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Research Article

An Inexpensive Route to Synthesize High-Purity CrO_2 for EMI Shielding in X-Band Frequencies

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Rod-shaped high-purity samples of CrO_2 have been synthesized by an inexpensive and simplified procedure. Here, we have prepared pure CrO_2 without applying any external pressure or control it during synthesis. The sample prepared exhibited an improvement in saturation magnetization values, 68 emu/g at 300 K, 136 emu/g at 80 K, and uniform grained microstructure. The complex permittivity, permeability, and microwave absorption properties of high-purity CrO_2 sample were investigated in the 8.2–12.2 GHz (X-band) microwave frequency range. Microwave measurements have shown the high shielding effectiveness due to absorption (SE_A) of 20.3 dB. The high value of SE_A suggests that CrO_2 can be used as a promising electromagnetic shielding, EMI, material in 8.2–12.2 GHz (X-band) microwave frequency range.

1. Introduction

The ferromagnetic chromium oxide (CrO_2) is considered to be one of the most promising candidates for new generation of spintronics devices [1–3] and is a well-established magnetoresistive material. CrO_2 is a peculiar compound, which behaves as a half-metallic ferromagnet, with a Curie temperature $T_c \sim 114^\circ C$ [4, 5]. It shows giant magnetoresistance (GMR) and optical properties for spintronics and optoelectronic devices [6]. There is an increased interest in shielding against electromagnetic radiation [7] in commercial, military equipments, scientific electronic devices, and communication instruments that are widely being used. The ferromagnetic CrO_2 with high permeability has been utilized in many microwave applications [8–12]. This study is inspired by the recent advances in the development of materials with magnetically controlled attenuation.

2. Experimental

The most widely accepted synthesis route for CrO_2 is initiated by using a highly hygroscopic compound CrO_3, which is treated at elevated pressures (270 GPa) in raw form or by mixing with other oxides of Cr and some catalysts that are often needed to bring down the working pressure [13–16]. In this paper, we report microwave absorption properties of high-purity sample of CrO_2 synthesized by a simplified procedure, where the pressure is not a control parameter, thus drastically reducing the cost of production. This synthesis technique involves a simple two-step process. The first step involves the preparation of intermediate precursors oxide, which can be prepared under ambient pressure by heating CrO_3 for 3 hours at a temperature of $250^\circ C$ in air. In a second step, the sample is sealed in an evacuated quartz tube at ambient pressure followed by palletization and subsequently treated in furnace at a temperature of $400^\circ C$ for 3 hours.

3. Results and Discussion

The XRD pattern of the calcined powder of CrO_2 determined by Rigaku Miniflex II, step size = 0.02, with Cu Kα radiation of wave length $\lambda = 1.5406$ Å, is shown in Figure 1(a). It is observed that the sample consists of the pure CrO_2 phase confirmed by PCPDFWIN card no. 76-1232. The lattice parameters corresponding to the tetragonal structure of

