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SHORT COMMUNICATION

NEW COMPLEX CERAMIC MATERIALS FOR MICROWAVE RESONATORS

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Dielectric materials based on the $BaTiO_3$ and $MgTiO_3$ with different dopants substituting Ba and Mg have been investigated. The influence of small additions on the microwave characteristic has been studied. The dielectric properties of the examined materials with partially replaced metal atoms (Ba or Mg) or Ti atoms has been determined. The influence of substitutes has been discussed in terms of discovering new material with optimal dielectric characteristics.

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Dielectrics like $BaTiO_3$ and $Ba_2Ti_9O_{20}$ are well known “classical materials” used for microwave resonators. They are used in microstrip design for frequency stabilization in microwave oscillators, filters, antenna devices, etc. They are most widely-used dielectrics. Moreover, considerable efforts have been directed towards improving their properties [1-3]. It is well known that materials like $Ba_2Ti_9O_{20}$ and $BaTi_4O_9$ made it possible to produce resonators with a quality factor Q of 3000-4000. Using materials like $(Ti, Zr)O_4$ and $(Zr, Sn)TiO_4$ it is possible to increase Q too [4, 5].

Dielectrics with exceptionally high Q values for microwave resonators have been synthesized on the base of some complex materials from the group of pseudo perovskites with formula:

$$Ba(M^{2+}Me^{5+})O_3\ ,\ M=Zn^{2+},\ Ni^{2+},\ Co^{2+},\ Ca^{2+},\ Me=Ta^{5+},\ Nb^{5+}$$

There are classic ferroelectrics, where Ti^{4+} is completely or partially substituted by the combination $M^{2+}Me^{5+}$ or $(M^{2+}Me^{5+})_{1-x}Zr^{4+}{}_x$ with an average of +4. These materials possess high dielectric constant and high Q values [6-8].

Dielectrics of $MgTiO_3$-$CaTiO_3$ system are of a particular interest due to their considerably low price and simple preparation technology. They possess high a quality factor (8000–10 000) which is comparable with that of the materials of $Ba(M^{2+}, Ta^{5+})O_3$ and $Ba(M^{2+}, Nb^{5+})_3$ type. The present scientific interest is directed toward the investigation of various compositions (substitution of elements) and improving their properties.

The aim of paper is to present and discuss the results of an investigation of the dependence of the dielectric properties of different ceramics on their composition.

High purity (99.9%) Mg, Ti, Nd, Ce, Zn and Zr oxides and Ca, Ba and Sr carbonates were used in the form of powders as starting materials. Milling and homogenization were carried out in a

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planet agate ball mill Fritsch for more than 6 h using distilled water as wetting agent. The mixtures were presintered in alundum crucibles in a muffle furnace at high temperatures (> 1200 °C) for about 3 h. The dried powder was mixed with polyvinyl alcohol serving as an organic plasticizer. The fraction was used to press pellets with a diameter of 5 to 10 mm and a thickness of 2 to 7 mm at a constant pressure of 2 tons/cm^2.

The microwave parameters (i.e. quality factor Q and dielectric constant ε) were measured by the resonance method in a test structure without losses using a sweep generator and a Hewlett-Packard amplitude frequency meter. Some of the compositions were studied by electron-microscope analysis on a Philips EM-400 apparatus at 80 kV by using the two-step replica method.

Fig. 1 presents the dependencies of the dielectric constant ε and the Q-factor on the Ti/Ba ratio. It may be seen that ε increases with an increase in the titanium content as represented by the Ti/Ba ratio.

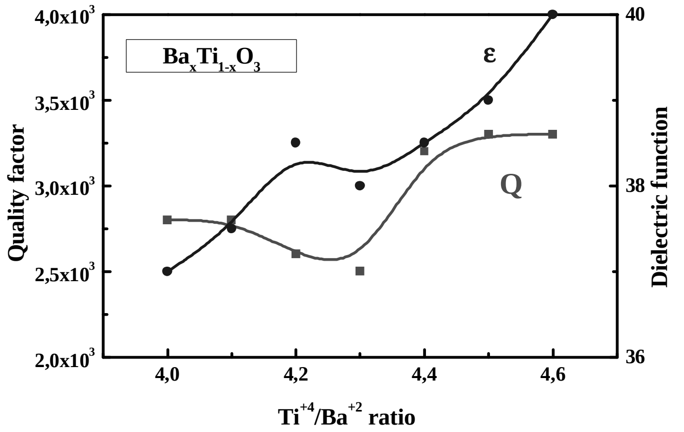

Fig. 1. Plots of quality factor Q and dielectric function ε against Ti/Ba ratio, measured at 9.9-10.1 GHz.

