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Thermobaric Synthesis, Structure, and Properties of $Dy_xCu_3V_4O_{12}$

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Abstract—The perovskite-like compound $Dy_xCu_3V_4O_{12}$ ($x = 0.67–0.75$) is synthesized under high pressure ($P = 4.0–9.0$ GPa) and temperature ($T = 1000°C$). Its crystal structure is determined (*Im*-3 space group, $Z = 2$, $a = 7.29348(7)$ Å) by means of powder X-ray diffraction. The basic lengths and bond angles are defined. It is found that the high-pressure phase of $Dy_xCu_3V_4O_{12}$ is characterized by metallic conductivity and paramagnetic properties.

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INTRODUCTION

Oxides with the perovskite-like or related structures are a class of compounds with a unique set of physical and chemical properties. It has been determined that $CaCu_3Mn_4O_{12}$ is a ferrimagnetic semiconductor with a high value of magnetoresistance at a relatively low magnetic field in the wide range of temperatures [1]. $CaCu_3Ti_4O_{12}$ forms a phase that is characterized by a giant dielectric constant (10^5) over a wide temperature range [2], and $CaCu_3V_4O_{12}$ shows metallic conductivity and an antiferromagnetic order at $T < 90$K [3]. Substitutions in the *A* sublattice also can lead to considerable changes in the properties of these materials. It is of interest to synthesize and study the properties of the previously unknown $Dy_xCu_3V_4O_{12}$. The aim of this work was to prepare samples and study the properties of the previously unknown $Dy_xCu_3V_4O_{12}$ phase.

EXPERIMENTAL

The samples were processed in high-pressure chambers on a DO-137A press. Dy_2O_3, V_2O_5, Cu_2O and ultradisperse electrolytic copper were used as starting reagents. The powder mixture, placed in a container and isolated from the heater with platinum foil, was compressed to a predetermined pressure and then heated to the required temperature. After annealing under pressure, the sample was tempered by dropping the temperature in the cell. The pressure was reduced and the sample was retrieved for testing.

The phase homogeneity of the final products of synthesis was controlled via X-ray diffraction. The X-ray diffraction patterns were recorded on an STADI-P automated diffractometer (STOE, Germany) in a range of 2θ angles of 2° to 120° with steps of 0.02° using a copper K_{α_1} radiation source, and on a Shimadzu XDR-7000 diffractometer in a range of the 2Θ angles of 5° to 80° with steps of 0.03° using a copper CuK_α radiation source. Polycrystalline silicon ($a = 5.43075(5)$ Å) was used as our external standard. The PDF2 base of powder standards (ICDD, United States) was used to identify possible impurity phases. The crystal structure of the investigated compounds was refined on the basis of the powder X-ray data using the GSAS program [4].

Electrical properties were studied by AC in the frequency range of 200 Hz to 200 kHz and in DC in a cell with two electrodes. Temperature studies of the electrical characteristics in the range of 10 K to 300 K were performed in a closed cycle autonomous cryostat with a DE-204SL two-stage cryogenic refrigerator based on the Gifford–McMahon cycle, using a water-cooled helium compressor. The accuracy of measuring cryogenic temperatures was 0.2 K.

Magnetic susceptibilities of the sample were measured on a VSM-5T magnetometer (Cryogenic Ltd.) in a temperature range of 8 to 300K and in a field of 1T (10000 Oe).

RESULTS AND DISCUSSION

Experiments on preparing the $Dy_xCu_3V_4O_{12}$ oxide were performed by varying the dysprosium content and the barothermal processing conditions. Analysis of the X-ray diffraction patterns showed that the dominant phase in the samples is cubic $Dy_xCu_3V_4O_{12}$ oxide ($x = 0.67–0.75$) (*Im*-3 space group, $Z = 2$, $a = 7.285–7.295$ Å). Nearly monophase samples of $Dy_{0.75}Cu_3V_4O_{12}$ were produced at a pressure of 9.0 GPa, a temperature of 1000°C, and a treatment time of 10 minutes.

Experimental, theoretical, and differential X-ray diffraction patterns of $Dy_{0.75}Cu_3V_4O_{12}$ are shown in Fig. 1. The X-ray scattering spectrum exhibits weak

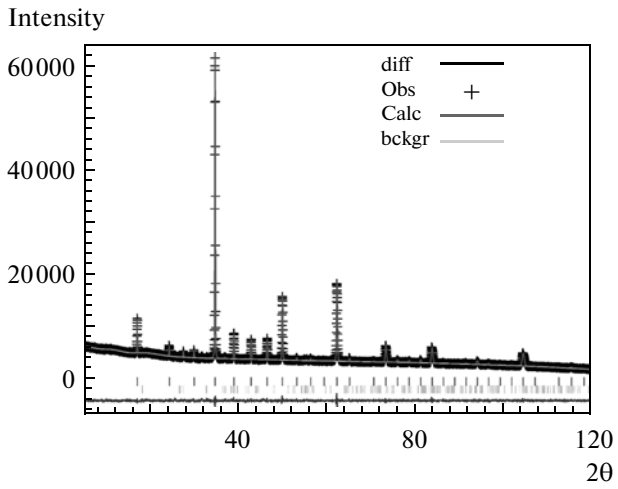

Fig. 1. XRD pattern of the $Dy_{0.75}Cu_3V_4O_{12}$ sample at p = 9.0 GPa, t = 1000°C, and τ = 10 min.

