OXIDE PEROVSKITE CRYSTALS FOR HTSC FILM SUBSTRATES MICROWAVE APPLICATIONS

A.S. BHALLA AND RUYAN GUO Materials Research Laboratory, The Pennsylvania State University University Park, PA 16802

ABSTRACT

The research focused upon generating new substrate materials for the deposition of superconducting yttrium barium cuprate (YBCO) has yielded several new hosts in complex perovskites, modified perovskites, and other structure families. New substrate candidates such as $Sr(Al_{1/2}Ta_{1/2})O_3$ and $Sr(Al_{1/2}Nb_{1/2})O_3$, $Ba(Mg_{1/3}Ta_{2/3})O_3$ in complex oxide perovskite structure family and their solid solutions with ternary perovskite LaAIO₃ and NdGaO₃ are reported. Conventional ceramic processing techniques were used to fabricate dense ceramic samples. A laser heated molten zone growth system was utilized for the test-growth of these candidate materials in single crystal fiber form to determine crystallographic structure, melting point, thermal, and dielectric properties as well as to make positive identification of twin free systems. Some of those candidate materials present an excellent combination of properties suitable for microwave HTSC substrate applications.

INTRODUCTION

There is great interest worldwide in the deposition of high quality thin films of high Tc superconductors (HTSC), using a whole variety of available deposition techniques. The selection of useful substrate materials is of first importance and is subjected to a number of constrains such as: thermal and chemical stability under the conditions used in the film processing and operating; suitable lattice parameter and ionic structure matching; thermal compatibility in terms of thermal expansion matching over the temperature range of film processing and operating; physical properties suitable for specific use (for instance the dielectric constant and loss for electronic devices and high thermal conductivity for high-power-density applications); commercial availability and if possible, low cost.

In addition to satisfy the general requirements, substrates to be used in microwave devices must be twin-free single crystals with potential to be grown in large size (2-4" wafer). Congruent melting compositions with modest melting temperatures are therefore favorable. The dielectric constant influences the propagation speed and the package dimensions therefore a moderately low dielectric constant (<25) is required. Because the conductor loss of the superconductor is diminished, the role of the dielectric loss becomes critically important. Very low dielectric loss (<10⁻⁴) is therefore demanded.

The potential application of YBCO superconductor to the development of ultra high density interconnect systems for a new generation of high speed high density multichip

modules dictates new requirements for the substrate design. An essential feature is the geometry of the X and Y layers of HTSC lines that must have geometries in cross section of order 2 x 1 μ meters thus necessitating a current carrying capability for the HTSC of ~10⁶ A/cm². For this current capability clearly the YBCO must be highly grain oriented very near to single crystal, so that the whole multilayer structure is in the form of highly oriented overgrowths on a single crystal substrate. Impedance characteristics for the interconnect structure dictate that the dielectrics used must be of low permittivity (ideally <10) if the geometry is to be preserved. Highly oriented thin films (2 μ m or above) will be needed for the separation of strip lines and ground plane structures. Dielectric loss requirements are a little less stringent than those required for the microwave applications; however, tan $\delta < 0.001$ is highly desirable at the 77K working temperature.

A family of substrates with the perovskite structure is most important as those materials are among the most obvious candidates for epitaxial growth of YBCO films. Substrates of perovskite structure usually have the ideal cubic (such as $SrTiO_3$), double cell cubic (such as Ba_2YSbO_6), hexagonal distorted pseudo cubic (such as $LaAlO_3$) or other pseudo cubic cells (such as NdGaO₃ that has the [GdFeO₃] structure with orthorhombic symmetry). SrTiO₃ crystals of high quality and large sizes, though are readily available and yield the best epitaxial quality thin films (primarily due to their close interatomic structure matching to the HTSC), have high dielectric constant (>300) arising from the phase transition near the working temperature (~110K). Another probably the most used substrate currently, LaAlO₃, though good in lattice matching and of reasonable dielectric properties, is heavily twinned and goes through a ferroelastic phase transition at ~435°C.¹ These macroscopic defects in the crystals are not tolerable in substrates used for complex microcircuits.

In our ongoing search for substrates suitable for microwave device and integrated circuit applications, the focus has been upon developing and identifying new substrate materials primarily with perovskite structures for the deposition of superconducting yttrium barium cuprate (YBCO) films. It became increasingly clear to us that the demand on the substrates to have a close "lattice match" was in many cases less appropriate.² Similarity in structure is a higher order criterion than simply lattice parameter matching though they are not independent.³ A wide range search for new low permittivity candidate materials using the predictive capability of the phenomenological ionic polarizability arguments is currently undertaking.⁴ The unique capabilities of a laser heated molten zone (LHMZ) growth system have been utilized for test-growth of candidate materials in single crystal fiber form to determine structure, thermal, and dielectric properties and make positive identification of twin free systems. This paper reports the combination of experimental and theoretical approaches in this field with focus on the complex oxide perovskites and related solid solutions.

