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# All-ceramic lead-free percolative composite with a colossal dielectric response

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## Abstract

All-ceramic lead-free percolative composite, comprising $RuO_2$ with high electrical conductivity denoted as the conductive phase and ferroelectric (K, Na)$NbO_3$ ceramics, was developed. Structural analysis revealed a uniform distribution of conductive ceramic grains within the ceramic matrix. Consequently, the dielectric response in the (K, Na)$NbO_3$–$RuO_2$ composite follows the predictions of the percolation theory. Thus, close to the percolation point exceptionally high values of the dielectric constant were obtained—values as high as 20,000 were detected at room temperature at 1 kHz. Fit of the data, obtained for samples of different compositions, revealed critical exponent and percolation point, which reasonably agree with the theoretically predicted values.

*Keywords:* Dielectric properties; Composites; Perovskites

## 1. Introduction

The theory of percolation in general explains a physical process in which a macroscopic magnitude is strongly modified as a result of small microscopic changes in connectivity.[1] One such process is the anomalous behaviour of a metal–insulator composite (a so-called percolative composite) near its percolation threshold, which is characterized by an abrupt discontinuity in the real part of the electrical conductivity.[2–4] Theory furthermore predicts that the dielectric constant of a composite comprising a conductive filler embedded in a dielectric matrix diverges at the percolation threshold, where the insulator–metal transition occurs.[2] The fact that the effective dielectric constant of the mixture is much larger than the dielectric constants of the individual constituents can intuitively be understood by a simple geometrical approach—close to the percolation point there are many conducting particles isolated by thin dielectric layers.

The development of high-dielectric-constant materials has in fact become one of the major scientific and technological issues, as the requirement for compact and low-cost systems, designed to control and store electrical charges, has increased substantially.[5,6] Such materials are highly desirable for use, not only as capacitor dielectrics, but also in a broad range of advanced electromechanical applications, such as actuators, sonars, and, particularly, as high-frequency transducers. The input electric energy that can be converted into strain energy is directly proportional to the dielectric constant of the electroactive material.[7] Thus, by increasing the dielectric constant the required electromechanical response can be induced under a much reduced electric field.

Very high dielectric constants can thus be achieved in metal–insulator composites close to the percolation point, however, up to now mainly organic percolative composites[8–11] and inorganic composites comprising metal particles dispersed in a dielectric matrix[12–17] have been developed. In organic percolative composites values of the dielectric constant as high as 7000 were obtained.[11] As the dielectric constant of a polymer is typically less than 100, i.e., far below the values of inorganic ferroelectrics, which reach several thousands, it is not surprising that the dielectric constant in percolative composites with an inorganic matrix can reach values as high as 80,000.[17]

Composites of ferroelectric ceramics and conductive ceramic particles could offer a major advantage in the development of high-dielectric-constant materials, as percolative systems comprising ceramics and metal particles are relatively sensitive to processing. The latter can be sintered in air only if a noble

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metal is used; however, if the conductive component is based on a non-noble metal, the system has to be fired in a neutral or reducing atmosphere. Such a procedure can negatively influence the electrical properties of ferroelectric ceramics, which are, due to the relatively high dielectric constant, very suitable for the matrix in a percolative system. For example, insulating ferroelectric $BaTiO_3$ or $Pb(Zr, Ti)O_3$ systems can, as a result of reduction, become semiconducting.[18] The combination of insulating and conducting ceramics is thus inherently better than the combination of oxide ceramics and metallic particles, as the all-oxide ceramic systems can be sintered in air. On the other hand, all-ceramic systems could suffer from reactions between both constituents during high-temperature sintering, resulting in new compounds or solid solutions with undesirable characteristics. The compatibility between the chosen ceramic matrix and the conductive ceramics must therefore be carefully evaluated.

