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Room temperature stabilisation of γ-$Bi_2VO_{5.5}$ and synthesis of the new fluorite phase f-Bi_2VO_5 by a mechanochemical activation method

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Mechanochemical activation followed by annealing at moderate temperatures results in the stabilisation at room temperature of the high ionic conductor oxide γ-$Bi_2VO_{5.5}$ belonging to the Bi–V^V–O_2 system, while in the Bi–V^{IV}–O_2 system a non-previously reported fluorite-type f-Bi_2VO_5 phase is isolated. All α-, β- and γ-$Bi_2VO_{5.5}$ and f-, α- and β-Bi_2VO_5, as well as amorphous powders with $2Bi_2O_3:V_2O_5$ and $Bi_2O_3:VO_2$ compositions, are studied by X-ray powder diffraction at ambient and high temperatures, thermal analysis and scanning electron microscopy.

Introduction

There is much interest in the bismuth–vanadium-(v) and -(iv) oxides $Bi_2VO_{5.5}$ and Bi_2VO_5, respectively, owing to their properties mainly as ionic conductors[1–5] and, also reported,[1,6] as ferroelectric materials. Both oxides exhibit three polymorphic phases (α, β and γ) obtained at increasing temperatures. From a structural point of view, all these compounds show an Aurivillius-related structure, with oxygen vacancies in the ReO_3 layer. The differences among the three polymorphs can be found in the ordering of the oxygen vacancies, these being disordered in the γ-phases. The α→β→γ transitions for the V^V oxide are reversible, occurring at *ca.* 450 and 650 °C on heating and showing hysteresis on thermal cycling. By contrast, for the Bi_2VO_5 these transitions are irreversible and occur at 690 and 850 °C, respectively. Since the high temperature γ-$Bi_2VO_{5.5}$ polymorph exhibits the largest ionic conductivity, numerous efforts have been devoted to stabilise this structure at room temperature. To date this has been done by partial substitution of the vanadium for iso- and alio-valent cations, of different sizes and valence states,[7,8] which leads to a deterioration of the physical properties, *e.g.* the ionic conductivity.

The conventional ceramic synthesis method has been the most widely applied to obtain all these oxides, but is problematic because high temperatures and long reaction times are needed. Thus new synthesis methods need to be developed in order to prevent changes in stoichiometry, as well as to facilitate the reactions, by lowering the reaction temperatures and times. The mechanochemical activation method seems to be able to fulfil these demands. It has been successfully applied to enhance the kinetics of compound formation and phase transformation, as well as to synthesise new materials,[9–11] with consequent improvement of the physicochemical characteristics of the resulting materials.[12,13]

While more than fifteen papers are published each year on $Bi_2VO_{5.5}$, references to Bi_2VO_5 are virtually limited to those of the present authors. In the same line, the present work reports the results of the mechanochemical activation synthesis method applied to obtain the technologically exciting $Bi_2VO_{5.5}$ and Bi_2VO_5 oxides. They are promising for use as alternative materials for a wide variety of applications, such as catalysts, gas sensors, solid state electrolytes, positive electrode materials for rechargeable batteries or high transition temperature ferroelectrics.

Experimental

About 3 g of stoichiometric mixtures of analytical grade Bi_2O_3 and V_2O_5 or VO_2 were homogenised by hand in an agate mortar and placed in a stainless-steel pot along with a 5 cm diameter steel ball. The sample was mechanochemically activated in air, for times ranging from one hour to three weeks, on a Fritsch vibrating mill (Pulverisette 0). Then the milled powders were characterised by differential thermal analysis (DTA) and X-ray powder diffraction (XRD) at ambient and high temperatures. Thermal treatments were carried out in air for V^V samples and under vacuum or N_2 for V^{IV}, in order to prevent oxidation of V^{IV} to V^V.

DTA curves were recorded up to 800 °C on a Seiko 320 instrument at a heating rate of 10 °C min^{-1}. About 10 mg of sample was used for each run with Al_2O_3 used as the reference material.

Powder X-ray diffraction patterns were performed at room temperature with a Siemens Kristalloflex 810 computer controlled diffractometer, and a D501 goniometer provided with a 2θ compensating slit and a graphite monochromator. Patterns were collected in the range 5–100°(2θ) with increments of 0.05°(2θ) and counting time of 4 s per step, the goniometer being controlled by a DACO-MPV2 computer. To collect X-ray diffraction patterns at high temperature, an Anton Paar HTK10 attachment mounted on a Philips PW 1310 diffractometer was used between 5 and 70°(2θ) with increments of 0.02°(2θ) and counting time of 2 s per step. Each sample was deposited on a platinum sheet placed on a tantalum strip, which acts as the heating element. The temperature was measured using a Pt–Pt (13% Rh) thermocouple welded onto the centre of the platinum sheet. The temperature was increased at a rate of 10 °C min^{-1} and stabilised for the measurements. Cu-Kα ($\lambda = 1.5418$ Å) radiation was used in all experiments.

