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Magnetoelectric and dielectric relaxation properties of the high Curie temperature composite $\text{Sr}_{1.9}\text{Ca}_{0.1}\text{NaNb}_5\text{O}_{15}–\text{CoFe}_2\text{O}_4$

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Abstract

A magnetoelectric (ME) composite ceramic $0.6\text{Sr}_{1.9}\text{Ca}_{0.1}\text{NaNb}_5\text{O}_{15}–0.4\text{CoFe}_2\text{O}_4$ (SCNN–CFO) was prepared by a conventional solid state reaction method. Remarkable dielectric constant dispersion with a Curie temperature of 270 $^\circ\text{C}$ was observed. This relaxor composite exhibits ferroelectric as well as ferrimagnetic hysteresis loops at room temperature. A significant ME coupling effect was observed. On the basis of our studies, it is demonstrated that the lead-free high Curie temperature SCNN–CFO relaxor composite material can be used in the future development of ME devices.

1. Introduction

In the past decades, there has been continued increasing interest in magnetoelectric (ME) materials due to their attractive physical properties and potential applications in actuators, transducers, field sensors and data storage devices [1–3]. Such materials display a spontaneous dielectric polarization as a response to an applied magnetic field or an induced magnetization driven by an external electric field. The prerequisite for the observation of the ME effect is the coexistence of magnetic and electric dipoles. Based on this primary requirement, the ME effect could be realized in composites consisting of both ferroelectric and ferro/ferrimagnetic phases, as first proposed by Van Suchetelene [4]. When designing these composites, the following issues should be considered: (a) a high Curie point for the ferroelectric phase, (b) a high Néel/Curie temperature for the ferri/ferromagnetic phase and (c) large piezoelectric as well as magnetostriective coefficients.

In this study, a new ceramic system based on tetragonal–tungsten–bronze (TTB) ferroelectric relaxor $\text{Sr}_{1.9}\text{Ca}_{0.1}\text{NaNb}_5\text{O}_{15}$ (SCNN) and Co-ferrite $\text{CoFe}_2\text{O}_4$ (CFO) as ferroelectric and ferrimagnetic components, respectively, was fabricated. To our knowledge, no similar ME composite systems have been reported. This selected composite system is attractive due to (i) the large spontaneous strain associated with the ferroelectric phase transition in SCNN as well as the strong elastic interaction between the two phases, (ii) the large magnetostriiction of the ferrimagnetic CFO phase, (iii) the high Curie temperature of SCNN (250–300 $^\circ\text{C}$) due to the introduction of Na ions in the void sites and the high Néel temperature of CFO (520 $^\circ\text{C}$) and (iv) its lead-free and environmental friendly components. In this paper, we demonstrate that this composite exhibits relaxor properties, room temperature ferroelectric and ferrimagnetic hysteresis loops and desirable ME coupling.

2. Experiment

The SCNN–CFO composites were prepared via a conventional solid state reaction method. $\text{SrCO}_3$, $\text{CaCO}_3$, $\text{Na}_2\text{CO}_3$ and $\text{Nb}_2\text{O}_5$ powders were ball milled and then calcined at 1250 $^\circ\text{C}$ in air for 6 h to prepare $\text{Sr}_{1.9}\text{Ca}_{0.1}\text{NaNb}_5\text{O}_{15}$ powder. On the other hand, a mixture of $\text{Co(CH}_3\text{COO})_2$ and $\text{Fe}_2\text{O}_3$ powders was calcined at 1200 $^\circ\text{C}$ in air for 6 h to create $\text{CoFe}_2\text{O}_4$ powder. Finally, the mixture of SCNN and CFO powders, in the molecular ratio of 6 : 4, was ball milled and pressed into discs. The composite ceramics were then obtained by sintering these discs at 1200 $^\circ\text{C}$ in air for 6 h.
The phase and structure of the sintered samples were observed by x-ray diffractometry (XRD) and scanning electron microscopy (SEM) with energy dispersive x-ray analysis (EDX). Their dielectric constant and loss were evaluated by using a precise impedance analyzer (HP 4294A). The magnetic properties of the samples were measured using a vibrating sample magnetometer (VSM). The ferroelectric hysteresis loop was characterized using a ferroelectric test tower (RT66A, Radiant Technologies). The ME effect of the composites was characterized using an in-house automated measurement system. Prior to the ME measurement, the samples were poled electrically under 30 kV cm\(^{-1}\) in silicon oil while cooled from 260\(^\circ\) C and magnetically poled under 2.5 kOe for 30 min at room temperature. Since this selected poling magnetic field is much larger than the coercive field of the SCNN–CFO composites (220 Oe), we believe that the composites had been magnetically poled.

