NEW DEFECT PYROCHLOR SOLID SOLUTION IN THE KBi$_2$M$_5$O$_{16}$ – TlBi$_2$M$_5$O$_{16}$ (M=Nb, Ta) SYSTEMS

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Abstract: synthesis and characterization of new solids solutions K$_{1-x}$Tl$_x$Bi$_2$M$_5$O$_{16}$ with (0≤x≤1; M=Nb, Ta) defect pyrochlore type. Two solid solutions K$_{1-x}$Tl$_x$Bi$_2$M$_5$O$_{16}$ (0≤x≤1; M=Nb, Ta) were prepared using solid state reaction method and characterized by x-ray diffraction and Infrared absorption spectroscopy. All compositions were indexed in the cubic system (space group Fd3m) and showed the defect pyrochlore-type structure like oxides as AB$_2$M$_5$O$_{16}$ (A=K, Tl; M=Nb, Ta) [1]. The cell parameter of the two defect pyrochlores solid solutions varies linearly with increasing x of compositions from a=10.5701(1) Å to a=10.5343(1) Å for K$_{1-x}$Tl$_x$Bi$_2$M$_5$O$_{16}$ (0≤x≤1) and from a=10.5489(1) Å to a=10.5144(1) Å for K$_{1-x}$Tl$_x$Bi$_2$Ta$_x$O$_{16}$ (0≤x≤1).

Résumé – Synthèse et caractérisation de nouvelles solutions solides K$_{1-x}$Tl$_x$Bi$_2$M$_5$O$_{16}$ (0≤x≤1; M=Nb, Ta) de type pyrochlore déficitaire. Deux solutions solides K$_{1-x}$Tl$_x$Bi$_2$M$_5$O$_{16}$ (0≤x≤1; M=Nb, Ta) ont été préparées à l’état solide et caractérisées par diffraction des rayons X et par spectroscopie d’absorption infrarouge. Toutes les compositions des solutions solides cristallisent dans le système cubique (groupe d’espace Fd3m) et appartiennent à la famille des pyrochlores déficitaires, AB$_2$M$_5$O$_{16}$ (A=K, Tl; M=Nb, Ta) [1]. Le paramètre de maille des deux solutions solides varie linéairement avec la composition x de a=10.5701(1) Å à a=10.5343(1) Å pour K$_{1-x}$Tl$_x$Bi$_2$M$_5$O$_{16}$ (0≤x≤1) et de a=10.5489(1) Å à a=10.5144(1) Å pour K$_{1-x}$Tl$_x$Bi$_2$Ta$_x$O$_{16}$ (0≤x≤1).

I. Introduction

Material pyrochlore and related phases have been characterized by many workers over the past several years, this as a result of the stability and diverse physical properties of this material. The pyrochlore structure with general formula A$_2$B$_2$O$_6$O’ [2-4] and with eight formula units per cell can be considered as interpenetrating networks completely independent B$_2$O$_6$ and A$_2$O’; this latter is not essential for the stability of the structure [5-7]. When the compounds processes a general formula A$_2$B$_2$O$_6$O’ the A cation retain the eight-fold coordination but the B cation are only in six-fold coordination. Thus the A ions are larger than the B ions in compound with this structure. The coordination polyhedra of th ions in the ideal case are AO’$_6$O”, BO”$_6$, OA$_2$B$_2$ and O’A’$_4$. The pyrochlore structure tolerates a high degree of non stoichiometry on the A cations and on the O’ anions sites particularly for A= Tl, Pb and Bi, AB$_2$O$_6$-type defect pyrochlores are obtain with all O’ atoms missing; also this type of defect pyrochlore are known for large univalent A cations such as Rb” [8]. So, by removing of A and O’ ions, a variety of deficient structures can be produced with, are know to occur with the general formula A$_2$-xB$_2$O$_{6+y}$ [9-11] with 0<x≤1 and/or 0≤y<1. In this work we report the preparation and characterization of a new defect pyrochlore solid solutions K$_{1-x}$Tl$_x$Bi$_2$M$_5$O$_{16}$ (0≤x≤1; M=Nb, Ta).