Dispersed particles of the milled and thermally treated powders were studied with an ISI-DS-130C scanning electron microscope (SEM), working at 18 kV.

Results and discussion

For both $2Bi_2O_3:V_2O_5$ and $Bi_2O_3:VO_2$ compositions, the X-ray diffraction patterns show that the mixture of starting oxides remains unchanged for very short milling times (up to 24 h). A gradual broadening of diffraction peaks occurs with increasing milling times, without appearance of peaks other than those of the starting oxides, up to 48 h in the former case and to five days in the latter, which indicates that an amorphization process is taking place. Finally, after three days and one week of mechanical activation for $2Bi_2O_3:V_2O_5$ and $Bi_2O_3:VO_2$ mixtures, respectively, only an amorphous phase is observed.

As can be observed in Fig. 1, DTA of amorphous $2Bi_2O_3:V_2O_5$ shows on heating the presence of a strong exothermic peak centred at 385 °C, and on cooling two small exothermic peaks centred at 542 and 353 °C. X-Ray diffraction patterns recorded at higher temperatures (Fig. 2) confirm the presence of the amorphous phase up to the temperature of the peak observed in DTA on heating, beyond which crystallised γ-$Bi_2VO_{5.5}$ is obtained that remains unaltered up to 650 °C. On cooling partial transformation of γ to β-$Bi_2VO_{5.5}$ is observed at 500 °C, after the first small exothermic peak, and finally to α-$Bi_2VO_{5.5}$ at 300 °C that appears as the only phase at room temperature. The α and β-$Bi_2VO_{5.5}$ phases were easily identified owing to the splitting of some diffraction lines in the α-phase, and because of their characteristic superlattice lines.

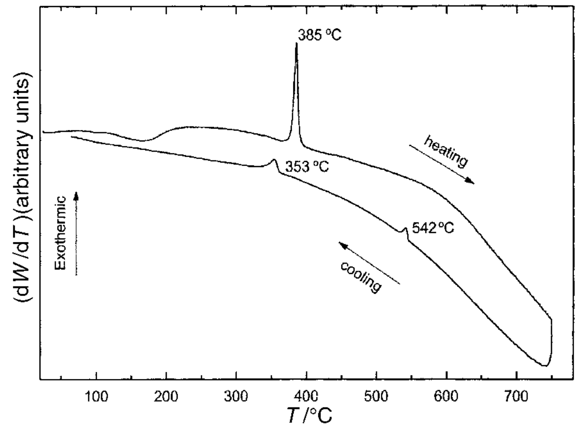

Fig. 1 Differential thermal analysis of $2Bi_2O_3:V_2O_5$ amorphous powder (mechanically activated).

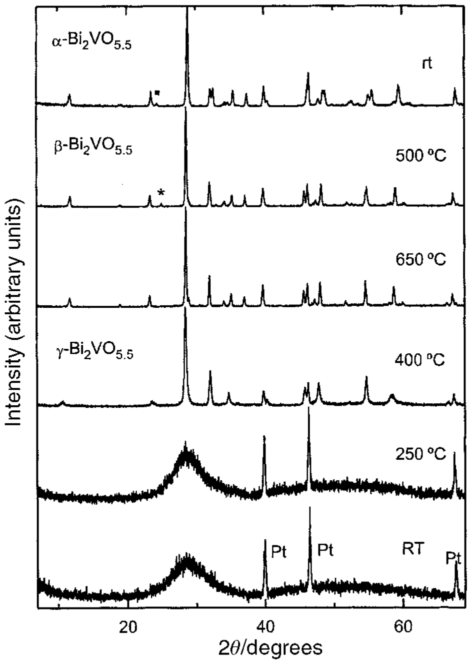

Fig. 2 X-Ray diffraction patterns at increasing/decreasing temperatures of $2Bi_2O_3:V_2O_5$ amorphous powder (mechanically activated). Pt = platinum; (*) high satellite line of β-$Bi_2VO_{5.5}$ phase; (●) high satellite line of α-$Bi_2VO_{5.5}$ phase; RT, starting room temperature; rt, final room temperature.