3. Results and discussion

Figure 1(a) shows a typical XRD pattern of the SCNN–CFO composites. Two distinct sets of diffraction peaks, corresponding to either the TTB phase of SCNN or the cubic spinel CFO phase, are observed. No other peaks corresponding to extra phases are identified. Furthermore, the SEM image shown in figure 1(b) displays the microstructure of the composites. A dense, crack-free composite with no observable pores is identified within the areas etched below the polished surface. As observed in the SEM micrograph, two different types of grain are recognized. The EDX results suggest that grains corresponding to the SCNN phase are rod-like shapes with an average width and length of 2–3 µm and 15 µm, respectively, while the relatively small spherical grains correspond to the uniformly distributed CFO phase. Hence, both the XRD and SEM results indicate that no observable chemical reaction or diffusion between the CFO and SCNN phases existed in these composites.

Figure 2 shows the variation in the dielectric constant of the composite as a function of the temperature measured at different frequencies. Higher dielectric constants are obtained at lower frequencies and all the dielectric constant curves are accompanied by an interesting temperature dependence. An increase in the dielectric constants is observed with increasing temperatures up to the transition temperature (270\(^\circ\) C) and then followed by a decrease in the dielectric constants with a further increase in temperature. As shown in figure 2, the dielectric constant curves of our samples display a broad temperature dependence in the vicinity of the transition temperature. Compared with pure SCNN ceramics, the SCNN–CFO composites display a larger frequency dependence, i.e. the rate of change in the dielectric constant with respect to frequency at a fixed temperature is larger in the SCNN–CFO composites than that observed in pure SCNN ceramics [5]. The high dielectric constants measured at low frequencies might be attributed to the interface between the ferroelectric and ferrimagnetic phases which have significantly different conductivities. These interfaces cause an additional polarization, the interface polarization, which boosts the dielectric constant [6]. As this interface polarization usually responds slowly to the external field, it is inactive at high frequencies (about 10\(^5\)–10\(^6\) Hz). Thus, it has no contribution to the dielectric constant at high frequencies, resulting in the decline of the dielectric constants.

Apart from the remarkable dispersion behaviour observed in the temperature dependence of the dielectric constants, a well-defined central peak is also observed in the Brillouin scattering spectrum of the composite (figure not shown).
addition to the observation of this central peak, the full-width at half-maximum of this peak increases significantly at around the Curie temperature. These two features suggest that the composites belong to relaxor-type composites [7]. Details of the Brillouin scattering will be discussed in another paper.

The phase transition feature of the composites was fitted using the modified Curie–Weiss law [8]:

$$\frac{1}{\varepsilon(f, T)} = \frac{1}{\varepsilon_m(f)} \left( 1 + \frac{[T - T_m(f)]^\gamma}{2\Delta^2} \right)^{-1},$$

This equation defines the diffuseness of the relaxor phase transition, where $\gamma$ (1 $< \gamma < 2$) is a constant which expresses the diffuseness exponent of the phase transition, indicating whether the phase transition is or not 'completely' diffusive. $\Delta$ is the peak broadening parameter that indicates the diffuseness degree, $\varepsilon_m$ is the dielectric permittivity maxima and $T_m$ is the temperature at the dielectric maxima. When $\gamma = 1$, the material follows an ideal Curie–Weiss law which shows validity in the case of normal ferroelectrics, whereas $\gamma = 2$ corresponds to the so-called 'complete' diffuse phase transition [9]. Figure 3 shows the plot of $\ln(\varepsilon_m/\varepsilon - 1)$ as a function of $\ln(T - T_m)$ at different frequencies. $\gamma$, obtained by a linear fitting to the experimental data, are found to be 1.73, 1.82, 1.84 and 1.93 for frequencies of 1 kHz, 10 kHz, 100 kHz and 1 MHz, respectively. These values are very close to 2, suggesting a large relaxation of the permittivity and demonstrating the relaxor behaviour of the SCNN–CFO composites.

