Solid State Sciences 12 (2010) 2134–2143

Contents lists available at ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie

Al^{3+}-modified elastic properties of copper ferrite

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ARTICLE INFO

Article history:
Received 5 June 2010
Received in revised form
30 August 2010
Accepted 10 September 2010
Available online 17 September 2010

Keywords:
Magnetic materials
Chemical synthesis
Ultrasonic measurements
Elastic properties
Microstructure

ABSTRACT

Ultrasonic pulse echo-overlap technique at 300 K (9 MHz) has been employed to study the elastic properties of Al^{3+}-substituted $CuFe_2O_4$ spinel ferrite system. The longitudinal and transverse wave velocities are used to compute elastic moduli and these are corrected to the zero porosity by employing different models. Contrary to expectation, the magnitude of elastic moduli is found to decrease by 75% with only 30% of Al^{3+}-substitution for Fe^{3+} in the system. The lowering of elastic stiffness is mainly due to residual stress-induced spontaneous cracking and presence of oxygen vacant sites in the material. The lower value of lattice energy for polycrystalline specimens as compared to their single crystalline counterparts have been explained in the light of an increase degree of disorientation at the grain boundary with Al^{3+}-substitution.

1. Introduction

It has been reported that copper ferrite ($CuFe_2O_4$) is an unique spinel because (i) due to a relatively small energy difference between Cu^{2+}-ions in the tetrahedral (A) and octahedral (B) sites, cation redistribution is possible and strongly dependent upon the annealing temperature, cooling rate, microstructure etc [1] (ii) the presence of Cu^{2+}-ions can provoke a collective Jahn–Teller distortion which is associated with the alignment of the Cu^{2+}-ions occupying the tetragonally distorted octahedral spinel lattice formed by the oxygen ions [2] (iii) it has two crystallographical spinel structure, the high temperature cubic phase and the low temperature tetragonal phase [1].

Various test techniques (distractive, semi-distractive and non-distractive) are available for complete characterization of the material. Among the various non-distractive techniques, Ultrasonic non-distractive testing and evaluation plays a key role in materials characterization [3]. Ultrasonic waves are important in research and applications. By employing coherent ultrasonic phonons of carefully controlled frequency and polarization several basic properties of solids have been investigated.

The study of propagation of ultrasonic waves in materials determines the elastic constant, which provides better understanding of the behaviour of the engineering materials. Elastic constants relate closely to many physical properties of solids, such as acoustic-phonon frequencies, internal stress, Debye temperature etc. Furthermore, they provide a sensitive probe of phase transitions and an indication of the nature of interatomic binding forces in the material [4].

During the last decade (2000–2010) there has been an upsurge in the study of various physical properties including elastic properties of the single [5–13] and double layered [14–16] perovskite structured manganites in polycrystalline form. The reports mainly focus on study of elastic anomalies associated with magnetic phase transition near the temperature of the charge-ordering transition and antiferromagnetic transition or structural phase transition as a function of temperature. The results have been explained in the light of spin–phonon interaction, different types of antiferromagnetic phase transition or mean field theory and the Jahn–Teller phenomenon.

There have been few research reports on other class of perovskite like ferrites: $SrFeO_3$ and $LaFeO_3$ [17], $SrZrO_3$ [18], single crystal of $Na_{0.5}Bi_{0.5}TiO_3$ [19], ferrite–perovskite composites of $xNi_{0.4}Zn_{0.6}Fe_2O_4$–$(1-x)$ $Pb_{0.95}Sr_{0.05}Zr_{0.53}Ti_{0.47}O_3$ [20], perovskite $La_{0.67}Ca_{0.33}MnO_3$:ZrO_2 composites [21] and brownmillerite ($Ca_2Fe_2O_5$) – a stoichiometric defect perovskites structure [22].

On the other hand limited number of research articles describing elastic properties of superconducting systems such as $RuSr_2GdCu_2O_8$, $YBa_2Cu_3O_{7-x}$, $(Er_{1-x}Pr_x)Ba_2Cu_3O_{6.9}$, $EuBa_2CuO_{7-\delta}$, $TlSr_2(Sr_{0.5}Y_{0.5})Cu_2O_7$, $DyBa_{2-x}Sr_xCu_3O_{7-x}$ are available in the literature [23–27].

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1293-2558/$ – see front matter
doi:10.1016/j.solidstatesciences.2010.09.012

Recent research reports on elastic properties of mixed spinel ferrite systems [28–33] just discuss the variation of elastic moduli as a function of substitution at 300 K. The variation has been explain on the basis of increase or decrease of strength of interatomic bonding without any emphasis on other structural and microstructural parameters like porosity, grain size, interionic distances, type of bonding, microcracks, oxygen vacancies etc.

Earlier, an excellent work has been carried out by Wang et al. [34] on elastic properties of $YBa_2Cu_3O_{7-x}$ ceramics with different oxygen contents. Zero porosity corrections of elastic moduli have been carried out by several methods for the effects of porosity and microcracking on the elastic properties. The correction methods were mainly based on the shape, size and distribution of the voids (pores) and cracks. They have clearly demonstrated that on increasing oxygen content ultrasonic wave velocities and elastic moduli increase to greater extent. The relationship between the porosity and elastic moduli of the Bi-Pb-2212 high Tc-superconductors has been studied by Reddy et al. [35]. They have employed eight theoretical models for calculating elastic moduli in void-free state. They have found $\sim$37% variation in the magnitude of non-porous value of Young's modulus determined from different semi-empirical relations. The origin, formation, types of microcracks and the factors that affect the microcracks characteristics have been studied by many workers for single-phase polycrystalline ceramics, granite and concrete. The various methods for microcracks evaluation and detection have been suggested [36–38].

