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Cobalt Aluminate ($CoAl_2O_4$) Derived from Co-Al-TEA Complex and Its Dielectric Behaviors

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Abstract: Cobalt aluminate ($CoAl_2O_4$) was successfully prepared through a Co-Al-TEA complex. The possible structure of the Co-Al-TEA complex determined by FTIR and MS was proposed as a trimetallic species consisting of one TEA group per metal center. The bluish-violet powders of $CoAl_2O_4$ generated by calcination at different temperatures ranging from 600 to 1200°C for 2 h in air were investigated by XRD, SEM and BET. The $CoAl_2O_4$ pellets sintered at 1300°C at different times were preliminarily studied for their dielectric property as a function of frequency (1 kHz – 1 MHz) at ambient temperature.

Keywords: Co-Al-TEA complex, $CoAl_2O_4$, dielectric property.

1. Introduction

Metal oxides containing transition metal ions are versatile materials which have received much attention in both science and engineering technology. They provide several technical applications, such as chemical sensors, heterogeneous catalysts and ion conductors. Among these materials, metal oxides having the spinel-type AB_2O_4 structure are often utilized as model systems due to their structural features which facilitate tailoring of relevant properties.

Cobalt aluminate ($CoAl_2O_4$) has received attention for various applications due to its scientific properties. It is commonly utilized as a humidity sensor [1], as a luminescent pigment [2] and as a material for electrical [3-4] and magnetic [5-7] instruments as well as for thin film technology [8]. Many methods have been developed to prepare the $CoAl_2O_4$ [9-15] that can provide many advantages over traditional methods, including an ability to control homogeneity and purity of product, to process at lower temperatures, and to control the size, shape and distribution of ceramic particles. Various synthesis routes for $CoAl_2O_4$ have been reported, such as the sol-gel formation method [9-10], heat induced collapse [11], solid-solid reaction [12-13], hydrothermal method, and thermal decomposition [15]. In addition, the simple and straightforward method or metal complex method was applied to prepare Mg-Al-TEA complex directly from $Al(OH)_3$, MgO and triethanolamine (TEA, $N(CH_2CH_2OH)_3$), as a precursor for $MgAl_2O_4$ [16]. The high purity and homogeneity of $MgAl_2O_4$ derived from a Mg-Al-TEA complex makes it a suitable as a humidity sensor material [16]. Recently, Laobuthee *et al.* [17] found that not only the metal oxides, but also metal chlorides, nitrates and acetate salts, can be used as the starting material to prepare $NiAl_2O_4$ spinel via the metal complex method.

The aim of this work was to prepare $CoAl_2O_4$ spinel via the metal complex method. The reaction condition was developed by using a low boiling point solvent, propan-1-ol, instead of a high boiling point solvent such as ethylene glycol. The dielectric property of $CoAl_2O_4$ was investigated at the ambient temperature as a function of frequencies. Moreover, the effect of sintering conditions on $CoAl_2O_4$ pellets on the dielectric constant and dielectric loss was also studied.

2. Experimental

2.1 Materials

Aluminum hydroxide hydrate ($Al(OH)_3.xH_2O$), cobalt chloride hexahydrate ($CoCl_2.6H_2O$) and cobalt acetate tetrahydrate ($Co(CH_3COO)_2.4H_2O$) were purchased from Aldrich Chemical Company. Propan-1-ol and butan-1-ol were purchased from Labscan Asia Co. Ltd. Triethanolamine (TEA, $N(CH_2CH_2OH)_3$, 99.5% purity) was purchased from Carlo Erba, in Barcelona, Spain and used as received. All products were moisture sensitive; thus, they were stored in desiccators.

2.2 Instruments

Fourier Transform infrared spectra were received by a Perkin-Elmer 2000-FTIR. Potassium bromide (KBr) acting as a non-absorbing medium was mixed with a solid sample (0.3-0.5 wt %) by an agate mortar and pestle to prepare a pellet specimen.

A mass spectrum of the Co-Al-TEA complex was obtained from an ESI-MS (Bruker Esquire mass spectrometer). Methanol was used as a solvent to prepare a Co-Al-TEA complex solution for mass analysis. The mass range was set from m/z of 100 to 1000.

The decomposition of the Co-Al-TEA complex was determined by thermogravimetric analysis (TGA, a Perkin-Elmer TGA 7). Each sample (10 mg) was heated by using a heating rate of 5°C/min in N_2 (20 psi) from 30-1000°C. The TGA balance flow meter was set at 20 psi N_2, while the purge flow meter was adjusted to 20 psi of synthetic air.