These composites also exhibit ferroelectric as well as ferrimagnetic hysteresis loops at room temperature. As shown in figure 4, SCNN–CFO composites show a well-defined ferroelectric loop with remanent polarization ($P_r$) and coercive fields ($E_c$) of about 9.5 $\mu$C cm$^{-2}$ and 19.1 kV cm$^{-1}$, respectively, at an applied electric field of 30 kV cm$^{-1}$. The composites are highly resistive with no breakdown under an applied electric field up to 30 kV cm$^{-1}$. In addition to the $P$–$E$ loop, a well-defined ferrimagnetic hysteresis loop is also displayed in figure 4. The saturation magnetization ($M_s$) of SCNN–CFO composites (33 emu cm$^{-3}$ for in-plane) is much smaller than that of pure CFO ceramics (350 emu cm$^{-3}$) due to the low volume concentration (22%) of the CFO in the composites. The magnitudes of the remnant magnetization ($M_r$) and the coercive field ($H_c$) for SCNN–CFO composites are found to be 5.2 emu cm$^{-3}$ and 206 Oe, respectively. The $H_c$ value for these composites is much lower than that of the pure CFO bulk (2 kOe) [10]. This is probably because the CFO magnetic domains can be easily switched in the non-magnetic environment inside the SCNN matrix, due to its relaxor inherent property and the difference in the thermal expansion coefficients between the SCNN and CFO phases [11]. This easy magnetization characteristic facilitates magnetic domain rotation and results in a larger magnetostriiction under very low magnetic fields, consequently leading to a strong ME coupling at the interface between the ferroelectric and ferrimagnetic phases. As expected, a significantly large piezoelectric charge coefficient ($d_{33}$) of 105 pC N$^{-1}$ was obtained using a quasi-static Berlincourt piezo meter.

The coexistence of the ferrimagnetic CFO and ferroelectric SCNN phases in these composites gives rise to a ME effect, which is characterized by their ME coupling coefficient $\alpha_E = dE/dH$. Figure 5 shows the frequency dependence of $\alpha_E$ at an applied ac magnetic field of 10 Oe. In our experiment, no dc bias magnetic fields were applied. From figure 5, it is noticed that $\alpha_E$ remains nearly constant in the frequency range 100 Hz–10 kHz and then increases rapidly after 10 kHz. A maximum $\alpha_E$ value of 58 mV cm$^{-1}$ Oe$^{-1}$ was obtained under zero dc bias with an 88 kHz magnetic field of 10 Oe. Following Petrov and co-workers [12, 13] the theoretical frequency dependence of the ME voltage coefficient is determined by the Debye formulae. The theoretical frequency dependence of the ME voltage coefficient presents a similar trend to that of the experimental data though the theoretical data are a little larger than the experimental data, especially in the range 5–20 kHz. These $\alpha_E$ values are comparable to those obtained in other ME systems such as BaTiO$_3$/CFO ($\alpha_E \approx$ 3 mV cm$^{-1}$ Oe$^{-1}$), PZT/LSMO ($\alpha_E \approx$ 4 mV cm$^{-1}$ Oe$^{-1}$) and Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$/Ba$_{0.5}$Pb$_{0.5}$Ti$_{0.5}$Zr$_{0.5}$O$_3$ ($\alpha_E \approx$ 0.2 mV cm$^{-1}$ Oe$^{-1}$) [14–16].
No dramatic gain was observed for two possible reasons: (1) the resonance frequency is expected to be higher than the highest frequency that our instrument can reach and (2) there is no resonance in the samples that we studied. This was confirmed by the frequency dependence of the electric impedance where no dramatic gain was observed between 1 and 100 kHz (not shown). Such behaviour is similar to that reported in [17–19]. The inset in figure 5 shows the dc bias magnetic field dependence of the ME coefficient. For two different ac frequencies of 5 and 25 kHz, with an increase in the dc bias magnetic field, \( \alpha_E \) increases before reaching its maximum near the coercive field and then drops and remains nearly constant beyond 1 kOe. The observed trend is similar to that reported in Dai et al’s work [19]. The present composites can work for frequencies up to and, probably, beyond 100 kHz without subjecting to redundant thermal-induced depolarization of the ferroelectric member due to its high Curie temperature. This permits promising applications in magnetic devices for these high Curie temperature composites.

4. Conclusion

Lead-free high Curie temperature SCNN relaxor is chemically compatible with CFO ferrite. Their composites have been electrically and magnetically poled to exhibit a significant ME effect. A remarkable dielectric constant dispersion spectrum with a Curie temperature of 270 °C was observed. A well-defined ferroelectric hysteresis loop with remanent polarization \( (P_r) \) and coercive fields \( (E_c) \) of about 9.5 \( \mu \)C cm\(^{-2} \) and 19.1 kV cm\(^{-1} \), respectively, and a ferrimagnetic hysteresis loop with remanent magnetization \( (M_r) \) and coercive field \( (H_c) \) of about 5.2 emu cm\(^{-3} \) and 206 Oe, respectively, were obtained for the same composite ceramic. A maximum ME coupling coefficient \( \alpha_E \) of 58 mV cm\(^{-1} \) Oe\(^{-1} \) was obtained under zero dc bias and an ac magnetic field of 10 Oe at 88 kHz. On the basis of our studies, it is suggested that lead-free high Curie temperature SCNN–CFO relaxor composites are potential candidate materials for ME devices.

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