After successful synthesis of the lead-based percolative system,[19] we report in this paper that exceptionally high dielectric constants were obtained by making use of the conductive percolative phenomenon also in all-ceramic composite made of lead-free conductive and ferroelectric systems—$K_{0.5}Na_{0.5}NbO_3$ was chosen as the matrix and $RuO_2$ as the conductive filler. These two systems have been selected as $RuO_2$ is a very good electrical conductor with a resistivity of $40 \times 10^{-8}$ Ωm[20,21] and as we found that there is no reaction between $K_{0.5}Na_{0.5}NbO_3$ and $RuO_2$ at temperatures even higher than 1000 °C.

## 2. Experimental

$K_{0.5}Na_{0.5}NbO_3$ (KNN) was prepared by solid-state synthesis from $K_2CO_3$ (99+%, Aldrich), $Na_2CO_3$ (99.95–100.05%, Alfa), and $Nb_2O_5$ (99.5%, Aldrich). A total of 2 wt.% of potassium–sodium germanate was added to lower the sintering-temperature of KNN. The powder mixtures were homogenized, calcined at 900 °C for 4 h and milled to yield submicron-sized powders. The phase composition was checked by X-ray powder diffraction using a Philips PW 1710 X-ray diffractometer with Cu Kα radiation. The X-ray spectra were measured from $2\Theta = 20°$ to $2\Theta = 70°$ KNN and $RuO_2$ (Alfa, 99.9%) were mixed in acetone in a ball mill. The powders were pressed into pellets and fired on platinum foils at 1000 °C for 2 h.

The fired KNN–$RuO_2$ samples were characterized using X-ray powder diffraction. A JEOL 5800 scanning electron microscope (SEM) equipped with a link ISIS 300 energy-dispersive X-ray analyzer (EDS) was used for the overall microstructural and compositional analyses. The samples prepared for the SEM were mounted in epoxy in a cross-sectional orientation and then polished using standard metallographic techniques. Prior to analysis in the SEM, the samples were coated with carbon to provide electrical conductivity and avoid charging effects. The microstructures of the polished samples were studied using back-scattered electron imaging and compositional contrast to distinguish between the phases that differ in density (average atomic number $Z$).

Samples having diameter of 5–6 mm with sputtered gold electrodes on both surfaces were used for dielectric measurements. The complex dielectric constant $\varepsilon^*(\nu,T) = \varepsilon' - i\varepsilon''$ was measured as a function of the frequency (20 Hz to 1 MHz) and temperature (heating and cooling rates of $\pm 0.5\,°C\,min^{-1}$) using an HP4284A precision LCR meter. The amplitude of the probing ac electric signal, applied to samples with a thickness of ≈3000 μm, was 1 V. The temperature was stabilized using a lock-in bridge technique with a Pt100 resistor as a thermometer. The real part of the complex ac-conductivity $\sigma^*(\nu,T) = \sigma' + i\sigma''$ was calculated via $\sigma' = 2\pi\nu\varepsilon_0\varepsilon''$ with $\varepsilon_0$ being the permittivity in vacuum.

## 3. Results and discussion

The microstructure of the KNN–$RuO_2$ composite with 15 vol.% of $RuO_2$ sintered at 1000 °C for 2 h is shown in Fig. 1. The grey KNN matrix consists of cubic-shaped grains; the light-grey inclusions are $RuO_2$ grains. The EDS microanalysis did not detect any solid solubility, which confirms the results obtained with X-ray analyses. The X-ray diffraction spectrum is presented in Fig. 2. The spectra of KNN and $RuO_2$ are added for comparison. It can be seen that only the peaks of the initial compounds are present in the fired sample. Furthermore, no shifts in the peaks' positions were observed. The results therefore indicate that KNN and $RuO_2$ are compatible at the firing temperature.

Structural analysis thus revealed a perfect percolative structure—there is no reaction and no solid solubility between constituents and the conductive filler is uniformly distributed throughout the matrix. Consequently, the dielectric response of the KNN–$RuO_2$ composite should follow the predictions of the percolation theory.

