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Preparations and Characterisations of Ceramics Based on Cesium Titanate

V. Peres, P. Fabry,* F. Genet

Laboratoire d'Ionique et d'Electrochimie du Solide de Grenoble,
ENSEEG, BP 75, 38402 Saint Martin d'Hères Cedex, France

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P. Dehaudt

Laboratoire de Radiométallurgie du Combustible, DRN/DTP/SECC, CEA-CENG,
Avenue des Martyrs, BP 85X 38041 Grenoble Cedex, France

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Abstract

Preparations of cesium titanates have been made by several routes: co-grinding, sol–gel and spray-drying. The results obtained with these different methods are compared. Electrical characterisations of pure $CsAlTiO_4$ *have shown that this compound is not a conductor at room temperature. Another phase,* $Cs_2Ti_6O_{13}$*, has been prepared. This last material has a slight conductivity (about* 2×10^{-7} *S cm*$^{-1}$ *at 200°C). Nevertheless, it is not stable in aqueous solution and it cannot be used in electrochemical applications in a water medium. If* $CsAlTiO_4$ *is synthesised without precautions, sizeable* $Cs_2Ti_6O_{13}$ *traces appear in the samples. Conductivity and stability in water of the mixed compound are intermediate between the characteristics of both pure materials.*

Verbindungen aus Caesium und Titanoxyd wurden durch verschiedene Verfahren vorbereitet: Pulverzerkleinerung, Sol–gel und Einspritzvergaser. Die Ergebnisse jedes einzelnen Verfahrens wurden verglichen. Elektrische Kenntlichmachungen der reinen $CsAlTiO_4$ *Phase zeigen, daß diese Verbindung in Zimmertemperatur nicht stromleitend ist.* $Cs_2Ti_6O_{13}$ *wurde ebenfalls vorbereitet. Dieser Stoff ist leicht stromleitend (2* × 10^{-7}*S cm*$^{-1}$ *bei 200°C). Er ist aber nicht wasserfest und darf deswegen nicht in wasservorkommenden elektrochemischen Anwendungen benutzt werden. Wenn* $CsAlTiO_4$ *ohne Vorsicht vorbereitet wird, sind nennenswerte Spuren von* $Cs_2Ti_6O_{13}$ *anwesend in den Mustern. Die Leitfähigkeit und die Wasserfestigkeit der Zweiphasenverbindung liegen dann zwischen den Charakteristiken der zwei reinen Stoffe.*

Des composés à base d'oxydes de césium et de titane ont été élaborés selon plusieurs procédés: par cobroyage de poudres, par la méthode sol–gel et par atomisation-séchage. Les résultats obtenus avec ces différents procédés sont comparés. Des caractérisations électriques de la phase pure de $CsAlTiO_4$ *ont montré que ce composé n'est pas conducteur à température ambiante.* $Cs_2Ti_6O_{13}$ *a également été synthétisé. Ce matériau possède une légère conductivité électrique (environ 2* × 10^{-7} *S cm*$^{-1}$ *à 200°C). Il n'est cependant pas stable dans l'eau et ne peut donc pas être utilisé dans des applications électrochimiques en milieu aqueux. Lorsque* $CsAlTiO_4$ *est préparé sans précaution, des traces notables de* $Cs_2Ti_6O_{13}$ *sont observées dans les échantillons. La conductivité et la stabilité dans l'eau du composé biphasé sont alors intermédiaires entre les caractéristiques des deux matériaux purs.*

1 Introduction

During the last decade, research on solid-state materials having an alkaline ionic conductivity has undergone a significant expansion. The applications which drive them are essentially electrochemical batteries. Since alkaline ions have a strong reducing power, it is possible to obtain batteries with a performing energy power, essentially for lithium

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* To whom correspondence should be addressed.

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which is the highest element of this chemical family. Bibliographic data are rich in this field.

Among solid-state ionics, certain ceramics are essentially covalent skeleton materials having conduction sites which are calibrated (1D or 3D materials). This structural particularity brings selectivity properties which can be very interesting in some applications, e.g. in electrochemical sensors. The use of such materials has been proposed as ion sensitive membranes, for instance in ion selective electrodes (ISE) or ion sensitive field effect transistors (ISFET).[1,2] The feasibility of such systems has been demonstrated with NASICON ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$)[3,4] which is a 3D-ionic conductor. Thin film technologies are applicable to micro-sensor devices: the dip-coating process has been proposed for instance to elaborate this material in a sol–gel route.[6,7]

Heavy alkalines are radioelements, such as Rb and Cs, which are produced from fission reactions in nuclear plants. For environment protection, it may be very interesting to have some sensors to detect them or to measure their concentration continuously. Today, sensors based on radioactivity measurements are used. There is no ISE based on solid membrane for Cs^+ analysis. Literature data are poor in the field of heavy-alkaline conductors. Not many solid-state cesium conductors are known.[8]