II. Experimental

The compounds K$_{1-x}$Tl$_x$Bi$_2$M$_5$O$_{16}$ (0≤x≤1; M=Nb, Ta) were prepared by usual solid solution from starting reagents Bi$_2$O$_3$, Nb$_2$O$_5$, Ta$_2$O$_5$, K$_2$CO$_3$ and Tl$_2$CO$_3$. Weighted quantities of the reactants were intimately mixed and ground in a agate mortar. In order to avoid a possible oxidization of Tl+ to Tl$^{3+}$, all compounds were treated under nitrogen atmosphere. Three thermal processings with intermittent regrinding at 300°C (6 hours) (to provoke the departure of CO$_2$ and in the same time to avoid volatilization of Tl$_2$CO$_3$ [12], 800°C (12 hours) ( to finish the decomposition of K$_2$CO$_3$) and 950 – 1000°C (12 hours) were necessary to obtain the final compounds. X-ray powder diffractions were obtained using Cu Kα line of a D5000 Siemens diffractometer with Bragg-Brentano
geometry and equipped with a back monochromator. The data were recorded between 10 and 120 (2θ) in steps of 0.04° with a count time of 72 s. Temperature programmed X-ray diffraction was performed on a Siemens D5000 diffractometer fitted out with an ANTON PARR furnace (CHTK10) and a linear detector (Elphyse 14°). The powders were ground in the presence of polyvinyl alcohol and polyethylene glycol and pressed into pellets (10mm in diameter and approximately 1.4 mm thick) using an uniaxial pressure (200 MPa). Before sintering, the pellets were heated at 500°C to evaporate the binder. The morphology of sintered materials was determined by SEM. The thermal gravimetric analysis (TGA) of powder samples was carried out using a SETARAM TG with a heating rate of 10°C/mn. The IR spectra were recorded between 4000 and 400 cm⁻¹ with 4 cm⁻¹ resolution using a Foirier-Transformed BOMEN MX spectrometer from dicks containing 2 mg of sample and 100 mg of KBr or CsCl. The densities were measured using ACCUPYC 13330 helium pycnometer.

III. Results And Discussions

III-1. Solid solution

In order to study the dielectric properties for compounds KBi₂M₅O₁₆ (M = Nb, Ta) [13] we have examined the morphology of sintered pellets (figure 1) we note for this two compound that pellets crack in contact with air. This phenomenon could be the result of the increase of the cell volume in relation with atmospheric humidity. To solve this problem of pellets cracking we however substitute the potassium by the thallium in the KBi₂M₅O₁₆ (M = Nb, Ta) for two reasons:

1) The size, in six-fold coordination, of thallium ion (rTl⁺(6) = 1.50Å) is relatively near to potassium ion (rK⁺(6) = 1.38Å).

2) Compounds KBi₂M₅O₁₆ and TlBi₂M₅O₁₆ (M = Nb, Ta) crystallize in the same structural type [1].

In spite of this substitution on one hand and by using of optimal conditions for sintering materials on the other hand, the pellet crack. So dielectrics properties can’t be determined because all prepared pellets crack at ambient temperature. However we have identify two solid solution Kₙ₋ₓTlₓBi₂M₅O₁₆ (0≤x≤1; M=Nb, Ta).

III-2. X-ray diffraction

All compound Kₙ₋ₓTlₓBi₂M₅O₁₆ (0≤x≤1; M=Nb, Ta) were prepared like compounds KBi₂M₅O₁₆ and TlBi₂M₅O₁₆ (M = Nb, Ta) [1]. The final products are yellow and white respectively for Kₙ₋ₓTlₓBi₂Nb₅O₁₆ and Kₙ₋ₓTlₓBi₂Ta₅O₁₆. Figure 2 shows the x-ray diffraction diagrams for the two solid solutions. They characterize a continuous solid solution crystallizing in the defect pyrochlore type structure (S.G. Fd3m).

The parameter exhibit a quasi-linear evolution with composition x. The substitution of K⁺ (1.38 Å) by Tl⁺ (1.50 Å) must normally induce an increasing of the cell parameter. Figure 3 shows an evolution of the cell parameter in the inverse sense. This could be the result of the action of two antagonistic phenomena: on one hand, the substitution by a bigger size cation (increase cell parameter) and on the other hand, composition rich with thallium present a slight hydration degree (decrease cell parameter); the consequence of these two effects is an appreciable reduction of cell parameter with x compositions. No significant change in the x-ray diffraction patterns of these compositions was observed, however a slight shift in the position of peaks was detected by the mean of high temperature diffraction patterns. In table I we give the cell parameter of extreme compounds (x=0 and x=1) for the two solid solutions at 25°C and at 500°C. Other effects of hydration are the change in the relative intensity of (311) Bragg peaks. Indeed, when hydration degree increase, relative intensity of (311) Bragg peaks increase as can be seen in figure 2. This phenomenon was also observed in NH₄NbWO₆ [14].
Figure 2. X-ray powder diffractograms of $K_{1-x}Tl_xBi_2M_5O_{16} (0 \leq x \leq 1)$

