Microstructures and electric characteristics of SrNdCoO$_4$ ceramics with K$_2$NiF$_4$ structure

Y. Y. Liu · X. M. Chen · X. Q. Liu · L. Li

Abstract SrNdCoO$_4$ ceramics with tetragonal K$_2$NiF$_4$ structure were prepared by a solid-state reaction process. The frequency and temperature dependence of dielectric and conductive properties were studied. A peak was found at ~325 °C on both dielectric constant (ε) and conductivity (σ) plots with temperature. After annealing in O$_2$, the peak of ε disappeared while that of σ just shifted a little toward high temperature side. So, some oxide vacancies existed in the polycrystalline SrNdCoO$_4$, which contributed much to ε but influenced σ only slightly in the measured temperature and frequency range. A lower resistivity of 3.7 Ωcm was obtained in SrNdCoO$_4$ ceramics sintered at 1150 °C.

Keywords K$_2$NiF$_4$ · Dielectric properties · Conductivity · Microstructure · SrNdCoO$_4$

1 Introduction

K$_2$NiF$_4$ is a kind of tetragonal layered perovskite with a space group I4/mmm and lattice constants of a=0.4006 and c=1.3076 nm [1]. The NiF$_6$ octahedra share corners with each other to make a two-dimensional perovskite array. The perovskite layers are interleaved with the rock salt KF layers in the c-direction. In light of the discovery of high temperature superconductivity [2] in the system La$_{2-x}$M$_x$CuO$_4$ (M=Ba, Sr, Ca), it is interesting to investigate other oxides possessing the K$_2$NiF$_4$ structure. Recently,

MRAlO$_4$ (M=Sr, Ca; R=La, Nd, Sm and Y) crystals and ceramics with K$_2$NiF$_4$ structure have attracted much scientific attention because of their interesting dielectric characteristics and their potential applications as substrates [3–6]. Moreover, these materials have been studied as good candidates of microwave dielectric materials in our group [7, 8].

On the other hand, the investigation on magnetic and electrical properties has also attracted great interest in K$_2$NiF$_4$-type oxides MRTO$_4$ (M=Sr, Ba; R=La, Nd; T=Mn, Fe, Ni) [9–14]. However, MRCoO$_4$ have been relatively less investigated and most known reports are related to spin state or spin and charge order [15, 16]. These materials could also indicate interesting properties.

In the present paper, SrNdCoO$_4$ ceramics with tetragonal K$_2$NiF$_4$ structure are prepared, and the dielectric properties and conductivity are characterized together with the microstructures.

2 Experimental

SrNdCoO$_4$ ceramics was prepared by a solid-state reaction. The starting materials Nd$_2$O$_3$ (99.9%), SrCO$_3$ (99.95%) and Co$_2$O$_3$ (99%) were mixed in appropriate stoichiometric proportions and then were ball milled in distilled water using zirconia media for 24 h. The slurry was dried and calcined at 1000 °C in air for 3 h. The resultant powders added with 6 wt% PVA (polyvinyl alcohol) were pressed into disc compacts of 12 mm in diameter and 1.6~2.0 mm in height. Finally, the pellets were sintered at 1150~1275 °C in air for 3 h. Annealing was carried out at 1000 °C in O$_2$ for 8 h.

Phase analysis was carried out by power X-ray diffraction (RIGAKU 2550/PC using CuKα radiation) and the

