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Preparation and Characterization of Lithium Copper Potassium Titanate

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Abstract

Lithium copper Potassium titanates were synthesized by solid state diffusion techniques. Calcinations and sintering temperatures were chosen according to their composition and chemistry. Circular pellets were made at 10 tons of hydraulic pressures and later sintered above the calcinations temperatures. The ingots were characterized by XRD, SEM, EDAX, electrical conductivity, thermoelectric power and dielectric properties. The particle size, grain sizes and defect densities have been estimated from XRD and SEM studies. Composition studies are performed with Energy dispersive X- ray analysis methods. The electrical conductivity, thermoelectric power and dielectric properties were carried from room temperature to 673K and frequencies are varied from 100Hz to 100 KHz. Ceramics systems have the best chance to become high-energy density capacitors. The low breakdown strength of ceramic capacitors is due to flaws, such as porosity, which cause electric field concentration and corona. Therefore, the energy density could easily be increased by eliminating flaws, i.e. pores, in the ceramic materials. The obtained results were discussed with acceptor-doped $CuTiO_3$, K_2TiO_3 and $LiTiO_3$ exhibited strong acceptor segregation in the Ti-rich grain boundaries. A liquid film was detected on the grain boundary. The Li content in the film was found four to five times higher than that of matrix grains. Such a film may promote the abnormal grain growth as observed in the 0.5% Li and potassium– doped Copper titanate.

Keywords: XRD= X-ray diffraction: SEM= Scanning Electron Microscope;

Introduction

Among many ferroelectrics titanates and tantalates occupy a special place owing to their diverse properties; high stability and low cost manufacturing have attracted much attention. Lithium Potassium copper titanate was prepared under high pressure and temperatures. The structural investigations of XRD, SEM, and EDAX are playing very important role in knowing the particle size and the composition of the prepared sample. The present study estimated the particle size 65Å, grain size 605Å. The experimental values reveal that the sample is monoclinic with space group P2 and the Bravais is primitive. The lattice parameters a= 15.04Å, b=18.642 and c= 2.347Å. The Miller indices are found (2 2 1. The typical interatomic spacing in crystals is 2.3161A.so the wide length of radiation used for crystal diffraction should be in the same range. X-rays have wavelengths in this range and therefore, diffracted by crystals. This property is widely used for the study of crystal structures. EDAX is an advanced technique to know the composition of the prepared compound. The SEM profiles helps in the estimation of grains size boundaries. Controlling porosity and surface activity is of greater importance in determining the humidity sensor electrical properties of ceramic products (1). Especially Potassium lithium titanate have been used as starting material for the preparation of various shape-controlled functions materials (2-4). The diffusion of atoms in a crystal can be studied well. The pervoskite structures and rutile structure of TiO_2described refered (5, 6).

Experimental details

Pure AR grade Li_2O, K_2CO_3, CuO and TiO_2 compounds were taken in stoichiometric. Pellet was synthesized in air by the high temperature solid-state reaction. Raw materials of a reagent grade Li_2O , K_2CO_3, CuO and TiO_2 were weighted on a electronic single pan balance (Afcost model) purity of powders higher than 99% .The reagent grade materials were mixed with agate mortar and pestle for two hours, dried and sintered. In an aluminum crucible the compound was kept and heated up to 690^0C in a carbon furnace. This was kept for several hours for homogenization of mixture. The resulted powders were made into pellet by using hydraulic press (Model 378, Kimaya Engineers Mumbai) and applied pressure of 10 tones and finally sintered .at 710^0C for eight hours. The suitable firing temperature can be determined by studying the shrinkage and apparent density of the pellet. The sintering process increases the mechanical strength of the pellet. These pellets were then annealed at 750^0C for about four hours under vacuum (10^2 torr) to remove the strain developed during mechanical stress. The two parallel faces were polished flat using silicon carbide (#200, #400, and #600) papers.

X-RAY diffraction method (XRD)

W.L. Bragg showed that the X-ray reflected from a lattice plane and the effect associated with it could be derived by the equation,

$$n\lambda = 2d \, \mathrm{Sin}\theta \text{ (Bragg's law)}$$

Where ‘n’ is an integer (the order) ,’λ’ is a wave length of the x-rays ‘d’ is the interplanar spacing and ‘θ’ is the angle of the incidence of x-rays beam on the lattice plane. The lattice parameters can be calculated by indexing the sharp peaks (assigning h, k, l values) and then using the relationship

$$\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right)d_{hkl}^2=1$$

From the positions, the relative intensities of the peaks or from the area under its profile, the position of atoms in a unit cell can be determined.