In this context, we have chosen to study materials having a hollandite-type structure, with 1D conductor sites, and other materials having a close chemical composition. Such a structure has been studied, essentially on potassium-based materials;[9,10] the better conductivity is generally about 10^{-5} S cm^{-1}. This order of magnitude is relatively low for amperometric applications (high ohmic drop), but on the other hand, it is sufficient for use in potentiometric sensors. For comparison, the conductivity of ISE sensitive membranes lies between 10^{-5} and 10^{-11} S cm^{-1}, respectively, for silver salts (Ag_2S) and glasses. From this point of view, NASICON is an exceptional material (σ = 10^{-3} S cm^{-1} at room temperature). ISE impedance is frequently in the range 1–10 MΩ.[11]

Several authors[12,13] have shown that hollandite compounds such as $K_xAl_xTi_{8-x}O_{16}$ are better conductors if aluminium is substituted by divalent cations (Mg or Zn). A very good ionic conductivity has been obtained on potassium compounds having a similar structure.[14] Nevertheless, the conductivity by Cs^+ will be certainly lower because it is a bigger ion. The results mentioned by Grigor'eva *et al.* illustrate very well this last point on hollandite structures with Li^+, K^+ and Rb^+.[15]

In the present work, we have characterised the priderite ($CsAlTiO_4$) which was first synthesised by Gatehouse.[16] Its structure is well identified: the symmetry is orthorhombic and the crystalline parameters are $a = 8{\cdot}978$ Å, $b = 5{\cdot}704$ Å and $c = 9{\cdot}962$ Å. Its theoretical volumic weight is 3·52 g cm^{-3}. By analogy with the works made on K^+-based materials and to improve the conductivity, we have also synthesised a Zn-doped compound: $Cs_xZn_{x/2}Ti_{8-x/2}O_{16}$. For the K^+-based materials, the x value varies from 1·4 to 2·2. We have then chosen x = 2 for this first study. There are no literature data related to this compound.

During the elaboration of these materials, $Cs_2Ti_6O_{13}$ was often observed and we have also characterised this compound to know its physico-chemical properties.

2 Experimental

To satisfy the quality criteria of chemical sensor membranes, it is necessary to use samples as pure as possible and especially which have a very good fired density.[4] In this purpose, we have made a comparative study of elaboration methods of $CsAlTiO_4$. Three ways have been used: powder co-grinding, sol–gel route and spray-drying technique.

2.1 Powder co-grinding (A-method)

The reactants were Al_2O_3 (Fluka® 99%), TiO_2 (Prolabo®, 99%) and $CsNO_3$ (Ventron®, 99·9%). First, the powders were co-ground in an agate mortar having a planetary movement. The powder was then burned a few hours at 800°C to eliminate water and nitrogen oxide vapours which would be harmful to a good densification during the sintering. Afterwards, the powder was disagglomerated in a mortar with an alumina ball, in an alcohol medium. The specific area of this powder measured by BET (Micrometrics Accusorb®) is 11 m^2 g^{-1}. Samples were pressed (P = 300 MPa) and sintered at 1000°C for 10 h.

The density obtained with this method is rather poor (64%). X-ray diffraction analysis has shown a sizeable fraction of $Cs_2Ti_6O_{13}$ compound (a few percent).

2.2 Sol–gel route (B-method)

Sol–gel routes using alkoxide precursors for ceramic elaboration (see, for instance, Ref. 17) have been extended with success to Na^+ and Li^+ ionic conductor synthesis.[18] This method allows to obtain powders having a large specific area with a narrow distribution of grain sizes. The sintering temperature can then be reduced by about 200–300°C below the usual one. The loss of volatised compounds is minimised by this means. For