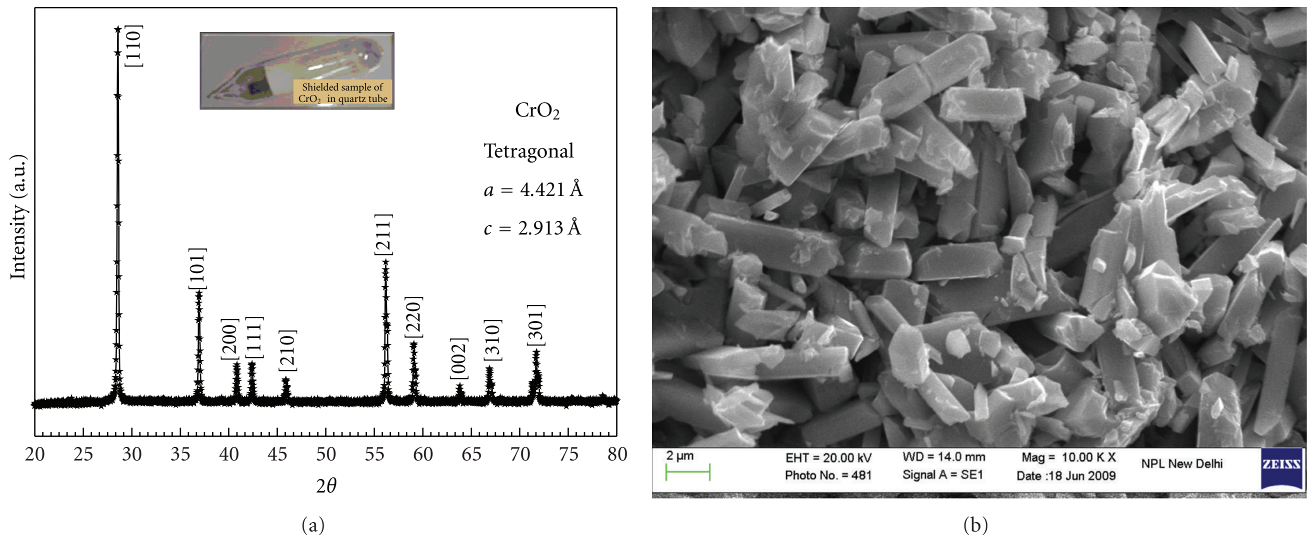

Figure 1: (a) XRD diffraction pattern of pure CrO_2 and shielded sample in quartz tube. (b) Scanning electron micrograph depicting long rod-like particles of CrO_2 (~4 μm).

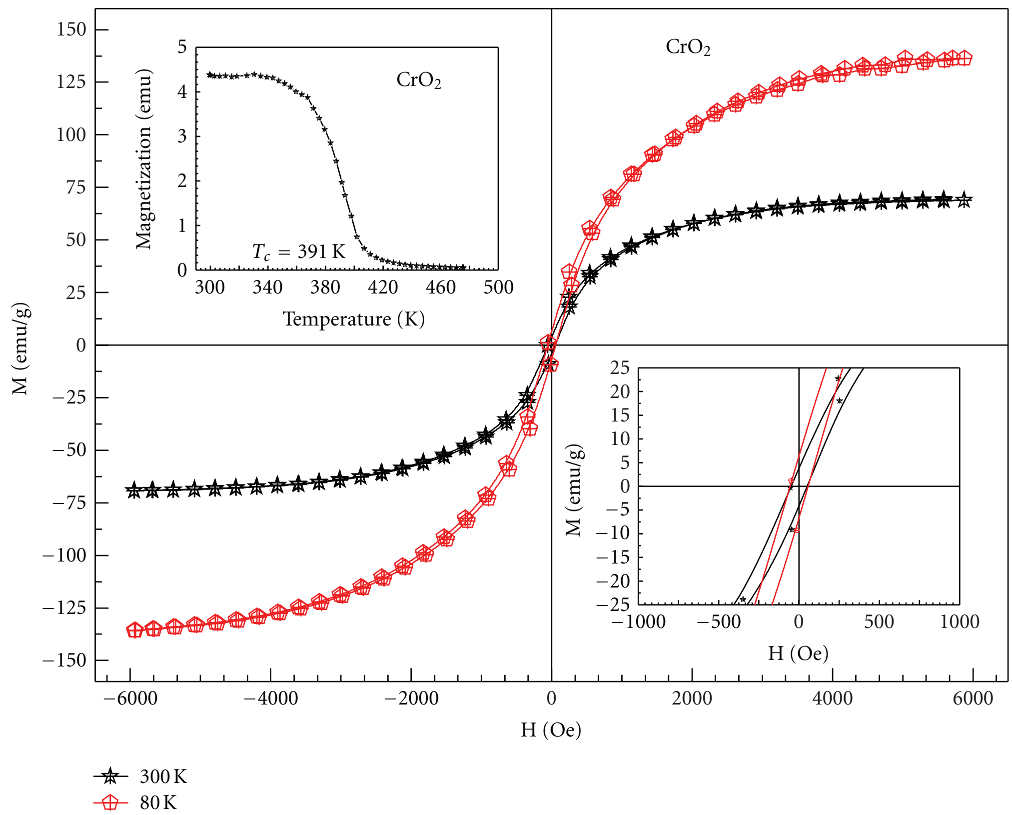

Figure 2: M-H curves at 300 K and 80 K and M-T curve (inset) of CrO_2 sample.

CrO_2 (P4$_2$/mnm) were calculated, a = 4.421 Å and c = 2.913 Å. Figure 1(b) shows the SEM micrograph of pure CrO_2 sample which depicts uniform grain size distribution.