Figure 3. Cell parameter variation versus composition of $K_{1-x}Tl_xBi_2M_5O_{16} (0 \leq x \leq 1)$

Tableau 1. Cell parameter at 25°C and at 500°C of $ABi_2M_5O_{16} (A= K, Tl; M= Nb, Ta)$

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Cell parameter at 25°C</th>
<th>Cell parameter at 500°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>KBi$_2$Nb$<em>2$O$</em>{16}$</td>
<td>10.5701(1)</td>
<td>10.5051(1)</td>
</tr>
<tr>
<td>TlBi$_2$Nb$<em>2$O$</em>{16}$</td>
<td>10.5343(1)</td>
<td>10.5093(1)</td>
</tr>
<tr>
<td>KBi$_2$Ta$<em>2$O$</em>{16}$</td>
<td>10.5389(1)</td>
<td>10.4684(1)</td>
</tr>
<tr>
<td>TlBi$_2$Ta$<em>2$O$</em>{16}$</td>
<td>10.5144(1)</td>
<td>10.4786(1)</td>
</tr>
</tbody>
</table>

III-3. TGA

The thermal gravimetric analysis (TGA) (figures.4) of the prepared powders of $K_{1-x}Tl_xBi_2M_5O_{16} (0 \leq x \leq 1; M= Nb, Ta)$ show that dehydration temperatures starts at about 50°C and are relatively low indicate the presence of water adsorbed and from 100°C to 400°C we assist to the loss of a bounded water. The effect of this insertion of water molecular is an appreciable increasing in the cell constants or cell volume. Table II gives the number of water moles adsorbed in each composition Compounds KNbWO$_6$
and KTaWO₆ prepared by Darriet and Al [15] are hygroscopic at ambient temperature; similar results have been obtained for other related pyrochlore such as K₃/2Cr₁/2Te₃/2O₆, 1/2H₂O [16, 17]. We note from x=1 to x=0, an increasing of weight losses $\Delta M$ (%) for the two solid solutions indicating that composition rich with K₂O retain atmospheric humidity more than Tl-containing pyrochlores.

**Figure 4.** TGA thermograms of KₓTlₓBi₂M₅O₁₆ (0≤x≤1; M=Nb, Ta)

**Tableau II.** Weight losses $\Delta M$ (%) and number of water moles of KₓTlₓBi₂M₅O₁₆ (M=Nb, Ta)

<table>
<thead>
<tr>
<th>Composition x</th>
<th>$\Delta M$ (%)</th>
<th>$n$ (H₂O)</th>
<th>$\Delta M$ (%)</th>
<th>$n$ (H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0</td>
<td>2.27</td>
<td>0.61</td>
<td>1.51</td>
<td>0.55</td>
</tr>
<tr>
<td>x = 0.25</td>
<td>1.73</td>
<td>0.48</td>
<td>1.21</td>
<td>0.48</td>
</tr>
<tr>
<td>x = 0.5</td>
<td>1.34</td>
<td>0.39</td>
<td>1.01</td>
<td>0.40</td>
</tr>
<tr>
<td>x = 0.75</td>
<td>0.96</td>
<td>0.28</td>
<td>0.83</td>
<td>0.33</td>
</tr>
<tr>
<td>x = 1</td>
<td>0.63</td>
<td>0.19</td>
<td>0.47</td>
<td>0.19</td>
</tr>
</tbody>
</table>

**Figure 5.** Variation of specific mass versus composition of KₓTlₓBi₂M₅O₁₆ (0≤x≤1; M=Nb, Ta)

**III-4. Specific mass measurements**

*Figure 5* shows a normal evolution with composition x. This is with a good agreement with the difference of molar weight of thallium (204.37 g/mol) and potassium (39.102 g/mol). The effect of hydration has been masked by the great difference between molar weights.

