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Effects of Diamagnetic Substitution on Heat Capacity of Double Spinel Ferrites

Grigor Tatishvili*, Mzia Khundadze, Vera Varazashvili**, Murman Dzotsenidze**, Rusudan Jorbenadze**, Lela Rokva****

* *Academy Member, National Academy of Sciences of Georgia; R. Agladze Institute of Inorganic Chemistry and Electrochemistry, Ivane Javakhishvili Tbilisi State University, Georgia*
** *Institute of Inorganic Chemistry and Electrochemistry, Ivane Javakhishvili Tbilisi State University, Georgia*

Abstract. This work aims to identify the effects of composition and temperature variables on the heat capacity of double ferrite systems. The isomorphic spinel series Me(1-x)ZnxFe$_2$O$_4$ (Me – Ni, Co, Li, Cu, Mg) is investigated. Heat capacity data obtained by calorimetric methods were presented as isotherms of heat capacity versus composition in the 300-1000 K range. In the paramagnetic region (T < Tc), all Me-Zn ferrite systems exhibit dome-shaped relationships between heat capacity Cp and composition (x), with maximum values near the equimolar region (x = 0.4 - 0.6). As the temperature rises, the maximum on the Cp-x curve moves toward the ferromagnetic component. In the paramagnetic region where T>Tc, Cp(x) isotherms display the shape without a maximum. In the CuZnF system, compositions with high Cu content (x=1.0, 0.8) show a noticeable influence of the cooperative Jahn-Teller effect and tetragonal distortion of the cubic lattice, leading to overestimated heat capacity values. *© 2026 Bull. Natl. Acad. Sci. Georg.*

Keywords: heat capacity, magnetic phase transitions, calorimetry, ferrites

Introduction

Complex systems of oxide ferrites capture ongoing interest due to their unique magnetic, electrical, and various other properties. Modifying the composition of ferrites significantly alters their properties in the desired direction, thus broadening the range of potential applications.

Among the various structural groups (such as spinel, perovskites, garnets, etc.), spinel-type ferrites are the most widely used. The cubic crystal structure of spinel ferrites arises from 64 tetrahedral (A) and 32 octahedral [B] sublattices, where ferrite-forming metal ions are situated according to their energy preferences and temperature (Brabers, 1995; Krupichka, 1973).

The distribution of cations in the sublattices is sensitive to temperature. As the temperature increases, the entropy component of free energy also rises, leading to redistribution of cations across the A- and B-sublattices, which is evident in the magnetic and thermal properties of ferrites. Additionally, as the temperature rises, a gradual ferromagnetic disordering process occurs, leading to a ferromagnetic-paramagnetic phase transition at the Curie (Néel) point, which affects the energetic characteristics of ferrites.

Currently, numerous new multicomponent compositions based on mixed spinel-type ferrites are being developed. Therefore, for the purposeful selection of the components of new developments, it is important to have initial data on the correlations between some fundamental parameters. From this perspective, it seems appropriate to identify the relationships between the cationic composition, magnetic parameters, and thermochemical characteristics in double ferrite systems that can be used to create new developments through cationic compilation.

This paper summarizes our studies on the thermal properties of complex ferrite systems. It focuses on a continuous series of solid solutions, including ferromagnetic inverse ferrites (Ni, Co, Li, Mg, Cu)Fe_2O_4 and diamagnetic normal spinel ferrite $ZnFe_2O_4$. Using zinc ferrite as a normal-type component enables us to observe the impact of diamagnetic dilution on the thermal and magnetic properties in these ferrite systems.

