



# Temperature independent low loss dielectrics based on quaternary pyrochlore oxides<sup>☆</sup>

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## ABSTRACT

Quaternary pyrochlore phases of the general formula  $\text{Bi}_{2-x}\text{Ca}_x\text{M}_{2-y}\text{M}'_y\text{O}_{7-x/2+y/2}$  ( $M = \text{Ti, Hf, Sn}$ ;  $M' = \text{Sb, Nb, Ta}$ ) were prepared by solid state reactions and characterized via structural and dielectric properties. The cubic  $a$ -lattice parameters show an expected linear relationship with the ionic radii of the substituted  $M$  cations. The solid solution  $\text{Bi}_{2-x}\text{Ca}_x\text{Sn}_{2-y}\text{Sb}_y\text{O}_{7-x/2+y/2}$  was analyzed by X-ray and neutron diffractions. The solubility limit is close to  $x = 1.3$ , and for  $x > 1.3$ , the reaction products contain a mixture of the pyrochlore phase and the  $\text{Ca}_2\text{Sb}_2\text{O}_7$  weberite phase. The refined formulas for compositions with nominal calcium content  $x = 0.5, 1.0$ , and  $1.5$  are  $\text{Bi}_{1.36}\text{Ca}_{0.64}\text{Sn}_{1.60}\text{Sb}_{0.40}\text{O}_{6.88}$ ,  $\text{Bi}_{0.82}\text{Ca}_{1.18}\text{Sn}_{1.10}\text{Sb}_{0.90}\text{O}_{6.86}$ , and  $\text{Bi}_{0.76}\text{Ca}_{1.24}\text{Sn}_{1.06}\text{Sb}_{0.94}\text{O}_{6.85}$  respectively, indicating slight oxygen deficiencies. Temperature and frequency independent dielectric constants and low loss are observed at 1 MHz. The dielectric constants vary from 16 to 98 depending on the composition. We have also prepared new cubic quaternary pyrochlores with the formula  $\text{BiCdMTeO}_7$ , where  $M = \text{Al, Cr, Ga, In, Fe, Mn, and Sc}$ . Magnetic property measurement shows paramagnetism in the  $M = \text{Cr}$  and  $\text{Mn}$  phases but antiferromagnetism with short-range correlations in the  $M = \text{Fe}$  phase. All these compositions are insulating. The measured dielectric constants and dielectric loss are independent of temperature and frequency.

## 1. Introduction

The growing ubiquity of small handheld and wearable electronic devices such as smart phones and biomedical sensors demands the use of more efficient and safer materials in these devices than what is available today. In 1965, Gordon E. Moore envisioned the role of integrated electronics in enabling these devices and predicted that the number of transistors per chip would double approximately every 18 months [1]. The future challenge in continuing this trend is to deliver component materials with significantly enhanced physical properties such as high linear dielectric constant, reduced loss tangent, lower leakage currents, and process compatibility. The dielectric properties of pyrochlore and related complex oxide materials are currently being studied due to their potential application as high- $\kappa$  dielectric materials in electronic devices.

The general formula of the pyrochlore structure is  $A_2M_2O_6O'$  with the ideal space group of  $Fd\bar{3}m$ , having 8 molecules per unit cell ( $Z = 8$ ) (Fig. 1). There are 4 crystallographically non-equivalent sites that can accommodate a vast array of elements. This structure is frequently described as a network of corner shared  $M_2O_6$  octahedra

interpenetration with  $A_2O'$  chains, where the  $A$  atom is 8-fold coordinated and the  $M$  atom is 6-fold coordinated [2]. Several quaternary compositions adopting the pyrochlore structure have been previously reported, including the series  $(\text{Ca}_x\text{M}_{1-x})_2(\text{Ti}_{1-x}\text{Nb}_x)_2\text{O}_7$  ( $M = \text{Bi, La, Pr, Nd, Sm, Dy, or Er}$ ),  $\text{CaErMMO}_7$ ,  $A^{\text{II}}A^{\text{III}}\text{TiSbO}_7$  ( $A^{\text{II}} = \text{Pb, Cd or Zn}$  and  $A^{\text{III}} = \text{Bi or RE}$ ), and  $A^{\text{II}}A^{\text{III}}M^{\text{IV}}M^{\text{V}}\text{O}_7$  ( $A^{\text{II}} = \text{Ba, Cd, Ca, Sr or Pb}$ ,  $A^{\text{III}} = \text{Bi, La or Sm}$ ,  $M^{\text{IV}} = \text{Ti, Zr, Hf or Sn}$ , and  $M^{\text{V}} = \text{Nb or Ta}$ ) [3–6].

