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Synthesis and characterisation of the new cubic phase $CsVTeO_5$ and re-investigation of the pyrochlore $CsVTeO_6$

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The compound $CsVTeO_5$ has been synthesized by solid state reactions and studied by X-ray powder diffraction. $CsVTeO_5$ is polymorphic with a cubic high temperature variety, space group $Fd\bar{3}m$ and $a = 10.482(2)$ Å. The observed X-ray powder pattern of this cubic phase is similar to the AB_2O_6 pyrochlore-type structure and also to those reported for $ATiXO_5$ phases (A = Rb, Cs, Tl and X = P, As). These phases correspond to the high temperature cubic polymorph of $KTiOPO_4$ (KTP). The framework of these cubic phases consists of randomly disordered TiO_6 octahedra and XO_4 (X = P, As) tetrahedra with the A^+ cation occupying large cavities within this framework. The cubic phase '$CsVTeO_6$' [$a = 10.483(1)$ Å], previously reported as a pyrochlore-type structure, corresponds in fact to $CsVTeO_5$. The cubic $CsVTeO_6$ phase, with a pyrochlore related structure, has also been synthesized and the structure was refined by Rietveld profiling of the X-ray data. The space group is $Fd\bar{3}m$ with $a = 10.077(1)$ Å. The value of the unit cell parameter is in good agreement with those reported for the $ABTeO_6$ pyrochlore series (A = K, Rb, Cs and B = Nb, Ta). The thermal stabilities of $CsVTeO_5$ and $CsVTeO_6$ under argon and oxygen atmospheres are discussed.

Introduction

The compounds of the type $MVTeO_5$ (M = Li, Na, K, Rb, and Ag)$^{1-3}$ have been reported previously. Except for the Li phase^3 which is orthorhombic, all the other compounds are isostructural with a monoclinic symmetry (space group $P2_1/c$). The structure, determined for $NaVTeO_5$ on a single crystal, is built up of $(VTeO_5)_n^{n-}$ chains separated by Na atoms. The corresponding oxidized phases $MVTeO_6$ (M = K, Rb or Cs)^4 crystallize with the well known cubic pyrochlore-type structure. As shown in Fig. 1(a), there is a large discrepancy of the *a*-lattice parameter for '$CsVTeO_6$' compared to the other compounds of this series. One should have observed a parameter close to *ca.* 10.1 Å instead of 10.483 Å as mentioned in ref. 4 and in the JCPDS-ICDD database (no. 41-1018). This prompted us to reinvestigate the compounds formation in the system Cs–V–Te–O. Our study shows that the '$CsVTeO_6$' reported in ref. 4 corresponds in fact to the formula $CsVTeO_5$. In this paper, we report the preparation and characterisation of the compounds $CsVTeO_5$ and $CsVTeO_6$.

Experimental

$CsVO_3$ was prepared by the equimolar reaction of Cs_2CO_3 (Aldrich 99.9%) and V_2O_5 (Aldrich 99.9%) heated in pure flowing oxygen at 500 °C for 24 h. $CsVO_3$ is a white powder which was stored in a dry box. Polycrystalline samples of $CsVTeO_5$ were then prepared *via* solid state reactions between $CsVO_3$ and TeO_2 (Aldrich 99.9%). The initial mixture was mixed in an agate mortar and heated in a gold crucible at 450 °C for 12 h under an argon atmosphere. Subsequently, the powder was ground and annealed at the same temperature for 12 h. After the final heating, the powder was quenched at 450 °C. The resulting microcrystalline product is a brown powder. $CsVTeO_6$ was prepared from $CsVO_3$ and $Te(OH)_6$ (Aldrich 99.9%). The mixtures was mixed and heated in a gold crucible at 450 °C for 12 h in pure flowing oxygen. In order to obtain the pure phase, the samples were then ground and heated for 12 h at the same temperature. $CsVTeO_6$ is a greenish grey powder.

