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The Effect of Ni-doping on The Thermal Expansion of β-Eucryptite Prepared by Sol-Gel Method

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ABSTRACT

β-eucryptite doped with Ni was prepared from tetraethylorthosilicate, aluminum nitrate, lithium chloride, and nickel chloride precursors using sol-gel method. Particle size analyzer, differential thermal analysis, thermogravimetric analysis, x-ray diffraction, and dilatometer were used to characterize the prepared powder and sintered specimens. It has been found that phase-pure β-eucryptite can be prepared using non-aqueous sol-gel method. The addition of Ni doesn't affect the phase purity of β-eucryptite; however, it has interesting effects on its thermal expansion behavior. The thermal expansion coefficient can be controlled, reduced or increased, based on the doping percent of Ni.

KEYWORDS: β-eucryptite, LAS system, negative thermal expansion, phase-pure ceramics.

INTRODUCTION

Low thermal expansion ($Li_2O–Al_2O_3–SiO_2$; LAS) system has several applications such as transparent cookware, optical materials, telescope mirror blanks, infrared transmitting electric range tops, wood-stove windows and fire door glazing where the dimensional stability and the ability to resist thermal shock are necessary [1-3].

The important crystalline phases in LAS system are β-eucryptite ($Li_2O– Al_2O_3–2SiO_2$), β-Spodumene ($Li_2O:Al_2O_3:4SiO_2$) and Petalite. β-eucryptite ($LiAlSiO_4$) has hexagonal crystal structure which is derivative of silica structure by the replacement of about one-half silicon ions with Al ions and the interstitial vacancies filled by Li^+ ions. β-eucryptite has high negative thermal expansion coefficient causing microcracking in the structure [2]. The reported coefficient of thermal expansion (CTE) of β-eucryptite is about -6.2 $\times 10^{-6}$°C [4]. This high value of CTE is due to the high negative thermal expansion along the c-axes (-18.4$\times 10^{-6}$ /°K) as compared with the positive expansion along a-axes (+8.6$\times 10^{-6}$ /°K). This contraction is attributed to the SiO_4 and AlO_4 tetrahedral tilting and flattening, and Si(Al)–O bond shortening [1, 2].

Approaches used to get body with controlled CTE depend on controlling the extrinsic structure or intrinsic structure. A negative thermal expansion material offsetting the positive thermal expansion in other material can give composites with low CTE material such as mullite or alumina with β-eucryptite or β-eucryptite with metal such as Cu [5-10]. Coexisting two phases with positive and negative thermal expansion are used in many approaches to synthesis body with low CTE [11-13]. The thermal expansion of β-eucryptite can be changed from negative to positive by doping it with Zn [14].

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In the current study, sol-gel method was deputized to prepare phase-pure and Ni-doped β-eucryptite. Sol-gel allows control of manufacturing processes at microscopic and macroscopic scales. The sol–gel technique has advantages over other methods, such as melt processing or solid-state reaction sintering. Besides high purity and lower sintering temperature, a high degree of homogeneity of the molecular scale product can be obtained using the sol–gel technique [15-16].

2. Experimental Procedure:

The powders of pure and Ni-doped β-eucryptite ($Li_2O:Al_2O_3:2SiO_2$) were prepared from lithium chloride (LiCl, Sigma Aldrich, 99%), aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$, THOMS BAKER,98%), tetraethylorthosilicate (TEOS), [($Si(OC_2H_5)_4$), Sigma Aldrich,99%)] precursors as course for lithia, alumina and silica, respectively, using sol gel method. To prepared non-aqueous silica solution, 10ml of TEOS was dissolved in 50 ml of ethanol. Non-aqueous aluminum nitrate solution was prepared by dissolving appropriate amounts of aluminum nitrate in ethanol to get a concentration of 0.67M. Lithium chloride dissolved in ethanol to get concentration of 0.02M. The solutions were mixed together according to the stoichiometric percent of (1:1:2) for pure β-eucryptite. To prepared Ni-doped β-eucryptite certain volume of solution of nickel chloride ($NiCl.6H_2O$, Sigma Aldrich, 99.99%) in ethanol was added to the solution on the expense of aluminum nitrate solution. A homogeneous solution was obtained after one hour of mixing using magnetic stirrer. 25ml of concentrated ammonia was added to the solution to obtain a gel after one hour of mixing. The gel was dried at 80˚C and crashed to obtain a powder. The powder was calcined in air at 700˚C for two hours at a heating rate of 10˚C/min. The calcined powder was grinded by pestle and mortar and sifted using sieve number 200 meshes. Subsequently 1% of PVA, as binder, was added the dried powder. Compact samples were obtained by pressing the powder in stainless steel die (6 × 6 × 60 mm) using uniaxial pressure of 200MPa. The compacts were sintered in air at 1200°C for 2 hours with a heating rate of 2.5°C/min.

