

## Synthesis of Nanosized $\text{Ag}_{0.9}\text{Li}_{0.1}(\text{Nb}_{0.7}\text{Ta}_{0.3})\text{O}_3$ Ceramic Powder and Investigation on its Property

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In this communication,  $\text{Ag}_{0.9}\text{Li}_{0.1}(\text{Nb}_{0.7}\text{Ta}_{0.3})\text{O}_3$  (ALNT) mixed oxide powder was synthesized by citrate wet chemical method. TG-DTA, XRD and TEM analyses showed that the reaction temperature was 800 °C, the calcining time was 3 h and the product was pure  $\text{Ag}_{0.9}\text{Li}_{0.1}(\text{Nb}_{0.7}\text{Ta}_{0.3})\text{O}_3$  in well-dispersed grain structure (35 nm in average). The dielectric constant of ceramic sample prepared under traditional techniques is 516, dielectric loss  $\text{tg}\delta$  is  $4.7 \times 10^{-4}$ .

**Key Words:** Citrate wet chemical method, Ceramic powder, Dielectric constant.

### INTRODUCTION

With the rapid development of microwave communication technology and miniaturization of electron apparatus, the demands on the capability of electron materials were getting higher and higher for not only the academia but also industries. The series microwave medium ceramic powder like  $\text{Ag}(\text{Nb}_y\text{Ta}_{1-y})\text{O}_3$  (ANT) drew more and more concern from the researchers due to its high dielectric constant<sup>1,2</sup>. If using alkali metals ion ( $\text{Na}^+$  or  $\text{Li}^+$ ) to replace  $\text{Ag}^+$  partly, the product was  $(\text{Ag}_x\text{Na}_{1-x})(\text{Nb}_y\text{Ta}_{1-y})\text{O}_3$  (ANNT) and  $(\text{Ag}_x\text{Li}_{1-x})(\text{Nb}_y\text{Ta}_{1-y})\text{O}_3$  (ALNT). The dielectric constant of  $\text{Ag}_{0.9}\text{Li}_{0.1}(\text{Nb}_{0.7}\text{Ta}_{0.3})\text{O}_3$  and  $(\text{Ag}_x\text{Li}_{1-x})(\text{Nb}_y\text{Ta}_{1-y})\text{O}_3$  was higher than that of  $\text{Ag}(\text{Nb}_y\text{Ta}_{1-y})\text{O}_3$  and dielectric wastage was significantly reduced, so the dielectric property of  $\text{Ag}_{0.9}\text{Li}_{0.1}(\text{Nb}_{0.7}\text{Ta}_{0.3})\text{O}_3$  and  $(\text{Ag}_x\text{Li}_{1-x})(\text{Nb}_y\text{Ta}_{1-y})\text{O}_3$  was better than that of  $\text{Ag}(\text{Nb}_y\text{Ta}_{1-y})\text{O}_3$ .

For solid-state reaction method, metal oxide was used as the raw material. As  $\text{Ag}_2\text{O}$  would decompose under high temperature during the reaction course, there was constantly mixture in the final product and the size of the powder was very large (normally more than 1  $\mu\text{m}$ ). Therefore, solid-state reaction method could not meet the high requirement of the industry any more.

Under wet chemical method condition, the substrate could be mixed homogeneously and the product was of small and uniform grain<sup>3-5</sup>. In this experiment,  $(\text{Ag}_x\text{Li}_{1-x})(\text{Nb}_y\text{Ta}_{1-y})\text{O}_3$  was synthesized by wet chemical method under milder conditions with hydrofluoric acid and nitric acid as the solvent. Citric acid could be the proper ligand to promote the formation of product. This paper will be focused on the preparation

conditions and dielectric properties of  $(\text{Ag}_x\text{Li}_{1-x})(\text{Nb}_y\text{Ta}_{1-y})\text{O}_3$  product.

### EXPERIMENTAL

$\text{Ta}_2\text{O}_5$  (analytical grade),  $\text{Nb}_2\text{O}_5$  (analytical grade), the citric acid chelation method.