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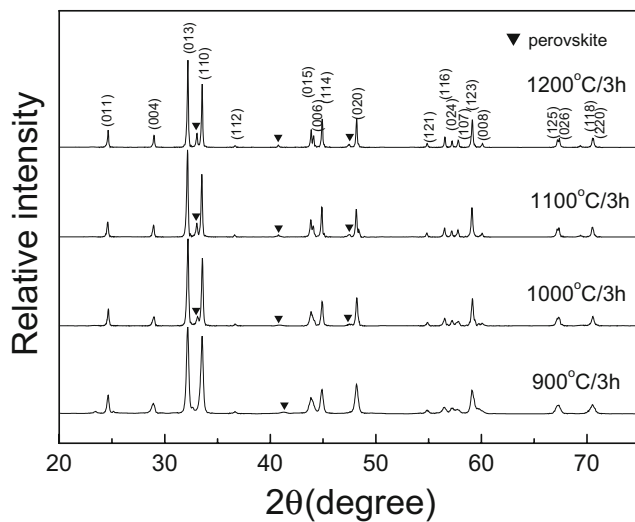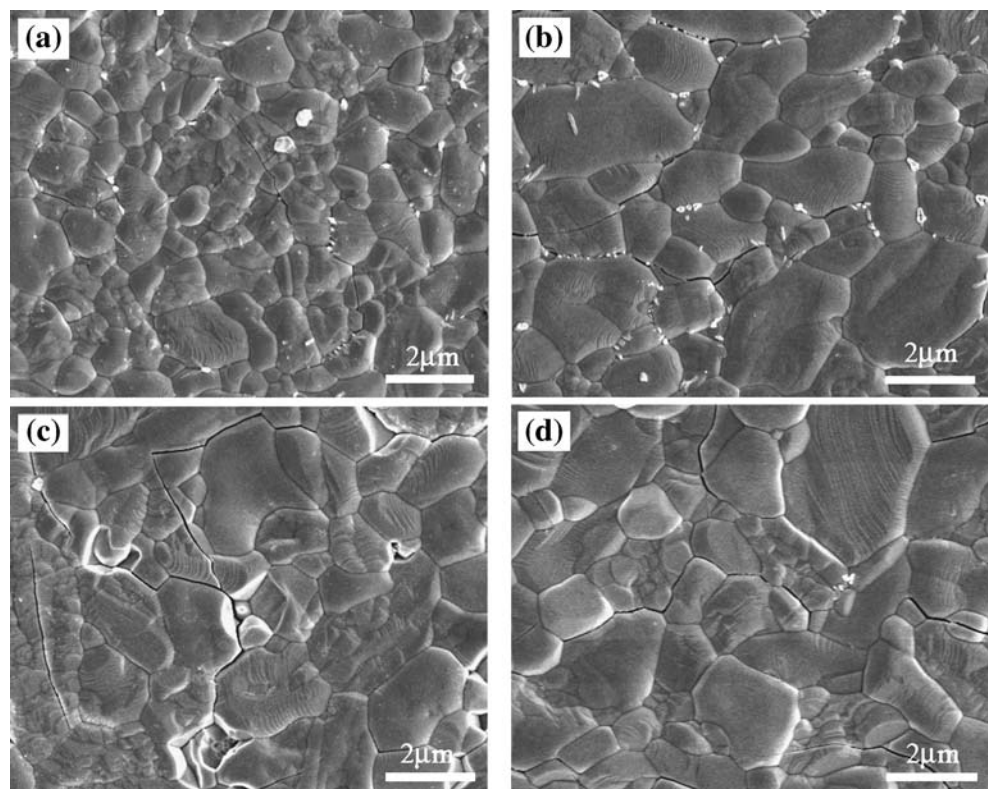Hangzhou 310027, China
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Fig. 1 XRD patterns of SrNdCoO$_4$ powders calcined at various temperatures

microstructures were observed by scanning electron microscope. The dielectric properties were evaluated at 10 kHz, 100 kHz and 1 MHz from 25 to 600 °C and by an LCR meter (HP 4284A) equipped with thermostat. Conductivity was evaluated at 10 kHz, 100 kHz and 1 MHz from −50 to 80 °C and from 25 to 80 °C by 4284A equipped with different thermostat. The room temperature conductivity was determined by a Digit Multimeter (Agilent 34401A). Silver paste was used as the electrodes.