3. Characterization:

Laser Particle Size Analyzer (PSA; Better size 2000) was used to evaluate the particle size and particle size distribution of the calcined powder. Differential Thermal Analysis (DTA; DSC PT- 1600), Thermogravimetry Analysis (TGA; STA PT- 1000) were used for thermal analyses. X-ray diffraction (XRD; XRD6000, SHIMADZU) was used to identify the phases present in samples. The obtained XRD patterns were indexed using the diffraction files of β-eucryptite (PDF: 01-070-1574). The measurements were performed in the range of 10–80° and the step size and time of reading were 0.01° and 2s, respectively. The coefficient of thermal expansion of the specimens was tested by dilatometer (Quickline^{TM} -05, USA) between 25 and 800˚C.

RESULTS AND DISCUSSION

Fig. 1 shows the particle size distribution of the calcined un-doped β-eucryptite, the powder has multimodal particle size distribution with main value of the particle size of 8.9 µm. Fig. 2 shows the XRD pattems of pure, 0.5% and 2.5%Ni-doped β-eucryptite calcined at 1200˚C for 2 hours using heating rate of 2.5°C/min. The β-eucryptite powder is well crystalline when it is calcined at 850°C. The obtained diffraction data are in full agreement with JCPDS (01-070-1574) for β-eucryptite indicating that the prepared samples are phase-pure β-eucryptite.

Fig. 3 shows the combined DTA and TGA thermographs of β-eucryptite. In DTA curve, two endothermic peaks were observed at ~130C° and ~230C°. These peaks are due to the evaporation of moisture, represented by ammonia and ethanol, occurred. The weight loss accompany with this process can be seen from TGA in two stages. The first stage, at the lower temperature, is marked by minor gradual weight lose, and the second stage, at temperature up to ~265°C, is characterized by major sudden weight lose due to the rapid evaporation caused by the high heating rate during the test. DTA curve of β-eucryptite has a sharp exothermic peak at ~270C° due to the oxidation of the $Si–CH_3$ group to Si–OH [17]. The oxidation process causes a noticeable weight loses by TGA. Another minor exothermic peak at ~700C° was observed, in DTA curve, which attributed to the crystallization of β-eucryptite.

Fig. 4a shows the thermal expansion of pure and Ni-doped samples. Samples with 0.5% and 1%Ni have negative thermal expansion lower than that of pure sample; moreover, they have higher order-disorder transition temperature. This indicates that the presence of Ni ions in the structure of β-eucryptite hinders the mechanisms of the negative thermal expansion. This can happen when the Ni ions substitute the Al and/or Si ions which have smaller atomic radiuses. This kind of substitution creates compressive stresses in the structure; thus, the thermal energy absorbed during the heating will be consumed for releasing these stresses rather than the thermal expansion. The samples with higher percents of Ni have higher negative thermal expansion than pure sample and lower order-disorder transition temperature. This is assigned to the enhancement of the thermal expansion mechanisms, involving the tilt of [SiO_4] and [AlO_4] tetrahedra, together with a positional disorder of Li^+ ions in the structure. This enhancement may be caused by the formation of vacancies in the structure to maintain the

charge balance which has been disturbed due to the difference in the oxidation state of Ni from one side and Al/Si from the other side.

The CTE was calculated according to the ASM C1470 [18], from the following equation:

$$\alpha = \frac{\Delta L}{L \times \Delta T} \quad (1)$$

where α is the main of linear expansion coefficient (CTE), $\Delta T = T_2 - T_1$, $\Delta L = L_2 - L_1$; L_2 is the length at temperature T_2, L_1 is the length at temperature T_1 (25˚C).Fig. 4b shows the CTE of pure and Ni-doped samples. It has been observed that all samples have variable CTE with temperature. However, the CET of the samples with Ni percent less than 1%is less variable than that of the samples with higher Ni percent. Fig. 5 shows the CTE behavior of Ni-doped samples at five different temperatures calculated according to eq. (1). All addition percent of doping gives zero CTE at 50˚C and maximum CTE at 800˚C.

