Proceedings of the ICSC-F'96 Jaszowiec '96

# DESIGN OF DIELECTRIC SUBSTRATES FOR HIGH $T_c$ SUPERCONDUCTOR FILMS

### A. BHALLA AND R. GUO

### Materials Research Laboratory, The Pennsylvania State University University Park, PA 16802, USA

Investigations on the design and engineering of candidate substrate materials suitable for high  $T_c$  superconductor thin film deposition and applications have yielded several exciting new hosts such as  $Ba(Mg_{1/3}Ta_{2/3})O_3$ ,  $Sr(Al_{1/2}Ta_{1/2})O_3$ , and  $Sr(Al_{1/2}Nb_{1/2})O_3$ . Dielectric properties, thermal expansion coefficients, melting temperatures and growth feasibility were tested for a wide range of substrate materials and solid solutions. These complex perovskite crystals and their associated solid solutions provide new options for ultra low loss, low permittivity substrates with close structural and thermal matching to the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-6</sub>. Several new materials have been tested for high  $T_c$  superconductor film depositions. A laser heated pedestal growth system has been used as an essential tool in producing single crystals for testing. Development on the predictive capability of the dielectric constant of ionic solids, by improving Shannon's approach, will also be discussed in this paper.

PACS numbers: 74.76.Bz, 73.61.Ng

#### 1. Introduction

The selection of useful substrate materials for the deposition of high  $T_c$  superconductors (IITSC) is of prime importance and is subjected to a number of constraints. In several microwave applications of the "ceramic dielectric substrates", important considerations have been given to the (a) materials' thermal properties such as thermal expansion and thermal conductivity, and (b) the electrical characteristics such as low dielectric loss, dielectric constants and dielectric coefficient with temperature. The main heart of the selection criteria are intended for the speed (in MCM devices) and the reduction of thermal effects on the signals. In case of the resonators the values of the constants are adjusted with the size of the required device. If we look for HTSC uses in such applications, the additional requirements from the substrates are demanded. For example, additional crystallographic matching parameters are required to deposit high quality oriented (preferably epitaxial) and hence high  $J_c$  high temperature superconducting films on the single crystal substrates. These parameters are summarized in Table I.

(7)

TABLE I

Dielectric property requirements for HTSC substrates.

	Multi-chip-modules (MCM)	Millimeter wave devices
Applications	Digital receivers, IR detectors, high performance computers	Oscillators; frequency discrimina- tors; phase shifters; delay lines etc.
Requirements	High speed, $v \propto 1/(\kappa)^{1/2}$ ; satisfy characteristic impedance $1/Z \propto (W/d)(\kappa)^{1/2}$ ; high packing den- sity (thinner film); low crosstalk (thinner film)	Narrow bandpass filters (high $Q$ ); low temperature coefficient of capacitance; compact designs (moderate $\kappa$ values)
Dielectric constant	$\kappa \approx 20$ or less is acceptable, how- ever, for film thickness $d \approx 1 \ \mu m$ , $\kappa < 10$ is required	$\kappa \approx 20-25$ desirable
Dielectric loss	$\tan \delta < 10^{-3}$ to maintain the di- electric loss much lower than the conductor loss	Ultra low loss, $\tan \delta < 10^{-4}$ (Q > 10,000)
Type of sub- strates	Single crystal films (2 $\mu$ m) in multi-layer integrated structure with HTSC films	Single crystal substrates 3" or 4" in diameter

CHARACTERISTICS

$\kappa \approx 2-25$ ,					
$Q \approx 10,000$					
at liq. N <sub>2</sub> & 10 GIIz					
$(\tan \delta \approx 10^{-4})$					

M.P.  $\approx 2100$  °C, Crystal growth: 2" dia. crystal available

Heavy	twinning;				
phase tran	sition				
≈ 500°C	(rhomb.)				
012 edge 3.792 Å					

Processability of HTSC thin film;  $\alpha$ , a O.K. but not perfect; no buffer layer needed

### CONSIDERING IT AS A MATERIAL

### TO BE IMPROVED UPON

COMMENTS & APPROACH

Lower  $\kappa$  and  $\tan \delta$ at liq. N<sub>2</sub> & freq.  $\geq 10 \text{ GHz}$  Lower M.P. (congruent), if possible the feasibility of crystal growth from Pt-crucible or other suitable/practical growth technique, sizes 4" desirable No twinning, if there is a  $T_c$  — it should be below liq. N<sub>2</sub>. (?)

 $\alpha$ , a match in temperature range 500 K — liq. N<sub>2</sub>

Fig. 1. The approach to replace or modify one of the most widely used substrate material —  $LaAlO_3$ .

Numerous candidate materials have been suggested for such purposes to achieve useful HTSC based devices. The most widely used candidate has been the crystals of LaAlO<sub>3</sub>. The serious problem of ferroelastic twinning in this material affects the quality of IITSC film and the device performance.

An additional factor, i.e., thermal expansion should also be considered rather seriously in selection of the single crystal substrate materials for HTSC. In this case, the films are deposited and oxidized at  $\approx 500^{\circ}$ C and the devices operate at liquid nitrogen temperatures. Therefore, for the less aging effects and high performance of the device point of view, thermal expansion matching over the temperature range from the deposition temperature to the operating liquid nitrogen are highly recommended.