The magnetic properties of a representative CrO_2 sample have been determined by the M-H hysteresis loop at 300 K and 80 K as shown in Figure 2. The saturation magnetization (Ms) value of the sample has been measured as 68 emu/g and 136 emu/g at 300 K and 80 K, respectively, by vibrating sample magnetometer (Lakeshore, 7304). The saturation magnetization value obtained in our samples is higher as reported by A. Bajpai and A. K. Nigam [15]. The coercive force is found nearly the same at 300 K and 80 K as shown

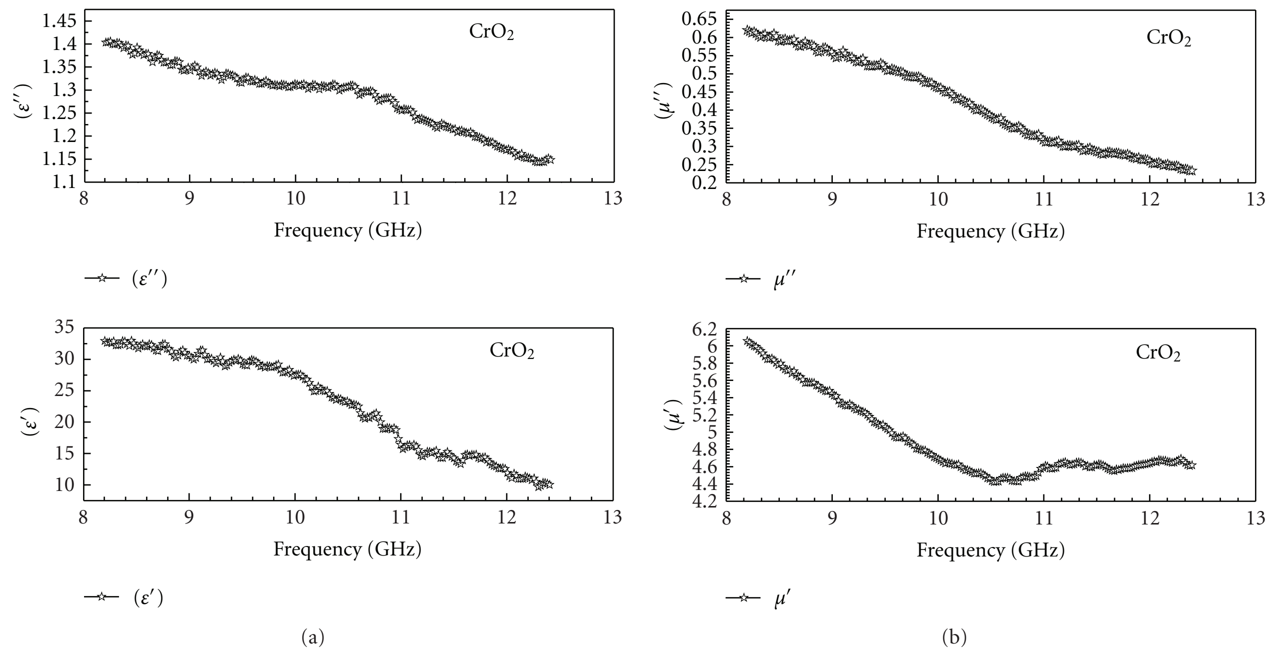

Figure 3: (a) Response of real and imaginary (a) permittivity, (b) permeability with frequency of pure CrO_2.

Table 1: Comparisons of relevant physical parameters as exhibited by our sample to that are reported in literatures.

Sample	Parameters	Reported values	Our values
CrO_2 (Rod shaped)	Structure (tetragonal)	$a = 4.420$ Å [15]	$a = 4.421$ Å
	Lattice parameters	$c = 2.915$ Å	$c = 2.913$ Å
	Magnetization (emu/g)	127–135 (at 5 K)	136 (at 80 K)
	Curie temperature (T_c)	114 K [6]	118 K
	Shielding effectiveness	Not reported	$SE_A = 20$ dB
			$SE_R = 10$ dB

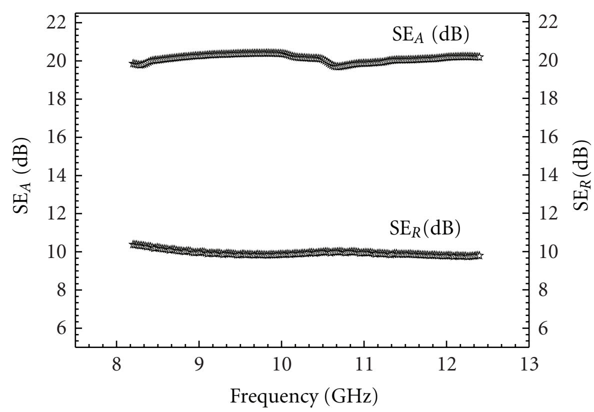

Figure 4: The variation of EMI shielding effectiveness of SE_A and SE_R versus frequency for CrO_2 samples.

in the inset of Figure 2. Curie temperature $T_c = 391$ K is depicted from M-T curve at 3 k Oe for CrO_2 sample as shown in the inset of Figure 2. Comparisons of relevant physical parameters as exhibited by our sample to those reported in literatures are given in Table 1.