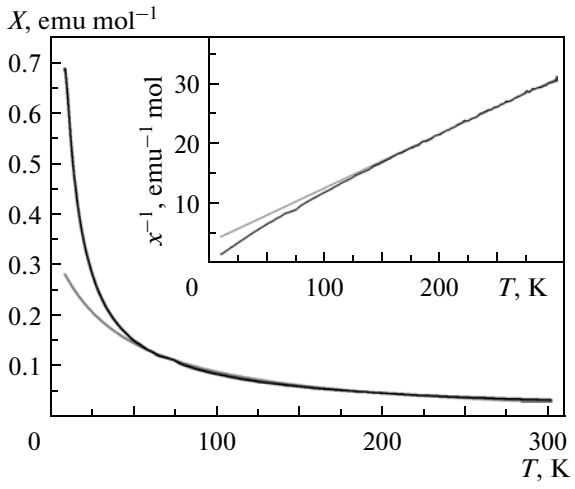

Fig. 2. Temperature dependence of the magnetic susceptibility of $Dy_{0.75}Cu_3V_4O_{12}$. (Insert: Temperature dependence of the reciprocal magnetic susceptibility of $Dy_{0.75}Cu_3V_4O_{12}$; the black curve represents the experimental values; the grey curve, the theoretical values from the Curie–Weiss law).

reflections that indicate the presence of traces of VO_2 and $CuVO_3$ in the sample. The crystal structure was determined, and the key bond lengths and angles calculated, on the basis of the X-ray data. The oxidation states of the elements in the crystal and its chemical formula, $Dy^{3+}_{0.875}\left[Cu^{2+}_{2.375}Cu^{1+}_{0.625}\right]V^{4+}_4O^{2-}$, were assessed. The results from structural determination are presented in Tables 1 and 2.

As is shown in Fig. 1, the temperature dependence of the magnetic susceptibility is typical of paramagnetics. The trend of the $\chi^{-1}(T)$ curve at temperatures above 100 K is linear and can be described using the Curie–Weiss law. The Curie constant C corresponds to an effective magnetic moment of $\mu_{eff} = 10.641\mu_B$. The theoretically calculated value of the squared magnetic moment is $\mu^2_{eff} = 100.7115\mu^2_B$, and the value of the effective magnetic moment per a formula unit is μ_{eff}=

Table 1. Structural and isotropic thermal parameters (Å^2) for $Dy_{0.75}Cu_3V_4O_{12}$

Atom		*x/a*	*y/b*	*z/c*	$U_{iso} \times 100$	Fraction
Dy	2*a*	0	0	0	3.3(2)	0.875(3)
Cu	6*b*	0	0.5	0.5	2.9(1)	1.0
V	8*c*	0.25	0.25	0.25	2.7(1)	1.0
O	24*g*	0	0.2988(4)	0.8191(4)	2.1(1)	1.0

Table 2. Shortest interatomic distances (*d*) and bond angles (ω) in $Dy_{0.75}Cu_3V_4O_{12}$

Distances, Å			Bond angles, °		Bond angles, °	
Dy-O	12×	2.548(3)	O–Dy–O	116.30(3)	O–V–O	91.4(1)
Expected		*2.463*	O–Dy–O	62.38(9)	O–V–O	88.6(1)
			O–Dy–O	63.70(3)		
Cu-O	4×	1.973(2)	O–Dy–O	117.62(9)	Dy–O–Cu	106.9(1)
Expected		*1.956*			Dy–O–V	88.7(1)
			O–Cu–O	83.9(2)	Cu–O–V	108.21(6)
V-O	6×	1.9249(7)	O–Cu–O	96.1(2)	V–O–V	142.6(1)
Expected		*1.960*				

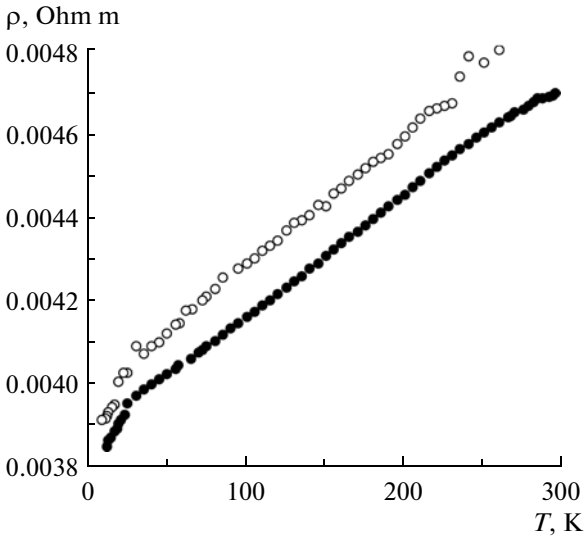

Fig. 3. Temperature dependences of $Dy_{0.75}Cu_3V_4O_{12}$ specific resistivity in a constant (dark dots) and an alternating electric field with a frequency of 4 kHz (white dots).

$10.036\mu_B$, respectively. The experimental value of the effective magnetic moment is thus quite close to the one obtained from our calculations.

CONCLUSIONS

Analysis of the temperature dependences of the electrical resistance in a constant electric field and an alternating field with a frequency of 4 kHz (Fig. 3) showed that $Dy_{0.75}Cu_3V_4O_{12}$ oxide is characterized by metallic conductivity. The resistivity changes slightly upon cooling from 300 K to 10 K. Similar behavior was observed for the electrical properties of the compound with a chemical composition of $Tm_{0.75}Cu_3V_4O_{12}$ [5].

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