We found that the tolerance factor of our compound is 0.84 (Goldth Smith factor) which is not exceeded beyond 0.9. Hence we conformed that all our samples crystallize in pervoskite structures refered (7, 8). If an X-ray beam sticks such a powder, may plane will be oriented. The specimen is usually rotated by an angle ‘θ’ on its own axis during exposure. The Ionic conditions are explained suitably as ref (9,10).

The Seifert X-ray powder diffract meter is used in the present study .The Cu Kα radiation ($\lambda = 1.5416 A^0$) was used for the phase identification. Transition metals oxides have been the subject of considerable attention, semiconduting (11,12) and swelling properties (13).

Scanning electron microscopy (SEM)

SEM is a powerful tool for the investigation of surface morphology of solids. The microstructure of the Lithium Potassium Copper titanate was studied in the present investigation employing JEOCJ.SM-35. Gold coated samples are mounted on a sample holder of SEM silverdag was used to make the sample conducting which was in contacted with the metal base of the sample holder. A Silverdag powder is a good electrical contact and also acts as a good adhesive, so that the pellet may not move when the sample holder is rotated. Both scattered and secondary emission electrons were used to give the image of samples.

Electrons dispersive analysis of X-rays (EDAX)

EDAX is studied for the investigation of composition of the sample for different magnification factors 2000K, 5000K and 10000K are available. from the Fig;2 and Fig;3 profiles indicates the composition of the elements in the prepared simple..

Results and discussions

The prepared sample was analyzed by X-ray diffraction for its structure determination Fig.1 gives that the intensity was drawn as a function of diffraction angle (2θ). In Fig.2 consists of three magnifications 0f 2.000K, 5.000K and 10.000K Scanning micrographs of prepared sample. The boundaries indicates that the material poly crystalline in nature with specific clear cut .non uniform boundaries. The same phenomena is observed in Fe-doped potassium Lithium titanate SEM images boundaries (14) The Fig.3.depicts the Energy dispersive analysis for x-rays profile which implies the composition of the material. More than 60% is occupied by oxygen. The remaining all covered by all the other components. Fig.4.depicts the 3D profile of the prepared sample with their molecules visible. How the atoms are oriented in their respective positions. Fig.5 &6 indicates the prepared sample dielectric constant and dielectric loss respectively. Fig.7. & 8 reveals the a.c.conductivity variation with frequency and temperature. It was observed that at high temperatures the conductivity is decreasing. But conductivity is at low temperatures. It is also observed that at high frequencies conductivity is decreasing. Fig 9 &10 depicts the dielectric loss and constant of the sample.

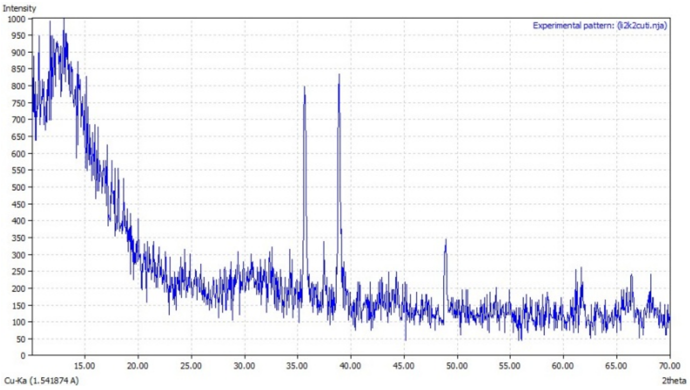


Figure 1: XRD profile of $Li_2K_2CuTiO_5$.