Results and Discussion

The samples examined are polycrystalline $Me_{1-x}Zn_xFe_2O_4$ ferrites, where Me = Ni, Co, Li, Cu, Mg, and x = 0; 1.0, 0.2; 0.4; 0.6; 0.8. They are prepared using a high-temperature (1500K) solid-state ceramic route. All samples exhibit a cubic spinel structure, and their crystal properties (as confir-

Table. Lattice parameter (a), Curie temperature (Tc), and magnetic moment (Ms) of ferrites

$M_{1x}Zn_xFe_2O_4$ (MeZnF)	x	a, (A°)	Tc (K)	Magnetic moment (300 K) M_s (σ_b)
NiZnF	0.0	8.340	858	2.29
	0.2	8.358	729	3.70
	0.4	8.383	623	5.00
	0.6	8.400	458	5.00
	0.8	8.417	323	3.10
	1.0	8.434	-	0.00
CoZnF	0.0	8.376	773	3.30
	0.2	8.364	669	4.50
	0.4	8.401	546	5.83
	0.5	8.402	423	6.17
	0.6	8.414	356	5.90
	0.8	8.425	223	4.10
	1.0	8. 433	-	0.00
LiZnF	0.0	8.330	903	2.47
	0.027	8.332	898	2.90
	0.097	8.340	833	3.40
	0.200	8.350	773	3.60
	0.368	8.366	658	4.50
	0.500	8.380	573	4.00
	0.692	8.400	413	2.00
	0.900	8.420	-	-
	1.000	8.434	-	-
CuZnF	0.0	8.254 (tetra. c/a=1.06)	755;761	1.8
	0.2	8.384	660	2.3
	0.4	8.396	510	2.3
	0.6	8.415	-	1.9
	0.8	8.432	-	1.3
	1.0	8.433	-	0.0
MgZnF	0.0	8.385	695	0.8
	0.2	8.389	585	1.9
	0.4	8.409	-	1.7
	0.6	8.410	-	0.9
	0.8	8.420	-	0.1
	1.0	8.435	-	0.0

med by X-ray analysis) match literature data. The temperature and air regimes, including a step-by-step cooling process, were employed to obtain a cation distribution within the sublattices that approaches the desired state of equilibrium.

The magnetic properties of the samples – the Curie temperature (T_c) and magnetic moments (M_s) – are also presented in Table. The Curie points were determined using the ballistic, thermogravimetric, and calorimetric methods. The magnetic moments (M) at near standard temperature were measured by the Sexsmith method (Chachanidze, 1990).

The thermodynamic properties – enthalpy (H_t) and heat capacity (C_p) – were studied using calorimetric methods: high-temperature adiabatic drop calorimetry for temperatures ranging from 298 to 1300 K and differential scanning calorimetry (DSC) for temperatures between 300 and 1000 K. The accuracy of recommended heat capacity data is about 2%.

The examined binary ferrite systems form a continuous series of solid solutions in which the ferromagnetic components NiF, CoF, LiF, CuF, and MgF are gradually substituted by the non-magnetic zinc ferrite ZnF. In terms of cation distribution over octahedral [B] and tetrahedral (A) positions, they can be conditionally divided into the following subgroups: a) normal spinel $(Me^{2+})[Me^{3+}]_2O_4$ (ZnF); b) inverse – $[Me^{2+}](Me^{3+})_2O_4$ (NiF, CoF, LiF); and c) mixed – $(Me^{2+}_x\ Me^{3+}_{1-x})[Me^{2+}_{1-x}\ Me^{3+}_{1+x}]O_4$ (MgF, CuF, MeZnF). The degree of inversion in intermediate compositions of double ferrites (MeZnF) is influenced by the Me/Zn ratio and temperature, affecting their magnetic and thermal properties. Regarding cationic composition, the investigated ferrite solutions can be classified into the following groups: spinel ferrites containing divalent ions – $Me_{(1-x)}Zn_xFe_2O_4$, where Me=Co, Ni, Cu, Mg; and ferrites containing monovalent lithium ions $Li_{0.5(1-0.5x)}Zn_xFe_{(2.5-0.5x)}O_4$.

The thermal characteristics of mixed oxides, such as ferrites, depend on numerous factors, including the radii and electronic configurations of cations, magnetic structure, phase transitions, and temperature. Heat capacity is one of the most useful quantities for clarifying the degree of influence of these factors.

The heat capacity of solids, including ferrites, can generally be expressed as a complex value:

$$C_p = C(v) + C(d) + C(ex), \qquad (1)$$

C(v) represents the lattice vibrational heat capacity, and C(d) is the difference between isobaric and isochoric heat capacities. An excess component, C(ex), can arise from structural phase transformations, cationic and magnetic disordering processes, Schottky, Jahn-Teller, or other effects. In the case of ferrimagnetic ferrites, the main component of C(ex) is the ferromagnetic part C_m, which indicates the energy required to reduce the initial magnetic order when heated.

