

Preparation and Characterisation of High Density, High Purity Lanthanum Aluminate Bulk Ceramics

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Abstract. In this work some methods for preparation of lanthanum aluminate bulk ceramics were compared. High purity lanthanum aluminate LaAlO₃ (LAO) ceramic samples of high density (>94%) were prepared via three different routes and the morphology, chemical and electrical properties of the samples were investigated. For high purity samples a sol-gel route A. Douy and P. Odier [1] and a thermal nitrate decomposition route Shaji Kumar et al. [2] were introduced to reduce unintentional doping by the preparation process to a minimum. As a standard route the mixed oxide process was chosen. In sol-gel and nitrate decomposition procedures the formation temperature of LaAlO₃ from its oxides was lowered by using reactive γ -alumina from the pyrolysis of initial aluminium nitrate instead of commonly used α -alumina (corundum) in the mixed oxide process. No commercial γ -alumina of sufficient purity is known.

Differences in the electrical behaviour of the samples were measured, indicating some correlations between the samples' different morphology, purity and its' preparation parameters.

Keywords: lanthanum aluminate, ceramics preparation, electrical properties

Introduction

Lanthanum aluminate LaAlO₃ (LAO) has received much attention due to its promising use as filter material in microwave applications [3] and substrate for high temperature super conductor (HTSL) thin films [4]. In fact single crystalline LAO of a relative permittivity of about 24 [5, 6] shows favourable electric, structural and thermal properties combined with high quality factors of the order 10^5 (10 GHz, 77 K) [7]. But preparation of single crystal LAO is an extremely demanding procedure, especially when single domain crystals are needed. Because of a second order phase transition of the LAO material at 500°C twinning occurs while cooling down the single crystal during its preparation process very easily.

The use of ceramic LAO samples instead of single crystals may provide the chance to reduce costs but with some compromise on quality factor, depending on the processing of those ceramics. Different LAO preparation routes are known widespreading from classical mixed oxide routes [8-10] to chemical approaches like sol-gel [11, 12] or decomposition methods [2, 13]. During the ceramic preparation processes listed milling provides an essential step. In case of the mixed oxide route milling effects an intensive mixing of La and Al-educt together, crushing large particles enhance interparticle diffusion and to receive a homogenous LAO powder after annealing the oxide mixture. In case of the chemical routes this feature is not necessary to be achieved by milling, because homogenisation is achieved by solvation. One feature of the milling step that concerns all three preparation routes is the powder deagglomeration during the ceramic processing.

Mixed oxide preparation provides the advantages of being an easy and inexpensive method. But there are some disadvantages. By grinding impurities are inserted into the ceramic powder the longer the milling process endures. Commonly a mixed oxide route needs high temperatures for LaAlO₃ formation caused by the use of fairly inert corundum as Al-donor. On the other side chemical preparation routes as mentioned above are more demanding. But their advantage is a procedure without need of intensive mechanical treatment

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for homogenisation of the ceramic powder that results in a higher powder purity.

For this reason we chose a thermal nitrate decomposition route of lanthanum and aluminium nitrates. The hydrates of those nitrates can be melted at low temperatures giving a homogenous salt mixture easily, so mechanical treatment as in a mixed oxide route is not necessary. Thermal decomposition of aluminium nitrate provides metastable γ -alumina being much more reactive than corundum, which reduces the sintering temperature of LaAlO₃. All reactions are performed in air. Moreover, lower temperatures have a larger potential to guide molecular scale parameters of the so prepared samples, i.e. grain size. Thus these features promised high purity LAO ceramics to produce easily. As a third method we chose a sol-gel synthesis for LAO preparation that also promised high purity.

In the passed years measurements were carried out to characterize the electrical properties of single crystalline LAO. Permittivity and loss tangent of single crystalline LAO are well known [7, 14, 15] today. But only few data are known about the electrical behaviour of LAO ceramics at time. McN Alford et al. comparative investigations between single crystals and polycrystalline LAO ceramics [16] show for polycrystalline ceramic samples always higher losses than for single crystals. But this difference can be very small. They both exhibit quasi-Debye losses indicating extrinsic loss mechanisms. However, attempts failed to isolate the influence of extrinsic origins like impurities and grain boundaries from each other.