Recently, several new materials have been suggested and are being tested. Our goal has been to design and develop new highly suitable substrates which are better than that of LaAlO<sub>3</sub> and thus the consideration for the development was based on the approach illustrated in Fig. 1. After a systematic structure-property relationship several promising new hosts such as  $Sr(Al_{1/2}Ta_{1/2})O_3$ ,  $Sr(Al_{1/2}Nb_{1/2})O_3$ , and  $Ba(Mg_{1/3}Ta_{2/3})O_3$  in complex oxide perovskite family have been developed and summarized in this paper.

In order to broaden the family of materials from which the candidates with broad range of dielectric properties can be selected for various microwave applications, an ion polarizability additivity rule (based on Shannon's model) was applied to predict the dielectric constant of large number of suitable HTSC substrates and the values are compared in some cases with the measured values (of dielectric constants).

#### 2. Experimental approach and results

### 2.1. Crystals of complex oxide perovskite compounds

Ceramic samples were prepared by solid state reaction, using conventional techniques. X-ray diffraction (XRD) technique was used extensively to characterize the crystallographic phases and to adjust the processing conditions. The laser heated molten zone (LHMZ) growth method has been shown to be a powerful method for rapidly growing small diameter single crystals, particularly oxides of high melting temperature, for both property studies and fiber devices [1–3]. The LHMZ equipment used in this investigation consisted of a power source (water cooled, tunable flowing gas  $CO_2$  55 W laser), an optical layout, and a growth section. The molten zone temperature during a stable growth was monitored using an optical pyrometer.

Radio frequency dielectric constants and the loss tangent were measured using a General Radio 1621 Capacitance Measurement System. Dielectric properties at microwave frequency were measured using resonance techniques equipped with an HP8510A network analyzer. Post resonance technique (the Hakki and Coleman technique) was used to measure the dielectric constants of the ceramic samples. Cavity perturbation technique was used for the measurements on samples of thin rod (e.g., single crystal fiber samples) or bar-shaped. The Q factors (of microwave frequency) at liquid nitrogen temperature were measured by a transmission resonance technique.

### 2.1.1. $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT)

Ceramics of complex perovskite oxides  $A(B1_{1/3}B2_{2/3})O_3$  type have been explored previously as the candidate materials with excellent microwave dielectric properties [4]. Ba(Mg<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> (BMT), in particular, was reported to have a dielectric constant  $\kappa \approx 25$  and dielectric  $Q \approx 16,800$  (one of the highest in the oxide family) at 10.5 GHz, in samples with 1 mol% Mn additive as a sintering aid [5]. BMT compound is one of the most refractory oxides known thus the growth of single crystals is difficult. A single crystal of BMT was grown from a  $BaF_2$ flux. It yielded a significantly higher dielectric constant ( $\approx 200$ ) [6], presumably attributable to the flux contamination. BMT single crystal fibers were grown successfully using our LHMZ technique. It grows congruently from the melt in the temperature range of 2900-3100°C. A high temperature phase of simple cubic perovskite was obtained at room temperature, in comparison to the hexagonal ordered perovskite structure usually obtained in ceramics (see Fig. 2). Dielectric properties of both the ceramic and the single crystal BMT were studied. BMT ceramic samples have ultra low dielectric loss ( $< 1 \times 10^{-5}$  at 90 K and 10 kHz) and good thermal compatibility ( $\alpha \approx 9.0 \times 10^{-6}$ /°C) with the YBCO superconductors. The single crystal BMT has a cubic lattice parameter a = 4.0877 Å. The dielectric constant increases and saturates as the bulk density approaches the theoretical density. Dielectric loss reduces with the enhancement of the ordering of the B-site. Single crystals of high temperature disordered cubic form preserve a moderate dielectric constant (26.0 at 10 GIIz) and low dielectric loss  $\tan \delta < 2.78 \times 10^{-4}$ at room temperature and 10 kHz and  $< 10^{-5}$  at 90 K) which make this material unique for microwave device applications.



Fig. 2. Typical X-ray diffraction pattern of Ba(Mg<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub>: (a) ceramic powder calcined at 1500°C for 3 h showing weak ordering; (b) ceramic sintered at 1655°C for 5 h showing strong B-site ordering; and (c) single crystal (powder) grown by LHMZ showing an ideal simple cubic perovskite structure with a = 4.0877 Å. BMT ceramic XRD patterns are indexed as a hexagonal perovskite structure with a = 5.7731(6) Å and c = 7.0941(2) Å.

The BMT lattice parameter of a = 4.0877 Å, represents a lattice mismatch of 5.3% to the b-axis of YBCO (b = 3.883 Å); this seems less ideal as a substrate for YBCO. However, there has been no clear cut-off for lattice parameter matches for "epitaxial" (or highly oriented) film deposition of YBCO. "Epitaxial" YBCO thin films on MgO single crystals (with mismatch of 8.5%) have been reported [7]. A BMT single crystal has a twin-free cubic perovskite structure which is advantageous as a substrate compared to some of the heavily twinned substrates, e.g., LaAlO<sub>3</sub> and NdAlO<sub>3</sub>. High temperature BMT single crystal grown by LHMZ is twin free, of moderate dielectric constant, low dielectric loss, and good thermal expansion matching and is therefore identified to be a potentially suitable substrate for the HTSC thin film deposition.