Determining the magnetic heat capacity of ferrites is a complex task because it reflects the combined effects of all sublattices, and none of the proposed methods offers the desired accuracy for antiferromagnetic multi-sublattice ferrites.

In our previous papers (Khundadze et al., 2021; Machaladze et al., 2023), we discussed the correlations between magnetic and thermal properties of double ferrite systems at standard temperatures. It was shown that as ferrimagnetic ferrites containing nickel, cobalt, copper, magnesium, and lithium are gradually diluted with diamagnetic zinc ferrite, the lattice parameter (a) increases monotonically, and the Curie temperature (T_c) decreases. However, the saturation magnetic moments (M_s) vary across the system in a dome-shaped curve, reaching a maximum in the region of equimolar compositions at x=0.4-0.6. This unusual behavior of spontaneous magnetization is explained based on the antiferromagnetic theory of ferrites. With an increase in zinc content to a certain limit (up to x=0.4-0.6), a redistribution of Fe and Zn cations occurs in the spinel sublattices, which increases the overall magnetic moment. Our study shows that the compositional dependencies of heat capacity $C_p(x)$ near standard temperature exhibit the same domed shape with a maximum at $x \approx 0.4$-0.6. The positions of the maxima on the heat capacity and magnetic moment curves coincide within the experimental error margins.

To separate and estimate the magnetic C_m component from the total heat capacity Cp (eq. 1), one must determine the value of the regular part C(reg) = C(v) + (Cd). However, the methods for evaluating the C(v) and C(d) components have limited accuracy for complex solid ferrite solutions. Nevertheless, for a qualitative understanding of this issue, it should be noted that in mixed double inverse ferrite (NiF/CoF) systems, a monotonic change is observed in the compositional dependence of magnetization, unlike double ferrites containing the normal zinc spinel, which display domed behavior.

To better clarify the influence of the magnetic component C_m on the total heat capacity of ferrimagnets, the relationships between composition and heat capacity of mixed ferrites are reviewed, with $C_p(x)$ shown as isotherms across a broad temperature range (300-1000K) (Fig.). Although all the compounds display a spinel structure, they are categorized into two distinct groups due to differences in the properties of the ferrite-forming metals.

a) NiZnF, CoZnF, LiZnF: Figure (a, b, c) illustrates the C_p-x isotherms for these systems. Curie temperatures are provided in the Table. We observe that the isotherms gradually change with increasing temperature. When all members of the ferrite systems are ferromagnets, the C_p-x curves display a dome shape with a maximum near equimolar compositions. As the temperature rises, compositions with a high Zn content progressively become paramagnetic. Consequently, the C_p-x curves change shape, and their maxima shift toward a higher content of ferromagnetic component. At temperatures where all compositions are paramagnetic (T>Tc), the C_p-x curve tends to become concave. Due to the disappearance of magnetic contributions C_m, the total heat capacity is represented solely by its lattice component C(reg), which has the smallest value at intermediate compositions. In this context, it should be noted that the result obtained for the microhardness of nickel-zinc ferrites can be viewed as an indirect confirmation of the above, as the maximum microhardness in intermediate compositions suggests that they have the highest bond energy and, consequently, the lowest lattice heat capacity.

Cobalt-zinc and lithium-zinc ferrite systems exhibit similar behavior (Fig. b). At lower temperatures, the $C_p(x)$ curves alter the shape of the dome, depending on the temperature of the ferrimagnetic-paramagnetic transformation in the compounds. In the temperature region where all compounds are paramagnetic, the C_p-x curves tend to have a concave shape.

b) MgZnF and CuZnF: For magnesium, copper, and zinc ions, the difference in the energy of preference to occupy positions A or B is negligible (Krupichka, 1973). Therefore, the entropic term of free energy becomes crucial in the distribution of cations, especially at temperatures overcoming the kinetic factor (T> 450 K). This makes the magnetic and energetic properties of magnesium-zinc and copper-zinc ferrites sensitive to synthesis processes. As a result, there is a significant spread in the published data on magnetic parameters. Therefore, as noted above, we applied the special synthesis modes to obtain a cation distribution close to equilibrium. As a result, the crystal and magnetic parameters of the obtained samples correspond to the published data.