The powder product obtained after pyrolyzing the Co-Al-TEA complex was spread on double-sided sticky tape, mounted on glass microscope slides and then characterized by XRD (Phillips P.W.1830 diffractrometer) using nickel-filtered CuK_α radiation. Diffraction patterns were recorded over a range of 2θ angles from 20-80° and identified using the Joint Committee on Powder Diffraction Standards (JCPDS) file No. 82-2252.

Scanning Electron Microscope (SEM, a JEOL JSM-6301F scanning microscope) operating at an acceleration voltage of 20 kV, a work distance of 15 mm and a magnification of 10,000x was used to identify the microstructure of powder samples. The samples were mounted on alumina stubs using a liquid carbon paste and then sputter-coated with Au to avoid particle charging.

The BET surface areas were calculated from the nitrogen adsorption isotherms at 77 K using a Micromeritics ASAP 2020 surface analyzer and a value of 0.162 nm^2 for the cross-section of the nitrogen molecule. Before measuring, the samples were degassed at 350°C under high vacuum for 20 h.

The dielectric constant and dielectric loss were measured by a precision LCR meter (Agilent E4980A) at room temperature and various frequencies (1 kHz – 10 kHz). The sample pellets were parallel polished and gold electrode deposited on both sides before measurement.

2.3 Methods

Aluminum hydroxide hydrate [$Al(OH)_3.xH_2O$ (53.2% as Al_2O_3, 19.164 g, 100 mmol)], cobalt chlorides [$CoCl_2.6H_2O$ (12.4505 g, 100 mmol)], triethanolamine (TEA, 40 ml, 300 mmol) and propan-1-ol as a solvent, were added into a two-neck, round bottom flask and then heated to 100°C to distill solvent off and water produced as a by-product during the reaction. The reaction was continuously distilled for approximately 6 h. The dark violet product was investigated by FTIR, ESI-MS and TGA. Furthermore, the Co-Al-TEA complex was calcined in a furnace at various temperatures (600, 700, 800, 900, 1000, and 1200°C) for 2 h. The powder products were stored in desiccators to avoid moisture absorbence and identified by XRD, SEM and BET.

$CoAl_2O_4$ powder was milled by an agate mortar and sieved at 45 microns for pressing into pellet form. In a stainless steel die with 10 mm diameter, the obtained powder was uniaxiallly pressed into green pellets (~30 MPa), and isostatically pressed at ~200 MPa. The dense pellets were prepared by sintering at 1300°C in air for various times (3, 4 and 5 h). X-ray diffraction analysis was carried out on polished samples.

Gold electrodes were painted onto both sides of the pellets using a gold paste and fired at 800°C for 2 h. The dielectric constant and dielectric loss at various frequencies, from 1 kHz to 1 MHz, were measured at room temperature.

3. Results and Discussion

A clear, violet-colored solution was obtained from the complete reaction of $Al(OH)_3$, $CoCl_2$ and TEA in 6 h. After removing the solvent, the solution became a dark violet, viscous product. The structure of the viscous product was determined using FTIR. Figure 1 shows the FTIR spectrum of the product. The peak position at 3420 cm^{-1} was attributed to the O-H stretching which might be due to the water adsorbed by the product. The C-H stretching band found at 2728 cm^{-1} was assigned for the $-CH_2-$ group in the product. The peak at 1383 cm^{-1} was assigned to the C-H bending band. The peaks at 1072 and 657 cm^{-1} were attributed to Al-O-C stretching vibration and Al-O stretching, respectively.

The possible structure of the complex was identified using electrospray ionization (ESI) techniques. The significant peak was generated at m/z = 586 as the parent ion (Figure 2).

By using the previous reports for the structural identification of the Mg-Al-TEA and the Ni-Al-TEA complexes [16-17] as well as the data obtained from FTIR and ESI-MS techniques, the possible structure of the product is proposed to be a trimetallic species, consisting of one TEA per metal ion and a chloride group (Figure 3).

