საქართველოს მეცნიერებათა ეროვნული აკადემიის მოამბე, ტ. 15, №2, 2021
BULLETIN OF THE GEORGIAN NATIONAL ACADEMY OF SCIENCES, vol. 15, no. 2, 2021

Physical Chemistry

Effect of Cationic Composition on Thermal and Magnetic Characteristics of Cobalt-Zinc Ferrites

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(Presented by Academy Member Vladimer Tsitsishvili)

The paper presents the results of calorimetric study of characteristics of ferromagnetic transformation, and heat capacity at standard temperature Cp(298.15) for the complex oxides $Co_{1-x}Zn_xFe_2O_4$ with spinel structure (x = 1, 0.2, 0.4, 0.5, 0.6, 0.8). The Curie temperature (Tc) and enthalpy of magnetic anomalies at the region of magnetic transitions (ΔHm) are the principal aim of the study. The investigation of ΔHm was carried out by using the high-temperature differential scanning calorimeter. Heat capacity at standard temperature Cp(298.15) was established by the high-temperature drop calorimeter and by DSC. The variation of magnetic characteristics (Curie temperature and enthalpy of ferromagnetic transition), and standard heat capacity in the $CoFe_2O_4$ – $ZnFe_2O_4$ isomorphic system is illustrated. The correlations of thermal characteristics with the saturation magnetic moment (Ms) and lattice parameter (a) are overviewed. *© 2021 Bull. Georg. Natl. Acad. Sci.*

Calorimeters, enthalpy, heat capacity, magnetic phase transitions

In recent decades, new complex oxide compositions with special magnetic, electrical and mechanical properties have been intensively developed. The area of practical application of multicomponent oxides is constantly expanding, especially after the development of new methods for their preparation by nanotechnology [1]. A targeted selection of new advanced compositions and predicting their properties is connected with the most urgent problem of revealing the effect of cationic substitution on certain physical properties in mixed oxide systems. In the frame of this problem, the estimation of influence of cation variables on thermal and magnetic characteristics in the isomorphic series $Co_{1-x}Zn_xFe_2O_4$ is the purpose of presented research.

In the ternary oxide system $CoO–ZnO–Fe_2O_3$ the compounds with spinel structure with general formula $Co_{1-x}Zn_xFe_2O_4$ are of particular interest. Cobalt ferrite is known to belong to the group of hard ferrites and is mainly applied for recording devises. However, the magnetic properties of Co ferrite can be modified if Co and Fe ions are replaced by cations of other metals which

contribute to their use in microwave and other technology [1–3]. It has been shown also that the gradual substitution of zinc ions for cobalt ions leads to the modification of structural and some magnetic characteristics of cobalt ferrite reducing the Curie temperature, and increasing the lattice parameters [3–5]. The Co/Zn cation ratio and their distribution over the octahedral and tetrahedral sublattices in the spinel structure significantly affects the magnetic structure and properties (magnetization, magnetic disordering process, magnetic anisotropy, etc.), thereby determining the energy parameters such as Curie temperature, the energy of ferromagnetic transformation and excess magnetic component of heat capacity.

The article presents the results of calorimetric study of thermal characteristics of ferromagnetic transformation of $Co_{1-x}Zn_xFe_2O_4$ spinels with x=1, 0.2, 0.4, 0.5, 0.6, 0.8. The new data of Curie temperature and enthalpy of magnetic transformation are the principal aim of the study. Using also the calorimetric data of standard heat capacity Cp(298.15), the variations of Curie temperature, enthalpy of magnetic transition, and heat capacity in the $CoFe_2O_4$–$ZnFe_2O_4$ isomorphic system are overviewed, and the correlations of these parameters with saturation magnetic moment (Ms) and lattice parameter (a) are discussed. The obtained correlations can be used to determine similar parameters for intermediate compositions by interpolation.

Experimental

Samples: The polycrystalline compositions $Co_{1-x}Zn_xFe_2O_4$ (x = 0, 1, 0.2, 0.4, 0.5, 0.6, 0.8) were fabricated by high-temperature synthesis using the starting oxides (Fe_2O_3, ZnO) and cobalt nitrate of high purity (~99.5%). The homogenized initial mixtures, in the form of compressed tablets, passed two repeated stages of calcination at 1500-1550K in air for 40-45 hours. The spinel structure and good stoichiometry of the products were confirmed using X-ray diffraction and chemical analysis.