The application of BMT as a substrate, beside its fiber crystals' applications for microwave antenna, may be restricted by the fact that single crystals are difficult to grow. Skull melting growth techniques [8], could presumably be used to grow BMT crystals of adequate sizes. The high melting temperature of BMT will not be a crucial issue, when the material is used as an insulating layer between the YBCO films in a multichip-module type of integrated structure, because vapor phase deposition techniques (e.g., laser ablation and metal-organic chemical vapor deposition, MOCVD) rather than liquid phase growth methods will be utilized.

### 2.1.2. $Sr(Al_{1/2}Ta_{1/2})O_3$ (SAT) and $Sr(Al_{1/2}Nb_{1/2})O_3$ (SAN)

The compounds of  $Sr(Al_{1/2}Ta_{1/2})O_3$  and  $Sr(Al_{1/2}Nb_{1/2})O_3$  were first prepared and tested to learn their crystallographic phases and melting behavior by the group at the AT&T Bell Labs [9]. Ceramic samples were identified to have double cell cubic perovskite structure with a = 7.795 Å and melting temperatures of 1900°C and 1790°C for SAT and SAN, respectively. On the basis of our understandings of the crystal chemistry-dielectric property relation of various oxide perovskites, and the reports by the Bell Labs group which showed both the SAN and SAT melt congruently and produce a single phase of the perovskite structure after melting, we selected the SAT and SAN as primary candidates in the  $A(B1_{1/2}B2_{1/2})O_3$  complex oxide perovskite family for crystal growth and to investigate their properties in relation to substrate applications.

Sr(Al<sub>1/2</sub>Ta<sub>1/2</sub>)O<sub>3</sub> and Sr(Al<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub> are grown using the LHMZ growth technique. Their crystallographic structures are found to be simple cubic perovskite with lattice parameters a = 3.8952 Å (SAT) and a = 3.8995 Å (SAN) which are of close lattice matching to the YBCO superconductors. No structural phase transitions or twins have been found and the average coefficients of the thermal expansion are in good matching with the YBCO superconductor materials. SAT currently represents one of the best potential HTSC substrate materials for microwave applications. The unique feature of this material is that it has desired dielectric properties (dielectric  $\kappa \approx 12$ , loss factor  $\tan \delta < 10^{-4}$ ) at the microwave frequencies with twin-free lattice and good thermal expansion matching along with chemical compatibility with the YBCO superconductors. Dielectric constants in RF region as measured on the dense ceramic samples of SAT and SAN at 23°C are shown in Fig. 3.



Fig. 3. Dielectric constants of SAT and SAN ceramics as functions of frequency at room temperature.

Our experimental results on the SAT composition (first reported at the Office of Naval Research Workshop on Substrates for HTSC, Williamsburg, VA, 1992) along with the earlier report on the congruent melting nature of the SAT and SAN compounds, have stimulated research works in the thin film area. MOCVD-derived SAT films grown at 850°C on LaAlO<sub>3</sub> were found to have exclusively (001) growth with in-plane orientation [10]. Using SAT polycrystalline materials as targets in a pulsed laser deposition process, Findikoglu et al. [11, 12] have reported high quality epitaxial (c-axis orientation) growth of thin films of SAT and multilayers of YBCO/SAT on (001) LaAlO<sub>3</sub> and MgO substrates. Dielectric constants of the SAT films ( $\approx 100-390$  nm thick), however, were reported to be  $\approx 23-30$ , notably higher than the value ( $\kappa \approx 12$ ) found in bulk ceramic materials. The deviations from perfect cation stoichiometry in films may be one of the causes for the discrepancy in value of the dielectric constants as the Al/Ta ratio in SAT films was found to be  $\approx 0.8$  rather than the stoichiometric ratio of unity [12, 13]. No dielectric loss data has been reported for the SAT films therefore direct comparison between the dielectric constants of the film and that of the bulk SAT sample is not intended.

#### 2.2. Solid solution of ternary and complex perovskite oxides

Further modification of the SAN and SAT compositions has been carried out to fine tune their properties, particularly reducing their melting temperatures (SAT: 1900  $\approx$  (1908±25) [9], and SAN: 1790  $\approx$  (1739±10) [9]) [13] for easier fabrication of the crystals and better control of the reduction problem of the Nb<sup>5+</sup> and Ta<sup>5+</sup>. This modification was also an attempt to overcome the twinning problem and to stabilize the cubic phase at room temperature in LaAlO<sub>3</sub> crystals.

LaAlO<sub>3</sub> has a rhombohedrally distorted perovskite  $(A^{3+}B^{3+}O_3 \text{ type})$  structure. Although the La<sup>3+</sup> ion generally prefers the 12-coordination-site, it has a tendency for 9-coordination. The distortion in the LaO<sub>12</sub> polyhedron is brought about by a slight displacement of the oxygen atoms away from the ideal positions of the cubic perovskite form, which is more clearly shown in other [rare-earth]<sup>3+</sup>AlO<sub>3</sub> family members when the A-site cation radii become even smaller, e.g., in the case of PrAlO<sub>3</sub> [14–16]. Figure 4 presents a classification of [A]<sup>3+</sup>[B]<sup>3+</sup>O<sub>3</sub> type compounds according to the constituent ionic radii (8-coordination cation radii



Fig. 4. Structure field map for  $[A]^{3+}[B]^{3+}O_3$  type compounds (Ref. [16]).

were used for A-site cations) focusing on the perovskite region. In fact, no ideal cubic perovskite structure but the rhombohedral [LaAlO<sub>3</sub>] and the orthorhombic [GdFeO<sub>3</sub>] structure have been reported in ternary compounds of the  $[A]^{3+}[B]^{3+}O_3$  type [17]. For aluminate compounds, rhombohedral symmetry is found when A-site is occupied by the largest  $A^{3+}$  cation,  $La^{3+}$ , and other  $[A]^{3+}[Al]^{3+}O_3$  compounds have even lower symmetry.