A similar study has been recently reported by Shantha *et al.*,[14,15] who carried out activation for $2Bi_2O_3:V_2O_5$ with a centrifugal ball mill. Their results show the progressive transformation of the starting oxides to $BiVO_4$ and to $Bi_2VO_{5.5}$, for 16 and 54 h of milling time, respectively. Despite an uncertainty owing to the broadening of diffraction lines in their X-ray patterns, these authors conclude that tetragonal γ-$Bi_2VO_{5.5}$ is formed. On the basis of these results it can be assumed that the mechanical activation process carried out by the method used here is more energetic, leading to the formation of an amorphous powder from the starting oxides, according to XRD analysis and the strong exothermic peak on the DTA curve can be assigned to crystallisation of this phase. In conclusion, the reactions taking place are summarised as follows:

on heating:

$$Bi_2O_3 : V_2O_5 \xrightarrow{\text{milling}} \text{amorphous} \xrightarrow{385\,^\circ C} \gamma\text{-}Bi_2VO_{5.5} \xrightarrow{650\,^\circ C} \gamma\text{-}Bi_2VO_{5.5}$$

on cooling:

$$\gamma\text{-}Bi_2VO_{5.5} \xrightarrow{542\,^\circ C} \beta\text{-}Bi_2VO_{5.5} \xrightarrow{353\,^\circ C} \alpha\text{-}Bi_2VO_{5.5}$$

Further thermal analyses confirmed the stability of the obtained γ-$Bi_2VO_{5.5}$ phase up to 500 °C without transitions on cooling to β and α-polymorphs. Fig. 3(a) shows the DTA curve of the amorphous phase which shows an exothermic crystallisation peak, while Fig. 3(b) shows the DTA curve of crystalline γ-$Bi_2VO_{5.5}$, obtained by annealing of the amorphous activated powder at 385 °C. γ-$Bi_2VO_{5.5}$ remains unaltered up to 500 °C after various heating–cooling cycles. By contrast, thermal analysis of γ-$Bi_2VO_{5.5}$ carried out up to 700 °C

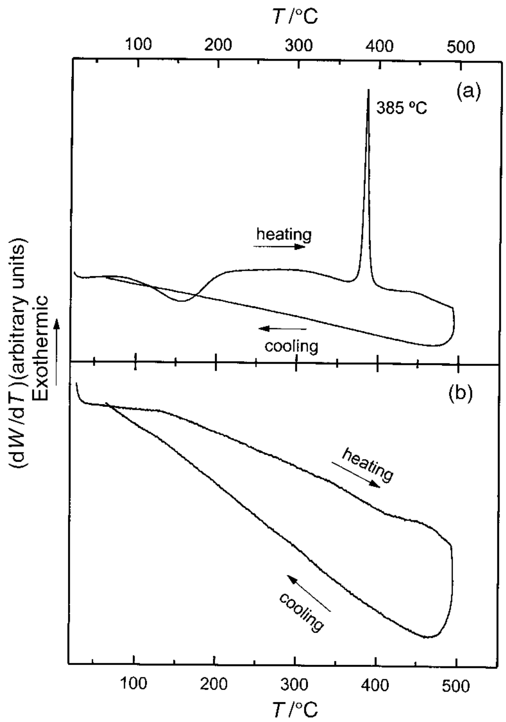

Fig. 3 Differential thermal analysis up to 500 °C of (a) $2Bi_2O_3:V_2O_5$ amorphous activated powder and (b) γ-$Bi_2VO_{5.5}$ obtained from the amorphous activated phase.

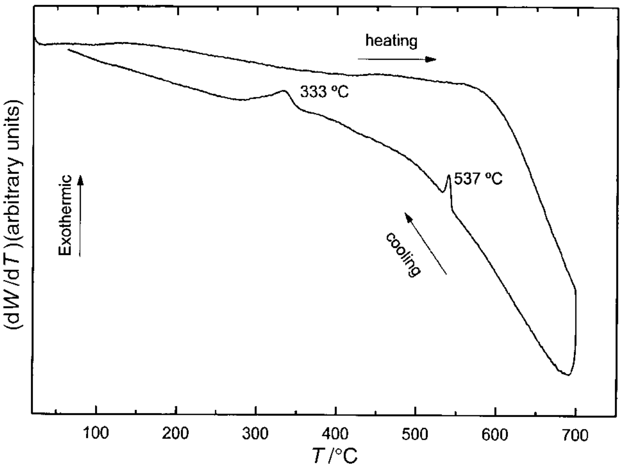

Fig. 4 Differential thermal analysis of γ-$Bi_2VO_{5.5}$ stabilised oxide up to 700 °C showing the $\gamma \rightarrow \beta \rightarrow \alpha$ transitions on cooling.