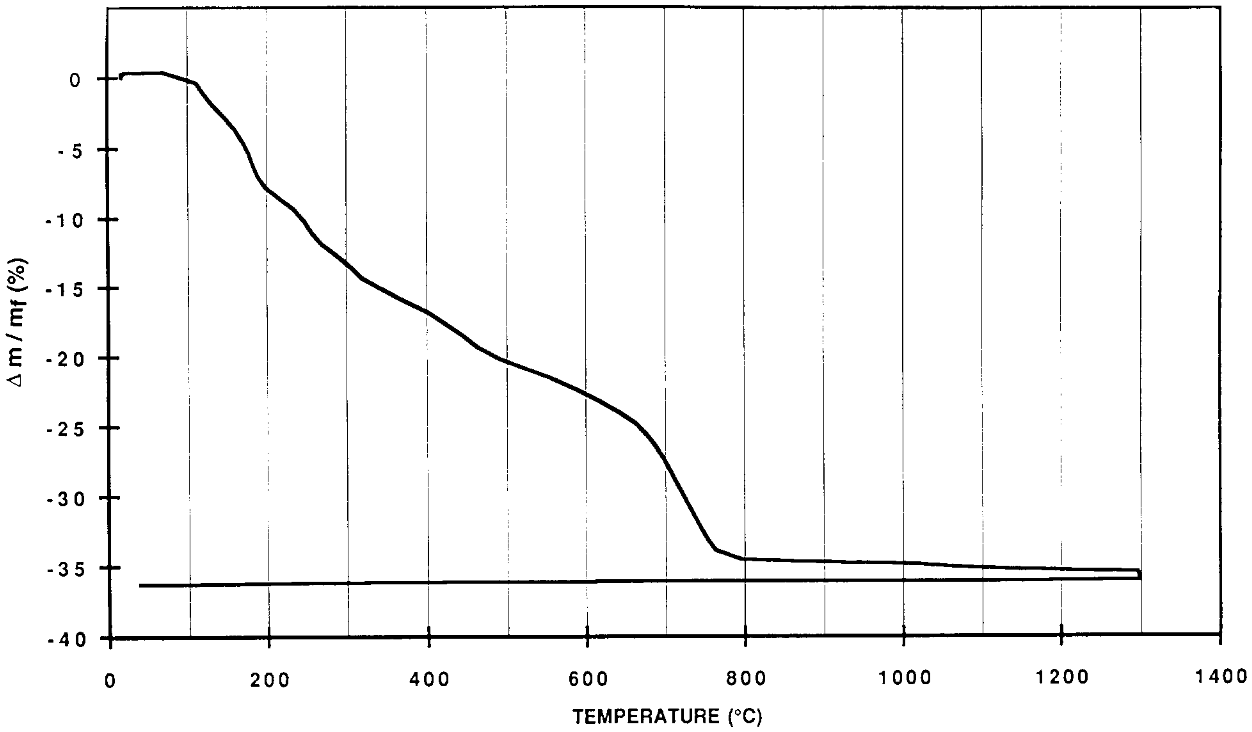


Fig. 1. Thermogravimetric analysis of $CsAlTiO_4$ powder synthesised by the sol–gel route.

$CsAlTiO_4$ sample elaboration, the used precursors were $Si(OC_2H_5)_4$ (Ventron®, 99%), $Al(OC_3H_7)_3$ (Fluka®, 98%), $Ti(OC_2H_5)_4$ (Merke®, 95%) and $CsNO_3$ (Ventron®, 99·9%). The main impurities of alkoxide compounds are the corresponding alcohols.

Silicium alkoxide (tetraethyl orthosilicate—TEOS) presents hydrolysis condensation kinetics which are very much slower than the Ti and Al alkoxide ones. So it is preferable to hydrolyse partly the TEOS, for instance by adding water very slowly, in the ratio of one water mol to one TEOS mol. The mixed alkoxide formation is so allowed and a better homogeneity of the material is favoured. In this purpose, the alkoxide solution was slightly shaken at 60°C for several hours in an alcohol medium (ethanol or propanol). Simultaneously, the $CsNO_3$ solution was maintained at 60°C, a water excess with a ratio sufficiently high to allow a complete hydrolysis reaction of all alkoxides (a minimum ratio of about 10 is recommended) was heated in the same way. Later, the

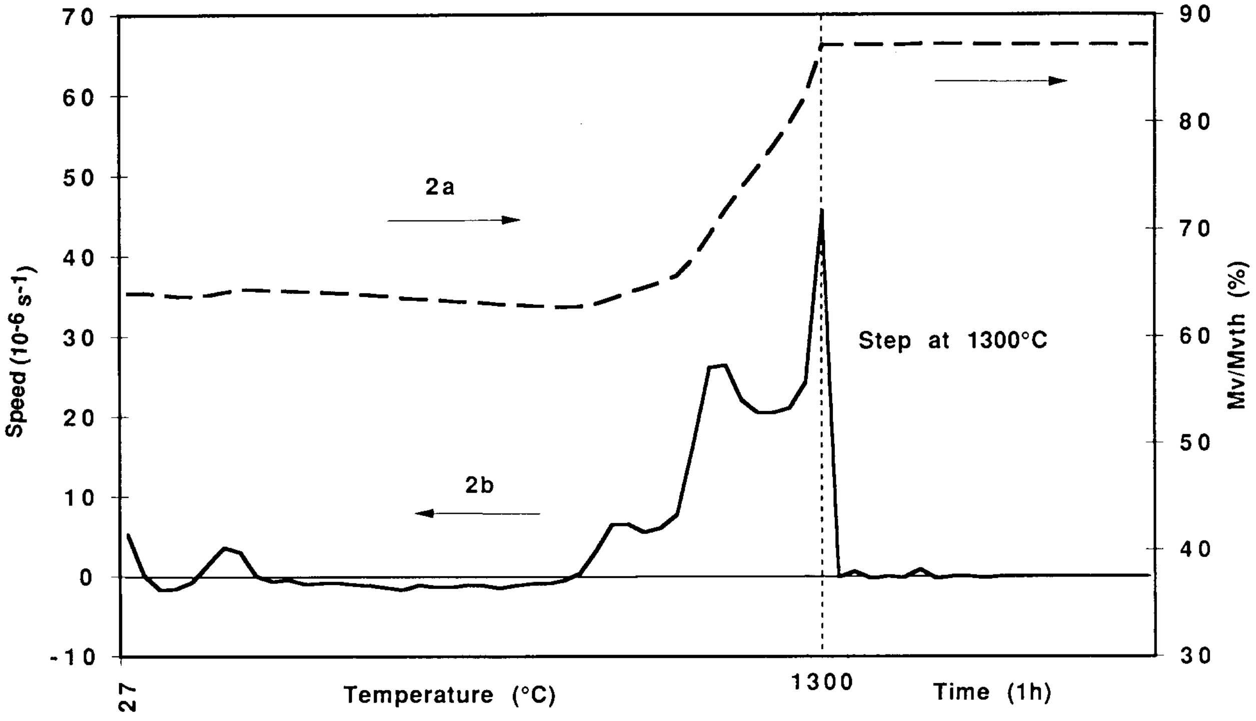


Fig. 2. Shrinkage study during the sintering of $CsAlTiO_4$ synthesised by the sol–gel route. (a) Specific weight relative to the theoretical value, and (b) densification velocity.