Our approach following this direction was to introduce "balanced" cation substitution simultaneously in the A- and B-sites to increase the average cation size at the A-site, hence to stabilize the 12-coordination of that position and consequently the cubic perovskite structure. The solid solution of ternary LaAlO<sub>3</sub> and complex oxides of  $Sr(Al_{1/2}Ta_{1/2})O_3$  or  $Sr(Al_{1/2}Nb_{1/2})O_3$  was chosen for investigation.

By forming crystalline solutions with compounds of low melting temperatures, it was expected that the crystalline solution would result in lower melting temperature and consequently avoid the reduction problem and permit growth in platinum crucibles. NdGaO<sub>3</sub> was found to have a melting temperature of  $\approx 1484 \pm 24^{\circ}$ C, and it was therefore selected as an end member of the crystalline solution series with SAT and/or SAN for the present studies. NdGaO<sub>3</sub> has the [GdFeO<sub>3</sub>] structure with orthorhombic symmetry. No twinning problems are reported in this material. YBCO thin films deposited on NdGaO<sub>3</sub> were of better quality compared to those deposited on LaAlO<sub>3</sub> substrates. However, the high dielectric loss in the NdGaO<sub>3</sub> is a limiting factor for the YBCO film applications in microwave devices.

Single crystal fibers of modified strontium aluminum tantalum oxide (1 - x)Sr(Al<sub>1/2</sub>Ta<sub>1/2</sub>)O<sub>3</sub>:xLaAlO<sub>3</sub> (SAT:LA) and (1 - x)Sr(Al<sub>1/2</sub>Ta<sub>1/2</sub>)O<sub>3</sub>: xNdGaO<sub>3</sub> (SAT:NG), and modified strontium aluminum niobium oxide (1 - x)Sr(Al<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub>:xNdGaO<sub>3</sub> (SAN:NG) and (1 - x)Sr(Al<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub>: xLaAlO<sub>3</sub> (SAN:LA) were grown using a laser heated molten zone growth technique [16]. 0.7SAT:0.3LA grows congruently and remains twin free simple cu-

bic perovskite structure (as the SAT) when cooled down to room temperature. 0.7SAT:0.3LA crystals have moderate dielectric constant ( $\kappa = 21.7$ ) and low dielectric loss ( $\tan \delta = 7.5 \times 10^{-5}$ ) at 10 kHz and 90 K. The reduction problem of Ta<sup>5+</sup> is eliminated (which is common in the case of SAT growth). 0.7SAT:0.3NG and 0.7SAN:0.3NG have lower melting temperatures and crystal growth is easier. NdGaO<sub>3</sub> addition to the SAT and SAN enhances the potential of SAT and SAN as large area substrates for HTSC growth. However, the dielectric constants increased from  $\kappa \approx 12$  to  $\kappa \approx 16$  (0.7SAT:0.3NG) and from  $\kappa \approx 18$  to  $\kappa \approx 23$ (0.7SAN:0.3NG) as a result of NdGaO<sub>3</sub> incorporation.

Our results further confirmed the report of Mateika et al. [18, 19] that the ideal cubic phase can be formed in  $(La,Sr)(Al,Ta)O_3$  compounds. It is interesting to notice that similar substitutions using [Ca,Ta] instead of [Sr,Ta] did not produce a compound with cubic structure. The average A-site cation radii of the [Ca,Ta] substitution is smaller than that of LaAlO<sub>3</sub> (ionic radii of  $Ca^{2+}$ ,  $La^{3+}$ , and  $Sr^{2+}$  are 1.14, 1.185, and 1.27 Å, respectively) [20], therefore, no stabilization effect on 12-coordination A-site is expected.

The cubic symmetry for the compound of SAT-NG and SAN-NG may be due to the fact that  $Ga^{3+}$  is almost of the same cation size as  $Ta^{5+}/Nb^{5+}$ . Slight reduction in the A-site cation size is accompanied by the slight increase in the B-site cation size and thus the cubic structure of SAN or SAT stays intact.

The ideal cubic perovskite structure can be stabilized in the case of ternary LaAlO<sub>3</sub> by forming a crystalline solution composition with cubic  $Sr(Al_{1/2}Ta_{1/2})O_3$ and Sr(Al<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub>. The mechanism of this type of stabilization is through introducing the compensated cation substitution in the form of  $[2La^{3+}] + [Al^{3+}] \rightarrow$  $[2A^{2+}] + [B^{5+}]$  with the  $A^{2+}$  cation having a radius larger than that of  $La^{3+}$  and therefore stabilizing the 12-coordinated A-site. Crystalline solutions of SAT-LA maintained or improved most of the dielectric and thermal properties of LaAlO<sub>3</sub> and gained the advantage of forming a twin free simple cubic structure and improved lattice compatibility. NdGaO3 is shown to be an effective end member to decrease the melting temperature of SAN and SAT without disturbing their simple cubic (twin free) crystal structure. Dielectric constants of SAN and SAT with addition of the NdGaO3 were increased; however, the dielectric loss factor still remained less than  $5 \times 10^{-4}$ . The results suggest that SAT-LA and SAN-LA are better candidates as substrate materials than LaAlO3 because the latter is intrinsically twinned. The growth of SAT-NG and SAN-NG are comparatively convenient as they have relatively low melting temperatures together with the relatively lower dielectric constants and the ideal lattice constants and thermal compatibility with the YBCO superconducting materials.

