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Ferroelectric transition and melting temperatures of new compounds: $CsTiOAsO_4$ and $Cs_xM_{1-x}TiOAs_yP_{1-y}O_4$ with $M \equiv K$ or Rb

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Abstract. We have synthesised, by the flux-growth method, millimetric crystals of new compounds isotype of $KTiOPO_4$ which also have non-linear optical properties: cesium titanyl arsenate $CsTiOAsO_4$ and the complete or incomplete solid solutions of general formula $Cs_xM_{1-x}TiOAs_yP_{1-y}O_4$ with $M \equiv K$ or Rb. The second harmonic generation test (SHG: 1.064 μm/0.532 μm) is positive for all these compounds. The ferroelectric transition temperatures are determined by measuring the temperatures at which the SHG disappears. The melting points of the compounds are also determined.

1. Introduction

We have synthesised new crystals for non-linear optics by the flux-growth method developed in our laboratory for $KTiOPO_4$ and isotypes [1, 2]. These compounds are the cesium titanyl arsenate $CsTiOAsO_4$ and the solid solutions having the general formula $Cs_xM_{1-x}TiOAs_yP_{1-y}O_4$ with $M \equiv K$ or Rb, $x = [Cs]/([Cs] + [M])$ and $y = [As]/([As] + [P])$, where [ ] represents the molar concentration of each element. The chemical compositions of the crystals are established by electronic microprobe analysis and are summarised in table 1. Thus, the substitution of the different alkali metals can probably be achieved in all proportions for the arsenate solid solutions but not necessarily for the phosphates in the chemical growth system previously used. Attempts to grow

Table 1. Chemical composition of the different crystals of solid solutions (§ 1).

Family	Alkali metal substitution: $x = [Cs]/([Cs] + [M])$ with $M \equiv K$ or Rb					
$Cs_xK_{1-x}TiOAsO_4$	0		0.15	0.31	0.62		1
$Cs_xRb_{1-x}TiOAsO_4$	0			0.33		0.91	1
$Cs_xK_{1-x}TiOPO_4$	0		0.10				
$Cs_xRb_{1-x}TiOPO_4$	0	0.05	0.10				
	Arsenic–phosphorus substitution: $y = [As]/([As] + [P])$						
$CsTiOAs_yP_{1-y}O_4$						0.88	1

$CsTiOPO_4$ were unsuccessful. From these experiments, transparent crystals measuring from about a hundred microns to a few millimetres have been synthesised.

The different limiting solid solutions which contain no cesium (corresponding to $x =$ 0) are already known [3–6] and are isotypes of KTP [7], a material known to be efficient in nonlinear optics.

We have measured the melting point and the ferroelectric transition temperature of these compounds, the latter by measuring the temperature where the SHG disappears.

2. Determination of the ferroelectric transition temperature

X-ray diffractometric investigations in our laboratory show that $CsTiOAsO_4$ belongs to the acentric point group mm2 with the space group $Pna2_1$ at room temperature [10]. Likewise $KTiOPO_4$ [11], its isotypes ($RbTiOPO_4$, $TlTiOPO_4$ [3], NH_4TiOPO_4 [4], $KTiOAsO_4$, $RbTiOAsO_4$, $TlTiOAsO_4$ [4, 6] and the solid solutions $K_xRb_{1-x}TiOPO_4$ [5, 8] and $KTiOP_yAs_{1-y}O_4$ [5] with $0 \leq x, y \leq 1$) belong to this point group.

According to Voronkova and co-workers [12] K-, Rb- and Tl $TiOPO_4$ have a second-order ferroelectric phase transition with a change of symmetry $Pna2_1$–$Pnam$. These authors studied the variation of relative dielectric permeability and SHG intensity on powder with temperature. They showed that the SHG intensity vanishes with the change of symmetry $Pna2_1$ (acentric)–$Pnam$ (centric); they also showed that the results of the two methods for the measurement of transition temperatures were similar.

The experimental method consists in grinding the samples to a grain size of about 50 μm. The fundamental wave (1.064 μm) emitted by a monomode, Q-switched YAG:Nd laser is focused on the warmed powder. The method consists of measuring the temperatures above which the frequency will no longer be doubled by the grains.