Pyrochlore related oxides with the formula  $A_2M_2O_7$  have been known to produce dielectric materials [2,7]. Dielectrics are materials that are characterized by their behavior in a parallel plate capacitor, ideally exhibiting no dc electrical conductivity. The dielectric constant is related to polarizability of constituent atoms and can be linked using the Clausius-Mossotti relationship (Equation (1)), where  $N$  is the number of polarizable species per unit volume,  $\kappa$  is the dielectric constant, and  $\epsilon_0$  is the permittivity of free space [8–10].

$$\frac{\kappa - 1}{\kappa + 2} = \frac{N\alpha}{3\epsilon_0} \quad (1)$$

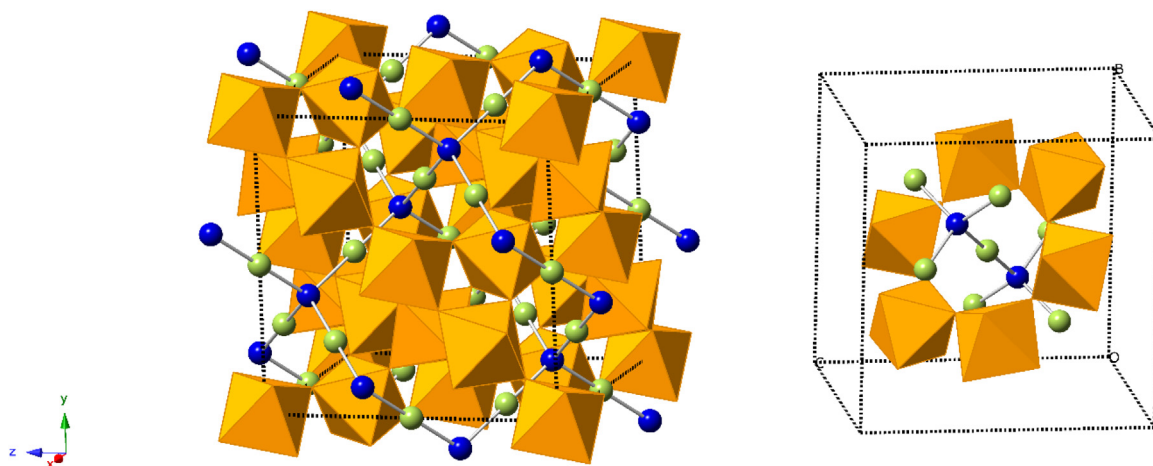
Polarizability is an additive quantity that includes many polarization mechanisms: electronic ( $\alpha_e$ ), ionic ( $\alpha_i$ ), dipolar ( $\alpha_D$ ), and space

<sup>☆</sup> Authors dedicate this paper to the memory of Professor G. V. Subba Rao. A review article titled "Oxide Pyrochlores – A Review" co-authored by M. A. Subramanian, G. Aravamudan and G. V. Subba Rao published in this journal is considered as an authoritative review in this field [Ref. 2 listed in this paper].

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**Fig. 1.** The pyrochlore structure,  $A_2M_2O_7$ , with a framework of corner shared octahedra and an interpenetrating network of  $A_2O'$  chains. A (16d sites) atoms are shown as light green,  $O'$  sites (8b) are shown as dark blue. The vertices of the octahedra are occupied by 48f oxygens (not shown) and the centers of the octahedra are occupied by  $M$  cations (16c sites). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

charge ( $\alpha_{sc}$ ) polarizability. The total dielectric polarizability includes ionic and electronic components (Equations (2) and (3)) [11–13]. The additivity rule explains the relationship of ionic to molecular polarizabilities in the same way that an ionic radius is related to the bond distance, but it does not always hold true for more complicated systems.

$$\alpha(M_2M'^{X_4}) = 2\alpha(MX) + \alpha(M'X_2) \quad (2)$$

$$\alpha(\text{Complex oxides}) = \sum \alpha(\text{simple oxides}) \quad (3)$$

The Clausius-Mossotti relationship can also be rewritten as Equation (4) (where  $V_m$  is the molar volume,  $b$  is  $4\pi/3$ , and  $\kappa'$  is the real part of the dielectric constant), and it applies to materials with cubic symmetry and relies on the additivity of the molecular or atomic polarizability [13–17].

$$\alpha = \frac{1}{b} \left( \frac{V_m(\kappa' - 1)}{(\kappa' + 2)} \right) \quad (4)$$

Equation (4) is very useful in calculating dielectric constants of materials where ionic and electronic polarizability dominate and can be compared with observed experimental data. A large deviation of the calculated dielectric constant from its measured value may be indicative of other possible polarization mechanisms (e.g. interfacial) contributing to the dielectric properties of the material as was shown in  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  [18].

A small dielectric loss is a large component of what characterizes a “good” dielectric. It is shown that  $\tan \delta$  depends on the measurement frequency and temperature of the material. In a perfect dielectric, the current leads the voltage by  $90^\circ$ , and the phase angle  $\theta$  is  $90^\circ$ . In a practical situation, this angle is smaller, by a factor of  $\tan \delta$ , correlating to the dielectric loss. The energy loss by a material is generally lost in the form of heat, and can occur through the formation of defects, ionic conductivity and electronic conductivity.