Other substrate candidates such as  $La(Mg_{2/3}Ta_{1/3})O_3$  [21],  $La(Mg_{1/2}Ti_{1/2})O_3$  [22],  $(Ca,Sr)(Ga,Nb)O_3$  [23] and a family of materials of the magnetoplumbite structures [24] have also been fabricated and their dielectric properties studied. These crystals and their associated solid solutions provide several new options for ultra low loss, low permittivity, twin free oxides with low congruent melting temperature, matching thermal expansion and excellent chemical compatibility.

### 2.3. Prediction of the dielectric constants of ionic materials

An ion polarizability additivity rule (Shannon [25]) was applied to calculate the dielectric constants of a large family of substrate materials (for HTSC films) and to compare with the measured dielectric constant values. The schematic approach of the ion polarizability rule applied by Shannon is summarized in Fig. 5.

The macroscopic dielectric constant and the molecular polarizability are connected through the Clausius-Mosotti relation

$$\alpha_{\rm D} = \frac{3}{4\pi} V_{\rm m} \frac{\kappa' - 1}{\kappa' + 2},\tag{1}$$

where  $\alpha_D$  is the dielectric polarizability and  $V_m$  is the molar volume in Å<sup>3</sup>. Much of the effort in this field has been, rather than trying to resolve the local field of each complex substance, to utilize the increasing pool of dielectric polarizabilities of substances with various compositions and structures. Dielectric polarizabilities and hence the dielectric constants of new materials/compounds whose dielectric constants have not been measured are potentially predictable by linear addition of the molecular polarizabilities of simpler substances (molecular polarizability additivity rule) [26-28] or ion polarizabilities of individual ions (ion polarizability additivity rule) [29, 28]. Review and comments about the application of polarizability additivity rules can be found in Shannon's paper [25].

TABLE II

Substance	Space gr. or sym.	Vm	$\kappa'_{exp}$	$\kappa'_{ m cal}$	$\Delta \alpha \%$	
Al <sub>2</sub> O <sub>3</sub>	R3ch	42.45	9.34,	10.05	0.06	
			9.34, 11.54			
CaF <sub>2</sub>	Fm3m	40.75	6.81	6.77	0.23	
MgO	Fm3m	18.68	9.65	9.86	-0.61	
Ba <sub>2</sub> YSbO <sub>6</sub>	cubic	139.53	25.0	23.71	0.63	
$\mathrm{Sr}(\mathrm{Ga}_{0.5}\mathrm{Ta}_{0.5})\mathrm{O}_3$	cubic	61.58	26.9	31.54	-1.60	
MgF <sub>2</sub>	P42/mnm	32.40	5.50	5.31	1.73	
$(Sr_{0.5}Ca_{0.5})(Ga_{0.5}Nb_{0.5})O_3$	cubic	58.64	32.0	25.41	2.32	
SiO <sub>2</sub> (quartz syn)	P6222	39.37	4.42,	4.26	3.10	
			4.41,		t i	
			4.6			
$\mathrm{Zr}_{0.72}\mathrm{Y}_{0.28}\mathrm{O}_{1.862}$	Pm3m	34.35	29	21.43	3.60	
BaZrO <sub>3</sub>	P23	73.10	43.0	27.59	3.72	
NdGaO3 (NG)	Pbn21	57.68	20–25	31.66	-3.80	

Comparison of calculated and experimental dielectric constants using ion polarizability additivity rule [25].