The SHG vanishing temperatures of the different compounds are given in figures 1 and 2. We observed a decrease in the number of grains in phase-matching positions with increasing temperature. This can be explained by a shrinking of the cone of phase-matching directions, caused by a progressive increase in the gap between the fundamental and harmonic index surfaces with increasing temperature. Indeed the refractive indices at the fundamental and harmonic frequencies can show dissimilar variation near the ferroelectric transition, particularly in this case because of the sharp anomaly of the dielectric permeability ε_{33} which is typical of second-order ferroelectric phase transitions [12]. Thus the SHG vanishing temperature is a lower bound of the ferroelectric transition temperature. It is possible that the index surfaces at the fundamental and harmonic frequencies are completely separate, which would not allow any direction for phase-matched SHG, the crystal still being in the acentric phase. This hypothetical situation is described by the index surfaces in figure 3 where $n_x(2\omega) > n_y(\omega)$ and $n_y(2\omega) > n_z(\omega)$. Thus there no longer exists any direction for which $n(\omega) = n(2\omega)$ (type I) and $n_1(\omega) + n_2(\omega) = 2n_3(2\omega)$ (type II) where $n(\omega)$, $n_1(\omega)$ and $n_2(\omega)$ are the refractive indices of the fundamental frequency and $n(2\omega)$ and $n_3(2\omega)$ those of the harmonic frequency. For example for $KTiOPO_4$ at room temperature, the shortest fundamental wavelength for type II SHG is 0.993 μm [13].

However, in [12] it was shown that the dielectric permittivity diverges and the SHG vanishes at the same temperature for K-, Rb- and Tl$TiOPO_4$. Therefore for these compounds, the refractive indices of the fundamental and harmonic frequencies have similar temperature behaviours even near to the ferroelectric transition.
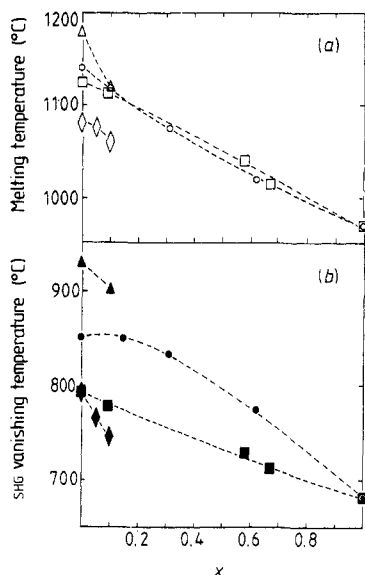
Figure 1. (a) Melting, and (b) SHG vanishing temperatures of alkali metal (M) solid solutions versus caesium concentration $x = [Cs]/([Cs] + [M])$. $\bigcirc$ $\bullet$, $Cs_xK_{1-x}TiOAsO_4$; $\square$ $\blacksquare$, $Cs_xRb_{1-x}TiOAsO_4$; $\triangle$ $\blacktriangle$, $Cs_xK_{1-x}TiOPO_4$; $\diamondsuit$ $\blacklozenge$, $Cs_xRb_{1-x}TiOPO_4$.
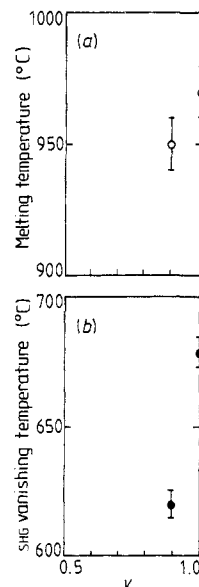

Figure 2. (a) Melting, and (b) SHG vanishing temperatures of arsenic–phosphorus substitution solid solutions $CsTiOAs_yP_{1-y}O_4$.
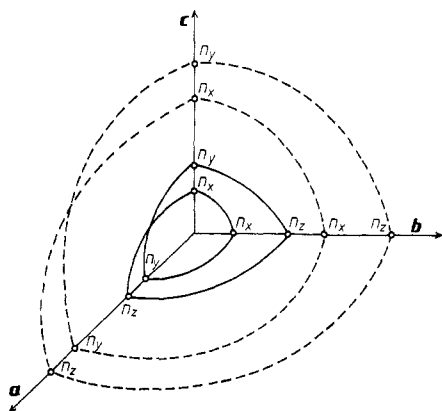

Figure 3. Hypothetical situation of fundamental (ω) (full curves) and harmonic (2ω) (broken curves) wave index surfaces of a biaxial crystal in which no phase matching direction for type I or type II SHG exists. a, b and c refer to the axes of the crystallographic frame.