The dependence of Q-factor on Ti/Ba ratio does not change in a regular manner. In general, the values of Q for Ti/Ba > 4.4 are higher than those for Ti/Ba < 4.4. The data for Q measured in the 9.9–10.1 GHz range differ negligibly from those presented in ref. [1] at 9.8 GHz. A comparison of these data with those reported in ref. [10] is not possible since the measurements in ref. [10] were performed at a considerably lower frequency (4 GHz). A sharp drop in Q values at Ti/Ba = 4.3 is observed. The dependence of ε on Ti/Ba ratio is also regular.

The increase in ε with Ti/Ba ratio is probably due to the increase of the Ti^{4+} polarization in the perovskite structure. The change in Q with Ti/Ba ratio may be attributed to structural reconstruction, which occurs at Ti/Ba > 4.3 as a result of replacement of $BaTi_4O_9$ phase by $Ba_2Ti_9O_{20}$ phase.

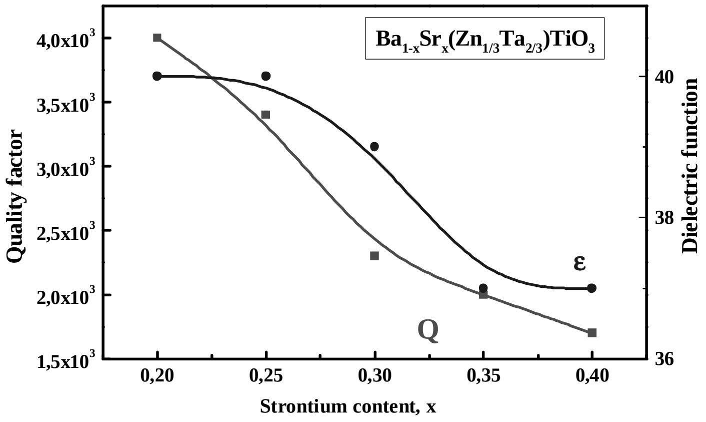

Fig. 2. Plots of the dependencies of quality factor Q and dielectric function ε on strontium content (measurements at 8 GHz).

Fig. 2 illustrates the dependencies of Q and ε on Ba content for constant Ti concentration. It may be seen from the figure that the Q values of perovskites, in which part of Ba content is substituted by Sr, is lower and decreases with Sr concentration x when Ti concentration is constant. Moreover, the decrease in Q roughly linearly decreases with an increase in Sr concentration. The trend of the dependence of ε on Sr content is similar to that of the plot of Q against Sr content. Obviously, addition of strontium leads to a worsening of the dielectric properties of the material. Dielectrics with partially substituted Ba atoms (x = 0.2-0.3) show better characteristics.

Fig. 3 presents the dependence of the dielectric constant ε and quality factor Q values on the composition of $Mg_{1-x}Ca_xTiO_3$ system. The value of the dielectric constant ε changes with Ca content x and follows the quadratic relation: $\varepsilon = A + B_1x + B_2x^2$ (where A, B_1 and B_2 are constants). The value for ε of $MgTiO_3$ is 16 and that of $CaTiO_3$ are 150.

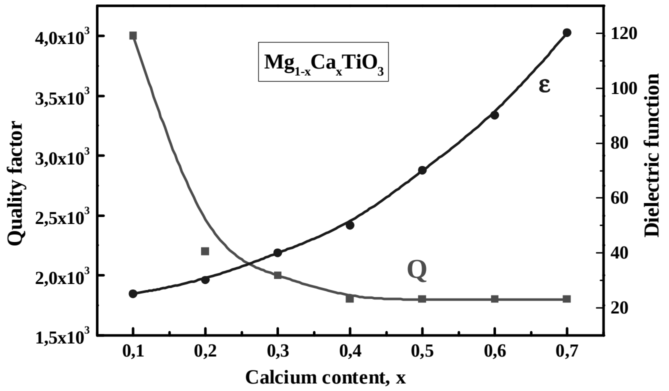

Fig. 3. Quality factor Q and dielectric function ε versus calcium content x (measured at 6-11 GHz).

The Q values steeply decrease for $x > 0.1$. The behavior of $Q(x)$ plot is exponential: $Q = Q_0 + K\exp(x/t)$, where Q_0, K and t are constants. This effect is most likely related to the increased share of $CaTiO_3$, which as well-known has considerably larger losses than $MgTiO_3$. Hence, above a certain amount of $CaTiO_3$, introduced in the system the losses strongly increase. At x = 0.1 (i.e. for $Mg_{0.9}Ca_{0.1}TiO_3$) the material obtained exhibits good parameters: ε = 23 and Q = 1800.