**General procedure:**  $\text{Ta}_2\text{O}_5$  and  $\text{Nb}_2\text{O}_5$  were mixed homogeneously in tetrafluoroethylene cup according to the stoichiometry of  $(\text{Ag}_x\text{Li}_{1-x})(\text{Nb}_y\text{Ta}_{1-y})\text{O}_3$  and dissolved completely by addition of hydrofluoric acid and nitric acid (*ca.* 1:2, number volume) in water bath. Then citric acid (analytical grade) was added and dissolved completely to make  $\text{H}_2\text{Cit}^-$  and  $\text{F}^-$  complex solution of  $\text{Ta}^{5+}$  and  $\text{Nb}^{5+}$ . To the proportion of  $(\text{Ag}_x\text{Li}_{1-x})(\text{Nb}_y\text{Ta}_{1-y})\text{O}_3$ , fresh made  $\text{Ag}^+$  and  $\text{Li}^+$  citric acid complex solution was added and stirred for *ca.* 3 h. Colorless and transparent solution could be formed during the reaction. The result solution was roasted with 250 W infrared lamp to evaporate the solvent and generate a white block. The white block was the precursor of  $(\text{Ag}_x\text{Li}_{1-x})(\text{Nb}_y\text{Ta}_{1-y})\text{O}_3$ . The precursor was grinded and heated with gradient increasing temperature at the rate of 2 °C/min till the temperature reaches 400 °C, after persistent heating for 2 h, all organic compounds will be carbonized. The yellow  $\text{Ag}_{0.9}\text{Li}_{0.1}(\text{Nb}_{0.7}\text{Ta}_{0.3})\text{O}_3$  powder will be formed after it was sintered at high temperature.

**Detection method:** X-Ray diffraction experiments were carried out on the BDX-3300 model X-ray diffract meter. The phase development of powder during heat treatment was determined by differential thermal analysis (DTA) (WCT-1 type). And the grain morphology and size distribution were observed by a transmission electron microscope (TEM) (Model: JEDL

100CXII). The formation of  $(\text{Ag}_x\text{Li}_{1-x})(\text{Nb}_y\text{Ta}_{1-y})\text{O}_3$  was provided by electric diffraction.

## RESULTS AND DISCUSSION

The XRD patterns of the products calcined at 800 °C for different time are showed in Fig. 1. The XRD pattern of the product was synthesized by the citric acid chelation method and was calcined at 800 °C for different hours. This was identical to the standard pattern of  $\text{Ag}_{0.9}\text{Li}_{0.1}(\text{Nb}_{0.7}\text{Ta}_{0.3})\text{O}_3$  synthesized by solid method<sup>2,6</sup>. We could concluded that the  $(\text{Ag}_x\text{Li}_{1-x})(\text{Nb}_y\text{Ta}_{1-y})\text{O}_3$  was synthesized after being calcined at 800 °C for 3 h. Compared to the other two, diffraction apexes of product calcined for 3 h were more aculeated. So we could determine the calcining temperature was 800 °C and the time was *ca.* 3 h.

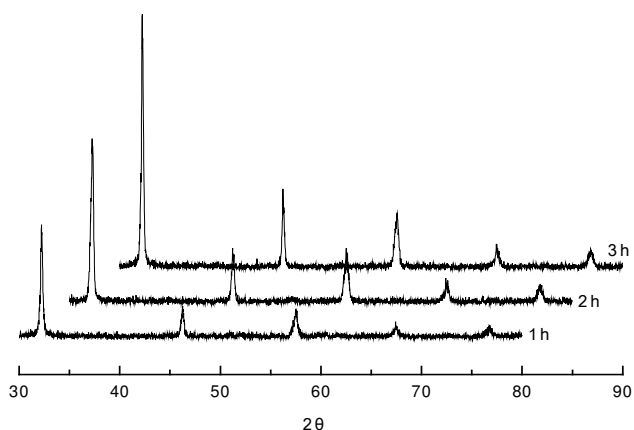


Fig. 1. XRD patters of  $(\text{Ag}_x\text{Li}_{1-x})(\text{Nb}_y\text{Ta}_{1-y})\text{O}_3$  calcined for different time

There is bright diffraction loop in the electron diffraction photograph and this shows the  $(\text{Ag}_x\text{Li}_{1-x})(\text{Nb}_y\text{Ta}_{1-y})\text{O}_3$  by the citric acid chelation method was synthesized (Fig. 2).