## TABLE II (cont.)

Substance	Space gr. or sym.	Vm	$\kappa'_{exp}$	$\kappa'_{\rm cal}$	$\Delta \alpha \%$
CaYAlO <sub>4</sub>	tetra	79.85	21.44,	15.54	3.80
			21.44,		
			16.12		
1/3SAN-1/3SAT-1/3NG	cubic	63.30	22.8	17.13	4.08
Nd <sub>0.39</sub> Sr <sub>0.61</sub> Al <sub>0.695</sub> Ta <sub>0.305</sub> O <sub>3</sub>		56.76	24.04	39.20	-4.79
La(MgAl11)O19	hex	296.86	13.50	10.81	5.03
GdAlO <sub>3</sub>		51.87	19.50	29.17	-5.03
LiBaF3	cubic	63.40	11.71	14.98	- 5.40
$0.7 \mathrm{Sr}(\mathrm{Al}_{0.5}\mathrm{Nb}_{0.5})\mathrm{O}_3 \!-\! 0.3 \mathrm{Nd}\mathrm{Ga}\mathrm{O}_3$	cubic	63.30	23.50	16.06	5.49
$0.7 \mathrm{Sr}(\mathrm{Al}_{0.5}\mathrm{Nb}_{0.5})\mathrm{O}_3 - 0.3 \mathrm{LaAlO}_3$	cubic	63.28	25.90	17.02	5.63
SrLaAlO <sub>4</sub>	tetra	88.99	16.70,	28.30	-6.19
			16.70,		
	1.	50.00	20.02	07.00	0.10
$Sr(Al_{0.5}Nb_{0.5})O_3$ (SAN)	Cubic	59.09	17.30	27.08	-0.19
KMgF <sub>3</sub>	Pm3m	63.00	5.98	0.97	-0.00
KZnF3	Pm3m	66.70	8.85	7.20	0.85
0.7Sr(Al <sub>0.5</sub> Ta <sub>0.5</sub> )O <sub>3</sub> $-0.3$ LaAlO <sub>3</sub>	cubic	58.08	21.9	45.52	-7.08
$La(Mg_{2/3}Ta_{1/3})O_3$	hex	74.33	24.1	14.56	7.30
Nd(MgGaAl10)O19	hex	296.50	14.9	10.60	7.37
$0.7 \mathrm{Sr}(\mathrm{Al}_{0.5}\mathrm{Ta}_{0.5})\mathrm{O}_3 - 0.3 \mathrm{LaAlO}_3$	cubic	57.89	21.9	47.94	-7.44
PrAlO <sub>3</sub>	R3-mr	53.25	25.0	64.81	-7.45
SmAlO <sub>3</sub>	Pbnm	52.30	19.0	38.53	- 8.03
BaSnO3	P23	69.40	18.0	36.06	- 8.37
LaGaO <sub>3</sub>	[GdFeO3]	59.10	25.0	81.33	-8.45
(Ba <sub>0.8</sub> Sr <sub>0.2</sub> )(Mg <sub>1/3</sub> Ta <sub>2/3</sub> )O <sub>3</sub>	cubic	67.48	25.9	91.67	-8.46
(Ba <sub>0.9</sub> Sr <sub>0.1</sub> )(Mg <sub>1/3</sub> Ta <sub>2/3</sub> )O <sub>3</sub>	cubic	67.84	25.3	123.65	-9.66
$CaGa_{12}O_{19}$	hex	301.48	9.70	15.12	-9.83
Ba(Mg <sub>1/3</sub> Ta <sub>2/3</sub> )O <sub>3</sub>	hex	68.59	24.6	138.91	-10.31
$La(Mg_{0.5}Ti_{0.5})O_3$	cubic	60.10	26.5	355.40	-10.83
NdAlO <sub>3</sub>	R3ch	52.80	17.50	46.89	-10.93
$CaGa_6Al_6O_{19}$	hex	302.00	18.2	10.72	11.43
$0.7 \mathrm{Sr}(\mathrm{Al}_{0.5}\mathrm{Ta}_{0.5})\mathrm{O}_3 - 0.3 \mathrm{NdGaO}_3$	cubic	57.90	16.3	42.22	-11.49
$LaAlO_3$	R3mr	54.40	23.8	406.86	-10.96
YAlO <sub>3</sub>	P63/mmc	61.69	16.83,	8.79	14.13
		1	16.83,		
		<b>_</b>	15.94	05.00	10.00
$Sr(Al_{0.5}Ta_{0.5})O_3$ (SAT)	cubic	59.09	11.78	37.36	-18.09



Fig. 5. Schematic approach of the ion polarizability additivity rule applied by Shannon [25].

The calculation results using Shannon's ion polarizability data [25] (Table III, second column) and the ion polarizability additivity rule are shown in Table II. Comparison of the calculated and experimental molar polarizability and dielectric constants are tabulated. All the materials chosen for this study could be effective substrates for IITSC thin films. Some materials which appeared in Shannon's database or calculation are also included for the sake of completeness. Most of the structural data, symmetry parameters and the molar volume  $(V_m)$ , are reasonably well established and the refined single crystal structure information used may be found in The Inorganic Crystal Structure Database (ICSD) [30]. Crystal structures and the molar volumes of new substrate materials are determined on available single crystal samples (grown by a laser heated pedestal growth technique) by X-ray diffraction. Ceramic samples of new substrate materials are also used, only for those well sintered samples having high density and cubic or pseudocubic symmetries. The experimental value of the dielectric constants were taken from Shannon's database wherever available, otherwise were our measurement results. Dielectric constants of new substrate materials are measured using a high precision capacitance measurement system (Gen Rad 1621) in frequency range 10<sup>3</sup>-10<sup>5</sup> Hz at room temperature and resonance technique or cavity perturbation techniques at

the microwave frequencies (GHz). Details regarding the synthesis, preparation, and properties of new substrate materials may be found in the referred publications.

Several observations on the results listed in Table II are worth mentioning for further discussions. First, it is strikingly apparent that small discrepancies in molar polarizability can many times cause large discrepancies in dielectric constant prediction which indicates that the  $V_{\rm m}$  value in dielectric constant prediction plays a significant role. Second, good agreements are usually seen in case of substances containing cations having high valence and small sizes, while large discrepancies are common in ternary systems which involve large cations in high coordination sites. Third, poor agreements are found in materials containing Nb or Ta ions such as Ba(Mg<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub>, Sr(Al<sub>1/2</sub>Ta<sub>1/2</sub>)O<sub>3</sub>, and Sr(Al<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub> and cations of rare-earth family such as LaAlO<sub>3</sub>.

### 2.3.1. Origin of large discrepancy in predicted dielectric constants values

Obviously any inaccuracy in dielectric constant measurements or structure parameter determinations are the up front cause for the discrepancies. All the data used in our calculation are believed to be the most reliable data available.

Besides experimental errors, large deviations from additivity rule using Shannon's ion polarizability data can sometimes be traced to, as pointed out by Shannon, unusual properties of the compounds such as ionic or electronic conductivity, the presence of dipolar impurities, or piezo- or ferroelectricity. However, above mentioned irregularities are presumably non existent in the substrate materials in current study.