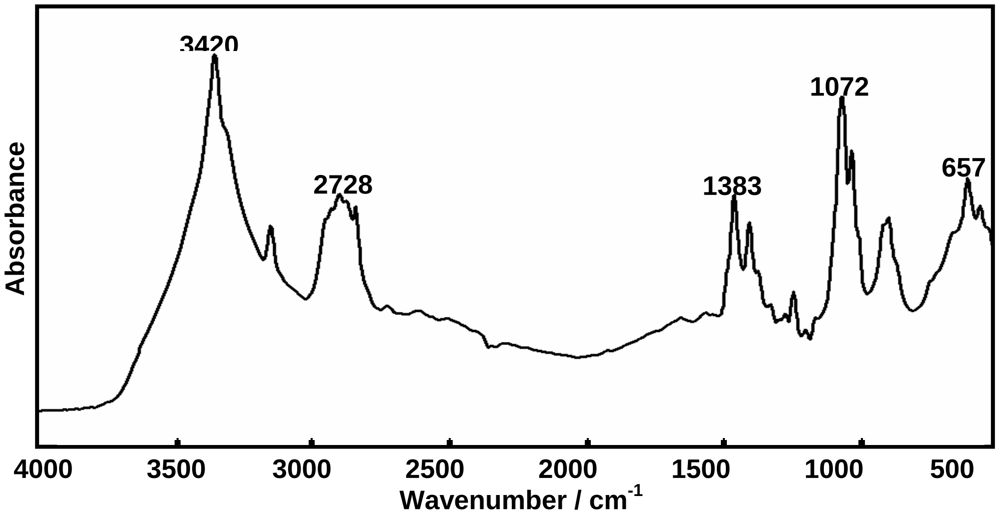

Figure 1. FTIR spectrum of the Co-Al-TEA complex.

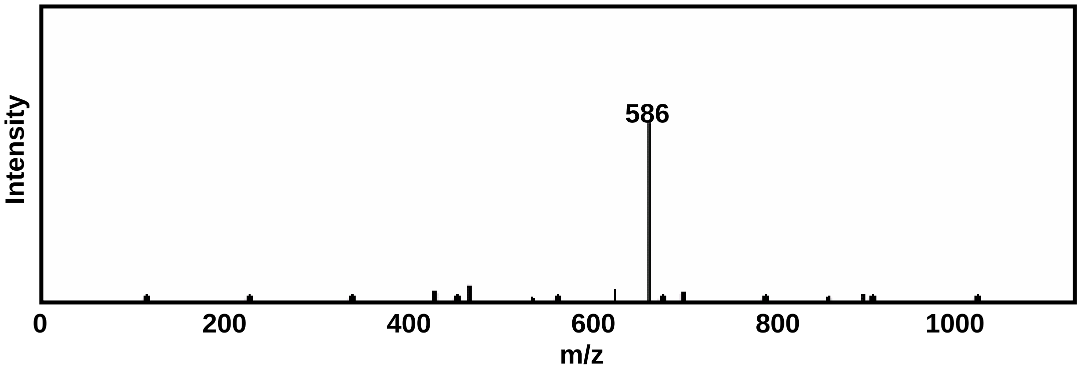

Figure 2. Mass spectrum (100% intensity) of the Co-Al-TEA complex.

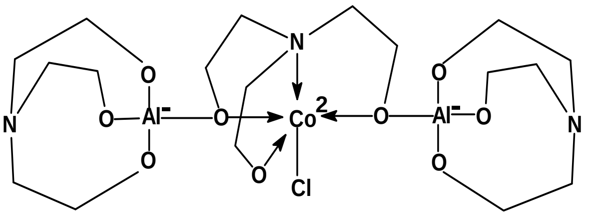

Figure 3. The possible structure of the Co-Al-TEA complex.

To obtain the powder product, the complex was calcined to remove the organic contents. The appropriate temperatures for calcination were found by TGA. Figure 4 shows the TGA thermogram of the Co-Al-TEA complex.

The TGA thermogram (Figure 4) shows three regions of mass loss. The first mass loss involved the decomposition of the organic ligand, which occurred between 80° and 250°C. In this step, volatiles and char were generated [16-17]. The obtained char was continuously oxidized by heating from 250° to 380°C as shown in the region of the second mass loss (Figure 4). The slight mass loss observed in the 380 to 800°C temperature range was ascribed to the burning of the residue organic contents.

Above 800°C, no mass loss was found, showing that the appropriate calcination temperature for preparing the powder product might be 800°C. The complex exhibited a final mass loss of 21% as shown in Figure 4.

Furthermore, based on the TGA result, the Co-Al-TEA complex was calcined at 600, 700, 800, 900, 1000 and 1200°C for 2 h to obtain the bluish-violet color of $CoAl_2O_4$. However, the powders obtained by calcination of Co-Al-TEA complexes at 600-700°C for 2 h contained a little carbon residue.