Magnesium-zinc and copper-zinc ferrites are weak ferromagnets (Table). This is also reflected in their heat capacity behavior. As a result, the ferrimagnetic-paramagnetic transition, marked by a lambda-shaped $C_p(T)$ curve with a peak at the Curie point, occurs only for the compositions rich in copper ions x=0, 0.2, and 0.4. As Tc decreases, the thermal effect of the magnetic transition also lessens, making the Cp curve less pronounced. Calorimetric measurements of these systems were performed using a slow temperature increase to minimize the quenching effect.

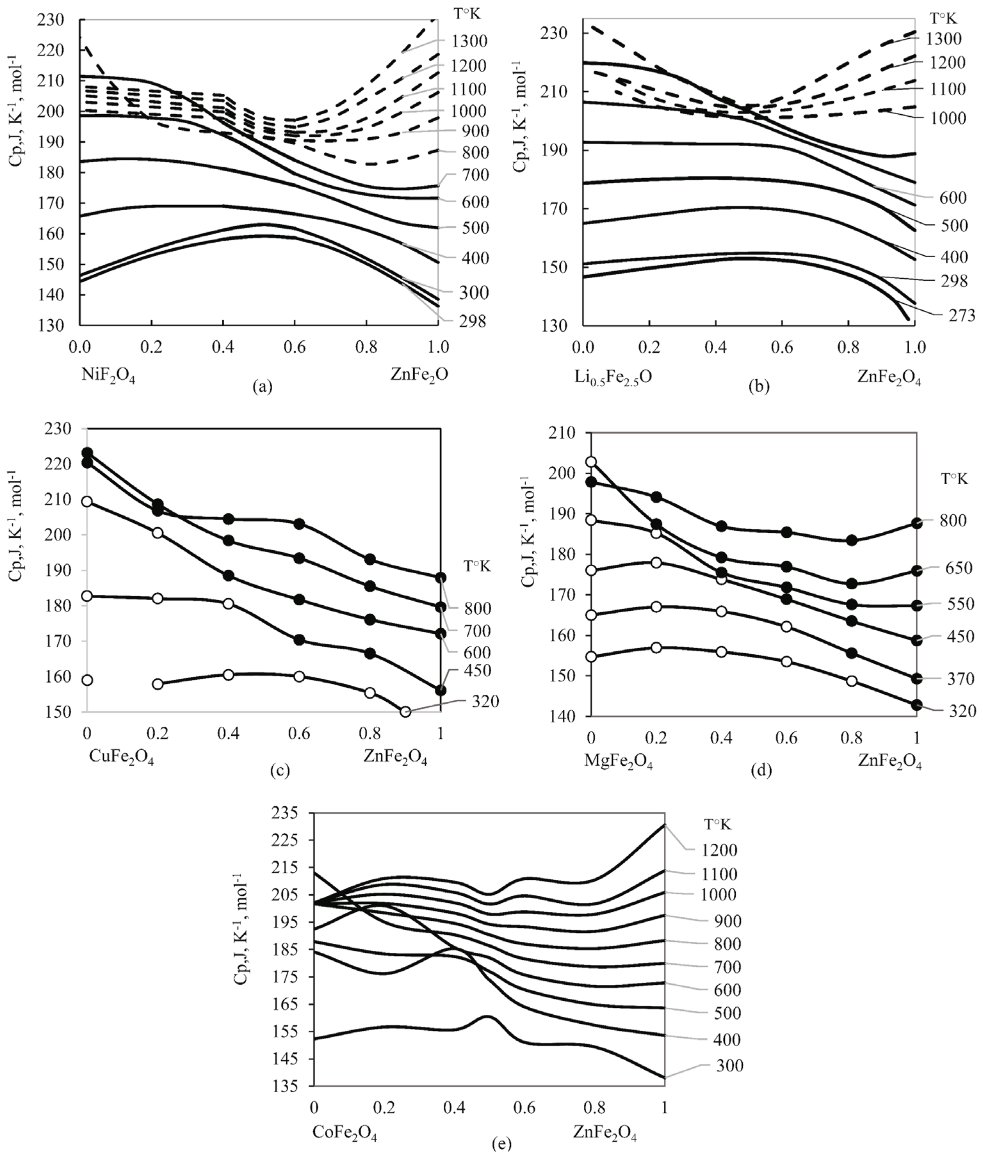

Fig. The isotherms of the compositional dependences of heat capacity of double ferrite systems $Me_{(1-x)}Zn_xFe_2O_4$.

The concentration dependences of the heat capacity for the MgZnF and CuZnF systems are generally similar to those of the first group ferrites (Fig. d, f). At temperatures where all compositions are ferrimagnetic, the C_p-x isotherms show a maximum at intermediate compositions, corresponding to the highest values of the magnetic component C_m of heat capacity. As the temperature increases, the $C_p(x)$ curve gradually shifts in the opposite direction, and in the paramagnetic region, the influence of the excess magnetic component on $C_p(x)$ disappears.

However, the copper-zinc ferrite CuZnF system differs somewhat from other spinel structures. Due to the Jahn-Teller effect (IT), in compositions with high Cu^{2+} content, a cooperative tetragonal macroscopic distortion of the initial cubic crystal structure occurs. This leads to the excess heat capacity anomaly and phase transition at the critical temperature TIT. Above TIT, the cooperative nature of the Jahn-Teller effect dissipates, and the system reverts to its initial cubic structure, although local tetragonal distortions of the polyhedral persist (Krupichka, 1973). In addition, ferromagnetic disordering occurs in the same temperature range, with a Lambda-type magnetic phase transformation at the Curie point T_c. As a result, a vast temperature region is formed where both heat capacity anomalies overlap. For copper ferrite, TIT >Tc (761 