After taking into consideration the oxygen polarizability dependence of the volume,  $V_{\rm ox}$ , the calculation in Table II was repeated using the refined ion polarizabilities given by Shannon [25] (Table III, first column). The improvement is insignificant and discrepancy is largely non corrected.

A critical question needed to be answered after examining the ion polarizability calculation is whether the assumption is valid that cation (and fluorine) polarizability is independent of the compound in which it is found.

There seems to be enough indication which suggests that the answer to this question is no. Evidence was presented by Safford and Silverman [31] that a change of coordination of an ion alters the molar refraction contribution of the ion or more correctly of the group immediately surrounding the ion. Fajans and co-workers [32] showed that the coordination number of  $Zn^{2+}$  is related to the molar volume (of  $Zn^{2+}$ ) and demonstrated a relationship between molar refraction and molar volume (of the cation). These authors showed that the  $Al^{3+}$  in fourfold coordination in glass or in certain crystals has a molar refraction contribution of 12.3 (calculated for  $Al_2O_3$ ), whereas in sixfold coordination it is 10.5. Kreidl [33] first indicated that MgO may assume both "basic" and "acidic" properties in glass. Differences in molar refractions were found for  $Mg^{2+}$  in sixfold coordination such as in periclase MgO where R = 4.538, and in fourfold coordination such as in spinel MgAl<sub>2</sub>O<sub>4</sub> where R = 5.18 [34]. For ions preferably found only in the same coordination, the dielectric polarizability of the ion remains relatively constant and the additivity rule applies well. Molar volumes of the compounds in these cases are all one need to calculate total polarizabilities of the compounds. Examples of this

TTT TTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTT	Τł	<b>IBI</b>	Æ	III
--	----	------------	---	-----

Compo-	Sym-	Lattice	κ	$\tan \delta$	$\alpha \times 10^{-6}$	Melting
sition	metry	constant	10 kHz	$10 \ \mathrm{kHz}$	[/°C]	point
		[Å]	90 K	90 K	$(at \approx 300 \text{ K})$	[°C]*
BMT	cubic	4.0877	25.9	$< 10^{-5}$	9.0	(> 2800)
(crystal)						`, ´,
SAT	cubic	3.8952	11.8	$4.2 \times 10^{-5}$	9.7	$1908 \pm 25$
SAN	cubic	3.8995	18.7	$2.2 \times 10^{-4}$	8.5	$1739 \pm 10$
SAT-LA	cubic	3.8727	21.7	$7.5 \times 10^{-5}$	7.7	$1830 \pm 22$
SAN-LA	cubic	3.8634	25.7	$2.8 \times 10^{-4}$	9.5	$1705 \pm 20$
SAT-NG	cubic	3.8866	16.0	$4.3 \times 10^{-4}$	8.8	$1767\pm31$
SAN-NG	cubic	3.8790	23.0	$5.2 \times 10^{-4}$	10.8	$1582 \pm 20$
$LaAlO_3$	rhomb.	a = 3.789	23	$7.5 \times 10^{-5}$	$8.2 \parallel [1\overline{1}0]$	$2040\pm9$
(crystal)		$\alpha = 90.12^{\circ}$			6.4    [001]	
$NdGaO_3$	ortho.	a = 5.426	23	$3.2 \times 10^{-4}$		$1484 \pm 24$
(crystal)		b = 5.502	(77 K,			
		c = 7.706	10 GHz)			

Properties of some newly proposed oxide perovskite substrate materials.

\*The melting point was determined rather simply using a strip furnace, with two operators using two separate optical pyrometers and averaging several readings per sample.

type would be the silicates and borates. For substances that contain cations which are found in different coordination, the difference in the dielectric polarizability is averaged when enough (unbiased) substances are used in the least squares fitting process and therefore good or fair additivity application can be obtained. Examples of this type may be identified as aluminates, and gallates. However, for cations like  $Cu^{2+}$ ,  $Ba^{2+}$ ,  $Re^{3+}$ ,  $Sb^{3+}$ ,  $As^{3+}$ ,  $Nb^{5+}$ ,  $Ta^{5+}$ , the ion polarizability data are scarce and single crystal data are not available, the uncertainties are larger because the ratio of the number of observed molar polarizabilities to refined ion polarizabilities is rather low and the observed total polarizabilities have larger errors (as also noted by Shannon).

#### 2.3.2. Modification proposed on current additivity approach

Following the above discussion, if the dielectric polarizability of a cation is dependent on individual compound, can a set of generally constant ion polarizability data be found and valid for use by the additivity rule for a broad range of compounds with various coordination combinations or crystallographic senses? Following the work of O'Keeffe [35] and Brown and Altermatt [36] on the apparent bond valences and their relations to bond lengths, we suggest reformulating of the ion polarizability additivity rule by normalizing each ion polarizability to its electrostatic valence status. In order to narrow down the differences between the calculated and measured values, we considered several new factors in Shannon's approach. One of the new approach defines the normalized ion polarizability which is applicable for estimation of the dielectric constants with higher precision once the refined crystal structure is known. The derivation of the modified ion polarizability data and the preliminary examination on ionic materials of broad range is content of a separate publication.