(Fig. 4) shows the $\gamma \rightarrow \beta \rightarrow \alpha$ transformations on cooling, in accordance with the XRD patterns (Fig. 2), at almost the same temperatures as observed for the amorphous powder. This is the first report on the stabilisation of γ-$Bi_2VO_{5.5}$ from room temperature up to 500 °C, without doping.

Fig. 5(a) shows an SEM image of the powder obtained by the mechanochemical activation of the $2Bi_2O_3:V_2O_5$ oxide mixture. The submicron size particles obtained are almost spherical, with no evidence for different types of particles arising from the two starting oxides. Fig. 5(b) shows the SEM image of the same powder after thermal treatment at 385 °C, which gives a well defined XRD pattern of the γ-$Bi_2VO_{5.5}$ phase (Fig. 2). The particle size observed in Fig. 5(a) could indicate that the amorphous XRD pattern of such an activated mixture has its origin in the amorphous character of the particles. Furthermore, the size reduction when the γ-$Bi_2VO_{5.5}$ phase appears could indicate that a crystallisation, and corresponding shrinkage, from amorphous particles with the same composition has taken place, rathre than an interdiffusion among the submicron size Bi_2O_3 and V_2O_5 particles. This would be in agreement with the very sharp peak of crystallisation observed by DTA (Fig. 1 and 3). However, only the local determination of the structure, by TEM, and analysis of the composition of the particles of the milled powder will fully clarify the effect of milling. Three pathways appear to be possible: (1) simple oxide particle fracture and straining by creation of a high defect concentration, (2) a more advanced stage consisting of the formation of double oxide amorphous particles or (3) a true mechanosynthesis of nanocrystals of γ-$Bi_2VO_{5.5}$.

Fig. 5(c) shows the particles after thermal treatment of the activated oxide mixture at 700 °C, well above the temperature of formation of the ordered α-$Bi_2VO_{5.5}$ phase (Fig. 2). A clear process of crystal growth has taken place and the particles obtained have a size of *ca.* 5 μm, much larger than in the previous samples.

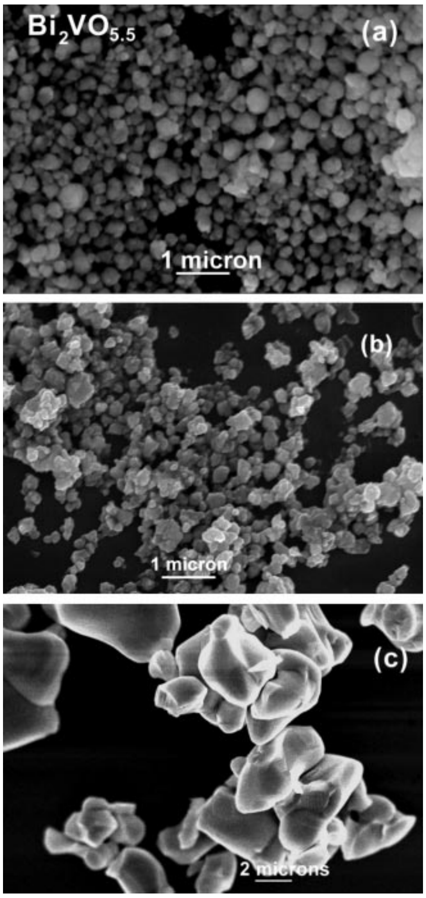

Fig. 5 SEM images of (a) $2Bi_2O_3:V_2O_5$ amorphous powder, (b) as (a) after annealing at 385 °C (γ-$Bi_2VO_{5.5}$) and (c) after further annealing at 700 °C (α-$Bi_2VO_{5.5}$).