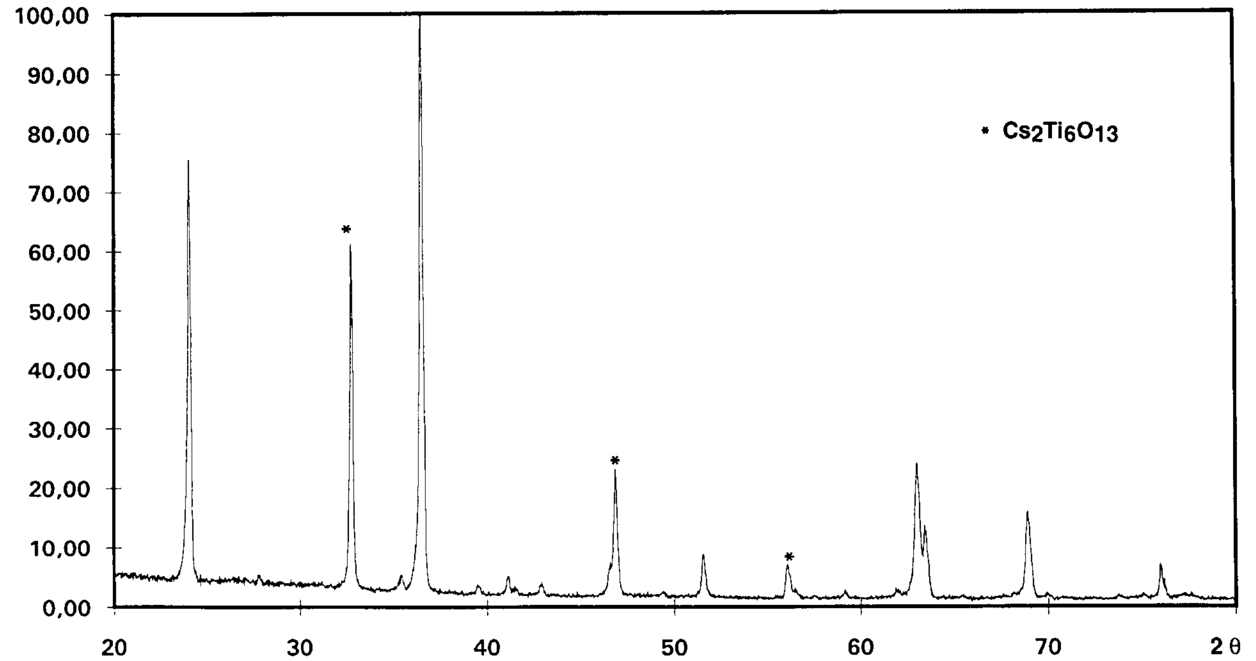


Fig. 3. Experimental X-ray spectrum of $Cs_2ZnTi_7O_{16}$.

solutions were quickly mixed by means of a strong mechanical agitator. To avoid agglomerate formation, water excess and agitation speed must be significant.

The drying step was made on a heating plate until it produced a creamy consistency; afterwards an azeotropic distillation was driven with toluene.[19] Finally, the xerogel was rinsed by alcohol and dried in a drying oven.

The specific area of this powder was very high (42 m^2 g^{-1}). An example of thermogravimetric analysis is shown on Fig. 1 (Setaram® TG 85.16–18). The weight loss (water, nitrogen oxides, burned organic compounds) is achieved at 750°C.

The compacity rate of the sintered pellets (1000°C, 2 h) was 83%. X-ray diffraction analysis has shown the $CsAlTiO_4$ spectrum and also traces of $Cs_2Ti_6O_{13}$.

To improve the density, the volatile compounds can be eliminated before by calcining the powder at about 700°C. After such treatment, the specific area was highly reduced (6 m^2 g^{-1}). Samples sintered at 1300–1400°C from this powder had a better purity: the formation of $Cs_2Ti_6O_{13}$ phase was not present, only a few slight traces of TiO_2 and Al_2O_3. The density was improved (89%). A shrinkage analysis made with a dilatometer (Adamel-Lhomargy® DI 24) has shown a slight densification at about 900°C and a sizeable shrinkage beyond 1300°C (Fig. 2). This experimental result explains the better performances obtained through this way.