The present study was undertaken to prepare high pure grade LAO ceramics that allow us to separate these effects. Initially we report about the preparation route being used, followed by an structural, chemical and electrical characterisation of our ceramic samples.

Experimental Procedure

Preparation Procedures

Mixed Oxide Route. In this common procedure aluminium oxide (99.95%, metals basis, Alfa Aesar) and lanthanum oxide (99.9%, metals basis, Alfa Aesar) were weighted and mixed together in a 1:1 molar ratio. Adding Isopropanol and zirconia balls the powders were mixed for 6 h. The mixture was transferred into

a corundum crucible and annealed at 1370° C for 12 h in air. The annealed powder was ground in an agate mortar down to <200 μ m particle size and milled in an additional step with a zirconia ball mill for 6 h down to a mean partice size of about 1 μ m. The powder then was pressed isostatically at 4000 bar and sintered at 1520°C for 12 h forming ceramic samples of 99,8% density. Samples prepared by this method will be denoted with the index **M**.

Nitrate Decomposition Route. Hydrates of the nitrates of aluminium and lanthanum Al(NO₃)₃·9H₂O (99.999%, Alfa Aesar) and La(NO₃)₃.6H₂O (99.99%, Alfa Aesar) were mixed in a stoichiometric amount of 1:1. The mixture was heated to 95°C for half an hour and stirred to become a clear colourless salt solution of its hydrate water. The solution then was quenched in an ice bath. The resulting melt was crushed and dried in vacuum over phosphoric anhydride for 5 days. By this treatment we got a white dry powder, we heated it in a special designed furnace up to 850°C passing two intermediary temperature steps at 200°C and 350°C of 1.5 h period at a time. Pyrolysis was observed accompanied by the formation of nitrous fumes. Chemical analysis indicates a negligible amount of nitrogen in the sample after pyrolysis. According to DSC spectra (Fig. 1) the combustion of the nitrates occurs at 390°C and 514°C. A LAO phase is formed at 910°C. The peak shown at 1020°C indicates the formation of α -Al₂O₃ corundum from the thermodynamic metastable γ -Al₂O₃ phase as



Fig. 1. DSC analysis of nitrate decomposition route pyrolysis, 910°C LAO formation, 1020°C corundum phase transformation.

side reaction. Experiments conducted at temperatures below 1100°C gave only low LAO content products due to the diffusion controlled LAO formation competing with the formation of corundum. Therefore a long time annealing step at temperatures over 1100°C following the pyrolysis step was added. After cooling to room temperature the resulting oxide mixture from the pyrolysis was annealed in a corundum crucible at 1200°C in air for 20 h. A dry ivory coloured powder was obtained that was carefully milled in a zirconia ball mill with isopropanol and dried at 80°C for 20 h. Ceramic samples then were formed by pressing the LAO powder isostatically at 4000 bar and sintering the green body at 1450°C for 15 h, receiving a white ceramic body of 94.2% to 98.2% density. Samples prepared by this method will be named with the index N.

Sol-Gel Route. Initially an aqueous 1:1 sol mixture of aluminium nitrate hydrate Al(NO₃)₃·9H₂O (99.999%, Alfa Aesar) and lanthanum nitrate hydrate La(NO₃)₃·6H₂O (99.99%, Alfa Aesar) was prepared as described in [1]. For complexing the cations citric acid as a chelating agens was added, improving the stability of the solutions. Then the pH was raised to neutralisation by addition of 25% ammoniasolution (Aldrich). After adding the organic monomers, acrylic acid amide (Aldrich), N,N'-methylene-bis-(acrylic acid amide) (Aldrich) and a catalyst, a,a'-azoiso-butyronitrile (Aldrich), the polymerisation was initiated by heating. To remove the organic compounds the resulting gel was pyrolized at 1000°C for 5 h remaining a fluffy greyish powder, which was transferred into a corundum crucible and annealed at 1200°C for 20 h in air. After this treatment a dry pink-ivory coloured powder was obtained and carefully milled with isopropanol in a zirconia ball mill and dried at 80°C for some hours. The dried powder then was pressed isostatically at 4000 bar and sintered at 1500°C for 15 h giving white ceramic samples of 95.2% to 97.2% density. Samples made by this method will be denoted with the index S.