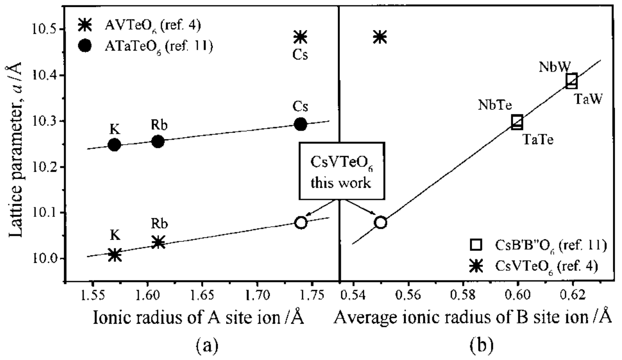

Fig. 1 Lattice parameter *vs.* ionic radius of A site ion and B site ion

Powder X-ray diffraction data were recorded at room temperature on a Philips X'pert MPD using Bragg–Brentano geometry with Cu-Kα radiation. Step scans were performed over the angular range $10 < 2\theta/° < 120$ with a step size of 0.02° and a counting time of 30 s. Profile refinements, using the Rietveld method, were carried out with the help of the Fullprof program.^{5}

Thermogravimetric analyses (TGA) were performed on a MTB10-8 Setaram balance with an accuracy $\Delta m = 0.01$ mg. Experiments were carried out under argon or oxygen atmospheres.

Results

$CsVTeO_5$

In Fig. 2, we show the evolution of the X-ray patterns with the heating temperature for the reaction of the equimolar mixture of $CsVO_3$ and TeO_2 under argon. The most important result is the observation of a very simple pattern at 450 °C. All the *d*-spacings observed in the X-ray diffraction pattern can be indexed with a face-centered cubic cell with $a = 10.482(2)$ Å. At intermediate temperatures, the X-ray pattern is complicated but one can assume that the cubic phase obtained by quenching at 450 °C corresponds to the high temperature form of $CsVTeO_5$. This assumption is corroborated by the thermal

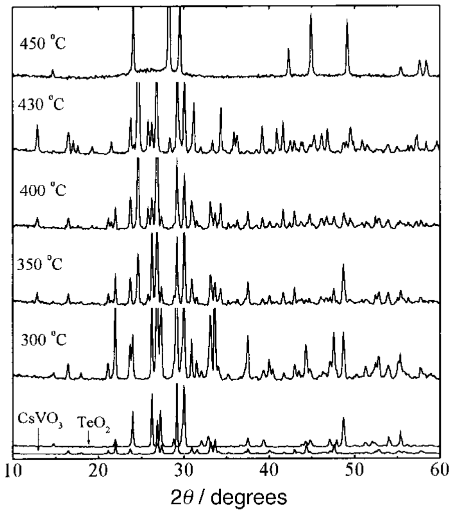

Fig. 2 XRD spectra of the reaction of $CsVO_3+TeO_2$ at different temperatures in Ar atmosphere

behavior of $CsVTeO_5$ (cubic) (Fig. 3). The cubic form is stable up to 200 °C but at higher temperature it progressively transforms to the low temperature variety which is observed as single phase between 350 and 400 °C. At higher temperature (450 °C) the cubic phase is re-stabilized. A profile fitting analysis of the cubic phase $CsVTeO_5$ is shown in Fig. 4. One can see that the X-ray pattern is very similar to the one normally observed for cubic AB_2O_6 with a pyrochlore-related structure. This explains why this phase was wrongly identified as '$CsVTeO_6$' with a pyrochlore structure.[4] In fact, the observed X-ray pattern for cubic $CsVTeO_5$ is also similar to those reported for $CsTiPO_5$,[6,7] $CsTiAsO_5$,[8] $RbTiPO_5$[9] and $TlTiPO_5$.[9] The symmetry of these phases is also cubic with the same space group $Fd\bar{3}m$. They correspond to the high temperature form of the well known KTP ($KTiOPO_4$) which is a nonlinear optical material of technological importance for frequency-doubling light *via* second harmonic generation. For example, $CsTiOPO_4$, which crystallizes at room temperature with the KTP-type structure, undergoes a phase transition to a cubic phase at 963 °C.[6,7] The cubic form corresponds to the highly disordered parent structure of the KTP compounds, with TiO_6 octahedra and XO_4 tetrahedra (X = As, P)[6] randomly disordered in the framework. For the cubic phase $CsVTeO_5$, if one assumes an average ionic radius corresponding to V^{5+} in the octahedra (0.54 Å)[10] and Te^{4+} with a coordination number CN = 4 (0.97 Å),[10] the variation of the a parameter for the series $CsBXO_5$ (B = Ti, V and X = As, P, Te) is linear as shown in Fig. 5.