$Cs_2ZnTi_7O_{16}$ has also been synthesised by this process. The Zn doping precursor was $Zn(NO_3)_2$ (Prolabo®). The specific area was less considerable (9 m^2 g^{-1}) than the previous result and it was even lower after burning at 700°C. The melting point of this compound has been determined at about 1300°C. It was then necessary to sinter the samples below this value (for instance 1150, 1200, 1225°C). The best performance was obtained for a sintering at 1200°C. The volumic weight was 3·66 g cm^{-3}. An X-ray diffraction pattern is given on Fig. 3. Sizeable $Cs_2Ti_6O_{13}$ traces are still visible.

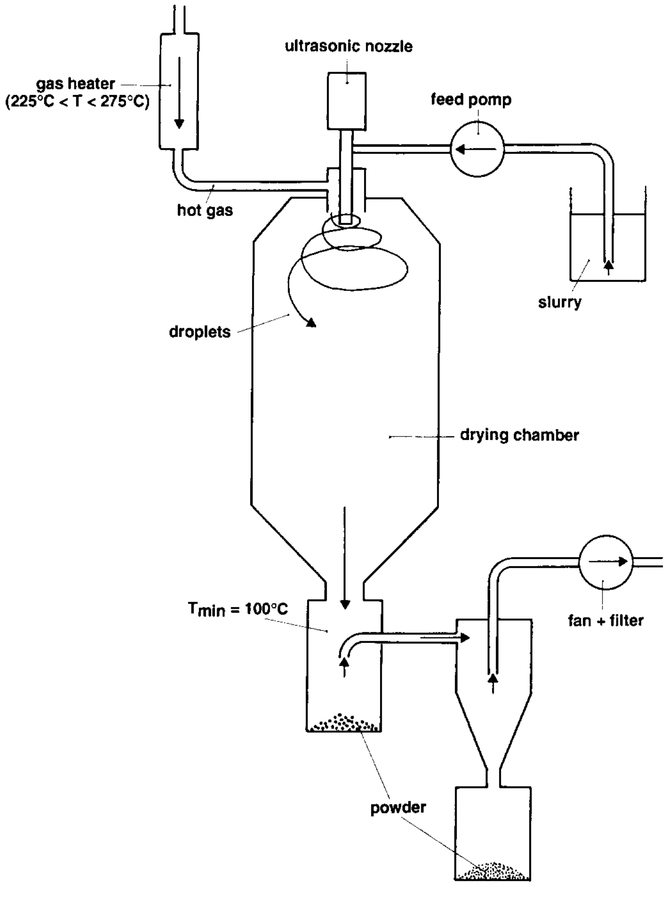
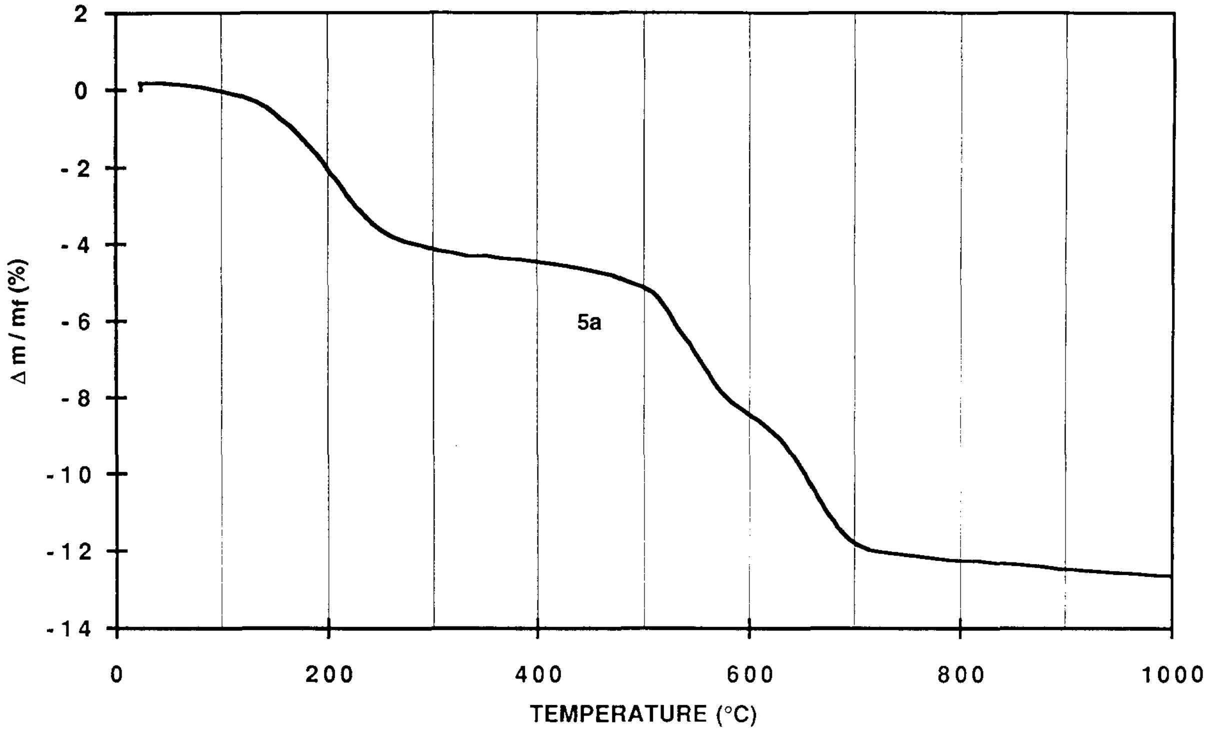


Fig. 4. Diagram of atomisation set-up.