Characterisation

Different methods including SEM, XRD, BSE and chemical analysis via ICP-OES were used to characterise the prepared powders as well as the ceramic samples chemical consistency and morphology. XRD spectra were made with an Phillips Xpert XRD spectrometer. SEM and BSE measurements were conducted on the ceramic samples using a Zeiss Gemini electron microscope applied with a back scattering electron detector from Oxford. SEM pictures of the ceramic samples show the polished samples surface. Also some pictures were made from freshly broken unpolished samples for an inside view. All BSE experiments were made on untreated samples splits for a phase distribution analysis.

The ceramic samples density was measured by an archimedes type densimeter.

For electrical characterisation Ceramic LAO samples of each preparation process described above and of cylindrical shape of average diameter 11 mm and average height 7.5 mm were inserted into a cylindrical, gold plated copper cavity on a poly-tetra-fluorine-ethylene (PTFE) spacer (Table 3). Transmission and reflection measurements were performed with a Hewlett-Packard 8722ES network analyzer using the $TE_{01\delta}$ dielectric resonator mode. For the circular symmetric $TE_{01\delta}$ mode the electric field is directed perpendicular to its c-axis aligned with cylinder axis mostly within the sample. This allows us to measure the in-plane dielectric properties $\varepsilon_{r,a,b}$ and tan $\delta_{a,b}$. Since ceramics are isotropic and single crystalline LAO's anisotropy of the dielectric permittivity is very small [14], we considered the permittivity of our samples to be isotropic.

Resonance frequency v_{res} and samples loss Q_{sample} were measured in the temperature range of 7 K to 300 K for various ceramic samples. For experimental data correction the cavity wall contribution R_S/G to the Q-factor and the samples filling factor κ_s was calculated using the finite element software MAFIA.

$$\frac{1}{Q_0} = \sum_i \kappa_i \frac{1}{Q_i} + \sum_{\text{surface}} \frac{R_S}{G}; \quad i = \text{sample, spacer}$$
(1)

with Q_0 = unloaded Quality factor; R_S = wall resistance (copper)

Powder Characterisation. The powders XRD spectra corroborate well with the spectrum of pure lanthanum aluminate [17] as depicted in Fig. 2 indicating the pure LAO phase in our samples. All the samples show some additional minor peak at $2\theta = 30^{\circ}$ correspondent to an La(OH)₃ excess due to inaccuracies while weighting the educts during preparation. Besides it is not unambiguous to derive this effect to intermediary La(OH)₃ as hydrolysis product due to the sensitivity of LAO to air humidity.



Fig. 2. XRD spectra of prepared LAO powders and reference spectrum (a): mixed oxide route (b): nitrate decomposition and (c): sol-gel.

By ICP-OES chemical analysis some differences of the powders purity were observed correlated to the preparation route. As shown in Table 1 the mixed oxide powders measured Zr content is ten times higher than the nitrate decomposition or the sol-gel powders

Table 1. Particle size and impurity level (ICP-OES) of prepared LAO powders

Powder sample	Mixed oxide	Nitrate dec.	Sol-gel
Particle size [nm]	-	200–300	200–300
La:Al-ratio	0.99	1.02	1.02
Zr content	>0.02%	<0.003%	<0.003%

due to a rub off of the milling balls during the milling process. By using the sol-gel and nitrate decomposition route this effect was reduced not only by the different milling time but also by the introduction of intermediary γ -Al₂O₃ instead of corundum as Al supplier of the mixed oxide route.