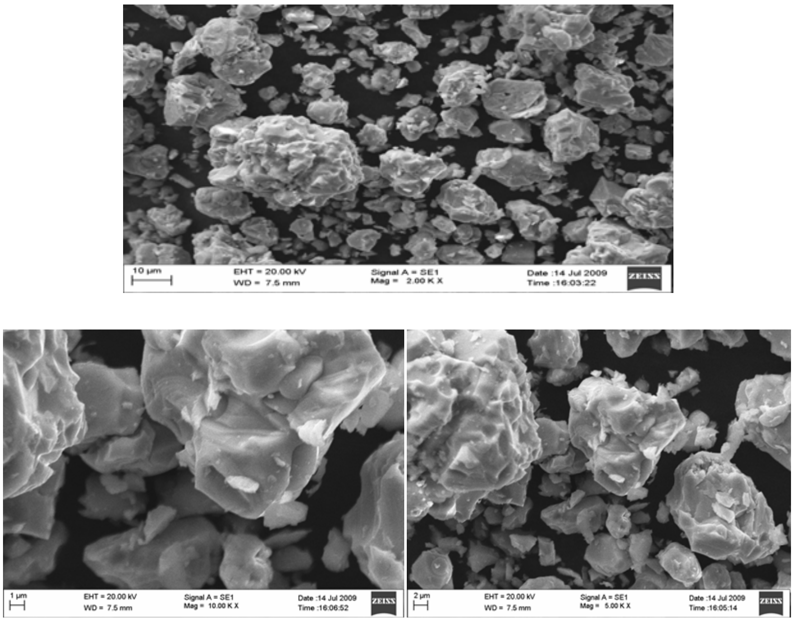
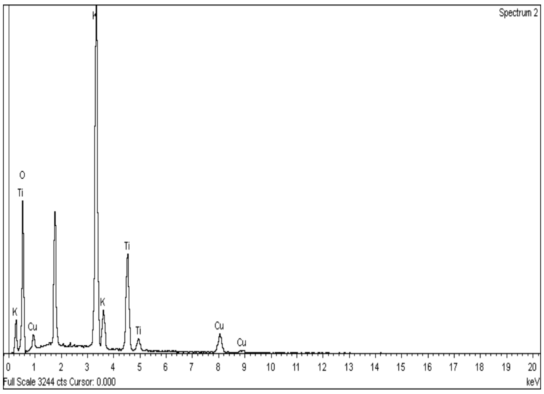


Figure 2: Depicts the SEM micrographs for 2.000K, 5.000K and 10.000K magnifications of Li_2K_2CuTiO

Composition of elements



Element	Weight %	Atomic%
O	41.03	63.12
K	24.15	15.14
Ti	12.46	6.38
Cu	16.26	6.27
Li	6.13	8.09
T Total	100.0	

Figure 3: EDAX profile of the $Li_2K_2CuTiO_5$.

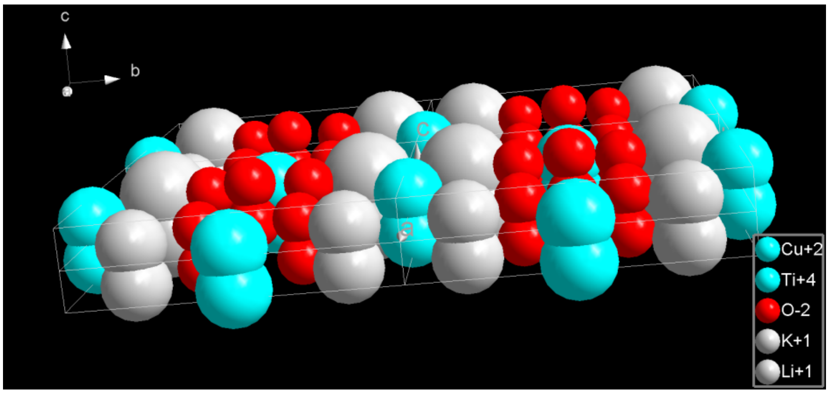


Figure 4: depicts the 3D profile of th $Li_2K_2CuTiO_5$e.

Thermoelectric power

It is well known that in the presence of a temperature gradient (ΔT), the distribution of carrier velocities varies across a material and thus there will be an electric field generated which ultimately gives rise to a thermo electromotive force (ΔV) (See beck effect).The thermo electric power flow and its impacts described (15-19).The thermoelectric power is defined as thermo – emf per unit temperature difference and is given by

$$S = \frac{\Delta V}{\Delta T}$$

Thermoelectric power measurements were used mainly for the determination of the nature of charge carriers and their density and the effective mass of the charge carriers. Using Einstein’s diffusion relation the electrical conductivity (σ) in these material cab be expressed as

$$\sigma = nq^2 D/KT \tag{1}$$

Where n is the charge carrier density and D is the diffusion coefficient, given by

$$D = \beta a^2 T^{-1} \tag{2}$$

Here β is the probability that a particle will leave its original plane and is structure dependent, **a** is the jump distance and T^{-1} is the probability that a jump will occur. If N is the number of sites to which the carrier can jump then

$$T^{-1} = NT_0^{-1} \exp(-\Delta G/KT) \tag{3}$$

Where the activation (Gibbs free) energy, ΔG is equal to the work required for the lattice to adjust such that the site at which the charge is located