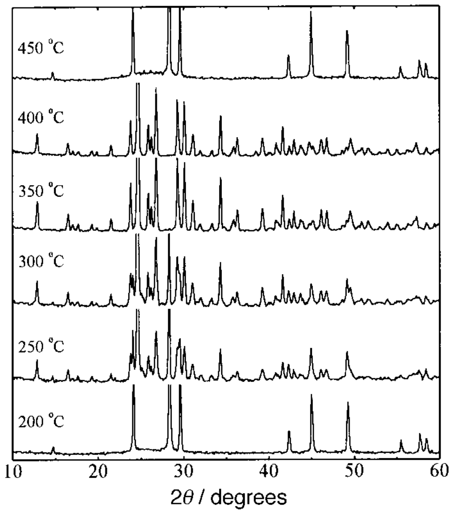

Fig. 3 Thermal behavior of $CsVTeO_5$ at different temperatures in Ar atmosphere

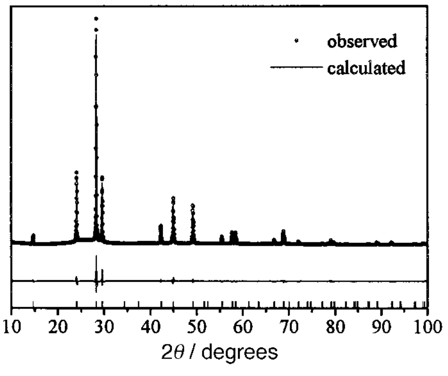

Fig. 4 Profile matching of the X-ray powder diffraction pattern of $CsVTeO_5$

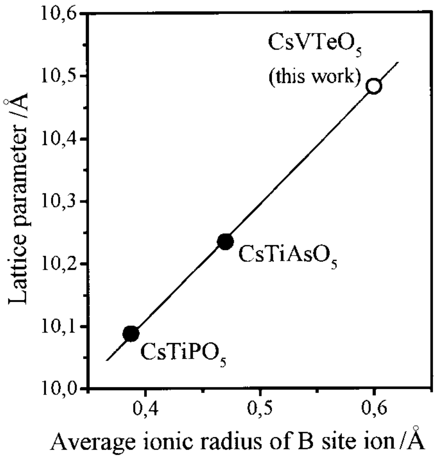

Fig. 5 Lattice parameter *vs.* average ionic radius of B site ion

$CsVTeO_6$

Fig. 6 shows the variation of the X-ray patterns with temperature of a equimolar mixture of $CsVO_3$ and $Te(OH)_6$ heated