#### 3. Summary

Oxide crystals with the perovskite structure are major candidates for YBCO film epitaxial deposition particularly if large size cubic, twin free crystals become available. SAT has already shown promise in high quality epitaxial YBCO film growth. With improved growth capability, the SAT and particularly its modified solid solutions may be more useful than the intrinsically twinned LaAlO<sub>3</sub>. Solid solutions between the known complex perovskite oxide and ternary end members, especially gallates, will provide large number of options to tailor the material for specific device applications. The property parameters of the newly proposed substrate materials of oxide perovskite family are summarized in Table III. LaAlO<sub>3</sub> and NdGaO<sub>3</sub> are also listed for comparison.

#### Acknowledgment

This work was supported by the Defense Advanced Research Projects Agency (DARPA) under the contract No. DN 00014-90-J-4140 and the Office of Naval Research (ONR) under the contract No. N00014-94-1-0641.

#### References

- J.S. Haggerty, W.P. Menashi, J.F. Wenckus, U.S. Patent No. 3 944 640, 16 March 1976; U.S. Patent No. 4 012 213, 15 March 1977.
- [2] R.S. Feigelson, MRS Bull. 13, 47 (1988).
- [3] J. Yamamoto, A.S. Bhalla, Mater. Res. Bull. 24, 761 (1989).
- [4] K. Wakino, Ferroelectrics 91, 69 (1989).
- [5] S. Nomura, K. Toyama, K. Kaneta, Jpn. J. Appl. Phys. 21, L624 (1982).
- [6] F. Galasso, J. Pinto, Nature 207, 70 (1965).
- [7] E.g., T. Terashima, K. Iijima, K. Yamamoto, K. Irata, Y. Bando, T. Takada, Jpn. J. Appl. Phys. 28, L987 (1989).
- [8] H.R. Harrison, J.M. Honig, Bull. Mater. Sci. 3, 247 (1981).
- [9] C.D. Brandle, V.J. Fratello, J. Mater. Res. 5, 2160 (1990).
- [10] B. Han, D.A. Neumayer, B.H. Goodreau, T.J. Marks, H. Zhang, V.P. Dravid, Chem. Mater. 6, 18 (1994).
- [11] A.T. Findikoglu, C. Doughty, S. Bhattacharya, Qi Li, X.X. Xi, T. Venkatesan, R.E. Fahey, A.J. Strauss, J.M. Phillips, Appl. Phys. Lett. 61, 1718 (1992).
- [12] A.T. Findikoglu, S. Bhattacharya, C. Doughty, M.S. Pambianchi, Qi Li, X.X. Xi, S.M. Anlage, R.E. Fahey, A.J. Strauss, J.M. Phillips, T. Venkatesan, *IEEE Trans. Appl. Superconductivity* 3, 1425 (1993).
- [13] R. Guo, A.S. Bhalla, J. Sheen, F. Ainger, E.C. Subbarao, S. Erdei, L.E. Cross, J. Mater. Res. 10, 18 (1995).
- [14] R.D. Burbank, J. Appl. Cryst. 3, 112 (1970).
- [15] O. Muller, R. Roy, The Major Ternary Structural Families, Springer-Verlag, Berlin 1974, p. 215.

- [16] R. Guo, P. Ravindranathan, U. Selvaraj, A.S. Bhalla, L.E. Cross, R. Roy, J. Mater. Sci. 29, 5054 (1994).
- [17] F.S. Galasso, Structure, Properties and Preparation of Perovskite-Type Compounds, Pergamon Press, Oxford 1969, p. 10.
- [18] S. Haussühl, D. Mateika, Cryst. Res. Technol. 26, 481 (1991).
- [19] D. Mateika, H. Kohler, H. Laudan, E. Völkel, J. Cryst. Growth 109, 447 (1991).
- [20] R.D. Shannon, C.T. Prewitt, Acta Crystallogr. B 25, 925 (1969); Acta Crystallogr. B 26, 1046 (1970).
- [21] P. Ravindranathan, A.S. Bhalla, to be published.
- [22] G. Harshe, A.S. Bhalla, L.E. Cross, Mater. Lett. 18, 173 (1994).
- [23] S. Erdei, L.E. Cross, F.W. Ainger, A.S. Bhalla, J. Cryst. Growth 139, 54 (1994).
- [24] R. Guo, A.S. Bhalla, to be published.
- [25] R.D. Shannon, J. Appl. Phys. 73, 348 (1993).
- [26] A. Heydweiller, Z. Phys. 3, 308 (1920).
- [27] D.A.A.S. Narayana Rao, Proc. Ind. Acad. Sci. A 30, 317 (1949).
- [28] A.C. Lasaga, R.T. Cygan, Am. Mineral. 67, 328 (1982).
- [29] R. Roberts, Phys. Rev. 76, 1215 (1949).
- [30] The Inorganic Crystal Structure Database (ICSD), copyrighted by Fachinformationszentrum-Karlsruhe, 7514 Eggenstein-Leopoldshafen 2, Karlsruhe, West Germany.
- [31] H.W. Safford, A. Silverman, J. Am. Ceram. Soc. 30, 203 (1947).
- [32] K. Fajans, N.J. Kreidl, J. Am. Ceram. Soc. 31, 105 (1948); K. Fajans, G. Joos, Z. Phys. 23, 1 (1923).
- [33] N.J. Kreidl, Glastchn. Ber. 7, 313 (1929).
- [34] Rustum Roy, J. Am. Chem. Soc. 72, 3307 (1950).
- [35] M. O'Keeffe, Structure and Bonding, Vol. 71, Springer-Verlag, Berlin 1989, p. 163.
- [36] I.D. Brown, D. Altermatt, Acta Crystallogr. B 41, 244 (1985).