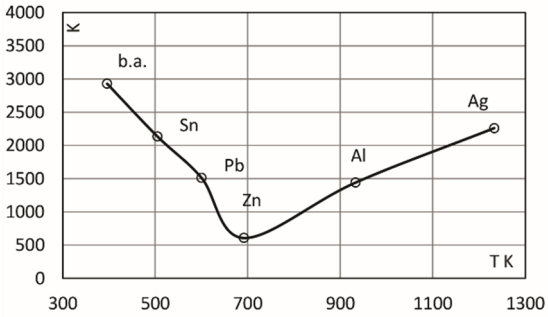
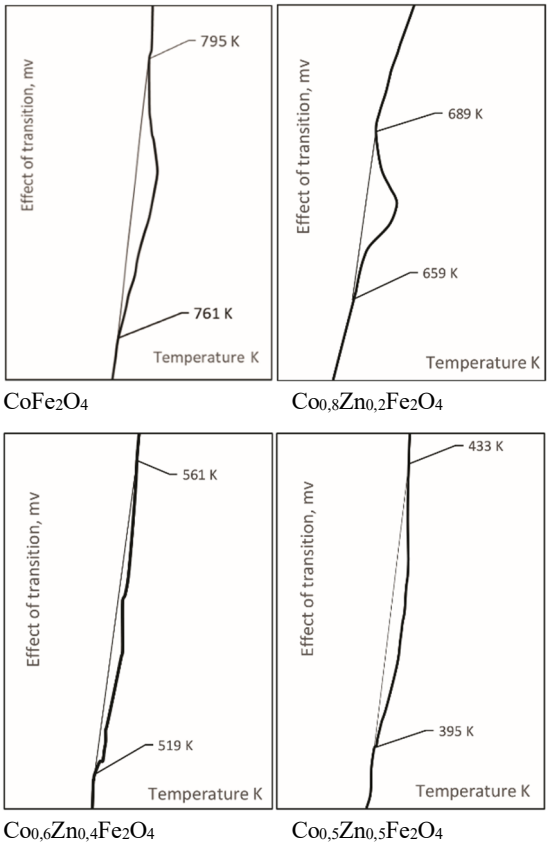


Fig. 1. Calibration curve of HT-1500.

Calorimetric Measurements. Investigation of high-temperature transformations was carried out on the calorimeter HT-I500 manufactured by "Seteram" (France). The calorimetric experiments were carried out in argon. The samples were weighed with an accuracy of 0.00005 g. Experiments were carried out in argon. The calorimetric detector with differential thermal battery Pt-Rd(10%)/Pt was used. Experimental conditions (heating rate, instrumental sensitivity, sample mass, etc.) were selected empirically so that the configuration of the experimental curve of thermal anomaly would give the minimum error at its assessment. The thermal constant of the calorimeter (K) at a given temperature was determined by the enthalpy of melting of the reference substances – benzoic acid, tin, lead, zinc, aluminum, and silver (Fig. 1). The heating rate was 200 K/hour (~3 K/min.), the sensitivity of the galvanometer -500 mv, the number of measurements for each substance was 5-8. The thermal effects correspondent to the anomalies in the region of transition (Fig.2), were calculated as:

$$\Delta H = K \cdot A \cdot \frac{M}{G} \frac{J}{mole}, \qquad (1)$$

where K is the calorimeter constant taken from the calibration graph (Fig. 1), A – experimental calorimetric thermal effect, M – molecular mass of the sample, G – weight of the sample. Standard deviation of enthalpy data is $S = \pm 2.5\%$. The experimental results are shown in Table 1 and Fig. 2.



$CoFe_2O_4$ $Co_{0,8}Zn_{0,2}Fe_2O_4$

$Co_{0,6}Zn_{0,4}Fe_2O_4$ $Co_{0,5}Zn_{0,5}Fe_2O_4$

Fig. 2. Experimental curves for enthalpy of ferromagnetic transitions of $Co_{1-x}Zn_xFe_2O_4$.

The heat capacity data for the standard temperature Cp (298.15) were estimated as $Cp = \frac{d\{H(T) - H(298.15)\}}{dT}$ using the equations of temperature dependence of enthalpy $H(T) - H(298.15) = f(T)$ obtained by the method of high-temperature drop calorimetry [6]. For the samples with x=0.8 and 0.6, having magnetic phase transition close to the standard temperature (see Table 1), a direct measurement of heat capacity was carried out using the differential scanning calorimetric (DSC-111) method [7], since the drop calorimeter has an increased error in this temperature area.

Results and Discussion

1. Enthalpy of ferromagnetic transition: The experimental calorimetric curves used for estimation of enthalpy of ferromagnetic transformation are shown in Fig. 2. Thermal effects are maximally manifested at the vicinity of Curie (T_c) temperatures. The peaks of anomalies on these curves correspond to T_c, and their values are given in Table 1. The calorimetric thermal effects are manifested most clearly for compositions with x=0 and x=0.2, while for compositions with x>0.4, the Curie points of which are in the least sensitive region of calorimetric measurements (T<350-400K), the thermal effects are too blurred and weak to be estimated with satisfactory accuracy.