The temperatures measured for K- and $RbTiOPO_4$, respectively $932 \pm 5\,°C$ and $795 \pm 5\,°C$, are very close to those given in [12], these being respectively $934 \pm 2\,°C$ and $790 \pm 2\,°C$. The temperatures for compounds of the four alkali metal substitution families decrease with the rise in caesium concentration based on those of alkali metals. Its evolution with the alkali metal concentration for the $Cs_xK_{1-x}TiOAsO_4$ family is non-linear, whereas it seems linear for $Cs_xRb_{1-x}TiOAsO_4$. It can be connected with the non-statistical distribution of the alkali metal atoms on the two crystallographic sites as shown for the family $K_xRb_{1-x}TiOPO_4$ [14]. The decrease of their ferroelectric transition temperatures is not linear from $KTiOPO_4$ to $RbTiOPO_4$ [15]. The current crystallo-

graphical studies will allow us to interpret the differences between the solid solutions $Cs_xK_{1-x}TiOAsO_4$ and $Cs_xRb_{1-x}TiOAsO_4$. It is difficult to discuss the phosphates $Cs_xK_{1-x}TiOPO_4$ and $Cs_xRb_{1-x}TiOPO_4$, because the range of x for solubility is restricted and its limits have yet to be established with certainty. The same applies to the arsenic–phosphorus substitution for which the ferroelectric transition temperature decreases from $CsTiOAsO_4$ to $CsTiOAs_{0.9}P_{0.1}O_4$. These results contrast with those obtained for the complete solid solutions $KTiOP_yAs_{1-y}O_4$ for which the ferroelectric transition temperature decreases from $KTiOPO_4$ to $KTiOAsO_4$ [15]. Furthermore substitution of arsenic by phosphorus with only $x = 0.1$ results in a drop in the ferroelectric transition temperature of 60 °C: this indicates that phosphorus and arsenic cannot be substituted in all proportions. The current synthesis experiments do not allow us to disprove this hypothesis.

3. Measurement of melting point

These measurements were carried out with millimetric crystals placed in a melting bench in alumina crucibles and silicium carbide heating resistance and were observed with a binocular magnifying glass. The melting temperatures are given in figures 1 and 2.

The melting point of $KTiOPO_4$ was found to be (1180 ± 10 °C); it is slightly greater than that found by Masse and co-workers [3] (1167 °C) and Jacco and co-workers [16] (1172 °C). These authors proceeded by DTA.

We observed that all the compounds become opaque approximately a hundred and fifty degrees below melting point. This opacity is probably due to a chemical decomposition which indicates that the melting is not congruent as for KTP [16]. We thus estimate the melting point to within around ±10 °C. despite an accuracy of about 1 °C. The melting point decreases with the rising caesium composition compared with potassium or rubidium for the alkali metal substitution families; the melting point also drops by arsenic–phosphorus substitution from $CsTiOAsO_4$ to $CsTiOAs_{0.9}P_{0.1}O_4$. The evolution of melting points is not proportional to the rate of substitution for the solid solutions $Cs_xK_{1-x}TiOAsO_4$, $Cs_xRb_{1-x}TiOAsO_4$ and $Cs_xRb_{1-x}TiOPO_4$.

4. Conclusions

The plots of melting and ferroelectric transition temperatures versus the chemical composition of the solid solution families studied show a similar form. The temperatures drop with rising caesium concentration compared with those of potassium or rubidium for the four alkali metal substitution families and fall from $CsTiOAsO_4$ to $CsTiOAs_{0.9}P_{0.1}O_4$. The evolution of melting and ferroelectric transition temperatures are not proportional to the atomic fraction of substitution for a few families of solid solutions; this can be interpreted by crystallographical studies now in progress, in particular on the non-statistical distribution of alkali metal atoms on the two sites.

The four compounds without caesium behave differently, depending on the alkali metal considered: the melting and ferroelectric transition temperatures of $KTiOPO_4$ are greater than those of $KTiOAsO_4$; on the other hand the ferroelectric transition temperatures of $RbTiOPO_4$ and $RbTiOAsO_4$ are equal while the melting point of $RbTiOPO_4$ is greater than that of $RbTiOAsO_4$.

The current optical studies will allow us to place $CsTiOAsO_4$ and the associated solid solutions among the other compounds used in non-linear optics, in particular $KTiOPO_4$ and BBO [17–19].

Acknowledgment

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