XRD was used to characterize the powders. Figure 5 shows the XRD patterns of the powders at various calcination temperatures. The calcined powders at each calcination temperature displayed reflections corresponding to the spinel structure of $CoAl_2O_4$ (JCPDS Powder Diffraction File No. 82-2252). The major peaks of $CoAl_2O_4$ were generated at 31, 36, 45, 55, 59, 65, 77 and 78, corresponding to *hkl* reflections at 220, 311, 400, 422, 511, 440, 620 and 533, respectively, as illustrated in Figure 5. The diffraction peaks of each powder became sharper and narrower with increasing calcination temperature, indicating an increase in the crystallite size.

The $CoAl_2O_4$ powders were confirmed by FTIR. Figure 6 shows the FTIR spectrum of the $CoAl_2O_4$ powders obtained after calcinating the Co-Al-TEA complex at 800°C for 2 h. Two characteristic peaks referred to vibrations of the atom in tetrahedral and octahedral holes were found at 555 and 671 cm^{-1} for Al-O and Co-O, respectively. The obtained results agreed with those reported previously [18].

The surface areas of $CoAl_2O_4$ measured by BET analysis are shown in Table 1. It was found that the surface area of the calcined powders decreased with increasing calcination temperature.

Table 1. BET surface area analysis.

Temperature (°C)	BET Surface Area (m^2/g)
600	139
700	124
800	63
900	56
1000	27
1200	9

The SEM micrographs of the spinel powders are shown in Figure 7. The powders were small with uniform particles at 600°C. With the temperature increased to 1200°C, the powders exhibited blocky particles with irregular shapes possibly due to the agglomeration generated during calcinating the Co-Al-TEA complex. In addition, the particle sizes ranged from submicrons to larger than ~ 2 µm.

In this study, the $CoAl_2O_4$ obtained from the Co-Al-TEA complex was subsequently investigated as to its dielectric properties. The powder of $CoAl_2O_4$ calcined at 800°C for 2 h was, therefore, used to prepare the pellets. The phase identification of pellets sintered at 1300°C with different times was carried out by XRD (Figure 8).

Comparing the XRD patterns of $CoAl_2O_4$ powder and pellets, it was found that the XRD patterns exhibited the same reflections. Moreover, the XRD patterns of each pellet were sharper and narrower with increasing sintering time (Figure 8).

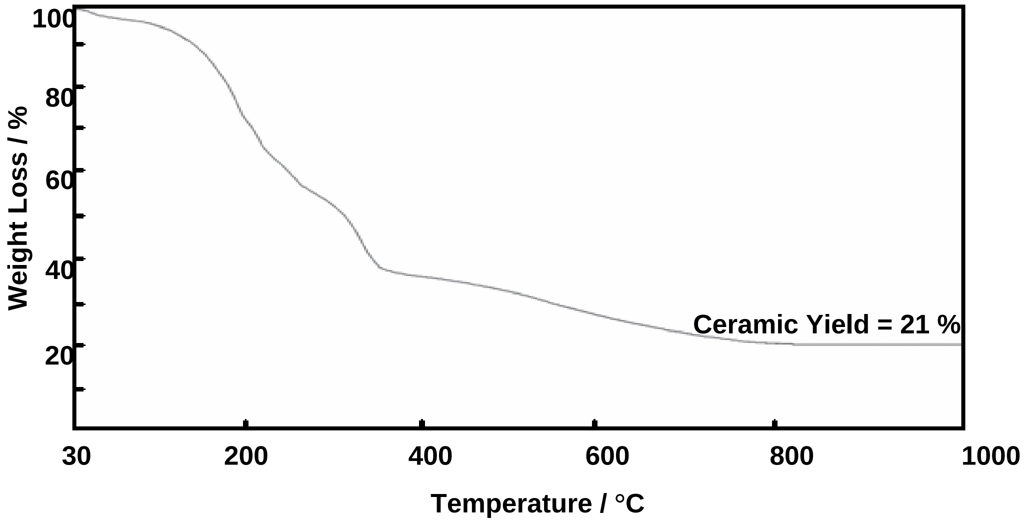

Figure 4. TGA thermogram of the Co-Al-TEA complex.

