Novel Route to Prepare Magnetic Material $Co_3V_2O_8$ and Structural Characterization

G. Celik, F. Kurtulus and H. Guler

Balikesir University, Science and Art Faculty, Chemistry Department, Cagis Yerleskesi, 10145 Balikesir, Turkey

$Co_3V_2O_8$ is a member of kagomé staircase oxides, represented by general formula $M_3V_2O_8$ (M = Ni, Co, Mn). It attracted great attention due to strong magnetic anisotropy, magnetic phase transition, genuine macroscopic quantum effects, strong quantum fluctuations, low-temperature ferroelectricity, field-induced magnetic transitions, complicated phase diagram and displays long-range magnetic order because of geometrical frustration. Different routes to prepare the frustrated magnetic material was reported such as floating zone technique and conventional high temperature method. $Co_3V_2O_8$ (International Centre for Diffraction Data (ICDD): 16-675) was synthesized with Co_3O_4 (ICDD: 80-1536) as binary phase by microwave assisted preparation using $Co(NO_3)_2 \cdot 6H_2O$ and NH_4VO_3. The synthesized material was characterization by powder X-ray diffraction, the Fourier transform infrared spectroscopy, and thermogravimetric–differential thermal analysis.

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1. Introduction

In recent years, Kagomé structure has drawn much attention due to extraordinary magnetic properties [1, 2]. General structural formula can be given by $M_3V_2O_8$ (M = Ni, Co, Mn). Attractive magnetic properties are based on frustrated lattice and strong quantum fluctuations. The crystal structure of kagomé staircase oxides was found to be orthorhombic system with space group *Cmca*. $Co_3V_2O_8$, a member of structure, is not a frustrated ferromagnetic in the low-temperature region [3, 4]. In the kagomé staircase structure of $Co_3V_2O_8$ there are two Co^{2+} sites, one located in the spines of the staircase and other at the cross-tie sites [5]. Studies on synthesis of $Co_3V_2O_8$ were performed, such as floating zone technique and high temperature solid-state reaction [1, 4]. The heating mechanism in microwave processing is fundamentally different from conventional processing. Microwave radiation is absorbed and converted to thermal energy. Heat is generated from inside the material, in contrast with conventional methods where heat is transferred from outside. This internal rapid heating allows a reduction of processing time and energy. The reaction rate is enhanced by one to two orders of magnitude [6–9]. The use of microwave energy as heating sources for the combustion reaction has many advantages such as fast reaction kinetic, cleanness and efficiency as well as economical and ecological aspects of the process due to the costs reduction in terms of energy and time [10].

In this work, we have developed an unreported microwave-assisted synthesis route for $Co_3V_2O_8$ (ICDD: 16-675). It was obtained in a short time (10 min) by using microwave electromagnetic radiation (2.45 GHz, 750 W).

2. Experimental procedure

2.1. Synthesis of magnetic material $Co_3V_2O_8$

Analytical grade cobalt nitrate nonahydrate $(Co(NO_3)_2 \cdot 6H_2O, > 99\%)$ and ammonium metavanadate $(NH_4VO_3 > 99\%)$ were purchased from Carlo Erba. Both chemicals were used without further purification. Reagents were grounded in an agate mortar with molar ratio 3:2, and transferred into a porcelain crucible in powder form and subjected to microwave treatment in a domestic microwave oven (2.45 GHz, 750 W) for about 10 min. The final product was homogenized and further analysis done.

2.2. Characterization with XRD, FTIR and TG/DTA

X-ray powder diffraction (XRD) analysis was performed using PANanalytical X'Pert PRO diffractometer with Cu K_α (1.5406 Å, 45 kV, and 30 mA) radiation. The Fourier transform infrared (FTIR) spectrum was taken on a Perkin Elmer Spectrum 100 FTIR spectrometer from 4000 to 650 cm^{-1}. Thermogravimetric–differential thermal analysis was carried out by Perkin Elmer Diamond TG/DTA. Siemens V12 domestic microwave oven was used.