The frequency dependence of the room-temperature dielectric constant $\varepsilon'$ and conductivity $\sigma'$ in KNN–$RuO_2$ composites with different $RuO_2$ volume concentrations ($p$) is shown in Fig. 3. While at higher frequencies $\sigma'$ increases, at lower frequencies values tend toward the dc-conductivity plateau. Such a behaviour corresponds to an equivalent circuit composed of two $R$–$C$ circuits connected in serial. The resistivity of the low-

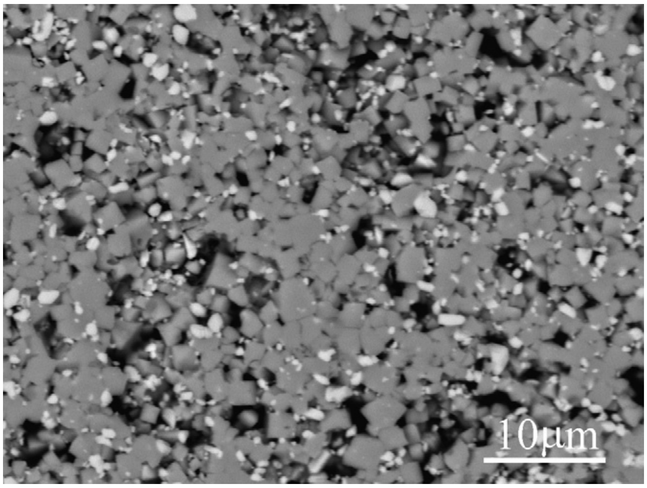

Fig. 1. Microstructure of the KNN–$RuO_2$ composite with 15 vol.% of $RuO_2$, sintered at 1000 °C. Light, conductive $RuO_2$ grains are uniformly dispersed in a grey, ferroelectric KNN matrix.

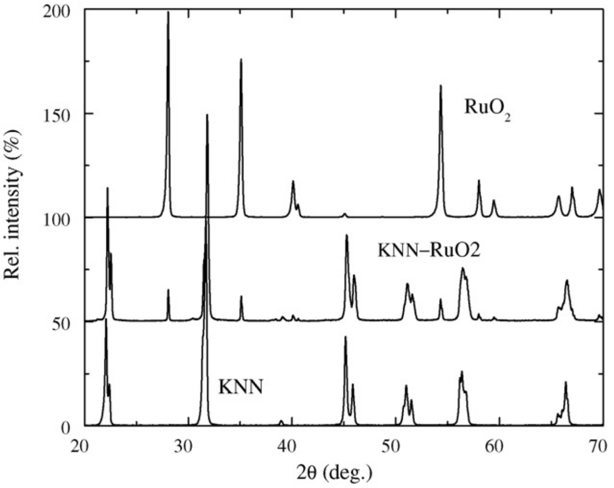

Fig. 2. X-ray diffraction spectrum of the KNN–$RuO_2$ composite with 20 vol.% of $RuO_2$, sintered at 1000 °C. The spectra of individual constituents are included.

frequency plateau is then $R_1 + R_2$, while at higher frequencies the conductivity follows a $\nu^2$ law if $R_2 \gg R_1$,[2] as is, evidently, the case in a percolative composite (then the value of the low-frequency plateau is just the resistivity of the matrix). Although a crossover from the plateau to the $\nu^2$ dependence has in fact been observed in the $Al_6Si_2O_{13}$–molybdenum ceramic–metal composite,[15] the increase here is weaker–the slope of the $\sigma'(\nu)$ curves in the frequency range $10^4$–$10^6$ Hz in the $p = 0.15$ sample and in the frequency range $10^5$–$10^6$ Hz in the $p = 0.175$ sample is slightly below 1. This is not surprising, as for granular systems, rather than modelling the spectra by various equivalent circuits with frequency-independent elements, more physically transparent models are needed in order to adequately describe their effective dielectric response.