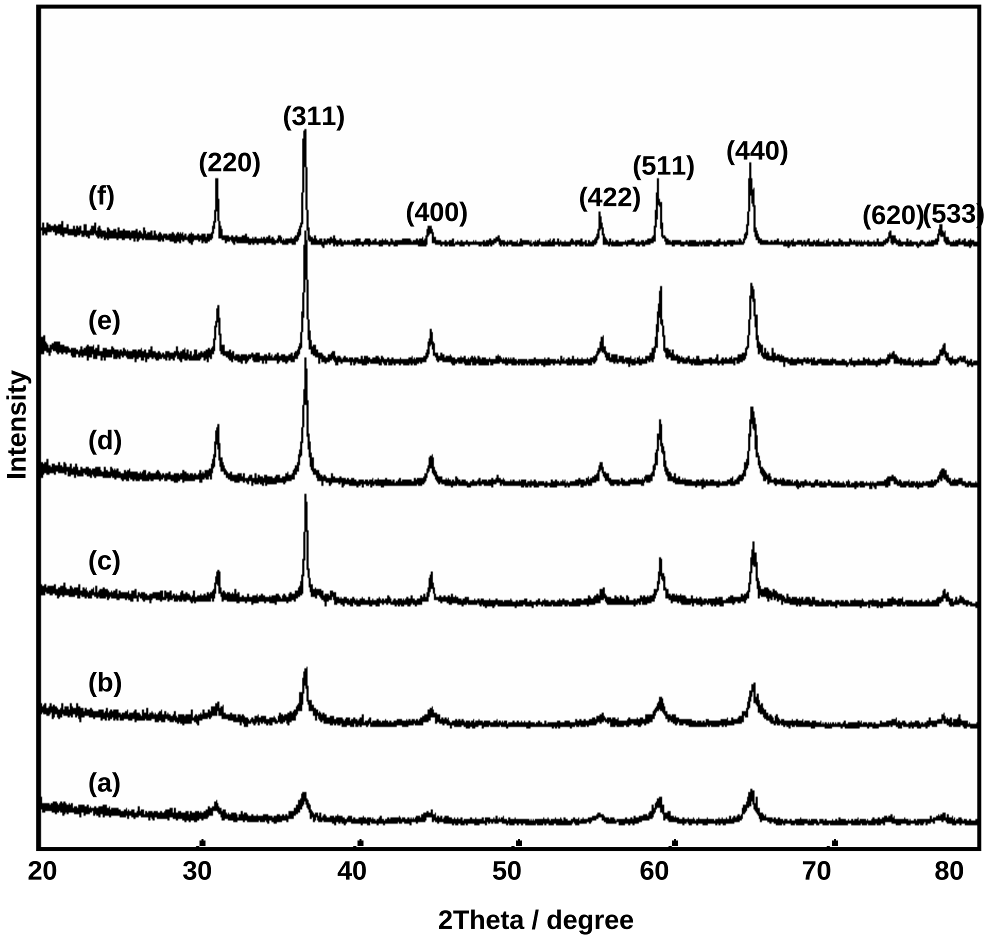

Figure 5. XRD patterns of $CoAl_2O_4$ powder obtained from the Co-Al-TEA complex by calcined for 2 h at (a) 600°C, (b) 700°C, (c) 800°C, (d) 900°C, (e) 1000°C and (f) 1200°C.