To our knowledge very few research reports are available on elastic properties of trivalent cation substituted ferrite systems [39–41]. In the case of Al^{3+} substituted Mg–Cu mixed ferrites [39], it is found that the magnitude of elastic moduli decreases with increase in Al^{3+}-content (x) for Fe^{3+} in the system. While in the case of substitution of Al^{3+} or Cr^{3+} for Fe^{3+} in $Ni_{1.05}Sn_{0.05}Fe_{1.9-x}$(Cr or Al)$_xO_4$ system [41] enhances the magnitude of Young's modulus, rigidity modulus, bulk modulus and Debye temperature. These lead to conclude that the Al^{3+}-substitution plays crucial role in influencing the elastic properties. Till today, there arose considerable interest in the synthesis and characterization of pure and substituted copper ferrite systems. The structural, magnetic, electrical and dielectric properties of typical compositions of the ferrite system $CuAl_xFe_{2-x}O_4$ have been carried out by different workers [42–47], but no efforts have been made to investigate the elastic behaviour of Al^{3+}-substituted $CuFe_2O_4$ in particular, the present work is important from fundamental research point of view. The Al^{3+}-ion possesses noble gas outer electron shell structure; it is less compressible than ions with a full or half filled d-shell (Zn^{2+}, In^{3+}, Sn^{4+} etc.) [48], thus it cannot easily accommodate in A-sites but statistically distributed among the available A- and B-sites.

2. Experimental details

2.1. Chemicals and materials

Copper oxide (CuO), ferric oxide (Fe_2O_3) and aluminum oxide (Al_2O_3), all 99.9% pure were procured from Sigma Aldrich India, Mumbai. Polyvinyl alcohol (PVA) and acetone, analytical regent (AR) grade, were purchased from Rankem (RFCL Ltd., New Delhi) used as the binder to make the pellets and cleaning purpose, respectively.

2.2. Synthesis procedure

According to the CuO-Fe_2O_3 phase diagram, $CuFe_2O_4$ is formed between 1000 °C and 1100 °C. The samples sintered below 1000 °C or above 1100 °C were mixed-phase [49]. Aluminum (Al^{3+})-modified copper ferrite ceramics with a general formula of $CuAl_xFe_{2-x}O_4$ ($x = 0.0$, 0.2, 0.4 and 0.6) were synthesized from high purity ingredients, namely CuO, Al_2O_3 and Fe_2O_3. The oxides were mixed thoroughly in stoichiometric proportions to yield the desired composition and then wet-ground by blending with an acetone in an agate mortar and pestle for 4 h. The mixture was dried and pressed into pellets under a pressure of 2×10^7 kg/m^2 using Hydraulic press (BIMPEX machines international, Mumbai, India). These pellets were pre-sintered at 1100 °C for 24 h and slowly cooled to room temperature. The samples were again powdered, pressed in to pellets, sintered in a muffle furnace (Therelek, India) at 1100 °C for 24 h and then slowly furnace cooled to room temperature at the rate of 2 °C/min. The pre-sintering and sintering processes were carried out under an air atmosphere.

2.3. Characterization

Room temperature (300 K) X-ray powder diffraction patterns were recorded with a Philips, Holland, Xpert MPD automated X-ray powder diffractometer using CuKα radiation ($\lambda = 0.15405$ nm), graphite monochromater, and Xe-filled proportional counter. Data were collected in a 2θ range of 5–85° at a scan speed of 2°/min. The elemental analysis of the powder samples was checked by energy dispersive analysis of X-rays (EDAX). The grain size determination and grain morphology of powdered samples were studied by scanning electron microscopy (SEM) (model: Philips, Holland, ESEM EDAX XL-30).

The important aspect of ultrasonic velocity and attenuation measurement in a material is the specimen preparation. Longitudinal and transverse wave velocity measurements were undertaken by the ultrasonic pulse echo-overlap technique (UPT). The radio frequency (rf) pulses generated by the pulse oscillator were applied to transmitting transducer, which converts them into acoustic pulses; these in turn, after propagating through the test samples, were converted into electrical signals by the receiving transducer. The amplified output signal was then displayed on a storage oscilloscope. The cuboids-shaped ferrite samples with 10 mm diameter and 3–4 mm thickness were polished to have flat and parallel faces. Ultrasonic pulses were generated and detected by an X-cut (longitudinal waves) and Y-cut (transverse waves) transducer with the carrier frequency of 9 MHz. The sample was bound to the quartz transducer using Nonaq stopcock grease so that intimate contact (no air gap) was established. A transducer correction was applied to the ultrasonic wave velocities. In all the cases, measurements were made on both sides of the specimen. The transit time of ultrasound was measured up to an accuracy of 1 μs using a digital storage oscilloscope (Matec 7700 system). The overall accuracy of these measurements is about 0.25% in velocity and about 0.5% in elastic moduli.

3. Results and discussion

3.1. EDAX, XRD and SEM studies on the $CuAl_xFe_{2-x}O_4$ system

High temperature prolong sintering may result in the loss of ingredients, which leads to non-stoichiometry in composition. This in turn shows unexpected behaviour; which cannot be explained on the basis of normal stoichiometry. Thus, it was essential to check the chemical stoichiometry of each composition. A representative Energy dispersive analysis of X-rays, (EDAX) pattern for typical composition $x = 0.4$ is shown in Fig. 1.

The results of EDAX confirm the expected stoichiometry, with small oxygen deficiency. No trace of any impurity was found indicating the purity of the samples. It is also clear that there is no loss of any ingredient after high temperature sintering. EDAX results suggest that the precursors have fully undergone the chemical reaction to form the expected ferrite composition. The reason for