The SEM pictures show morphological differences of the sample powders that affects ceramic samples properties described later. Due to the preparation route dependent content of organic compounds and water, more or less porous products are obtained. As seen in picture 3(a) and (b) nitrate decomposition gives a dense powder of about 200-300 nm particle size but of inconsistent shape. However milling is necessary to destroy agglomerates of the nitrate route powder (Fig. 3(a)-(c)). The sol-gel powder shows leaf like porous structures (Fig. 4(a) and (b)) due to elimination of huge amounts of organic compounds and water during gel-pyrolysis. Milling destroys these structures leaving a fluffy powder of 200-300 nm particles of uniform shape but some reagglomeration after drying the powder still is a problem (Fig. 4(c)).

Ceramic Sample Characterisation. For all samples the density exceeded 94%, the ceramic bodies were between uniform white to ivory colour. Via mixed oxide route a sample density of 99.8% was achieved. The nitrate decomposition and sol-gel methods gave ceramic samples of up to 98.2% density.

In confirmation to the experimental density data SEM analysis of the prepared ceramic samples present dense surfaces. Surprisingly, experimental data suggest that the grain size of the ceramic samples is not correlated with the powders particle size. For all samples the grain size was found to be between 2 μ m and 5.5 μ m (Figs. 5–7). On the samples surface no voids and cracks between neighbouring grains were found, even not in the grains itself (Figs. 5(b), 6(b) and 7(b)). To take a look inside the ceramic bodies one of each preparation routes sample was broken. In contrast to the M samples inner surface the S and N inner surfaces show some holes and a grainy surface



Fig. 3. SEM pictures of nitrate decomposition powder processing at different resolutions; (a): powder after pyrolysis and (b) and (c): powder after milling.



Fig. 4. SEM pictures of sol-gel powder after pyrolysis at different resolutions; (a) and (b): powder after pyrolysis and (c): powder after milling.



Fig. 5. SEM pictures of a ceramic *M* sample ($\delta = 99.8\%$) at different resolutions, polished surface (a) and (b), inner surface (c).

(Figs. 5(c), 6(c) and 7(c)). This gives evidence of a less strong structure of the S and N ceramics than of the M ceramic.

XRD spectra of the ceramic samples as well as the prepared LAO powders corroborate well with literature data (Fig. 8). X-ray spectra of the prepared LAO powder indicate LaAlO₃ as major phase. No significant

differences in the samples spectra of the three different preparation routes were found. Within an 2% error these results indicate LAO as major component in all cases.

For BSE measurements we broke one ceramic sample of each preparation route and observed the fresh surface of the break. The BSE pictures indicate



Fig. 6. SEM pictures of a ceramic N sample ($\delta = 94.9\%$) at different resolutions, polished surface (a) and (b), break (c).



Fig. 7. SEM pictures of a ceramic S sample ($\delta = 95.2\%$) at different resolutions, polished surface (a) and (b), inner surface (c).

phase homogeneity and a uniform distribution of La and Al on all the samples surfaces, rejecting second phases like corundum (Al_2O_3), $LaAl_{11}O_{18}$ or La_2O_3 . (Fig. 9).

Samples chemical characterisation given by ICP-OES measurements correspond with the XRD results. An Al:La-ratio of 1:1 of all samples was found within an 2% error range (Table 1).

Electrical Characterisation of the Ceramic Samples. The obtained resonance frequencies were situated at 4.3–5.8 GHz at room temperature, decreasing monotonously with temperature. For all samples of different preparation routes the temperature dependencies of v_{res} exhibit the same shape. A correlation be-

Table 2. Grain size and density of prepared LAO ceramic samples

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Ceramic sample	М	Ν	S	
Grain size [µm] Density [%]	2–5.5 99.8	2–5.5 94.2–98.2	2–5.5 95.2–97.2	

tween the preparation method and the resonance frequencies temperature dependence could not be found (Fig. 10).