The complex permittivity, permeability, and S_{11} (S_{22}), S_{21} (S_{12}) measurements were carried out on an Agilent E8362B vector network analyzer in the microwave frequency range of 8.2–12.2 GHz (X-band). The rectangular pellet of 2 mm thickness with a dimension to fit the waveguide dimensions has been prepared for microwave measurements. From S_{11} and S_{21} measurements, the reflectivity (R), transmissivity (T), and absorptivity (A) were calculated. The real and imaginary parts of complex permittivity (ε' and ε'') and permeability (μ' and μ'') versus frequency are shown in Figures 3(a) and 3(b). Compared with conventional ferrite materials, the CrO_2 exhibits larger saturation magnetization and complex permeability value in X-band frequency range. In CrO_2 sample, permittivity and permeability are found to be decreasing with an increase in frequency because the dipole present in the system cannot reorient themselves along with the applied electric field. The CrO_2 sample shows highest real permittivity ($\varepsilon' = 33$), imaginary part ($\varepsilon'' = 1.4$), and permeability ($\mu' = 6$) which ultimately enhances the shielding effect. Magnetic materials with high permeability have been utilized in many microwave applications. The EMI shielding effectiveness (SE) of a material is defined as the ratio of transmitted power to incident power and is given by SE (dB) $= -10\log(P_t/P_0)$, where P_t and P_0 are the transmitted and incident electromagnetic powers, respectively. For a shielding material, total $SE = SE_R + SE_A + SE_M$, where SE_R is due to reflection, SE_A is due to absorption, and SE_M is due to multiple reflections. In two-port network, S parameters S_{11} (S_{22}), S_{21} (S_{12}) represent the reflection and the transmission coefficients $T = |E_T/E_I|^2 = |S_{21}|^2 = |S_{12}|^2$, $R = |E_R/E_I|^2|S_{11}|^2 = |S_{22}|^2$ and absorption coefficient $(A) = 1 - R - T$. Here, A is given with respect to the power of the incident EM wave. If the effect of multiple reflections between both interfaces of the material is negligible, the relative intensity of the effectively incident EM wave inside the material after reflection is treated equally to $1 - R$. Hence, the effective absorbance [17] (A_{eff}) can be described as $A_{\text{eff}} = (1 - R - T)/(1 - R)$ with respect to the power of the effectively incident EM wave inside the shielding material. It is convenient to express the reflectance and effective absorbance in the form of $-10\log(1 - R)$ and $-10\log(1 - A_{\text{eff}})$ in decibel (dB), respectively, which results in SE_R and SE_A as $SE_R = -10\log(1 - R)$ and $SE_A = -10\log(1 - A_{\text{eff}}) = -10\log[T/(1 - R)]$.

Figure 4 shows the variation of EMI shielding effectiveness of SE_A and SE_R versus frequency for CrO_2 sample. It explicitly confirms that the pure CrO_2 possesses much more effective electromagnetic absorbing effect compared to γ-iron and ferrites [18–20]. CrO_2 has shielding effectiveness mainly due to absorption, which is found in maximum ~20 dB. The shielding effectiveness due to reflection was nominal and of value ~10 dB.

4. Conclusions

In conclusion, the pure phase CrO_2 can be prepared by an inexpensive and simplified procedure adopted. Structural and magnetic properties are compatible as reported earlier [6, 15]. These CrO_2 have a relatively uniform dimension and well-defined rod-shaped structure. The microwave absorption properties strongly depend on the intrinsic properties of CrO_2. The value of EMI shielding effectiveness due to absorption SE_A (~20 dB) is quite interesting for strategic technology applications.

References

[1] Y. Ji, G. J. Strijkers, F. Y. Yang et al., "Determination of the spin polarization of half-metallic CrO_2 by point contact Andreev reflection," *Physical Review Letters*, vol. 86, no. 24, pp. 5585–5588, 2001.

[2] R. J. Soulen Jr., J. M. Byers, M. S. Osofsky et al., "Measuring the spin polarization of a metal with a superconducting point contact," *Science*, vol. 282, no. 5386, pp. 85–88, 1998.