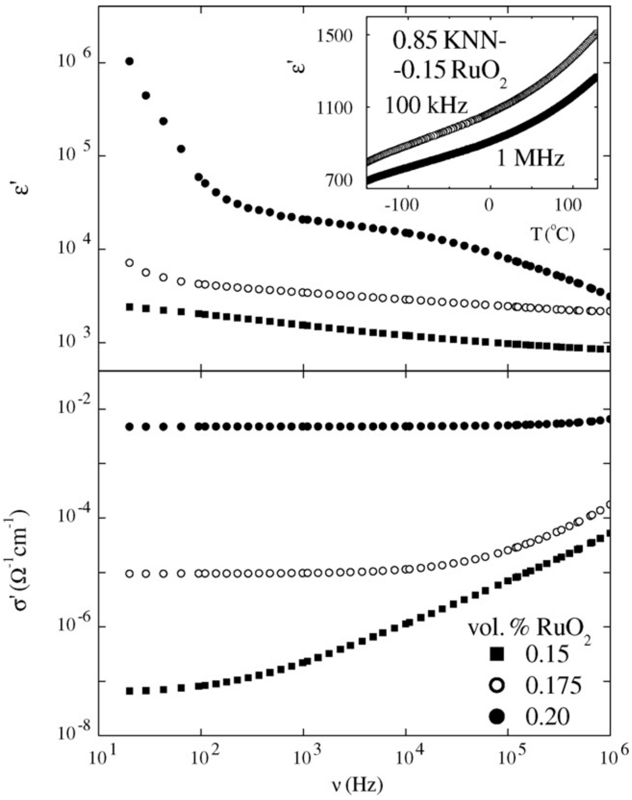

Fig. 3. Frequency dependence of the dielectric constant $\varepsilon'$ and conductivity $\sigma'$ measured at room temperature for KNN–$RuO_2$ samples with different volume concentrations of $RuO_2$. The inset shows $\varepsilon'$ measured as a function of the temperature at two frequencies in the 0.85 KNN–0.15 $RuO_2$ sample.

By using the effective medium theory (EMT) it has thus been derived already more than three decades ago that the ac conductivity in a random system follows a $\nu^s$ behaviour with $s < 1$.[22] Later, a rather general approach has been formulated in the limit of EMT,[23] which states that for any two-component composite with sharp particle boundaries the dielectric response can be composed of two additive parts. One part describes the sum of the original bulk responses weighted by the relative volumes, while the second part describes the localized particles affected by the depolarization field which depends on particle shape and its surroundings. Within EMT, the spherical shape of inclusions leads to a percolation threshold of 1/3,[24] thus a more general particle form and topology is needed to describe smaller threshold, as is frequently observed (also in our case, as is just going to be shown). However, the detected dielectric response can also be qualitatively understood: While at lower frequencies the conductivity of the $RuO_2$ inclusions is effectively blocked, at higher frequencies most of their charge carriers have no time to feel the blocking boundaries. The effective ac-conductivity therefore increases with frequency, and would increase up to the high-frequency plateau corresponding to the value of the $RuO_2$ conductivity. As even for an inhomogeneous system the Kramers–Kronig relations must be satisfied, the increasing $\sigma'$ parts of spectra contribute to the static dielectric constant via a strong dielectric relaxation.

The inset to Fig. 3 shows the temperature dependence of $\varepsilon'$ detected at two frequencies in the $p = 0.15$ sample in the temperature range −150 °C to 130 °C. Although, due to the increasing conductivity, $\varepsilon'$ increases at higher temperatures, the detected response is rather smooth around room temperature, i.e., in the range most interesting for eventual applications.

Evidently, values of $\varepsilon'$ strongly increase with a larger $RuO_2$ content. This is depicted in Fig. 4, which shows the evolution of the $\varepsilon'$ (measured at room temperature at a frequency of 1 kHz) versus the $RuO_2$ volume concentration. The solid line represents the fit of the experimental data to an expression derived from general percolation theories.[2–4]

$$\varepsilon' = \varepsilon_m \left( \frac{p_c - p}{p_c} \right)^{-q}, \tag{1}$$

which has been, up to now, successfully applied to several organic and inorganic percolative composites.[8–17] Here, $\varepsilon_m$ is the real part of the complex dielectric constant of an insulator matrix, $p$ is the volume concentration of the conductive admixture, $p_c$ is the percolation threshold for the conduction (unambiguously defined in the ideal composite with the zero-conductivity of the matrix via $\sigma_{dc} = 0$ for $p < p_c$), and $q$ is the critical exponent. Several values for the percolation-critical exponents and the threshold value have been proposed on the basis of theoretical derivations[1–4] or numerical calculations.[25,26]