However, some differences were observed in the temperature dependencies of the Q_{sample} values. Experimental data suggest a large impact of the preparation process on the quality of the produced ceramics. For the mixed oxide samples the quality behaviour versus temperature exhibits an overlapped curve with the smallest quality value of 6750 at RT but 30650 at

Table 3. Geometrical data, quality Q_{sample} and resonance frequency v_{res} of electrically characterized ceramic LAO samples

Sample	М	Ν	S	
Diameter (mm)	11.5	11.0	11.5	
Height (mm)	5.9	7.5	7.7	
$\rho(\%)$	99.8	94.9	95.2	
vres.RT (MHz)	5612	5694	5520	
$v_{res,10}$ K (MHz)	5664	5745	5574	
Q _{sample.RT}	6750	12120	5320	
Q _{sample,10} K	30650	25850	22140	



Fig. 8. XRD spectra of prepared LAO ceramics and reference spectrum (a): mixed oxide route (b): nitrate decomposition and (c): solgel.

10 K. In contrast to the other preparation routes the M samples curve exhibits a steep decrease at 50 K to 75 K (Fig. 11) indicating extrinsic loss contributions in that temperature regime. Between 100 K and RT the M samples quality factor does not change significantly.

Two broad minima at 120 K and at 250 K are detected corresponding with many loss contributions.

Experimental Q_{sample} -curves of the S and N samples exhibit different behaviour. Both samples show quality values of more than 22000 at 10 K but their Q_{sample} curves decrease more constantly across the whole temperature range measured.

A step around 40 K in the temperature dependence of the N samples quality factor indicates some extrinsic loss contributions. But compared to the large extrinsic contribution the M samples quality behaviour shows below 75 K this small step exhibits only a minor influence of extrinsic loss processes on the N samples quality factor at low temperatures. Above 50 K to room temperature the N samples quality decreases merely following a straight line indicating intrinsic losses as dominating contribution. It should be mentioned that at RT the N samples exhibits a quality factor of 12120 that is compared to the other samples quality factor at that temperature surprisingly high.

Over a large temperature regime the experimental S samples Q_{sample} -curve resembles more the N than the M samples curve by magnitude. These experimental data suggest some loss contributions similar to the N samples. But the some differences the S Q_{sample}-curve show should also be mentioned. In the low temperature regime the temperature dependence of the quality factor shows no step but decreases continuously. Between 70 K and 150 K the S samples quality factor keeps almost constant in temperature, in contrast to the decrease the N samples Q_{sample}-curve shows. Above 150 K the quality factor again decreases with nearly constant steepness. With Qsample-values of 22140 at 10 K and 5320 RT the S sample shows the lowest quality factor of all. These differences suggest some additional loss contributions of the S sample compared to the N sample, especially at temperatures of 150 K and above. However experimental data are not sufficient to reveal more detail about the physical nature of these additional loss contributions.

Results and Discussion

Using the three preparation routes described in the previous sections LAO powders and ceramics of a variety of densities and purity levels were fabricated. Both the powders and ceramics XRD spectra indicate pure LAO as main phase within an 2% error. No significant difference between the powder samples spectra and



Fig. 9. BSE pictures of ceramic samples (a) mixed oxide (b) nitrate decomposition route and (c) sol-gel route.



Fig. 10. Ceramic samples resonance frequency ν_{res} versus temperature T.

the ceramics spectra were detected, which means that no recrystalisation process from the LAO back to the educts during the ceramic firing occurs. A uniformly LAO phase distribution confirmed by BSE data also indicates that in all preparation routes a complete conversion of the educts to LAO took place as desired. Some minor peaks in the XRD spectra were attributed to La(OH)₃ from an La-excess due to inaccuracies while weighting the educts during preparation. These peaks also may be correlated with La(OH)₃ located at the ceramics surface as hydrolysis product due to the sensitivity of LAO to air humidity.