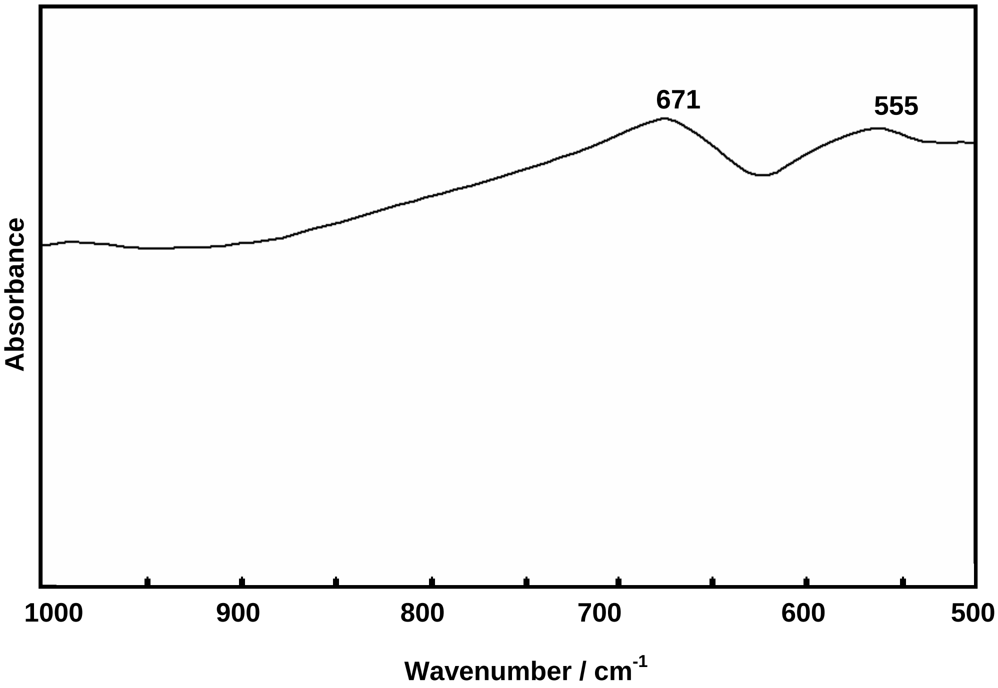

Figure 6. FTIR spectrum of $CoAl_2O_4$ calcined at 800°C for 2 h.