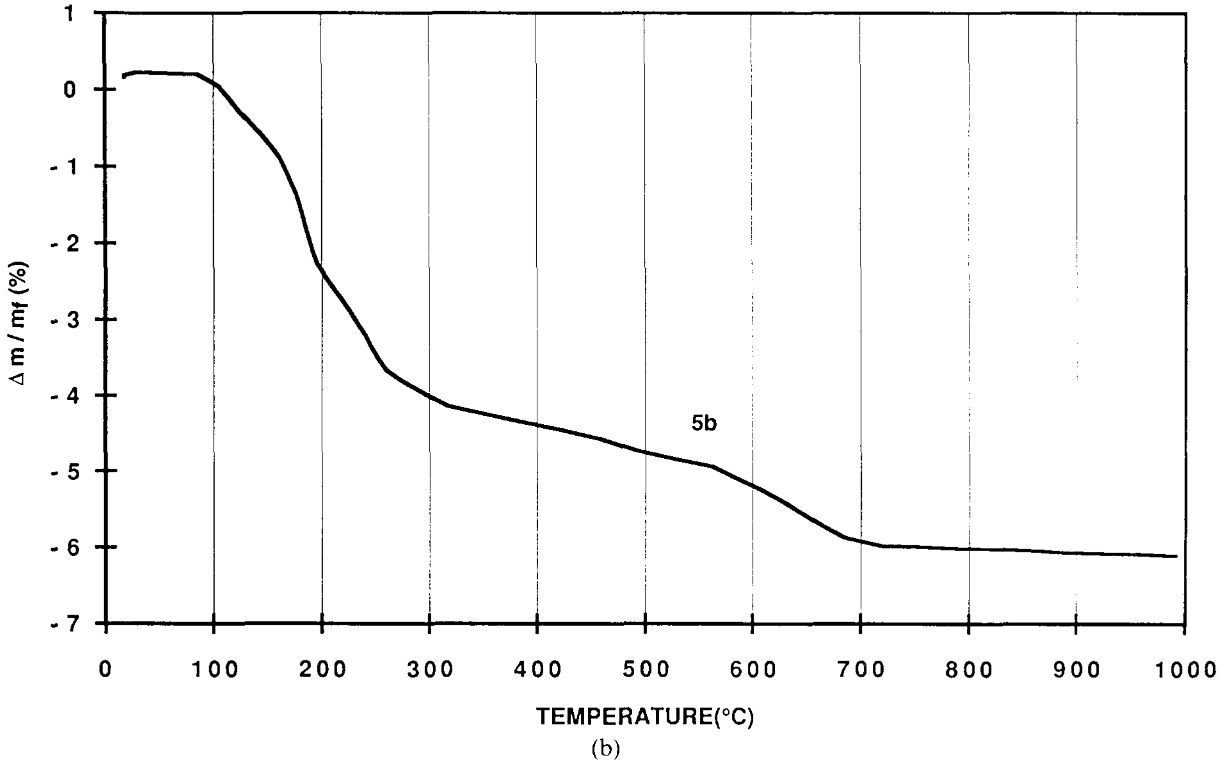


Fig. 5. Thermogravimetric analysis of $CsAlTiO_4$ powder synthesised by atomisation method. (a) No-calcined $CsAlTiO_4$ powder, and (b) calcined $CsAlTiO_4$ powder (400°C).

2.3 Spray-drying technic (C-method)

This process is relatively recent.[20] It consists in drying a slurry by a flux of hot gas. The powder consists mainly of spherical particles having a very small size. The specific area is generally high. This process is very well adapted to continuous powder productions. A schematic view of set-up is shown in Fig. 4. A piezoelectric ceramics (20 kHz) generates small droplets (about 50 μm) which are pulsed by a hot gas into the reactor.

The slurry was obtained by mixing TiO_2 and Al_2O_3 powders in an aqueous solution of cesium carbonate. In this way, the specific area of the powder was 5 m^2 g^{-1}. This value was not modified after burning at 700°C. Thermogravimetric analysis have shown similar water loss, before and after the burning treatment of the powder. This is certainly due to hygroscopic properties of the reactives. On the other hand, weight losses between 200 and 700°C were clearly