[3] R. A. de Groot, F. M. Mueller, P. G. V. Engen, and K. H. J. Buschow, "New class of materials: half-metallic ferromagnets," *Physical Review Letters*, vol. 50, no. 25, pp. 2024–2027, 1983.

[4] H. Y. Hwang and S. W. Cheong, "Enhanced intergrain tunneling magnetoresistance in half-metallic CrO_2 films," *Science*, vol. 278, no. 5343, pp. 1607–1609, 1997.

[5] R. M. Costescu, D. G. Cahill, F. H. Fabreguette, Z. A. Sechrist, and S. M. George, "Ultra-low thermal conductivity in W/Al_2O_3 nanolaminates," *Science*, vol. 303, no. 5660, pp. 989–990, 2004.

[6] S. Biswas and S. Ram, "Synthesis of shape-controlled ferromagnetic CrO_2 nanoparticles by reaction in micelles of Cr^{6+}–PVA polymer chelates," *Materials Chemistry and Physics*, vol. 100, no. 1, pp. 6–9, 2006.

[7] C. R. Paul, *Introduction to Electromagnetic Compatibility*, Wiley, New York, NY, USA, 1992.

[8] Y. Naito and K. Suetaki, "Application of ferrite to electromagnetic wave absorber and its characteristics," *IEEE Transactions on Microwave Theory and Techniques*, vol. 19, no. 1, pp. 65–72, 1971.

[9] H. M. Musal and H. T. Hahn, "Thin-layer electromagnetic absorber design," *IEEE Transactions on Magnetics*, vol. 25, no. 5, pp. 3851–3853, 1989.

[10] C. A. Grimes and D. M. Grimes, "A brief discussion of EMI shielding materials," in *Proceedings of the IEEE Aerospace Applications Conference*, pp. 217–226, Steamboat Springs, Colo, USA, January 1993.

[11] K. J. Vinoy and R. M. Jha, "Trends in radar absorbing materials technology," *Sadhana*, vol. 20, no. 5, pp. 815–850, 1995.

[12] E. F. Knott, J. F. Shaeffer, and M. T. Tuley, *Radar Cross Section*, Artech House, Boston, Mass, USA, 1993.

[13] B. L. Chamberland, "Chemical rubber company critical reviews in solid state and materials sciences," *Critical Reviews in Solid State and Materials Sciences*, vol. 7, no. 1, 1977.

[14] A. Bajpai and A. K. Nigam, Nigam, Indian Patent Appl. No. 783/MUM/2002 and International patent application filed with PCT Appl. No. PCT/IN03/ 00278.

[15] A. Bajpai and A. K. Nigam, "Synthesis of high-purity samples of CrO_2 by a simple route," *Applied Physics Letters*, vol. 87, no. 22, Article ID 222502, pp. 1–3, 2005.

[16] P. Norby, A. N. Christensen, H. Fjellvåg, and M. Nielsen, "The crystal structure of Cr_8O_21 determined from powder diffraction data: thermal transformation and magnetic properties of a chromium-chromate-tetrachromate," *Journal of Solid State Chemistry*, vol. 94, no. 2, pp. 281–293, 1991.

[17] A. Ohlan, K. Singh, A. Chandra, and S. K. Dhawan, "Microwave absorption properties of conducting polymer composite with barium ferrite nanoparticles in 12.4-18 GHz," *Applied Physics Letters*, vol. 93, no. 5, Article ID 053114, 2008.

[18] B.-W. Li, Y. Shen, Z.-X. Yue, and C.-W. Nan, "Enhanced microwave absorption in nickel/hexagonal-ferrite/polymer composites," *Applied Physics Letters*, vol. 89, no. 13, Article ID 132504, 3 pages, 2006.

[19] K. Singh, A. Ohlan, R. K. Kotnala, A. K. Bakhshi, and S. K. Dhawan, "Dielectric and magnetic properties of conducting ferromagnetic composite of polyaniline with γ-Fe_2O_3 nanoparticles," *Materials Chemistry and Physics*, vol. 112, no. 2, pp. 651–658, 2008.

[20] S. P. Gairola, V. Verma, L. Kumar, M. A Dar, S. Annapoorni, and R. K. Kotnala, "Enhanced microwave absorption properties in polyaniline and nano-ferrite composite in X-band," *Synthetic Metals*, vol. 160, no. 21-22, pp. 2315–2318, 2010.