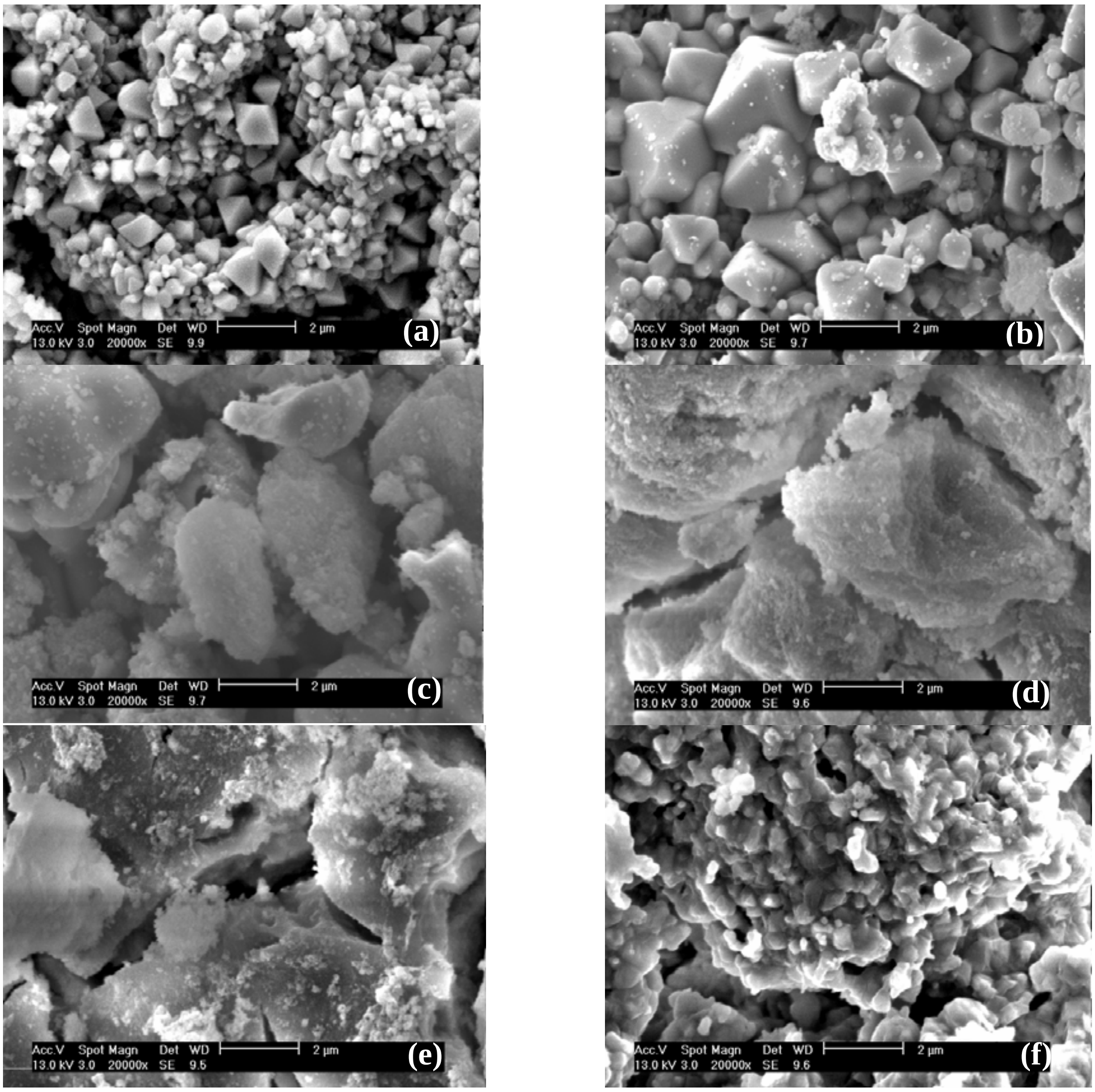

Figure 7. SEM micrographs of $CoAl_2O_4$ powder obtained from the Co-Al-TEA complex calcined for 2 h at (a) 600°C, (b) 700°C, (c) 800°C, (d) 900°C, (e) 1000°C and (f) 1200°C.

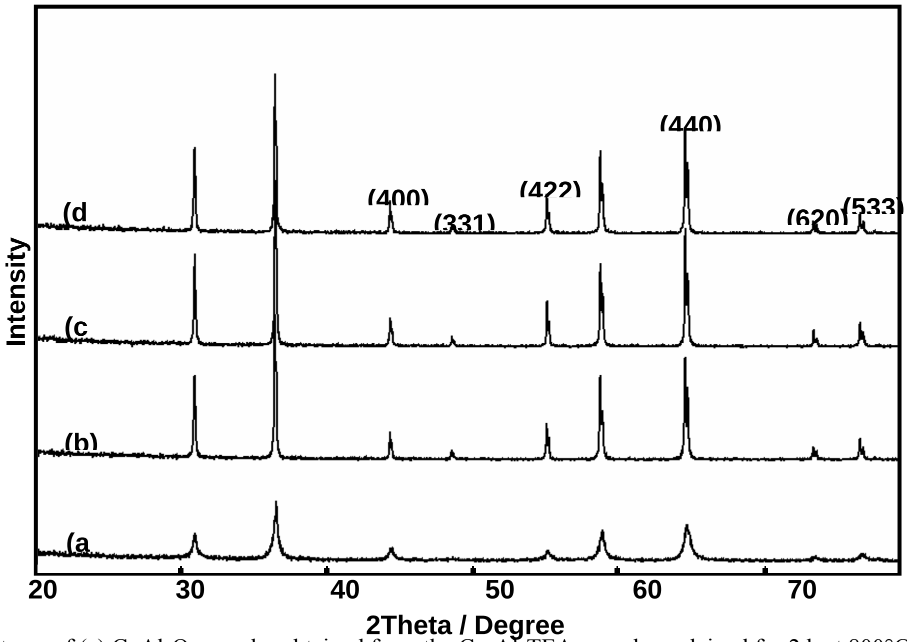

Figure 8. XRD patterns of (a) $CoAl_2O_4$ powder obtained from the Co-Al-TEA complex calcined for 2 h at 800°C, (b) $CoAl_2O_4$ pellet sintered at 1300°C for 3 h, (c) $CoAl_2O_4$ pellet sintered at 1300°C for 4 h, and $CoAl_2O_4$ pellet sintered at 1300°C for 5 h.

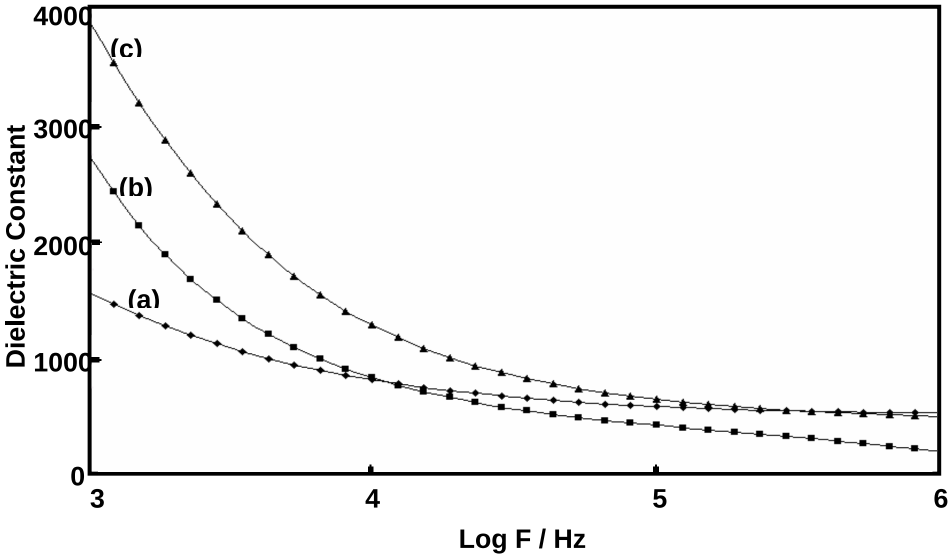

Figure 9. The dielectric constant (ε′) measured at various frequencies of the $CoAl_2O_4$ pellets sintered at 1300°C for (a) 3 h, (b) 4 h and (c) 5 h.