CRYSTALS OF COMPLEX OXIDE PEROVSKITE COMPOUNDS

Ceramic samples were prepared by solid state reaction, using conventional techniques. X-ray diffraction technique was used extensively to characterize the crystallographic phases and to adjust the processing conditions. The laser heated molten zone 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.^{5,6,7} The LHMZ equipment used in this investigation consisted of a power source (water cooled, tunable flowing gas CO_2 55W 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.

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

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.⁸ $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT), in particular, was reported to have a dielectric constant κ ~25 and dielectric Q~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.⁹ 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 BaF₂ flux. It yielded a significantly higher dielectric constant (~200),¹⁰ 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. 1). Dielectric properties of both the ceramic and the single crystal BMT were studied. BMT ceramic samples have ultra low dielectric loss ($<1x10^{-5}$ at 90K and 10kHz) and good thermal compatibility ($\alpha \sim 9.0x10^{-6}/^{\circ}$ C) with the YBCO superconductors. The single crystal BMT has a cubic lattice parameter a=4.0877Å. 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 10GHz) and low dielectric loss tan δ (2.78x10⁻⁴ at room temperature and 10kHz and $<10^{-5}$ at 90K) that make this material unique for microwave device applications.

The BMT lattice parameter of a=4.0877Å, represents a lattice mismatch of 5.3% to the b-axis of YBCO (b=3.883Å); 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.¹¹ A BMT single crystal has a twin-

free cubic perovskite structure that is advantageous as a substrate compared to some of the heavily twinned substrates, e.g., $LaAlO_3$ and $NdAlO_3$. 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,¹² 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) rather than liquid phase growth methods will be utilized.



Fig. 1. Typical x-ray diffraction pattern of Ba(Mg_{1/3}Ta_{2/3})O₃: (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.

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

The compounds of $Sr(Al_{1/2}Ta_{1/2})O_3$ (SAT) and $Sr(Al_{1/2}Nb_{1/2})O_3$ (SAN) were first prepared and tested to learn their crystallographic phases and melting behavior by the group at the AT & T Bell Labs.¹³ Ceramic samples were identified to have double cell cubic perovskite structure with a=7.795Å 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 that 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_{1/2}Ta_{1/2})O₃ (SAT) and Sr(Al_{1/2}Nb_{1/2})O₃ (SAN) are grown using the LHMZ growth technique. Their crystallographic structures are found to be simple cubic perovskite with lattice parameters a=3.8952Å (SAT) and a=3.8995Å (SAN) that 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 κ ~12, loss factor tan δ <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.2.



Fig. 2. Dielectric constants of SAT and SAN ceramics as functions of frequency at room temperature.

Our experimental results on the SAT composition 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 LaAlO₃ were found to have exclusively (001) growth with in-plane orientation.¹⁴ Using SAT polycrystalline materials as targets in a pulsed laser deposition process, Findikoglu *et al.*^{15,16} have reported high quality epitaxial (c-axis orientation) growth of thin films of SAT and multilayers of YBCO/SAT on (001) LaAlO₃ and MgO substrates. Dielectric constants of the SAT films (~100-390nm thick), however, were reported to be ~23-30, notably higher than the value (κ ~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 ~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.

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: $1900 - (1908 \pm 25)^{13}$, and SAN: $1790 - (1739 \pm 10)^{13})^{17}$ for easier fabrication of the crystals and better control of the reduction problem of the Nb⁵⁺ and Ta⁵⁺. This modification was also an attempt to overcome the twinning problem and to stabilize the cubic phase at room temperature in LaAlO₃ crystals.