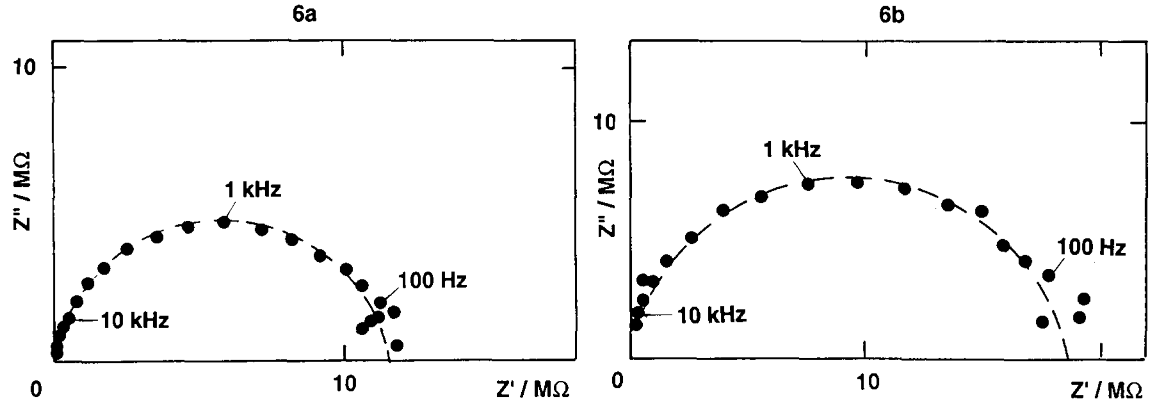


Fig. 6. Examples of impedance diagram obtained on $CsAlTiO_4$ sintered at 1000°C. Sampled synthesize by (a) by the co-grinding method, and (b) the sol–gel route.

lower for the burned powder (see Figs 5a and b). To improve the densification, we have used burned powders to elaborate our samples, because they do not produce a great quantity of gas during the sintering.

In this case, the shrinkage took place at about 1000°C. Beyond this temperature, the sintering did not advance. The pellets sintered at a temperature higher than 1100°C were crumbly and all the more so the higher the sintering temperature. The best result have been obtained for a sintering at 1000°C for 1 h. The density was 94%. X-ray diffraction showed the $CsAlTiO_4$ spectrum only, without other phases.

Because the spray-drying technique has given the best results on priderite compound (density and purity), we have also used this method to synthesise $Cs_2Ti_6O_{13}$. The powder obtained was very hygroscopic and, as agglomerates were formed very quickly in ambient air, it was necessary to keep it in a desiccator. The shrinkage was observed essentially at about 1000°C. X-ray diffraction analysis has given a spectrum slightly shifted in comparison with the JCPDS data. We have also observed TiO_2 traces and some $Cs_2Ti_5O_{11}$ pics. The specific weight of the samples was 3·92 g cm^{-3}.

3 Results

Conductivity measurements have been made by impedance spectroscopy in the frequency range 5 Hz to 13 MHz (Impedance Analyser H.P.® 4192A). The input impedance of this set-up is about 10^9 Ω. During the measurements, the samples were inserted in a cell under vacuum with graphite electrodes. The temperature range is room temperature to 200°C (Buchi® furnace).

For the samples of $CsAlTiO_4$ synthesised from oxides (A-method) and sol–gel (B-method), as previously mentioned, significant traces of $Cs_2Ti_6O_{13}$ have been observed. The conductivity was measurable only at high temperature, its value at 200°C was $2{\cdot}5 \times 10^{-8}$ S cm^{-1} for the A-method and $1{\cdot}7 \times 10^{-8}$ S cm^{-1} for the B-method. Examples of impedance diagrams are plotted in Fig. 6. Such diagrams are typically those which are generally obtained on a material having monophasic-conductivity properties (only one relaxation time). Their characteristic frequencies (frequency corresponding to the maximum in the imaginary part of the impedance) are around 1 kHz.

If the powder is first calcined (improved B-method), $Cs_2Ti_6O_{13}$ was not observed (only TiO_2

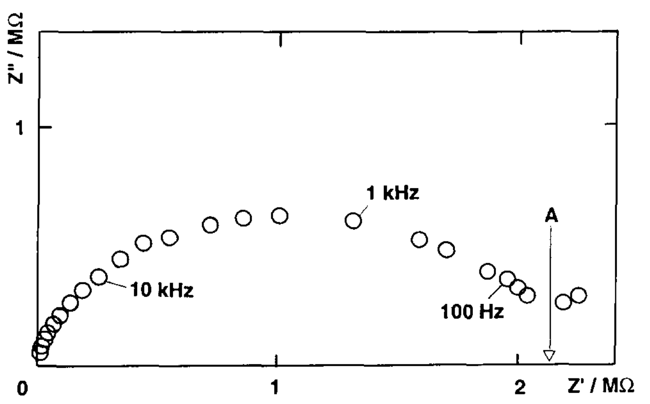


Fig. 7. Example of impedance diagram obtained on $Cs_2Ti_6O_{13}$ at 200°C.