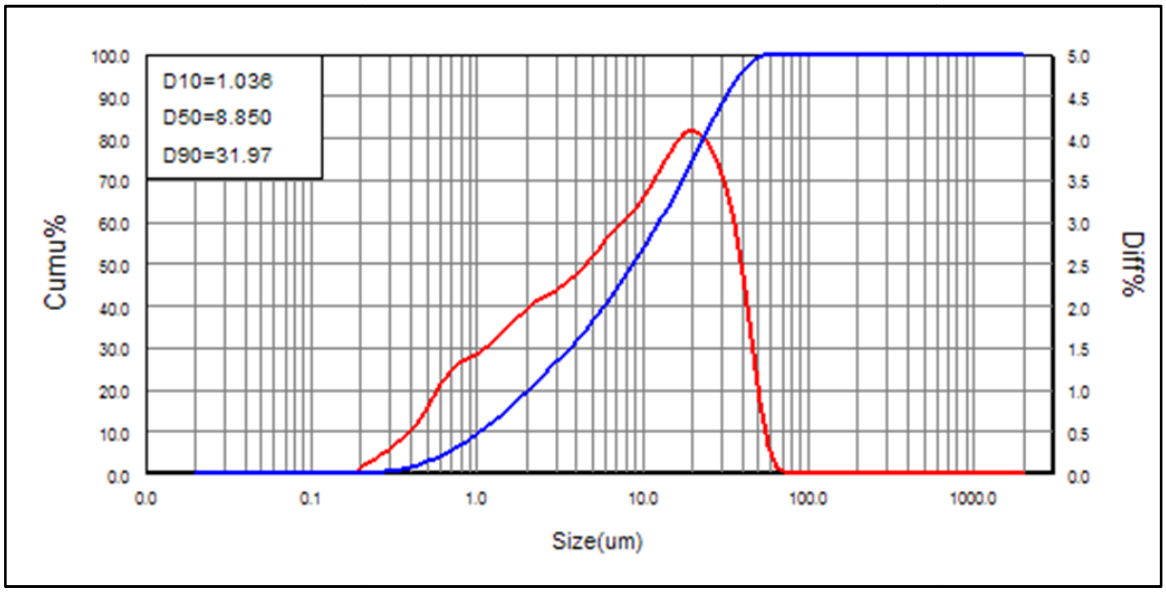


Fig. 1: particle size distribution of un-doped β-eucryptite

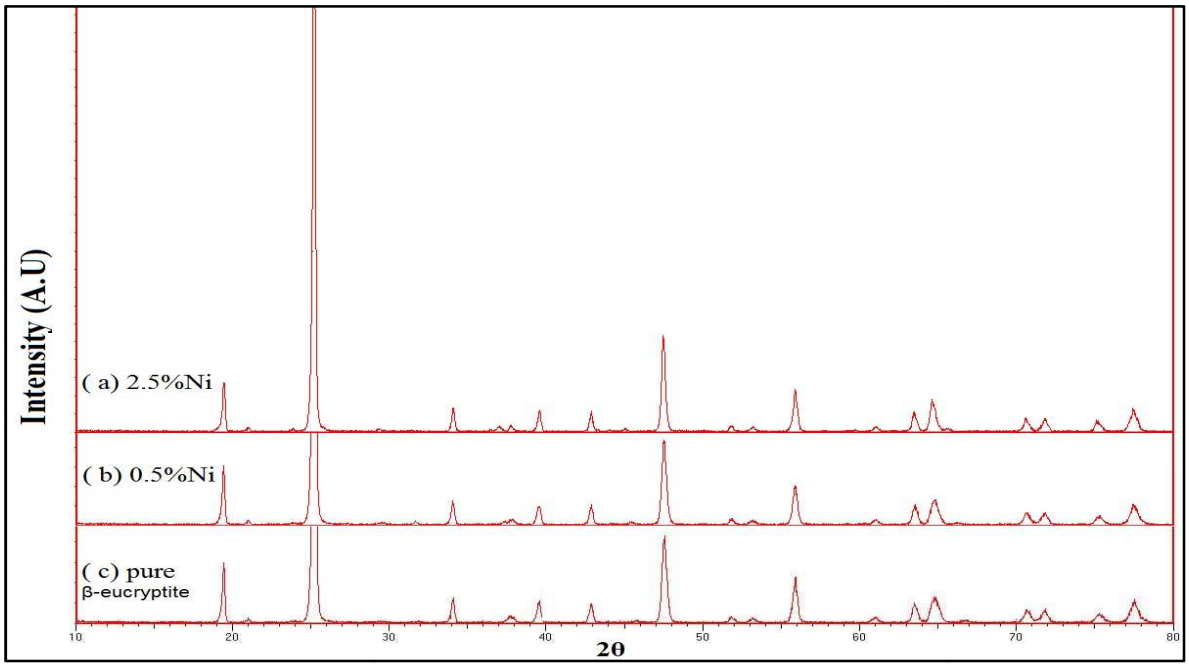