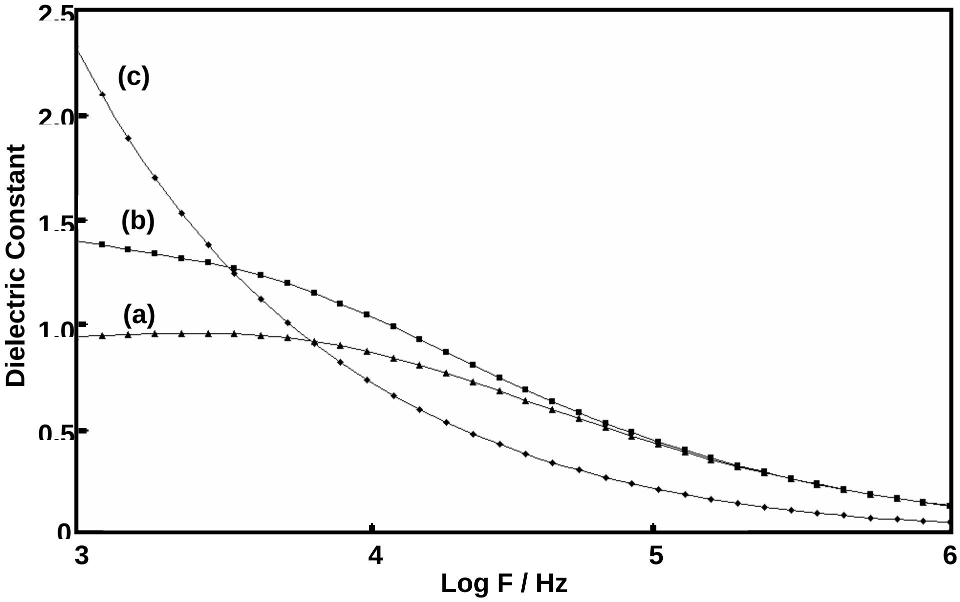

Figure 10. The dielectric loss (ε″) measured at various frequencies of the $CoAl_2O_4$ pellets sintered at 1300°C for (a) 3 h, (b) 4 h and (c) 5 h.

Figures 9 and 10 exhibit the variation of the dielectric constant and dielectric loss as a function of frequency. The dielectric constant of $CoAl_2O_4$ pellets illustrated frequency dispersion and relaxation with increasing frequency. The dielectric losses of $CoAl_2O_4$ families was quite high and showed conductivity behavior at frequencies of 10^3-10^4 Hz suggesting their use as dielectric materials at 1 MHz or higher. As soaking time increased, the dielectric constant of $CoAl_2O_4$ pellets was enhanced. However, considering the dielectric loss, the electrical behavior at a low frequency range was dominated by the ionic conductivity. The dielectric behavior was exhibited at a low frequency, higher than 10^4 Hz, indicating the potential use as a dielectric material at a high frequency range. A dielectric constant of about 500 at 1 MHz was shown for all samples with low losses.

4. Conclusion

The Co-Al-TEA complex was successfully prepared from $Al(OH)_3$, $CoCl_2$, TEA in propan-1-ol. By calcinating the Co-Al-TEA complex at temperatures ranging from 600-1200°C for 2 h, a pure and homogeneous $CoAl_2O_4$ was obtained. The pellets prepared from the powder of $CoAl_2O_4$ calcined at 800°C for 2 h was used to investigate the dielectric property. Ionic conductive behavior was observed at low frequency range but the ionic mobility was suppressed at higher frequencies starting from 10^4 Hz. The application of this material as a dielectric material is preferred at a high frequency range, represented by a high dielectric constant of 500 and low loss at 1 MHz. The increment of pellet soaking time is one means to possibly improve the dielectric properties of $CoAl_2O_4$ pellets.

Acknowledgements

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