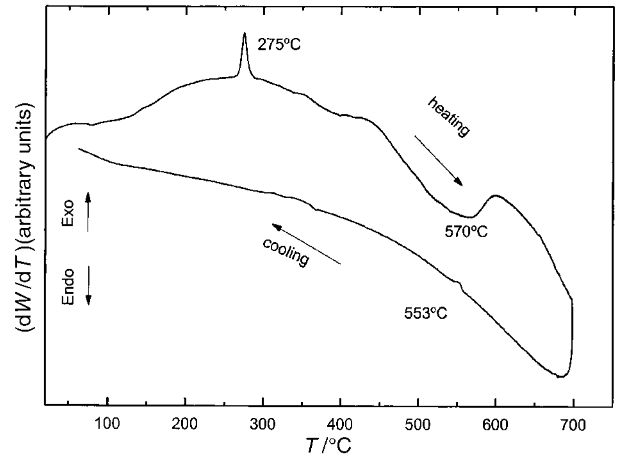

Fig. 6 Differential thermal analysis of $Bi_2O_3:VO_2$ amorphous powder (mechanically activated).

The amorphous product obtained by mechanochemical activation of $Bi_2O_3:VO_2$ is black similarly to VO_2 whereas for $2Bi_2O_3:V_2O_5$ the amorphous product was dark yellow. This fact suggests that the V^{IV} valence state remains unaltered in the course of milling. Such high stability of V^{IV} was previously observed during milling when V_2O_5 is present,[15,16] in which partial conversion of V^{V} to V^{IV} occurred. Fig. 6 shows the DTA curve, recorded under N_2, and Fig. 7 the X-ray diffraction patterns at increasing/decreasing temperatures, recorded under vacuum, of amorphous $Bi_2O_3:VO_2$. By analogy with the $2Bi_2O_3:V_2O_5$ mixture, the first observed exothermic peak on heating is attributed to crystallisation. In this case the crystalline phase exhibits a fluorite structure and constitutes a new polymorph of Bi_2VO_5. Then, the fluorite phase transforms, as revealed by a large endothermic effect, to a mixture of α- and β-Bi_2VO_5.[4,5] γ-Bi_2VO_5 is, however, not observed since it is expected to form between 775 and 800 °C.[17] On cooling only a very weak exothermic effect is observed, attributed to the $\beta \rightarrow \alpha$ transition, so that α-Bi_2VO_5 is obtained as a pure phase on cooling to room temperature.

The chemical reactions occurring are understood as follows:

on heating:

$$\begin{aligned} Bi_2O_3 : VO_2 &\xrightarrow{\text{milling}} \text{amorphous} \xrightarrow{275\,^{\circ}C} \text{f-}Bi_2VO_5 \\ &\xrightarrow{570\,^{\circ}C} \alpha\text{-} + \beta\text{-}Bi_2VO_5 \end{aligned}$$

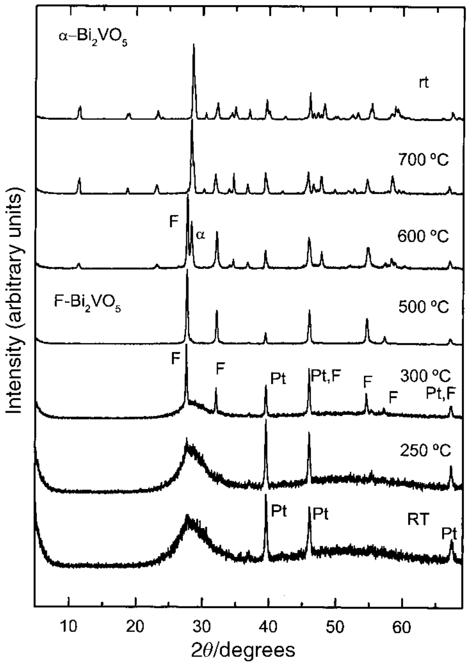

Fig. 7 X-Ray diffraction patterns at increasing/decreasing temperatures of $Bi_2O_3:VO_2$ amorphous powder (mechanically activated). Pt = platinum; F = Bi_2VO_5 fluorite; RT, starting room temperature; rt, final room temperature.

on cooling:

$$\alpha\text{-} + \beta\text{-}Bi_2VO_5 \xrightarrow{553\,^{\circ}C} \alpha\text{-}Bi_2VO_5$$

Formation of fluorite-phases as intermediate products in the synthesis of different Aurivillius-like materials has recently been reported, upon employing the mechanochemical activation method.[12,18] Here, annealing under vacuum at 275 °C of the amorphous powder obtained by mechanochemical activation of $Bi_2O_3:VO_2$ leads to a well crystallised Bi_2VO_5 fluorite phase. Its X-ray diffraction pattern (Fig. 8) has been indexed assuming cubic symmetry with space group $Fm\bar{3}m$ (no. 225) and unit-cell parameter $a = 5.5456(9)$ Å.

The full structural study of this new oxygen deficient Bi_2VO_5 fluorite type structure phase by TEM and X-ray and neutron diffraction is in progress and will be reported separately.