3. Results and discussion

The X-ray powder diffraction pattern of $Co_3V_2O_8$ is given in Fig. 1. The results of comparison of the XRD pattern with the standard ICDD correspond to $Co_3V_2O_8$ (ICDD: 16-675). The material is crystallized in cubic system with the cell parameter a = 8.314 Å. The expected reaction is as follows:
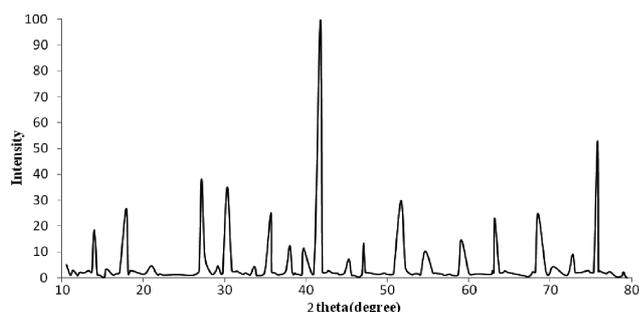
Fig. 1.   Powder XRD pattern of $Co_3V_2O_8$.

$$3Co(NO_3)_2 \cdot 6H_2O + 2NH_4VO_3 \rightarrow Co_3V_2O_8$$
$$+2NH_3 + 6NO_2 + (3/2)O_2 + 19H_2O.$$
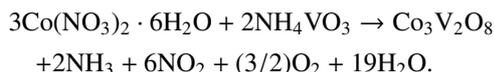
FTIR spectra of the product are presented in Fig. 2. The peak at 759 cm^{-1} belongs to V–O vibration frequency [11]. The strongest one is generally observed in the range 600–500 cm^{-1}, and it corresponds to stretching vibration of the metal at the tetrahedral site. The lowest peak in the range 450–386 cm^{-1} corresponds to stretching vibration of the metal at the octahedral site [12].
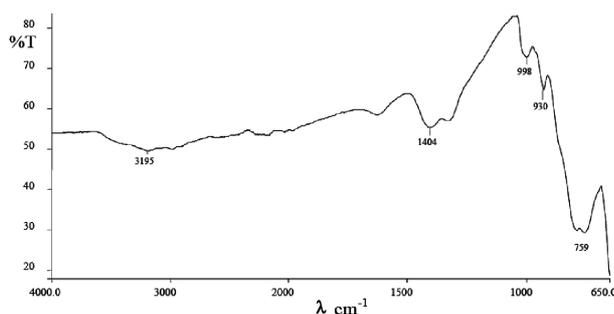
Fig. 2.   FTIR spectrum of $Co_3V_2O_8$.
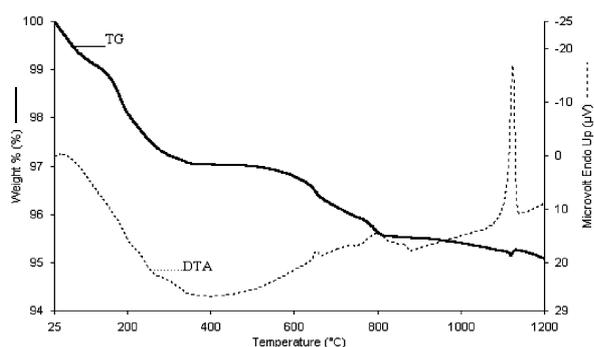
Fig. 3.   TG/DTA curves of pure $Co_3V_2O_8$.

TG/DTA curves of $Co_3V_2O_8$ are given in Fig. 3. Mass loss of the material was due only to about surface water, so $Co_3V_2O_8$ was very stable in the range of 25–1200 °C.

4. Conclusion

The highlight of this work, is the synthesis of pure powder crystal of $Co_3V_2O_8$ by microwave method with using $Co(NO_3)_2 \cdot 6H_2O$ and NH_4VO_3 as starting materials in a molar ratio 3:2. XRD results correspond to $Co_3V_2O_8$ (ICDD:16-675) which is crystallized cubic system with the cell parameter $a = 8.314$ Å. The presence of characteristic peaks and groups confirm the crystal structure. TG/DTA curves confirmed the stability of the $Co_3V_2O_8$.

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