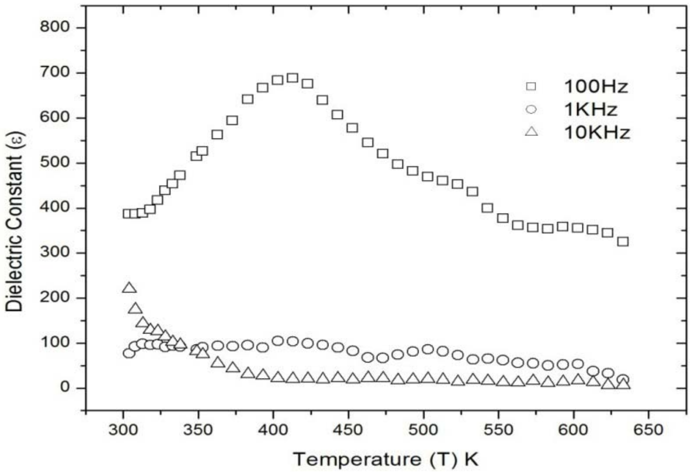


Figure 5: Depicts the dielectric constant of $Li_2K_2CuTiO_5$.

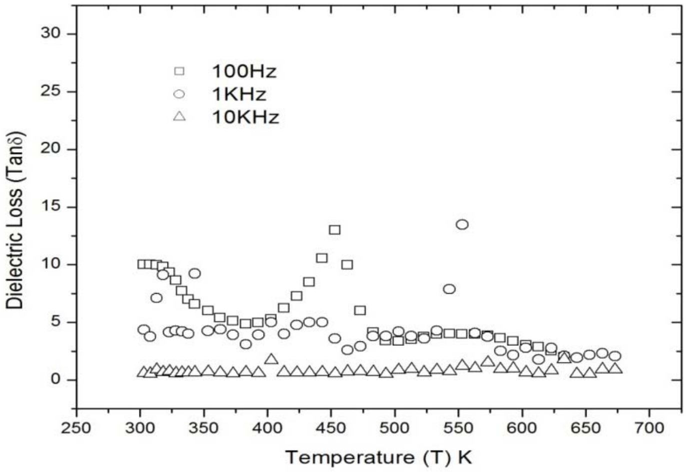


Figure 6: depicts the dielectric loss of Li_2K_2CuT.

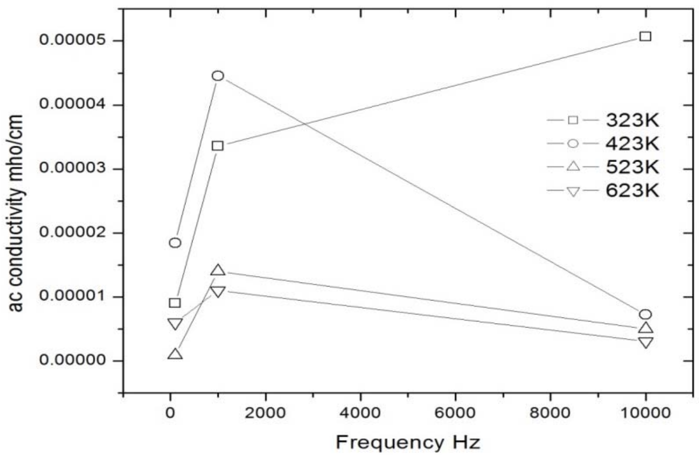


Figure 7: Variation of ac conductivity with frequency.