Compared to the mixed oxide method the two chemical preparation routes nitrate decomposition and solgel give ceramic samples of strongly reduced Zr content due to the lack of extensive milling of α -Al₂O₃ corundum containing educt mixtures of high Mohs hardness. But this advantage is compromised by a lower ceram-



Fig. 11. Ceramic samples quality Qsample temperature dependencies.

ics density and an increased La:Al-ratio inaccuracy. An explanation for the reduced density of the chemical route ceramics is given by the morphology of its powders described above. Some agglomeration and the larger variation of particle sizes of the "soft" nitrate decomposition and sol-gel powders leads to an increased inner porosity of the resulting ceramics in contrast to the "hard", intensely milled corundum powder of the mixed oxide process resulting more dense ceramic bodies due to less agglomerated ceramic powders of uniform particle size. Moreover experimental data suggest that the sol-gel process and the nitrate decomposition route gives more porous ceramic samples due to the larger amount of organic compounds and water to remove during powder processing. The decreased La:Al-accuracy is mainly due to some indefinite water content of the nitrate-hydrate educts, especially when these salts were stored for a longer time. Unfortunately La(NO₃)₃·6H₂O and in particular Al(NO₃)₃·9H₂O are required to prepare a melt (nitrate decomposition route) and a stable, pH controlled solution (sol-gel route) for sample homogenisation. Here the sol-gel process provides more variety concerning the choice of educts than the nitrate route.

Taking a high quality factor as primary feature of a ceramic in this work the chemical preparation routes described outperform the common mixed oxide process because the measured S and N samples Q-values are much higher than M samples. Remarkably in this connection it is that the M sample features the highest density and lowest structural defect rate of all samples measured but also the highest impurity level. Since both extrinsic effects, structural defects and impurities, are supposed to contribute to one samples loss the experimental data suggest that the impurity level seems of major influence on the ceramics quality factor and structural defects play a minor role at least at higher temperatures.

It should be mentioned that single crystalline LAO samples measured by Zuccaro [7] exhibit quality factors higher by two or three times at RT and one magnitude at 10 K than the polycrystalline samples of this work. So the absolute values of the experimental quality data presented here should be considered with care.

Until now, no enough data are collected to take a closer look inside or even identify the loss behaviour of the LAO ceramics material. But by comparison of the shape of the ceramics quality-temperature dependence presented here with the single crystals Q(T)-dependence being presented in previous works [7, 18, 19] some preliminary hypothesis should be allowed.

Since the single crystals low temperature peak described by Zuccaro [7] may be related to an impact of some extrinsic loss mechanisms it is supposed that also the low temperature steps of the ceramic samples M and N described above are related to extrinsic loss too. Such behaviour can not be fully explained by the intrinsic phonon processes [19] but impurities from the milling steps and grain boundary effects may give a contribution by means of some defect dipole relaxation processes [7, 18]. Further examinations are needed and already planned to provide a closer look. At higher temperatures the N ceramics and within some range the S ceramics quality temperature behaviour resembles that of the single crystal by an overlapped shape but of much lower absolute value. Consequently, the experimental curves provide no indication on one single extrinsic defect dipole loss contribution as they do in the low temperature regime but it seems not unambiguous that there are several effects additional to intrinsic phonon processes that contribute to the samples quality factor. In comparison with the single crystal, the ceramics experimental Q-values give rise that some extrinsic losses provide the samples quality factor also at higher temperatures. In this context the steep quality decrease of the S-samples above 160 K was considered to be a superposition of some extrinsic effects. Future experiments should give a more detailed insight.