Hafnium containing materials, such as pyrochlore  $\text{Ho}_2\text{Hf}_2\text{O}_7$ , have been suggested as an emerging advanced dielectric material [19]. This hafnate has dielectric constant of  $\sim 20$ , and a low dielectric loss of  $\sim 0.1\%$ , with temperature and voltage independence at 100 kHz. These materials can potentially find applications as high- $\kappa$  dielectrics in complementary metal-oxide-semiconductor (CMOS) devices [19].  $\text{SiO}_2$  is the current standard for gate dielectrics, but a higher dielectric constant is required. In the simplified model for a parallel plate capacitor, the capacitance is inversely related to the thickness of the material. This is shown in Equation (5), where  $\kappa$  is the dielectric constant,  $C$  is the capacitance,  $\epsilon_0$  is the permittivity of free space,  $A$  is the area of the capacitor and  $t$  is the thickness.

$$C = \frac{\kappa\epsilon_0 A}{t} \quad (5)$$

For  $\text{SiO}_2$  based materials, higher capacitance requires a decreased thickness which increases the leakage current and deteriorates the device performance. If the dielectric constant is larger, a material with the same thickness can supply a higher capacitance. Finding a material with an improved dielectric constant without sacrificing other important properties of gate dielectrics (interface quality, reliability, band gap, etc.) is difficult, as  $\text{SiO}_2$  based materials can only be reduced in size to a certain extent [20]. Other compounds such as the ferroelectric  $\text{HfO}_2$  based materials are of recent interest due to potential applications as ferroelectric random-access memory (FeRAM) materials, with reported dielectric constants of  $\sim 30$  [21,22].

In this article we present on the synthesis and characterization (dielectric and magnetic properties) of several new quaternary pyrochlores with general formulas  $\text{Bi}_{2-x}\text{Ca}_x\text{M}_{2-y}\text{M}'_y\text{O}_{7-x/2+y/2}$  ( $M = \text{Ti, Hf, Sn}$ ;  $M' = \text{Sb, Nb, Ta}$ ) and  $\text{CdBiMTeO}_7$  ( $M = \text{Al, Cr, Ga, In, Sc, Mn, and Fe}$ ).

## 2. Experimental

### 2.1. Synthesis

Polycrystalline samples of  $\text{Bi}_{2-x}\text{Ca}_x\text{M}_{2-y}\text{M}'_y\text{O}_{7-x/2+y/2}$  ( $M = \text{Ti, Hf, Sn}$ ;  $M' = \text{Sb, Nb, Ta}$ ) were prepared through standard solid state synthesis. Stoichiometric quantities of  $\text{Bi}_2\text{O}_3$  (Sigma-Aldrich, 99.9%),  $\text{CaCO}_3$  (Sigma-Aldrich, 99.0%),  $\text{TiO}_2$  (Sigma-Aldrich, 99.9%),  $\text{HfO}_2$  (Johnson Matthey, 99.95%),  $\text{SnO}_2$  (Sigma-Aldrich, 99.9%),  $\text{Sb}_2\text{O}_3$  (Johnson Matthey, Grade 1),  $\text{Nb}_2\text{O}_5$  (Aldrich, 99.99%), and  $\text{Ta}_2\text{O}_5$  (Aldrich, 99.99%) were mixed thoroughly using an agate mortar and pestle. The pelletized mixture was then placed in an alumina crucible and heated from  $900$  to  $1300^\circ\text{C}$  for 12–24 h in air. The samples were reground and reheated repeatedly to complete the reaction. Polycrystalline samples of  $\text{BCdMTeO}_7$ ,  $M = \text{Al, Cr, Ga, In, Fe, Mn, and Sc}$ , were prepared by solid state reactions as well.  $\text{CdO}$  (Baker analyzed, 99.1%),  $\text{Bi}_2\text{O}_3$  (Aldrich, 99.99%), and oxides of  $M_2\text{O}_3$  including  $\text{Al}_2\text{O}_3$  (Cerac, 99.99%),  $\text{Cr}_2\text{O}_3$  (Aldrich, 99%),  $\text{Ga}_2\text{O}_3$  (Aldrich, 99.99%),  $\text{In}_2\text{O}_3$  (Aldrich, 99.99%),  $\text{Sc}_2\text{O}_3$  (Standford Materials Corporation, 99.999%),  $\text{Mn}_2\text{O}_3$  (Johnson Matthey, 98%), and  $\text{Fe}_2\text{O}_3$  (Alfa, 99.99%) were used as reactants. Stoichiometric mixtures of reactants were ground, pressed into pellets and heated at  $600^\circ\text{C}$  for 12 h,  $700^\circ\text{C}$  for 12 h,  $800^\circ\text{C}$  for 12 h, and  $850^\circ\text{C}$  for 12 h in gold containers with intermediate grindings.

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