In $Mg_{0.8}Ca_{0.2}Ce_xTi_{1-x}O_3$ system the maximum of the dielectric constant corresponds to the minimum of the Q values (Fig. 4). Two maximum-minimum pairs are observed in the investigated concentration range. There is a well-defined maximum in $Q(x)$ plot at x = 0.1. It is suggested that this maximum is most likely due to some oxidation-reduction process occurring in the system as well as to the optimal grain size. The oxidation-reduction process during the solid state reaction proceeds most likely in the direction of electron compensation. Thus, from the results presented above it may be concluded that the addition of new substitutes and complexity of the composition lead to an increase in the dielectric characteristics to infinity.

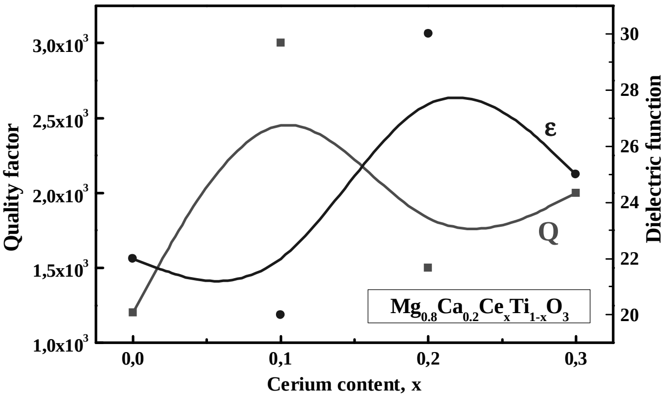

Fig. 4. Quality factor Q and dielectric function ε versus cerium content x (measured at 10-11.9 GHz).

The dependence of the dielectric constant *ε* and the *Q* value on neodymium content *x* in the $Mg(Ca_{1.7}Nd_{0.2})_xTi_{1-x}O_3$ system is presented in Fig. 5. The maximum in the values of *Q* corresponds to the minimum in *ε* values. The considerably higher value of Q is probably due to the increased density and the maximum deviation from the electron equilibrium.

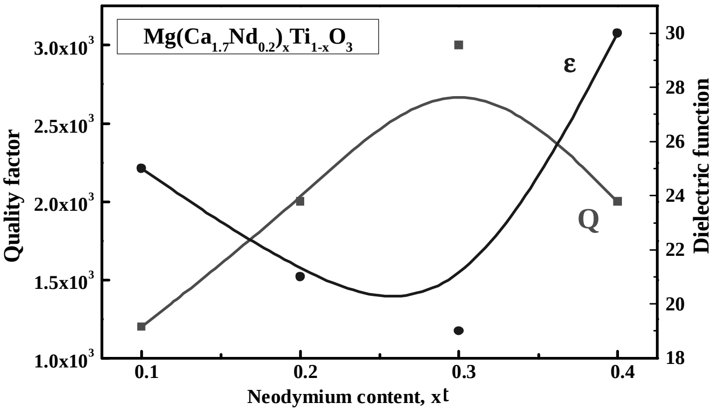

Fig. 5. Quality factor and dielectric function vs. neodymium content (measured at 10-11.9 GHz).

In general, the dependencies of *Q* and *ε* on Ti content are similar for $MgMTiO_3$ systems (M = Ca, Ce or Nd). At constant Ti concentration, the Q values depend on the concentration of M and Mg. At constant Mg content, a decrease in the Q value is associated with an increase in Ti concentration.

Ferroelectrics from the systems $BaTiO_3$ and $MgTiO_3$ with different compositions have been investigated. The values of dielectric characteristics (quality factor and dielectric constant) were measured as a function of composition. By substituting Ba and Mg with new metal atoms one can produce materials for microwave resonators with better characteristics and lower price of production.

References

[1] D. Hennings, P. Schnable, Phil. J. Res. **38**, 295, (1983).
[2] C. Tsironis, Electron Letters **18**, 741, (1983).
[3] C. Tsironis, IEEE MTT **33**, 310, (1985).
[4] K. Wakino, H. Tamura, T. Konoike, Y. Sakabe, K. Wakino, J. Amer. Ceram. Soc. **67**, C-59, (1984).
[5] J. Plourde, IEEE MTT **29**, 754, (1981).
[6] K. Wakino, J. Amer. Soc. **69**, 34, (1986).
[7] K. Sasazawa, N. Yamaoka, Jap. J. Appl. Phys. **24**, 124, (1985).
[8] K. Matsumoto, T. Miuga, K. Tanaka, H. Ichimura, Proc. IEEE International Symposium on Applications of ferroelectrics Digest **6**, 118, (1986).
[9] H. Bryan, J. Amer. Ceram. Soc. **57**, 522, (1974).
[10] P. Kell, J. Amer. Ceram. Soc. **57**, 352, (1973).