and 660K, respectively) (Samadashvili, 2002). Even a slight increase in zinc content (up to 5%) disrupts the cooperative nature of the Jahn-Teller effect due to an increase in the lattice parameter. In compounds where x>0.2, no critical point TIT is observed, and only a magnetic anomaly with the Curie point T_c appears. It is notable that changes in zinc content similarly affect ferromagnetic ordering; the Curie point decreases as the zinc content increases. On $C_p(T)$ curves, the ferromagnetic anomaly is evident only for compositions with x = 0, 0.2, 0.4 (760, 660, 505K, respectively), followed by a gradual decrease in the corresponding heat capacity peaks. The combined effect of two anomalies spanning a fairly wide temperature range (300-760 K) makes it impossible to reliably separate them from each other and to estimate their corresponding contributions to heat capacity.

Overlapping processes are reflected in the isotherms of the compositional dependence Cp(x) of CuZnF, making them somewhat different from those considered earlier. In addition to the ferromagnetic part, the influence of excess heat capacity caused by the Jahn-Teller effect is also evident, since the heat capacity of compounds with x = 0 and 0.2 on the Cp(x) isotherms exceeds the values expected from the direction of the Cp(x) curve above these compositions, both at standard temperatures and in a certain range above 300 K. For copper ferrite, the excess heat capacity associated with the Jahn-Teller effect at 300 K is approximately 8±1.5 J/Kmol, which is 5% of the total Cp. In the region with high zinc content x >0.6, no cooperative IT effect is evident, and the shape of the Cp(x) isotherms approaches that of other ferrite systems, with maxima at x=0.5-0.6, reflecting the influence of the ferromagnetic factor. No thermal effect with a notable heat capacity peak associated with the IT effect is observed in Cp(T) of these compositions. However, based on general assumptions about the nature of this phenomenon (Krepichka, 1973), one can expect the influence of local distortions of polyhedra associated with the Jahn-Teller "dynamic" effect.