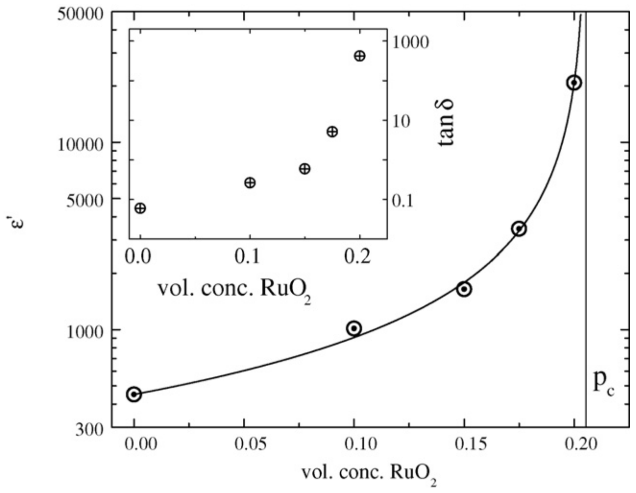

Fig. 4. Evolution of the real part of the dielectric constant vs. the $RuO_2$ volume concentration, measured at room temperature at a frequency of 1 kHz. The solid line represents fit of the experimental data to Eq. (1), while the vertical line indicates the percolation threshold, $P_c$ The inset shows the dependence of the dielectric loss factor on the $RuO_2$ volume concentration.

While standard percolation theories on three-dimensional lattices assume $q = 0.9$ and $p_c \approx 0.16$,[2,3] rather different values (usually a much higher $p_c$) have been experimentally detected in various percolative systems.[8–17] This can be explained in terms of the continuous percolation theory.[1] In our system the fit yields $q = 1.05 \pm 0.04$ and $p_c = 0.205 \pm 0.004$ It is noteworthy that value of $q = 1$ is obtained in the framework of the effective medium approach regardless of the space dimensionality,[2] however, the most important fact is that the exact fit in Fig. 4 further confirms the perfect outgrowth of the KNN–$RuO_2$ composite. A significant fraction of porosity, which can clearly be seen in Fig. 1 and is many times observed in KNN-based ceramic composites,[27] undoubtedly alters the dielectric response, i.e., decreases the dielectric constant. Nevertheless, the obtained dielectric constant is near the percolation threshold for two orders of magnitude higher than in the pure KNN ceramics. It should also be stressed out that, by definition, the electrical conductivity undergoes an abrupt discontinuity at the percolation point, and, consequently, the dielectric loss factor $\tan\delta = \varepsilon''/\varepsilon'$ becomes extremely high. This can clearly be seen in the inset to Fig. 4. However, dielectric losses in samples with lower $RuO_2$ concentration ($p \leq 015$), where dielectric constant is still much higher than in the pure KNN ceramics, are supposedly acceptable for applications.

## 4. Summary

Lead-free percolative composite, based on conductive $RuO_2$ and ferroelectric KNN ceramic systems, was developed. The structural analysis revealed that there were no chemical reactions between the constituents during processing, which resulted in a perfect percolative structure—conductive ceramic grains are uniformly distributed throughout the ceramic matrix. Consequently, the dielectric response in the developed KNN–$RuO_2$ composite follows the predictions of the percolation theory. The dielectric constant actually diverges on approaching the percolation threshold and values as high as 20,000 were detected at room temperature at a measuring frequency of 1 kHz, thus being for two orders of magnitude higher than in the pure KNN ceramics. These results demonstrate the potential of all-ceramic percolative composites for use as high-dielectric-constant materials in electronic and electromechanical applications.

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