3 Results and discussion

As shown in Fig. 1, SrNdCoO$_4$ powders with K$_2$NiF$_4$ structure can be synthesized at 900 °C and sharp peaks suggesting enough crystallization form at 1000 °C, but some peaks for perovskite phase exist, probably originating from (Sr, Nd) CoO$_{3-\delta}$, and cannot be removed by increasing the calcining temperature, which also occurs in La$_{2-x}$Sr$_x$CoO$_4$ [17]. The equilibrium transformation to a pure SrNdCoO$_4$ phase can be expressed as:

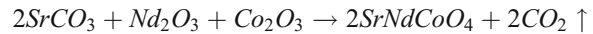$$2SrCO_3 + Nd_2O_3 + Co_2O_3 \rightarrow 2SrNdCoO_4 + 2CO_2 \uparrow$$

Figure 2 shows the SEM micrographs of SrNdCoO$_4$ ceramics sintered at various temperatures in air for 3 h. The SrNdCoO$_4$ ceramics are well sintered at the temperatures investigated here. As the sintering temperature increases from 1200 °C to 1225 °C, the grains grow obviously from ~0.7 to ~1.5 μm. When the sintering temperature increases further, the grains change slightly. Some smaller grains can be observed on the boundary of main phase grains, and these smaller grains might be the peroveskite secondary phase which is detected by XRD analysis. The content of this secondary phase decreases rapidly with further increasing the sintering temperature and becomes very little for the samples sintered at 1250 and 1275 °C.
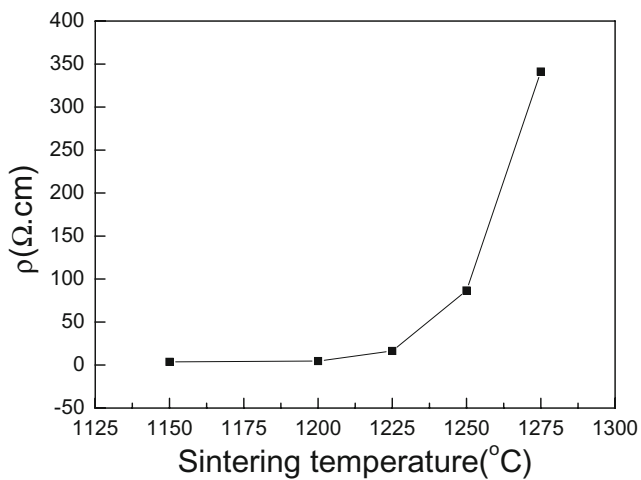
Fig. 2 SEM micrographs of SrNdCoO$_4$ ceramics sintered at (a) 1200 °C, (b) 1225 °C, (c) 1250 °C and (d) 1275 °C

Fig. 3 Room temperature resistivity of SrNdCoO$_4$ ceramics as function of sintering temperature

Figure 3 shows the effect of sintering temperature on the room temperature DC resistivity of SrNdCoO$_4$ ceramics. The resistivity enhances monotonously with increasing the sintering temperature. The variation of room temperature dielectric characteristics (see Table 1) indicates a variation tendency very closely related to that of resistivity. With increasing sintering temperature, both the dielectric constant and loss decreases, while the reduced conductivity (higher resistivity) is observed. That is, the semiconducting nature greatly contributes to the high dielectric constant. With respect to the monotonous increase of resistivity, several factors should be considered. With increasing the sintering temperature, the ceramics becomes dense due to the elimination of porosity. Meanwhile, the grain grows gradually and the content of oxygen vacancies increases with reoxidation during cooling of the sintering process becoming insufficient. All these factors tend to decrease the resistivity of the semiconducting materials. Besides, the content of the second phase decreases with increasing sintering temperature. Based on above analysis, the reason for the monotonous increase of resistivity should be that the second phase, whose content decreases with sintering temperature increasing as shown in Fig. 2, has higher conductivity than SrNdCoO$_4$.