Conclusion

The gradual dissolution of spinel-type ferrimagnetic ferrites by diamagnetic zinc ferrite creates an isomorphic series of solid solutions. The factors that determine their magnetic and thermal properties include the characteristics of the structure-forming cations, the proportion of zinc content, and temperature. To identify the influence of these factors on thermodynamic properties, the heat capacity (C_p) of double spinel ferrite systems $Me_{(1-x)}Zn_xFe_2O_4$ (Me = Ni, Co, Li, Cu, Mg) was examined as a function of composition and temperature. The Curie temperature decreases smoothly in all systems as the zinc content increases. The compositional dependences of heat capacity (C_p-x) for double ferrite systems are presented as isotherms ranging from 300 to 1000 K. At temperatures where all compositions are ferrimagnetic, the influence of the excess magnetic component (Cm) creates a dome-like compositional dependence of total heat capacity Cp(x), featuring a maximum near equimolar compositions. This aligns with the behavior of magnetic moments in the systems. The maximum $C_p(x)$ curve gradually shifts toward ferromagnetic compositions as the temperature increases. In the paramagnetic temperature region, where no magnetic heat capacity components are present, isotherms tend to form a curve without a maximum. In copper-zinc ferrites, the influence of the cooperative Jahn-Teller (IT) effect is manifested in compositions with high copper content (Cu < 5%), causing tetragonal distortion of the cubic lattice and overestimating heat capacity values.

ფიზიკური ქიმია

დიამაგნიტური ჩანაცვლების ეფექტი შპინელის ტიპის ფერიტების თბოტევადობაზე

გ. ტატიშვილი*, მ. ხუნდაძე, ვ. ვარაზაშვილი**, მ. ძოწენიძე**, რ. ჯორბენაძე**, ლ. როყვა****

* *აკადემიის წევრი, საქართველოს მეცნიერებათა ეროვნული აკადემია; ივანე ჯავახიშვილის სახ. თბილისის სახელმწიფო უნივერსიტეტი, რ. აგლაძის არაორგანული ქიმიისა და ელექტროქიმიის ინსტიტუტი, საქართველო*

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

ნაშრომში განხილულია თბოტევადობაზე კომპოზიციური და ტემპერატურის ცვლილების გავლენა შპინელის სტრუქტურის ფერიტების ორმაგ იზომორფულ სისტემებში – $Me_{(1-x)}ZnxFe_2O_4$ (Me – Ni, Co, Li, Cu, Mg). თბოტევადობის მონაცემები წარმოდგენილია როგორც შედგენილობისა და ტემპერატურის ფუნქცია და ილუსტრირებულია იზოთერმების სახით 300-1000 K დიაპაზონში. პარამაგნიტურ რეგიონში კიურის ტემპერატურამდე (T<Tc), Me-Zn ფერიტის ყველა სისტემა ხასიათდება გუმბათის ფორმის კორელაციებით თბოტევადობა Cp-სა და შემადგენლობას (x) შორის, მაქსიმალური მნიშვნელობებით ეკვიმოლარულ უბანზე (x = 0,4 – 0,6). მსგავსი სახის დამოკიდებულება აღინიშნება მაგნიტური მომენტების კომპოზიციურ ცვლილებებში. ტემპერატურის მატებასთან ერთად, Cp-x დამოკიდებულების მაქსიმუმი გადაინაცვლებს მაღალი კიურის ტემპერატურის მქონე კომპოზიციების მიმართულებით, რაც დაკავშირებულია საერთო თბოტევადობიდან მისი ფერომაგნიტური მდგენელის თანდათანობით გამორთვასთან. პარამაგნიტურ T>Tc რეგიონში, Cp(x) იზოთერმებს აღარ ახასიათებს მრუდი მაქსიმუმით, რაც მიუთითებს საერთო თბოტევადობაში მაგნიტური მდგენელის მნიშვნელოვან წვლილზე. სპილენძის თუთიის CuZnF სისტემაში, სპილენძის მაღალი შემცველობის მქონე კომპოზიციებისთვის, აღინიშნება კოოპერატიული Jahn-Teller ეფექტის შესამჩნევი გავლენა, რაც უკავშირდება თბოტევადობის გაზრდილ მნიშვნელობებს.

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