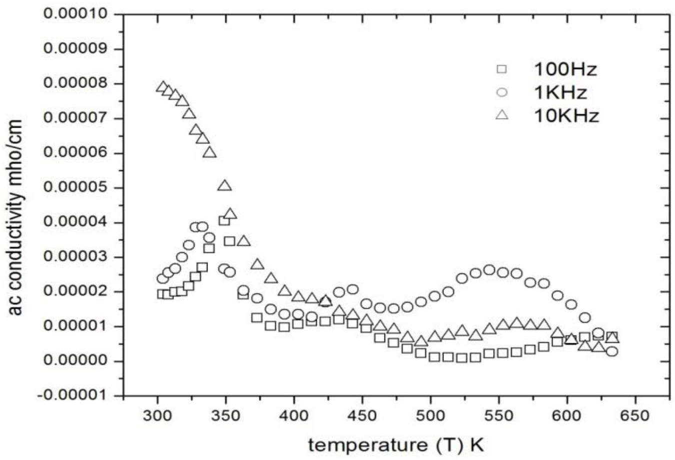


Figure 8: Variation of ac conductivity with temparature.

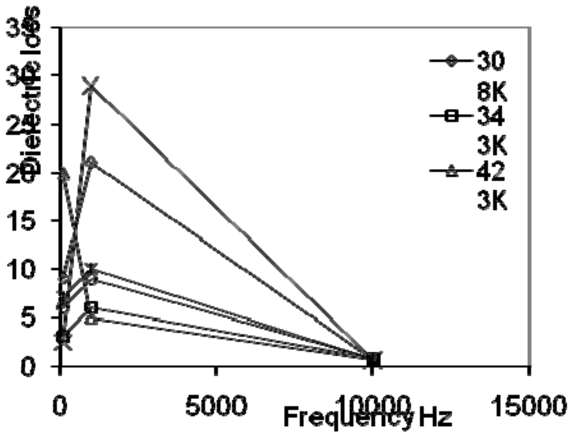


Figure 9: depicts the dielectric loss with frequency.

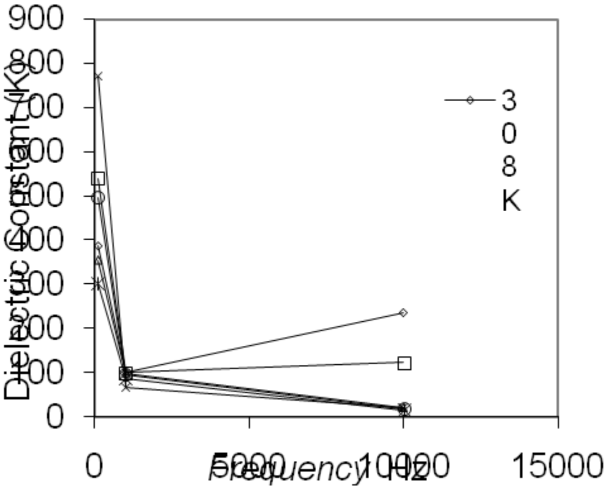


Figure 10: depicts the dielectric constant with frequency.

Conclusions

XRD profile of the sample estimated the particle size 65Å, and the Lattice constants are a= 15.04Å, b=18.642 and c= 2.347Å. The SEM profile clearly indicates the boundaries of the particles and the grain size was 605Å. With the help of EDAX profiles estimated the composition of the pellet. Most of the composition contains 60% oxygen 10-20% potassium and the remaining is copper. The electrical conductivity (σ)values are 965, 1746 & 5350x10^{-6} mhos/cm and the activation energies (E_a) 0.09, 0.3 & 0.34eV for 343K, 373K and 673Krespectively. Thermal electric power (TEP) 384,226 & 593 μV/K for 343K, 443K & 543K temperatures respectively. The electron densities also calculated as 1.8x 10 ^{16}, 2.3x 10 ^{16} and 6x 10 ^{16} for 343K, 473K & 623K temperatures respectively. The dielectric constant 'K' values are 538, 385 and 357 for 100Hz, 101, 70, 33 for 1KHz and 23, 34 ,165 for 10KHz and the dielectric losses (Tan delta) values are 1.39, 2.68 , 41 for 100Hz, 0.51, 0.87, 9.5 for 1KHz and 0.48, 0.62 and 2.2 for 10KHz at 323K, 523K and 623K temperatures respectively. The a.c. conductivity values calculated as 2.16647E5, 1.1417E5 8.5778E7 for 100Hz, 3.3533E3, 1.7056E5, 2.38877E5 for 1KHz and 7.11137E5, 1.71102E5, 8.48916E5 for 323K, 423K and 523K temperatures respectively.

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