Figure 4 shows the frequency dependence of dielectric properties for SrNdCoO$_4$ ceramics sintered at different
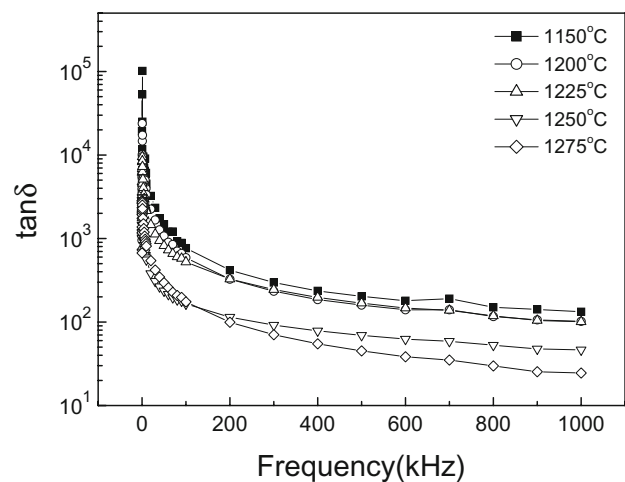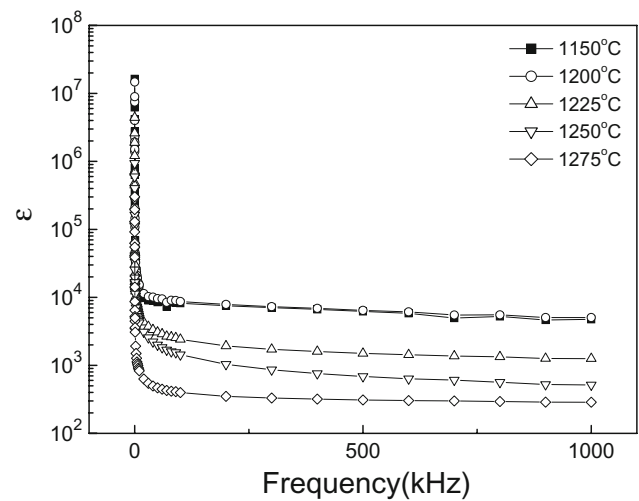

Fig. 4 Dielectric characteristics of dense SrNdCoO$_4$ ceramics sintered at various temperatures as function of frequency (30~10^6 Hz)

temperatures. With increasing frequency, dielectric constant reduces quickly at first then tends to be a stable state, and the dielectric loss shows a peak value at 10^2~10^3 Hz then changes like the dielectric constant for all samples. The drop-off of ε and the peak of tanδ at low frequency should be caused by some slow polarization mechanism. Due to conduction mechanism in the material, charge carriers have to be considered in the polarization mechanisms and the loss from the conductivity becomes dominant in the total

Table 1 Room temperature electric properties of SrNdCoO$_4$ ceramics sintered at various temperatures.

Sintering temperature (°C)	ε				Tanδ		Resistivity (Ωcm)
	10 kHz	100 kHz	1 MHz	10 kHz	100 kHz	1 MHz	
1150	14,003	8,204	4,750	4,536	766	132	3.72
1200	10,989	6,212	3,697	4,380	773	130	4.64
1225	5,852	2,411	1,256	2,152	522	101	16.35
1250	3,271	1,078	424	829	252	64	86.67
1275	765	355	255	810	174	24	341.3

dielectric loss. So, the dielectric constant and dielectric loss changes in accord with the conductivity as function of the sintering temperature as shown in Fig. 3.