Fig. 2: x-ray of β-eucryptite: (a) doped with 2.5%Ni, (b) doped with 0.5%Ni and (c) un-doped

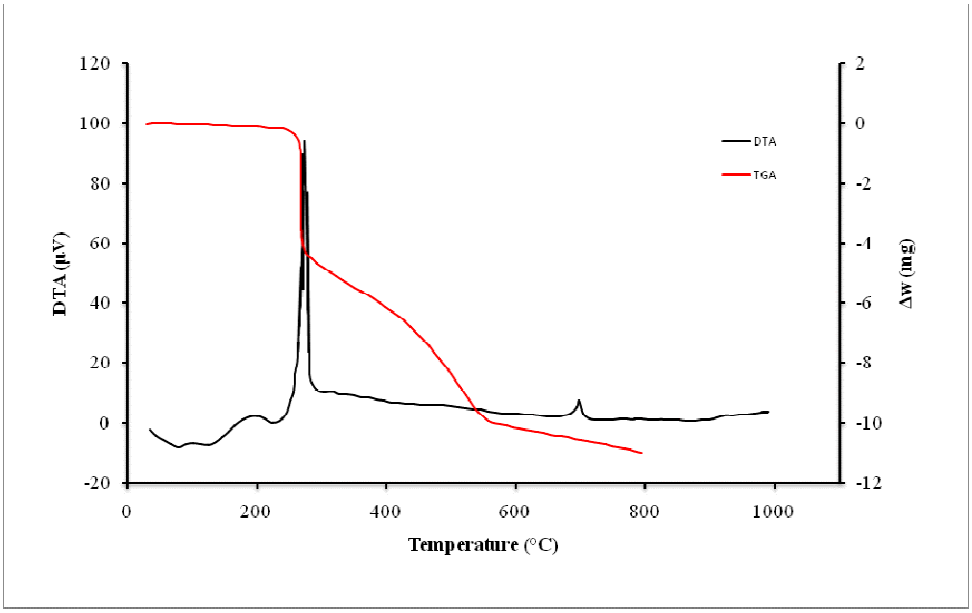
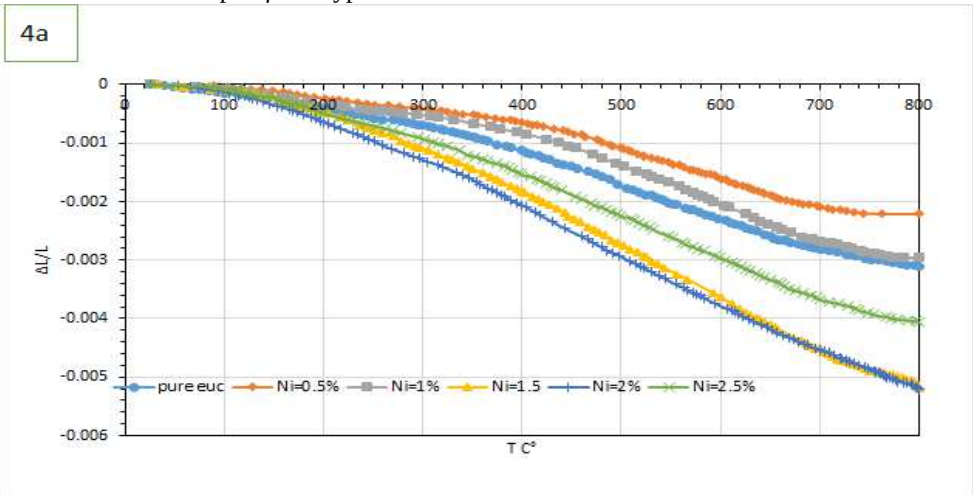