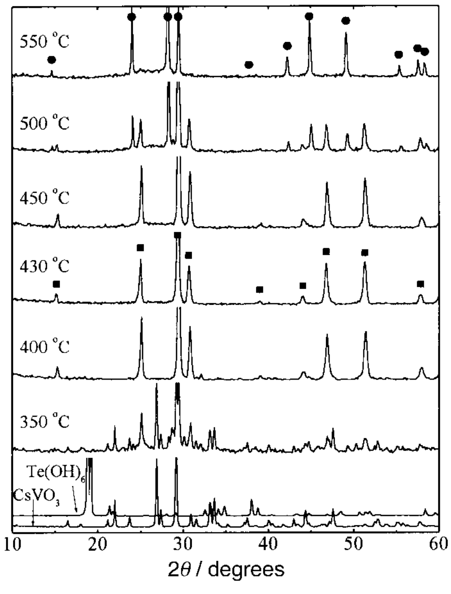

Fig. 6 XRD spectra of $CsVO_3+Te(OH)_6$ at different temperatures in O_2 atmosphere (■: $CsVTeO_6$, ●: $CsVTeO_5$)

Table 1 Atomic coordinates for $CsVTeO_6$

atom	site	x	y	z	$B_{iso}/Å^2$
Cs	8b	3/8	3/8	3/8	0.87(4)
V,Te	16c	0	0	0	0.01(4)
O	48f	0.3162(5)	1/8	1/8	0.12(19)

under an oxygen atmosphere. The cubic phase $CsVTeO_6$ is formed at around 400 °C and is stable up to 450 °C (Fig. 6). At higher temperature $CsVTeO_6$ loses one oxygen giving rise to the $CsVTeO_5$ cubic phase. The transformation is complete at 550 °C. Analysis of the X-ray powder diffraction data indicates that $CsVTeO_6$ is isostructural with AB_2O_6 cubic pyrochlore. The lattice parameter refined from the X-ray powder pattern is $a = 10.077(1)$ Å. The variations of the a parameter of the $ABTeO_6$ series[11] with the ionic radius of the A^+ cations (A = K, Rb, Cs) and the average ionic radius of the (BB′) ions[10] are given in Fig. 1(a) and (b). The value obtained for $CsVTeO_6$ agrees very well with the lines [Fig. 1(a), (b)].

The structural refinement of $CsVTeO_6$ was carried out in the space group $Fd\bar{3}m$ (no. 227) with the origin at the centre ($\bar{3}m$). The caesium atom occupies the 8b position (3/8,3/8,3/8), the (V,Te) atoms are located in the 16c position (0,0,0) and the oxygen atom occupies the 48f position [$x = 0.3162(5)$,1/8,1/8]. The refined atomic positions and isotropic displacement factors are listed in Table 1. The final R values are $R_I = 4.29\%$, $R_P = 9.82\%$ and $R_{wP} = 13.5\%$. The observed, calculated and difference X-ray diffraction profiles are shown in Fig. 7. The values of the main bond lengths are: Cs—O = 3.112(2) Å and 3.612(3) Å, (V,Te)—O = 1.902(3) Å. These are comparable to the sums of ionic radii of Shannon.[10]

Discussion

It has been shown above that the cubic phase prepared by quenching under argon at 450 °C or under oxygen at 550 °C corresponds in fact to the compound $CsVTeO_5$. The true $CsVTeO_6$ phase can be only prepared under an oxygen atmosphere and at a temperature lower than 450 °C. At higher temperature, there is a loss of oxygen and the compound $CsVTeO_5$ is stabilized as a decomposition product of $CsVTeO_6$. The observed weight loss of 3.8% is in good agreement with the theoretical value (3.9%) coresponding to the loss of one oxygen atom. Experimentally, the a-lattice parameter increases from 10.077(1) Å for $CsVTeO_6$ to 10.482(2) Å for $CsVTeO_5$. This change agrees very well with the variation of the ionic radii of Te^{4+} (0.97 Å) and Te^{6+} (0.56 Å).[10]

$CsVTeO_6$ is isostructural with the mineral pyrochlore. Alternative descriptions of the structure have been reviewed elsewhere.[12,13] One of these descriptions considers the structure as consisting of octahedral layers equivalent to those in hexagonal tungsten bronze (HTB) [Fig. 8(a)] and isolated octahedra placed on the top of the centers of the characteristic HTB-type triangles [Fig. 8(b)]. These layers are stacked perpendicular to the [111] direction of the cubic unit cell which corresponds to the [001] direction of the hexagonal unit cell of HTB. Each two equivalent (HTB-type or isolated octahedra) layers are shifted by (1/3) $[120]_{hex}$ relative to each other.