The temperature dependence of dielectric constant at 10 kHz, 100 kHz and 1 MHz is given in Fig. 5. The dielectric constant shows a peak at 325 °C in the as-sintered samples,
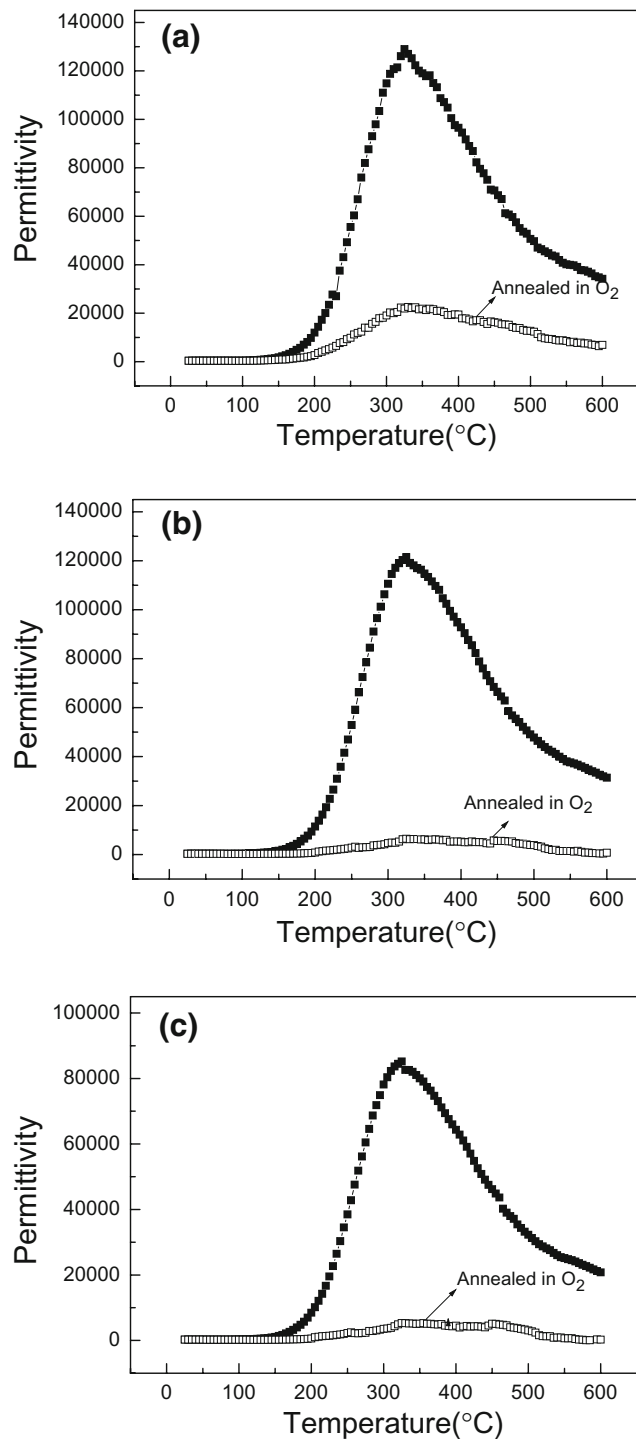
and this peak becomes very flat at 10 kHz and almost disappears at 100 kHz and 1 MHz after annealing in O_2. Therefore, the dielectric peak should be related to the inhomogeneities especially the microstructure with conducting grains surrounded by the relatively insulating grain boundaries. That is, oxygen vacancies will be formed when the $SrNdCoO_4$ ceramics are sintered at high temperatures in air, and these oxygen vacancies may be eliminated partially or entirely during cooling due to the reoxidation. When the grains grown to a critical size or above, usually sintered at the higher sintering temperature, the reoxidation process during cooling might not be able to penetrate the grains, especially if the cooling is not slow enough. As the final result, the special microstructure with oxygen vacancy-free grain boundaries and oxygen deficient grains forms [18]. This inhomogeneous microstructure is similar to that in grain boundary capacitors, and will result in the large effective dielectric constant [19]. The dielectric constant will increase with more charge carriers accumulated at the interface between grains and relatively insulating boundaries at higher temperature. However, when the temperature is enough high for oxygen vacancies to make long-range motion, the polarization of interface charges becomes deactivated, which decreases the effective dielectric constant. So, the oxygen vacancies should be responsible to the dielectric peak around 325 °C for the present material. These interpretations are strongly supported by the results for $SrNdCoO_4$ ceramics annealed in oxygen. The dielectric peak at 325 °C almost disappears in the samples annealed in oxygen due to the elimination of oxygen vacancies and the subsequent vanishing of the inhomogeneous microstructures.