Fig. 9(a) shows an SEM image of the powder obtained by mechanochemical activation of the $Bi_2O_3:VO_2$ oxide mixture, which, again, shows almost spherical particles and in which the two oxides cannot be distinguished. Fig. 9(b) shows an SEM image of the activated mixture after thermal treatment at 275 °C, which results in formation of the fluorite phase (Fig. 8). Together with phase formation, a process of crystal growth has taken place, which would explain the wide DTA signal (Fig. 6). Fig. 9(c) shows the SEM image of the activated mixture after thermal treatment at 700 °C, in which large crystals, of *ca.* 3–5 μm in size, of α-Bi_2VO_5 can be observed.

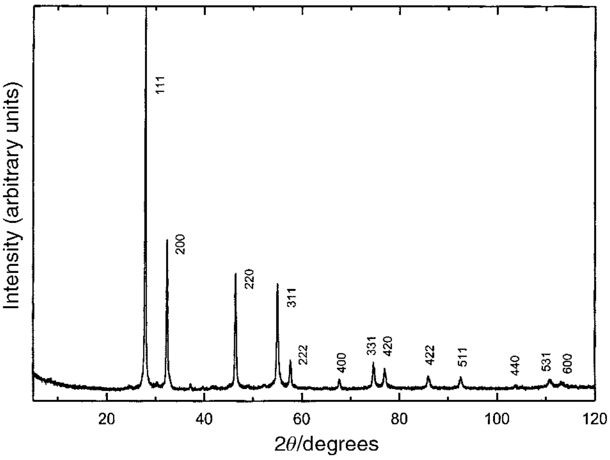

Fig. 8 X-Ray powder diffraction pattern of the single f-Bi_2VO_5 fluorite phase.

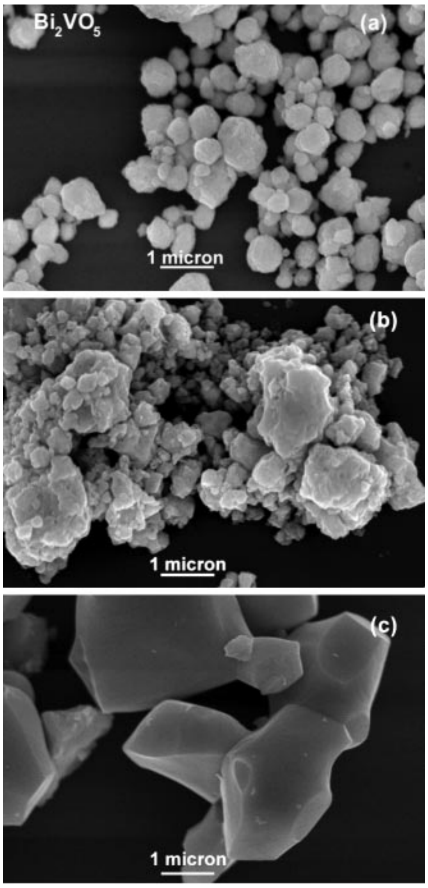

Fig. 9 SEM images of (a) $Bi_2O_3:VO_2$ amorphous powder, (b) as (a) after annealing at 275 °C (fluorite-Bi_2VO_5) and (c) after further annealing at 700 °C (α-Bi_2VO_5).

The homogeneity, in terms of both size and shape, of the powder particles of the $2Bi_2O_3:V_2O_5$ and $Bi_2O_3:VO_2$ amorphous mixtures [Fig. 5(a) and 9(a)] obtained by milling suggests a promising method for the synthesis of non-textured and isotropic ceramics. In particular, piezoelectric properties have been already shown to be improved[12] when ceramics of Aurivillius type structure are prepared from amorphous precursors.

Conclusions

In conclusion, the mechanochemical activation of $2Bi_2O_3:V_2O_5$ and $Bi_2O_3:VO_2$ oxide mixtures by milling, to give amorphous powders has proved to be a novel and effective method to isolate new room-temperature stable phases, not available by conventional chemical routes.

Highly ionic conducting γ-$Bi_2VO_{5.5}$ has been prepared at 385 °C, obtained without doping for the first time, and its stability has been demonstrated up to a temperature of 500 °C.

A new polymorphic fluorite-Bi_2VO_5, stable up to 550 °C, has also been prepared at 275 °C.

The amorphous mixtures are promising precursors for the synthesis of isotropic ceramics in the search for improvement of potential piezoelectric and ionic conducting properties.

Acknowledgements

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