LaAlO₃ has a rhombohedrally distorted perovskite $(A^{3+}B^{3+}O_3 \text{ type})$ structure. Although the La³⁺ ion generally prefers the 12-coordination-site, it has a tendency for 9-coordination. The distortion in the LaO₁₂ polyhedron is brought about by a slight displacement of the oxygen atoms away from the ideal positions of the cubic perovskite form, that is more clearly shown in other [rear-earth]³⁺AlO₃ family members when the A-site cation radii become even smaller, e.g., in the case of PrAlO₃.^{18, 19}. Fig. 3 presents a classification of $[A]^{3+}[B]^{3+}O_3$ type compounds according to the constituent ionic radii (8coordination cation radii were used for A-site cations) focusing on the perovskite region. In fact, no ideal cubic perovskite structure but the rhombohedral [LaAlO₃] and the orthorhombic [GdFeO₃] structure have been reported in ternary compounds of the $[A]^{3+}[B]^{3+}O_3$ type.²⁰ For aluminate compounds, rhombohedral symmetry is found when A-site is occupied by the largest A³⁺ cation, La³⁺, 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 LaAlO₃ 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. NdGaO₃ was found to have a melting temperature of ~1484 \pm 24°C, and it was therefore selected as an end member of the crystalline solution series with SAT and/or SAN for the present studies. NdGaO₃ has the [GdFeO₃] structure with orthorhombic symmetry. No twinning problems are reported in this material. YBCO thin films deposited on NdGaO₃ were of better quality compared to those deposited on LaAlO₃ substrates. However, the high dielectric loss in the NdGaO₃ is a limiting factor for the YBCO film applications in microwave devices.



Fig. 3. Structure field map for $[A]^{3+}[B]^{3+}O_3$ type compounds (ref. 19).

Single crystal fibers of modified strontium aluminum oxide tantalum $(1-x)Sr(Al_{1/2}Ta_{1/2})O_3:xLaAlO_3$ $(1-x)Sr(Al_{1/2}Ta_{1/2})O_3:xNdGaO_3$ (SAT:LA) and niobium (SAT:NG), and modified strontium aluminum oxide (SAN:NG) $(1-x)Sr(Al_{1/2}Nb_{1/2})O_3:xNdGaO_3$ and $(1-x)Sr(Al_{1/2}Nb_{1/2})O_3:xLaAlO_3$ (SAN:LA) were grown using a laser heated molten zone growth technique.²¹ 0.7SAT:0.3LA grows congruently and remains twin free simple cubic perovskite structure (as the SAT) when cooled down to room temperature. 0.7SAT:0.3LA crystals have moderate dielectric constant (κ =21.7) and low dielectric loss (tan δ =7.5x10⁻⁵) at 10 kHz and 90K. The reduction problem of Ta^{5+} 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. NdGaO₃ 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 $\kappa \sim 12$ to $\kappa \sim 16$ (0.7SAT:0.3NG) and from $\kappa \sim 18$ to $\kappa \sim 23$ (0.7SAN:0.3NG) as a result of NdGaO₃ incorporation.

Our results further confirmed the report of Mateika *et al.*^{22,23} 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 LaAlO₃ (ionic radii of Ca²⁺, La³⁺, and Sr²⁺ are 1.14, 1.185, and 1.27Å, respectively),²⁴ 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 of 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 LaAlO₃ by a crystalline solution composition with cubic $Sr(Al_{1/2}Ta_{1/2})O_3$ forming and $Sr(Al_{1/2}Nb_{1/2})O_3$. 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 A²⁺ cation having a radius larger than that of La³⁺ and therefore stabilizing the 12-coordinated A-site. Crystalline solutions of SAT-LA maintained or improved most of the dielectric and thermal properties of LaAlO₃ 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 5×10^{-4} . The results suggesting 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 $La(Mg_{2/3}Ta_{1/3})O_3$ ²⁵ $La(Mg_{1/2}Ti_{1/2})O_3$ ²⁶ (Ca,Sr)(Ga,Nb)O₃²⁷ and a family of materials of the magnetoplumbite structures²⁸ 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.

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 LaAlO₃. 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 I. LaAlO₃ and NdGaO₃ are also listed for comparison.

Compositio n	symmetry	Lattice Constant (Å)	к 10kHz 90K	tanδ 10kHz 90K	α (x10 ⁻⁶ /°C) (@~300K)	Melting Point (°C) *
BMT (crystal)	Cubic	4.0877	25.9	<10-5	9.0	(>2800)
SAT	Cubic	3.8952	11.8	4.2x10 ⁻⁵	9.7	1908±25
SAN	Cubic	3.8995	18.7	2.2x10 ⁻⁴	8.5	1739±10
SAT-LA	Cubic	3.8727	21.7	7.5x10 ⁻⁵	7.7	1830±22
SAN-LA	Cubic	3.8634	25.7	2.8x10-4	9.5	1705+20
SAT-NG	Cubic	3.8866	16.0	4.3x10-4	8.8	1767±31
SAN-NG	Cubic	3.8790	23.0	5.2x10-4	10.8	1582±20
LaAlO ₃ (crystal)	Rhomb.	a=3.789 a=90.12°	23	7.5x10 ⁻⁵	8.2//[110] 6.4//[001]	2040±9
NdGaO ₃ (crystal)	Ortho.	a=5.426 b=5.502 c=7.706	23 (77K,10GHz)	3.2x10 ⁻⁴		1484±24

TABLE I. 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.