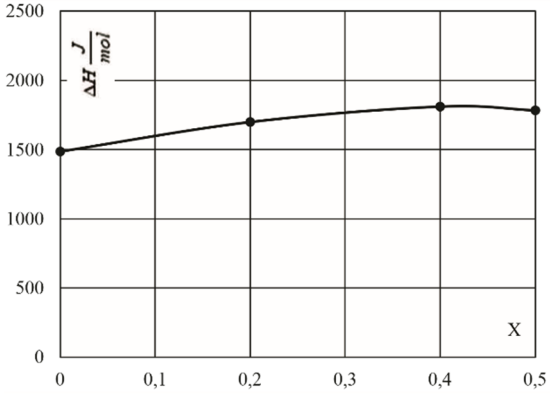


Fig. 3. Enthalpy of magnetic transition of $Co_{1-x}Zn_xFe_2O_4$.

Table 1. Characteristics of cobalt-zinc ferrites $Co_{1-x}Zn_xFe_2O_4$

x	a (°A) [3,4]	Curie temperature T_c K	ΔH (transition) J/mole	Heat capacity Cp(298.15) J/K.mole	Magnetic moment M_s (n_B)
0	8.475	780	1487	152.1 [6]	3.75
0.2	8.485	670	1699	156.3	4,95
0.4	8.495	540	1812	154.8	5,83
0.5	8.504	420	1783	154.5	6,17
0.6	8.508	356 [3]	-	149.7	5.80
0.8	8.515	223 [3]	-	149.1	4.10
1.0	8.527	-	-	138.0 [6]	0.00

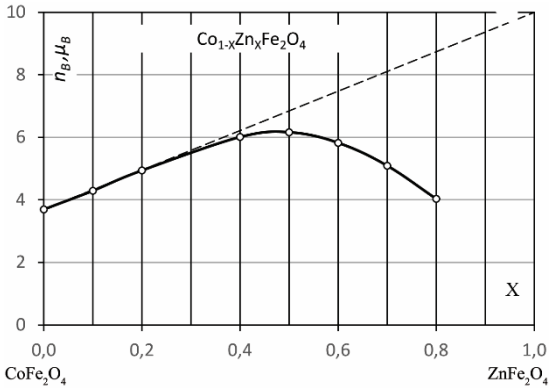


Fig. 4. Magnetic moments of $Co_{1-x}Zn_xFe_2O_4$.

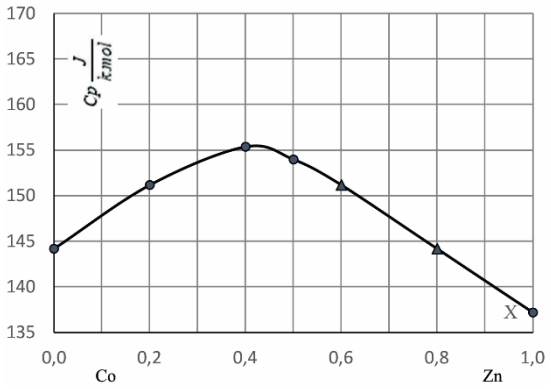


Fig. 5. Heat capacity (J/K.mole) of $Co_{1-x}Zn_xFe_2O_4$.

When saturated with zinc ions, the Curie point of Co-Zn ferrites gradually decreases. The similar behavior was identified also for other spinel series (Ni-Zn; Li-Zn) [6], and therefore we can assume that this is typical for complex oxide solid solutions.

The data given in Table 1 show the relationship between the Curie point (T_c) and the lattice parameter (a) – an increase in the lattice parameter of spinel-type structure leads to a linear decrease in the Curie point. Consequently, the effect of the size factor on T_c is obvious, since an increase in the distance between structure-forming paramagnetic cations leads to weakening of the magnetic exchange interactions between them [2]. In Table 1 the values of the enthalpy of the ferromagnetic transformations ΔH_m, estimated by corresponding calorimetric effects (Fig. 2), are given as well. The shape of the curve of the compositional dependence of enthalpy of magnetic transformation (Fig. 3) generally coincides with the change in the curve of magnetic moment in the Co-Zn ferrite system (Fig. 4, Table 1). This is in accordance of equation 2 which illustrates the dependence between magnetic energy and magnetic moments [2] for antiferromagnetic ferrites with sub-lattice structure:

$$E(mag) = -0.5 \cdot \Sigma n_i \cdot M_i^2 \qquad (2)$$

(n_i – the constant of crystal fields in sublattices, M_i – magnetic moment of sublattices).