**III-5. Infrared spectroscopy**

The group theoretical analysis for optical and acoustical modes from correlation method and taking account the symmetry conditions of pyrochlore structure [18] are given in table III.
Table III. Factor group analysis for the zone center vibrational modes of pyrochlore $A_2B_2O_6$O’

<table>
<thead>
<tr>
<th>Ion</th>
<th>Number of equivalent positions (Wyckoff notation)</th>
<th>Site group Symmetry</th>
<th>Irreducible Representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>16(c)</td>
<td>D3d</td>
<td>$A_{2u} \oplus E_u \oplus 2F_{1u} \oplus F_{2u}$</td>
</tr>
<tr>
<td>B</td>
<td>16(d)</td>
<td>D3d</td>
<td>$A_{2u} \oplus E_u \oplus 2F_{1u} \oplus F_{2u}$</td>
</tr>
<tr>
<td>O</td>
<td>48(f)</td>
<td>C2v</td>
<td>$A_{1g} \oplus E_g \oplus 2F_{1g} \oplus 3F_{2g} \oplus A_{2u} \oplus E_u \oplus 3F_{1u} \oplus 2F_{2u}$</td>
</tr>
<tr>
<td>O’</td>
<td>8(a)</td>
<td>Td</td>
<td>$F_{1u} \oplus F_{2g}$</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td></td>
<td>$\Gamma = A_{1g} \oplus E_g \oplus 2F_{1g} \oplus 4F_{2g} \oplus 3A_{2u} \oplus 3E_u \oplus 8F_{1u} \oplus 4F_{2u}$</td>
</tr>
<tr>
<td></td>
<td>Acoustic</td>
<td>$\Gamma_{ac} = F_{1u}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Raman</td>
<td>$\Gamma_{r} = A_{1g} \oplus E_g \oplus 4F_{2g}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Infrared</td>
<td>$\Gamma_{ir} = 7F_{1u}$</td>
<td></td>
</tr>
</tbody>
</table>

So, out of these 26 normal modes, only $A_{1g}$, $E_g$, $4F_{2g}$ are Raman active, $7F_{1u}$ are infrared active and $F_{1u}$ acoustical. The IR spectrum recorded between 300 and 4000 cm$^{-1}$ for $K_{1-x}Tl_xBi_2Nb_5O_{16}$ and $K_{1-x}Tl_xBi_2Ta_5O_{16}$, are represented in figure 6. We note at first that these spectrum are similar to those of $ABi_2M_5O_{16}$ ($A = K$, Tl; $M = Nb$, Ta) pyrochlore prepared by [19]. The strong vibrational modes at about 390-400 cm$^{-1}$ and 550-670 cm$^{-1}$ have been assigned to fundamental $M$---$O$ (With $M = Nb$, Ta) stretching and $O$---$M$---$O$ bonding vibrations (all of $F_{1u}$ symmetry) [20]. $M$---$O$ stretching are usually broadened with shoulder near 600 cm$^{-1}$ and 700 cm$^{-1}$ for $M = Nb$ and Ta respectively as for $Cd_2M_2O_7$ ($M = Nb$, Ta) [21]. This may be due to distortions in the $MO_6$ octahedra: The $M$---$O$ bands which should actually exhibit the same length seems to be different. The band at about 812-833 cm$^{-1}$ is not attributed; it may be due to the local defect in the structure. The absorption bond at 3500 cm$^{-1}$ is related to $O$---$H$ stretching vibrations, whereas the bond near to 1630 cm$^{-1}$ represents $H$---$O$---$H$ bonding vibration of water, showing that hydrogen, at least partly, occurs as molecular water in the two defect pyrochlore solid solutions. This result is consistent with the well-known depending on the nature of the large cation $A$ [17, 22].
IV. CONCLUSION

In this work we have determined the existence of two solid solutions $K_{1-x}Tl_xBi_2M_5O_{16}$ ($0 \leq x \leq 1$ and $M = Nb, Ta$) inside the systems $KBi_2M_5O_{16}$ - $TlBi_2M_5O_{16}$ ($M = Nb, Ta$). The structure of all composition is isotypic with defect pyrochlore like $ABi_2M_5O_{16}$ ($A = K$, $Tl$ and $M = Nb$, $Ta$) compounds [1]. Infrared spectra, TGA and high temperature diffraction patterns show the existence of water in all compositions of $K_{1-x}Tl_xBi_2M_5O_{16}$ ($0 \leq x \leq 1$ and $M = Nb$, $Ta$). As a consequence hydration we note a slight increase in the unit cell volume; this phenomenon is responsible of cracking of all sintered pellets destined to dielectrics measurements.

V. REFERENCES


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