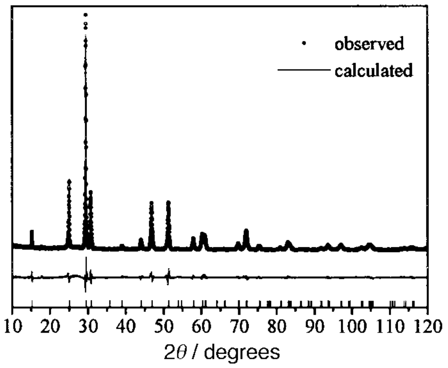

Fig. 7 Observed, calculated and difference X-ray powder diffraction patterns of $CsVTeO_6$

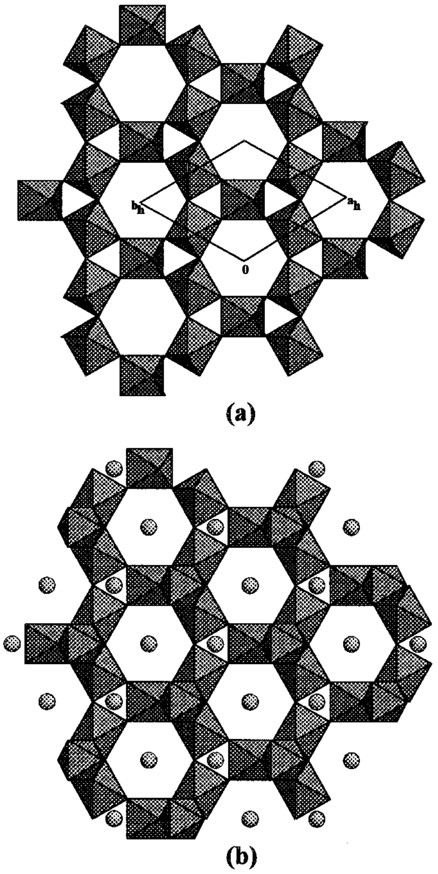

Fig. 8 (a) Representation of a HTB-type layer perpendicular to $(001)_{hex}$ and (b) layer of isolated octahedra on top of HTP layer

A tentative structural arrangement for $CsTiXO_5$ phases has been proposed from a combination of X-ray and neutron data.[8] The structure consists of randomly disordered TiO_6 octahedra and XO_4 (X = P, As) tetrahedra with the caesium atoms occupying large cavities within the framework. The caesium and titanium atoms are in the same positions as in the AB_2O_6 pyrochlore-type structure. The X atoms are shifted off from the center of the octahedra in a 96h position ($-x$, x, 0) with $x \approx 0.04$ (for $CsTiAsO_5$). The consequence of this displacement is that the oxygen atoms occupy split sites near the 48f position of the pyrochlore-type structure. This disordered structure can be directly related to that of the orthorhombic KTP-type structure.[8] A preliminary refinement of the $CsVTeO_5$ structure with oxygen at the 48f position, caesium atom in the 8b position and the vanadium and the tellurium atoms occupying the 16c position converges to $R_I = 4.5\%$ with an unacceptably high thermal parameter (B value) for the oxygen. A refinement based on a split position for the metal atoms with the vanadium in the 16c position (1/2 occupied) and the tellurium in the 96h position (1/12 occupied) gives a significant improvement in R_I (3.9%). Although single crystal refinements are necessary to substantiate the above results, the powder refinement seems to indicate that the tellurium atoms are located in the 'tetrahedral' site. In addition, it is possible that the tellurium atoms, with a chemically active lone pair of electrons [Te^{4+}: ($5s^2$)], should be off-center in the tetrahedra as expected for the 96h position.

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