The variation of resistivity with temperature in $SrNdCoO_4$ ceramics (see Fig. 6) indicates a close correlation with that of dielectric constant. A very similar variation tendency is

Fig. 5 Dielectric constant of dense $SrNdCoO_4$ ceramics as function of temperature at (**a**) 10 kHz, (**b**) 100 kHz and (**c**) 1 MHz
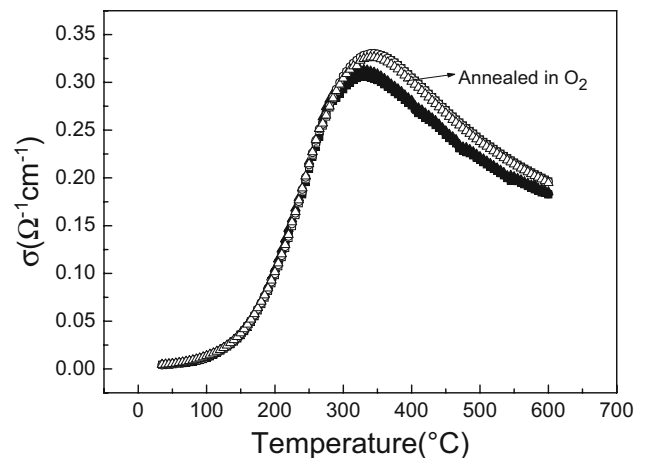

Fig. 6 Conductivity of dense $SrNdCoO_4$ ceramics as function of temperature at 10 kHz, 100 kHz and 1 MHz

observed, and a peak of conductivity is indicated at 330 °C which is slightly higher than that for dielectric constant. This correlation suggests again that the semiconducting nature contribute greatly to the high dielectric constant. However, the effects of oxygen annealing on the conductivity significantly differ from that for dielectric constant. The effects of oxygen annealing on conductivity of the present material is slight, the peak of conductivity cannot be eliminated and only a shift of peak temperature can be obtained by oxygen annealing. This result can be understood as follows. There are two kinds of conductive mechanism existing in this system, which are the intrinsic conductivity and the conductivity from oxygen vacancies, and the latter contributes little compared to the former. As a result, the oxygen annealing shows little influence on the conductivity. Noted that, the semiconductor-to-metal transition related to the peak is very similar to that in the $La_{2-x}Sr_xNiO_4$ system and is supposed to arise from the delocalized $d_{x^2-y^2}$ orbitals [20].

4 Conclusion

Dense $SrNdCoO_4$ ceramics with tetragonal K_2NiF_4 structure can be created by sintering at 1225 to 1275 °C in air for 3 h. The large dielectric constant of $SrNdCoO_4$ is attributed to the semiconducting nature and it is enhanced by the inhomogeneous microstructure. A dielectric peak was found at 325 °C, and it could be eliminated by annealing in oxygen. Meanwhile, a peak of conductivity was also observed at 335 °C, and it could not be eliminated by annealing in oxygen but indicated a shifting to 345 °C. A resistivity of 3.7 Ωcm was obtained in $SrNdCoO_4$ ceramics sintered at 1150 °C. The higher conductivity in $SrNdCoO_4$ ceramics sintered at lower sintering temperature is assumed to result from the second phase and its higher conductivity. The highly resistive sample sintered at 1275 °C has a high loss of 810 at 10 kHz and might have prospective dielectric applications such as wave absorbing materials.

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