Summary

Ceramic lanthanum aluminate (LAO) samples have been produced by three different preparation routes, mixed oxide, nitrate decomposition and sol-gel. Chemical routes, nitrate decomposition and a sol-gel processing, were shown to provide high pure ceramic samples of sufficient density and of moderate to high quality factor at higher temperatures. In the mixed oxide route a good powder homogeneity compromised an increased impurity level. So common mixed oxide processing provided high density ceramic samples but of lower quality factor at higher temperatures. The advantage by the sol-gel and nitrate route is the homogeneity of its powder without intensive milling, but resulting ceramics provide an increased porosity and a weaker structure due to powder agglomeration and increased variation of particle size. Those ceramic samples were found to be of less density than mixed oxide ceramics but surprisingly exhibit lower dielectric loss at microwave frequencies except at very low temperature, where a freeze out of most extrinsic loss contributions is expected. Electrical investigations on our LAO samples give evidence that in case of the mixed oxide route sample extrinsic loss effects attributed to impurities are of major influence on samples quality than loss contributions of structural origin. In contrast the chemical route samples quality is supposed to be governed by structural defects increasing intrinsic phonon processes over the whole temperature range.

For all samples described experimental data suggest intrinsic and extrinsic loss mechanisms coexisting to contribute to the samples quality, but of different magnitude correlated to the preparation process. Further experiments shall provide a closer look how doping affects the quality and loss behaviour of the ceramic material in detail. Also chemical route preparation methods should be modified to obtain a better particle size control for ceramics of increased density.

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References

- 1. A. Douy and P. Odier, Mat. Res. Bull., 24, 1119 (1989).
- M.D. Shaji Kumar, T.M. Srinivasan, C. Subramanian and P. Ramasamy, *Ceramics International*, 23, 419 (1997).
- N. Klein, A. Scholen, N. Tellmann, C. Zuccaro and K. Urban, IEEE Trans. Microwave Theory Tech., 44, 1369 (1996).
- G. Müller, B. Aschermann, H. Chaloupka, W. Diete, M. Getta, B. Gurzinski, M. Hein, M. Jeck, T. Kaiser, S. Kolesov, H. Piel, H. Schlick and R. Theisejans, *IEEE Trans. Appl. Supercond.*, 4, 143 (1994).
- 5. G.A. Samara, J. Appl. Phys., 68, 4214 (1990).
- T. Tonaka, M. Sato, H. Asano and S. Kubo, *J. Supercond.*, 4, 283 (1991).

- C. Zuccaro, M. Winter, N. Klein and K. Urban, J. Appl. Phys., 82, 5695 (1997).
- V.A. Presnov, M.A. Rubashov, M.P. Yakubenya, V.V. Strganov and O.M. Ivleva, C.A., 61, 5171(1964).
- I.A. Bonder and N.V. Vinogradona, Bull. Acad. Sci. USSR., 5, 785 (1964).
- T.A. Vanderah, C.K. Lowe-Ma and D.R. Gagnon, J. Am. Ceram. Soc., 77, 3125 (1994).
- Jae-Myong Jung and Seung-Bin Park, J. Mat. Sci. Letters, 15, 2012 (1996).
- 12. P. Peshev and V. Slavova, Mat. Res. Bull., 29, 255 (1994).
- 13. A.K. Adak and P. Pramanik, Mat. Letters, 30, 269 (1997).
- J. Krupka, R.G. Geyer, M. Kuhn and J.H. Hinken, *IEEE Trans.* Microwave Theory Tech., 42, 1886 (1994).
- Yu.G. Makeev, A.P. Motornenko, N.T. Cherpak, I.P. Babijchuk and M.B. Kosmyna, *Tech. Phys. Letters*, 28, 221 (2002).
- N. McN Alford, J. Breeze, X. Wang, S.J. Penn, S. Dalla, S.J. Webb, N. Ljepojevic and X. Aupi, *J. European Ceram. Soc.*, 21, 2605 (2001).
- 17. JCPDS
- C. Zuccaro, Mikrowellenabsorption in Dielektrika und Hochtemperatursupraleitern f
 ür Resonatoren hoher G
 üte, (Ph.D. Thesis, RWTH Aachen, 1999).
- V.L. Gurevich, A.K. Tagantsev, Advances in Physics, 40, 719 (1991).