Ba, Sr, \text{ and } Pb$ ), the size of ionic radius of the  $A$  cation influences strongly the  $BO_6$  stretching modes near  $750$  and  $870\text{ cm}^{-1}$ . 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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