2. Heat capacity at standard temperature. The data of heat capacity were determined based on high-temperature enthalpy functions $H(T) - H(298.15) = f(T)$ valid for the temperature interval from 298K up to T_c and expressed by the equation suggested by N. Landia [8, 9]:

$$Cp = \left(27.6 + b \cdot T^n + c \cdot T^k\right) \cdot m \frac{J}{K \cdot mole} \qquad (3)$$

(m – the number of atoms in molecule in our case is 7). The corresponding coefficients are shown in Table 2. The heat capacity data at standard temperature Cp (298.15) are presented in Table 1. For compositions with x = 0.8 and 0.6, the values

Table 2. Coefficients of heat capacity equation (3) for $Co_{1-X}Zn_XFe_2O_4$

x	Temperature range	-b	-n	c	k
0.8	298-1300	135.1559	0.14	$5.5997192*10^{-2}$	1
0.6	298-356	$3.6013720*10^{9}$	3.21	$-3.5367652*10^{-15}$	6
0.5	298-418	35280427	2.41	$-4.5551949*10^{-8}$	2.8
0.4	298-548	$5.7981230*10^{9}$	3.31	$-2.2312008*10^{-7}$	2.7
0.2	298-662	2541.3329	0.56	21.626669	0.2

obtained by direct determination of the heat capacity on DSC are recommended.

The compositional dependence of the standard heat capacity is shown in Fig. 5. The maximum value of Cp (298.15) appears for compositions with x=0.4-0.5. A similar type of change in heat capacity, depending on the composition, was revealed earlier for a number of spinel systems (Ni-Zn, Li-Zn) [6,7]. The Cp(298.15) curve correlates with the form of the composition-magnetic moment dependence shown in Fig. 4 and indicates a significant influence of magnetic component on the energy parameters.

Conclusion

For the purposeful selection of compositions with certain characteristics, the effect of cation variables on thermophysical properties of cobalt-zinc ferrites was studied using various calorimetric techniques. The Curie point – (Tc), enthalpy of magnetic transformation (Hm) and the heat capacity at standard temperature (Cp298.15) were established. The correlations between composition, structural parameters, thermal and magnetic properties have been elucidated and discussed.

ფიზიკური ქიმია

კატიონური შემადგენლობის გავლენა კობალტ-თუთიის ფერიტების თერმულ და მაგნიტურ მახასიათებლებზე

მ. ხუნდაძე*, ვ. ვარაზაშვილი*, თ. მაჩალაძე*, თ. მირიანაშვილი*, რ. ჯორბენაძე*

*ივანე ჯავახიშვილის სახ. თბილისის სახელმწიფო უნივერსიტეტი, რ. აგლაძის არაორგანული ქიმიისა და ელექტროქიმიის ინსტიტუტი, თბილისი, საქართველო

(წარმოდგენილია აკადემიის წევრის ვ. ციციშვილის მიერ)

Co/Zn კატიონების თანაფარდობა და მათი განაწილება შპინელის სტრუქტურაში ასახვას პოულობს $Co_{1-x}Zn_xFe_2O_4$ ჯგუფის ფერიტების თერმულ და მაგნიტურ მახასიათებლებზე. სტატიაში პირველად არის წარმოდგენილი $Co_{1-x}Zn_xFe_2O_4$ (x = 1, 0.2, 0.4, 0.5, 0.6, 0.8) სისტემის შპინელების ფერომაგნიტური გარდაქმნის თერმული მახასიათებლების კალორიმეტრიული კვლევის შედეგები. კიურის ტემპერატურა (T_c) და ფერომაგნიტური გარდაქმნის ენტალპია (ΔH_m) შესწავლილია მაღალტემპერატურული დიფერენციალური სკანირების კალორიმეტრის გამოყენებით (HT-1500 "Setaram"). დადგენილია კიურის წერტილისა და მაგნიტური ენთალპიის ცვლილების ხასიათი, როგორც Co/Zn თანაფარდობის ფუნქცია და გამოვლენილია მაგნიტური ენთალპიის კორელაცია გაჯერების მაგნიტურ მომენტთან (Ms). სტანდარტულ ტემპერატურაზე თბოტევადობის Cp(298.15) მნიშვნელობები დადგენილია მაღალტემპერატურული შერევის კალორიმეტრისა და DSC მეთოდის გამოყენებით. $CoFe_2O_4 - ZnFe_2O_4$ იზომორფულ

სისტემაში სტანდარტული თბოტევადობის ცვლილება ავლენს კორელაციას ნაერთის მაგნიტურ მომენტთან, სტრუქტურულ პარამეტრსა და შპინელის სტრუქტურაში კატიონების განაწილების სახესთან. წარმოდგენილი კორელაციები საშუალებას იძლევა შეფასდეს შესწავლილი მახასიათებლების მნიშვნელობები Co-Zn ფერიტების შუალედური, ექსპერიმენტულად შეუსწავლელი, კომპოზიციებისათვის.

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Received March, 2021