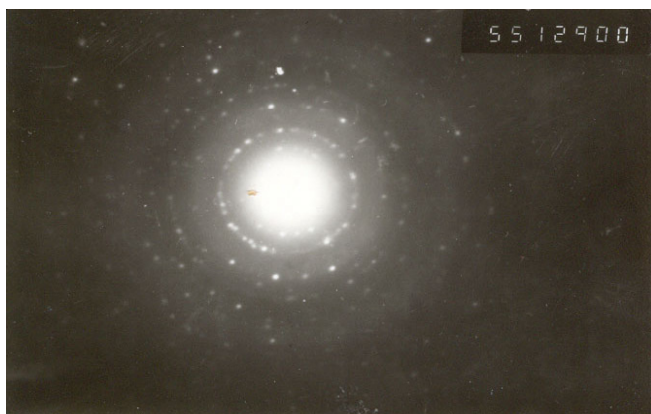


Fig. 2. Electron diffraction pattern of  $(\text{Ag}_x\text{Li}_{1-x})(\text{Nb}_y\text{Ta}_{1-y})\text{O}_3$  particulate made by citric method

The TEM micrograph indicates that the product synthesized by the citric acid chelation method was composed of well-dispersed grain (35 nm, averagely), having a relatively narrow grains size distribution (Fig. 3).

$(\text{Ag}_x\text{Li}_{1-x})(\text{Nb}_y\text{Ta}_{1-y})\text{O}_3$  powder was calcined at 800 °C for 2 h by traditional techniques and sintered to porcelain in air will form a 10 mm-diameter flan. The SEM photograph of the

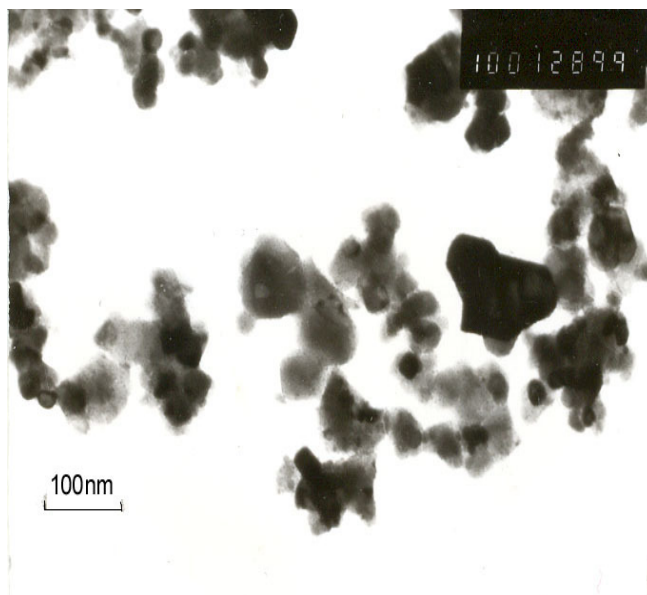


Fig. 3. TEM micrographs of the products obtained by citric acid ligand method

porcelain calcined under 1040 °C for 1 h is Fig. 4. Compared to Fig. 5 (the SEM photograph of the porcelain synthesized by solid method), it shows that the porcelain by the citric acid chelation method was more compact and well-proportioned than porcelain by solid method.

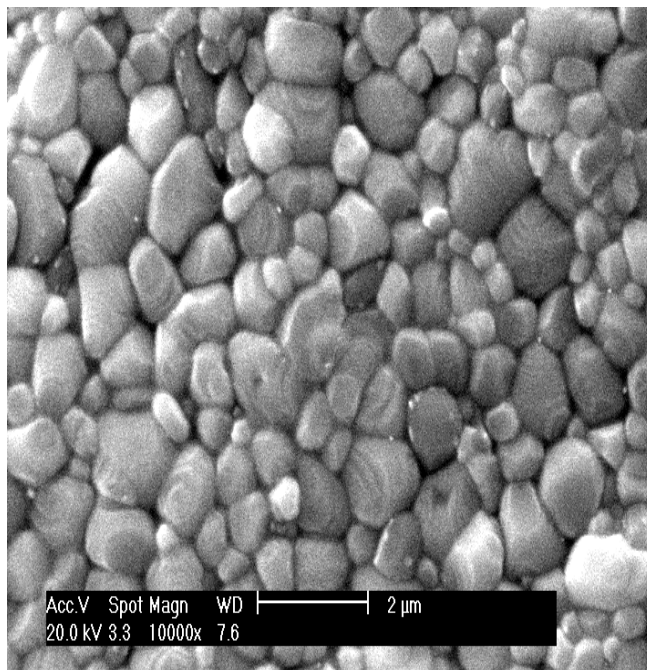


Fig. 4. SEM of the  $(\text{Ag}_x\text{Li}_{1-x})(\text{Nb}_y\text{Ta}_{1-y})\text{O}_3$  ceramic surface made by citric method