ACKNOWLEDGMENT

This work was supported by the Defense Advanced Research Projects Agency (DARPA) under the contract No. DN 00014-90-J-4140.

REFERENCES

- ¹ E.A. Wood, Amer. Min. 36 768 (1951).
- ² R. Roy, Ruyan Guo, A. S. Bhalla, and L.E. Cross, J. Vac. Sci. Technol. A. 12(2) 269 (1994).
- ³ Ruyan Guo, A.S. Bhalla, L.E. Cross, and R. Roy, J. Mat. Res. 9(7), 1644 (1994).
- ⁴ Ruyan Guo, A.S. Bhalla, R. Roy, and L.E. Cross, *Ferroelectrics* 155(1-4) 43 (1994).
- ⁵ J.S. Haggerty, W.P. Menashi and J.F. Wenckus, U.S. Patent No. 3 944 640 (16 March 1976); U.S. Patent No. 4 012 213 (15 March 1977).

- ⁶ R.S. Feigelson, MRS Bull. 13 47 (1988).
- J. Yamamoto and A.S. Bhalla, Mat. Res. Bull. 24 761 (1989).
- ⁸ K. Wakino, Ferroelectrics 91 69 (1989).
- ⁹ S. Nomura, K. Toyama, and K. Kaneta, Jpn. J. Appl. Phys. 21(10) L624 (1982).
- ¹⁰ F. Galasso and J. Pinto, *Nature* vol. 207 No. 4992, 70 (1965).
- ¹¹ e.g., T. Terashima, K. Iijima, K. Yamamoto, K. Irata, Y. Bando, and T. Takada, Jpn. J. Appl. Phys. 28, L987 (1989).
- ¹² H.R. Harrison and J.M. Honig, Bull. Mater. Sci. 3(3), 247 (1981).
- ¹³ C.D. Brandle and V.J. Fratello, J. Mater. Res. 5(10), 2160 (1990).
- ¹⁴ B. Han, D. A. Neumayer, B.H. Goodreau, T. J. Marks, H. Zhang, and V.P. Dravid, *Chem. Mater.* (in press).
- ¹⁵ A.T. Findikoglu, C. Doughty, S. Bhattacharya, Qi Li, X.X. Xi, T. Venkatesan, R.E. Fahey, A.J. Strauss, and J. M. Phillips, *Appl. Phys. Lett.* 61 1718 (1992).
- ¹⁶ 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, and T. Venkatesan, *IEEE Trans. Appl. Superconductivity*, 3(1) 1425 (1993).
- ¹⁷ R. Guo, A.S. Bhalla, J. Sheen, F. Ainger, E.C. Subbarao, S. Erdei, and L.E. Cross, *J. Mat. Res.* (in press, 1994).
- ¹⁸ R.D. Burbank, J. Appl. Cryst. 3 112 (1970).
- ¹⁹ O. Muller and R. Roy, in "The major ternary structural families" (Springer-Verlag, Berlin, Heidelberg, New York 1974) p.215.
- ²⁰ F.S. Galasso, in "Structure, properties and preparation of perovskite-type compounds" (Pergamon Press, Oxford, London, Edinburgh, Now York, Toronto, Sydney, Paris, Braunschweig 1969) p.10.
- ²¹ R. Guo, P. Ravindranathan, U. Selvaraj, A.S. Bhalla, L.E. Cross, and R. Roy, J. Mater. Sci. (in press, 1994).
- ²² S. Haussühl and D. Mateika, Crystal. Res. Technol. 26(4) 481 (1991).
- ²³ D. Mateika, H. Kohler, H. Laudan and E. Völkel, J. Cryst. Growth 109 447 (1991).
- ²⁴ R.D. Shannon and C.T. Prewitt, Acta Cryst. **B25** (1969) 925; Acta Cryst. **B26** 1046 (1970).
- ²⁵ P. Ravindranathan and A.S. Bhalla *et al.* (to be published).
- ²⁶ G. Harshe, A.S. Bhalla, and L.E. Cross, *Materials Letters* 18(4), 173 (1994).
- ²⁷ S. Erdei, L.E. Cross, F.W. Ainger, and A.S. Bhalla, J. Cryst. Growth 139, 54 (1994).
- ²⁸ R. Guo and A.S. Bhalla (to be published).