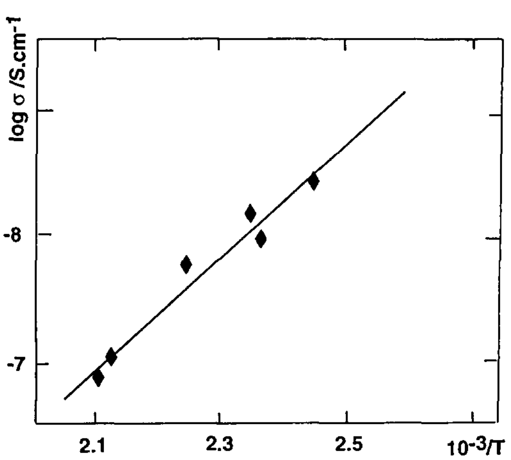


Fig. 8. Resistivity of $Cs_2Ti_6O_{13}$ as a function of reciprocal temperature.

and Al_2O_{13} traces are noticeable). In this case, the conductivity is not measurable with our set-up, even if the temperature is about 200°C. That means that the conductivity of this material is lower than 10^{-10} S cm^{-1}. In the same way, the samples sintered from spray-drying (C-method), which were obtained without traces of $Cs_2Ti_6O_{13}$, were not conductors.

The conductivity of $Cs_2ZnTi_7O_{16}$ synthesised by the B-method was $2{\cdot}3 \times 10^{-8}$ S cm^{-1} at 200°C. It is close to the value of Cs_2AlTiO_4 synthesised by the A- and B-methods. As mentioned before, sizeable traces of $Cs_2Ti_6O_{13}$ were also observed in this material.

$Cs_2Ti_6O_{13}$, synthesised by the C-method, has also been characterised and the conductivity values were clearly higher ($\sigma = 2{\cdot}10^{-7}$ S cm^{-1} at 200°C). An example of impedance diagram is plotted in Fig. 7. Its shape shows several relaxation times of conductivity phenomena with characteristic frequencies around the preceding one (1 kHz). We can suppose that there is another conducting phase in the sample which could be $Cs_2Ti_5O_{11}$, in accordance with the X-ray analysis. The equivalent conductivity values quoted in Fig. 8 have been calculated from the total resistance (A-point in Fig. 7). The activation energy is about 40 kJ mol^{-1} (i.e. about 0·4 eV). The conductivity value extrapolated at room temperature is about 10^{-12} to 10^{-13} S cm^{-1}.

4 Discussion

From our results, pure $CsAlTiO_4$ is practically not a conductor. On the other hand, the conductivity of pure $Cs_2Ti_6O_{13}$ is certainly higher than $2{\cdot}10^{-7}$ S cm^{-1} at 200°C because our experimental values were determined from the total resistance of the samples. The conductivity value obtained on $CsAlTiO_4$ samples synthesised by the A- and B-methods are undoubtedly due to the $Cs_2Ti_6O_{13}$ traces. The conductivity ratio between both phases corresponds to a first order to the composition proportion. The characteristic frequencies of these compounds are around the same value (1 kHz). This point is in agreement with an identical conductive phase.

A solubility study has shown that pure $CsAlTiO_4$ is not soluble in water (no weight loss has been noticed after several days of immersion). On the other hand, $Cs_2Ti_6O_{13}$ is soluble: the pellet spontaneously dissolved. A slight solubility of samples composed of both phases have been also observed: a weight loss of 2% after 48 hours of immersion. The water action is also observable by increasing roughness on the sample surface. This result is in accordance with the order of magnitude of the conductivity ratio (difference between pure $CsAlTiO_4$ and the impure phase) and the composition ratio (X-ray analysis).

The bad stability of $Cs_2Ti_6O_{13}$ (and of $Cs_2Ti_5O_{11}$) in water can be explained by a lamelar structure. Such crystalline structure has been identified by Grey *et al.* (21) with a = 3·825 Å, b = 17·271 Å and c = 2·961 Å as parameters (orthorhombic symmetry) for $Cs_2Ti_6O_{13}$. Nevertheless, the theoretical specific weight calculated from these parameters is too high (for instance 13·6 g cm^{-3} for 2 molecules per unit cell) in comparison with our experimental value (3·92 g cm^{-3}). It can be mentioned that Anderson *et al.* have proposed monoclinic symmetry for $Rb_2Ti_6O_{13}$ which is a compound isomorphic to $Na_2Ti_6O_{13}$.[22] The specific weight of $Rb_2Ti_6O_{13}$ should be 4·07 g cm^{-3}, it is close to our experimental value for $CS_2Ti_6O_{13}$. In such a structure, the fast deterioration of the compound in water is difficult to interpret. The structure of $Cs_2Ti_6O_{13}$ seems to be an open problem.

5 Conclusion

If $CsAlTiO_4$ is carefully synthesized, without interference phases, it is not a conductor. It cannot be of any utility in electrochemical applications. Thin films, with for instance a 0·1 micrometer thick and a 1 cm^2 area, would have an impedance higher than 10^{10}–10^{11} Ω. This is a value too high for sensor applications, potentiometric devices included.[11]

The conductivity of $Cs_2Ti_6O_{13}$ is better. Unfortunately, this material is dissolved in water. It cannot be used as ionosensitive membrane for aqueous analysis. As no deterioration in an alcohol medium has been noticed, this compound can eventually have some applications in such a solvant. With the same geometric parameters mentioned before the impedance of thin films would be of the order of 10^6 Ω at room temperature. Such a value is reasonable. Thin films elaborations of this material can be considered, for instance by the dip-coating process as proposed for NASICON compounds.[6,7]

A di-phasic mixture of both compounds should not be particularly advantageous, because the samples are still slowly damaged by water.

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