Fig. 3: DTA and TGA of un-doped β-eucryptite



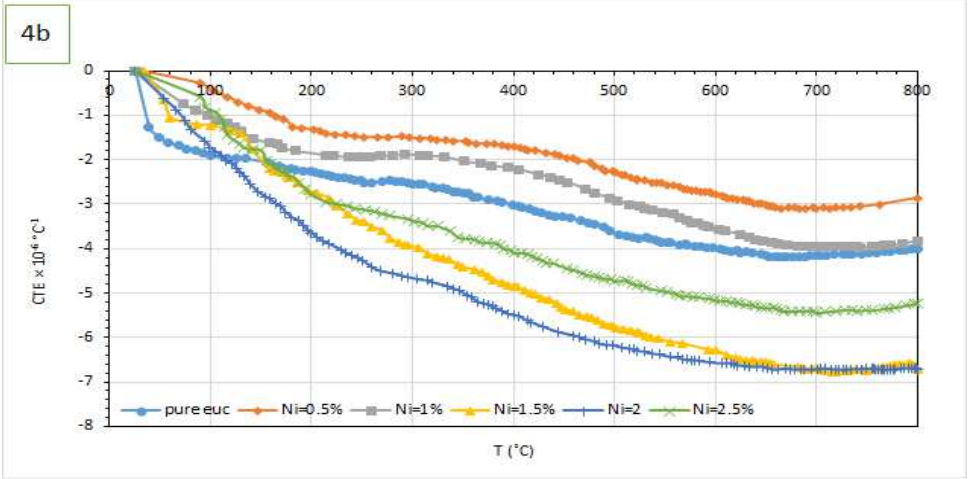


Fig. 4: (a) Thermal expansion of pure and Ni-doped samples,(b) CTE of pure and Ni-doped samples measured between 25˚C and 800˚C.

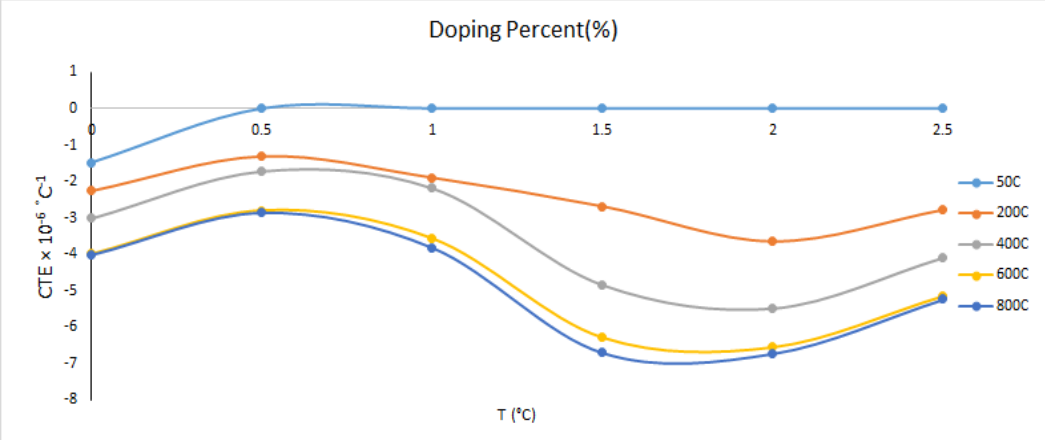


Fig. 5: effect of Ni-doping percent on the CTE of β-eucryptite at five different temperatures

Conclusion:

Phase pure β-eucryptite, pure and doped with Ni, can be prepared from non-aqueous solutions of TEOS, aluminum nitrate, lithium chloride, and nickel chloride via sol-gel method. The CTE of β-eucryptite can be reduced by the addition of Ni with a molar percent less than 1%, the higher molar percent increases the negative CTE of β-eucryptite. All addition percent of doping gives zero CTE at 50˚C and maximum CTE at 800˚C.

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