Electricity loss was determined by HP4278A, capacitance was determined by HP85A and dielectric constant was determined by capacitance Wayne Keer Multi Bridge6425 testing appearance and Mc-710p circulation box were applied to measure capacitance under different temperature. ZC36 type high temperature measuring appearance was applied to measure the insulation resistance and the insulation resistance rate  $\rho_v$

TABLE-1  
DIELECTRICITY CAPABILITY COMPARISON OF ALNT POWDER MADE BY DIFFERENT METHODS

Synthesizing method	Tangent of wastage angle $\text{tg}\delta (\times 10^{-4})$	Dielectricity constant $\epsilon$	insulation resistance rate $\rho_v (\Omega \text{ cm})$	Capacity temperature coefficient $\alpha_c (\text{ppm}/^\circ\text{C})$
Citric acid method	4.7	516	$> 10^{12}$	-480
Solid-state reaction method	8.0	415	$> 10^{12}$	-760

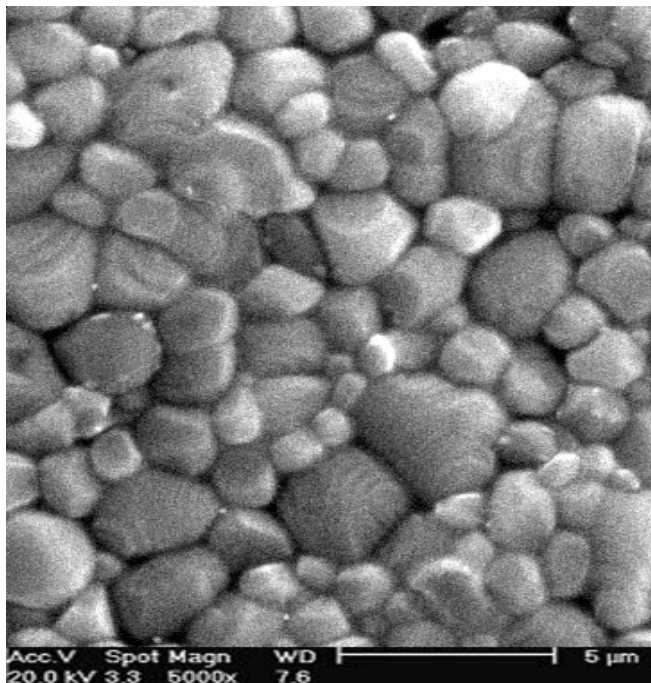


Fig. 5. SEM of the  $(\text{Ag}_x \text{Li}_{1-x})(\text{Nb}_y \text{Ta}_{1-y})\text{O}_3$  ceramic surface made by solid method

could be calculated. Dielectric capability of  $(\text{Ag}_x \text{Li}_{1-x})(\text{Nb}_y \text{Ta}_{1-y})\text{O}_3$  was showed in Table-1 and compared to the compound was made by solid-state reaction method. According

to the data, we could observe the dielectric constant of  $(\text{Ag}_x \text{Li}_{1-x})(\text{Nb}_y \text{Ta}_{1-y})\text{O}_3$  synthesized by this method became higher and dielectric loss improved remarkably.

### Conclusion

As discussed above, the  $(\text{Ag}_x \text{Li}_{1-x})(\text{Nb}_y \text{Ta}_{1-y})\text{O}_3$  product could be synthesized by citric acid chelation wet chemical method at lower temperature. Well-proportioned and well-distracted powder could be obtained. Compared to  $(\text{Ag}_x \text{Li}_{1-x})(\text{Nb}_y \text{Ta}_{1-y})\text{O}_3$  made by solid method, the powder was much smaller, the dielectric constant was much higher and dielectric loss improved remarkably. This method showed a considerable application potential for the syntheses of  $(\text{Ag}_x \text{Li}_{1-x})(\text{Nb}_y \text{Ta}_{1-y})\text{O}_3$  series mixed oxide ceramic powders with better properties.

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