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The role of cerium in potassium titanyl phosphate ($KTiOPO_4$)

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Abstract

The role of cerium in potassium titanyl phosphate ($KTiOPO_4$), where it increases its optical transmission in the visible region, is explained. A comparison with the afterglow-reducing role of cerium in phosphors for computed tomography is made.

1. Introduction

Potassium titanyl phosphate ($KTiOPO_4$) is a non-linear optical material of great interest [1] and shows a very unusual titanate luminescence [2]. This compound has a weak optical absorption in the visible spectral region [3] which is undesirable for its application as a non-linear optical material. Oxygen annealing seems to be a possible way to reduce this absorption [4]. Recently, the addition of cerium was reported to reduce this absorption considerably [3], but an explanation of the effect was not proposed.

It is the purpose of this note to present an explanation of the optical absorption of $KTiOPO_4$ in the visible region and to propose a mechanism for the role that cerium plays in its reduction. It will be shown that the role of cerium in $KTiOPO_4$ is strongly analogous to its role in some computed tomography phosphors [5] where it is used to reduce the afterglow of the luminescence [6].

2. Experimental results

Figure 1 shows the transmission spectra of flux-grown $KTiOPO_4$ crystals with and without cerium addition to the flux. This figure has been derived from data in ref. 3. The cerium content of the crystals was determined to be 5 ppm by weight [3].

3. Discussion

In contrast to the authors of ref. 3, we believe that a straightforward interpretation of the data is obvious. In the first place it is possible to assign the absorption bands in the spectrum. The strong optical absorption for $\lambda < 400$ nm is due to charge transfer transitions in the titanate groups [2]. The bands in the visible region cannot be due to $KTiOPO_4$ itself. Obviously they must be ascribed to defects. Since several authors have observed this absorption [3], it is unlikely that it is due to impurities, so that defects related to the composition of the compound remain as the most obvious explanation.

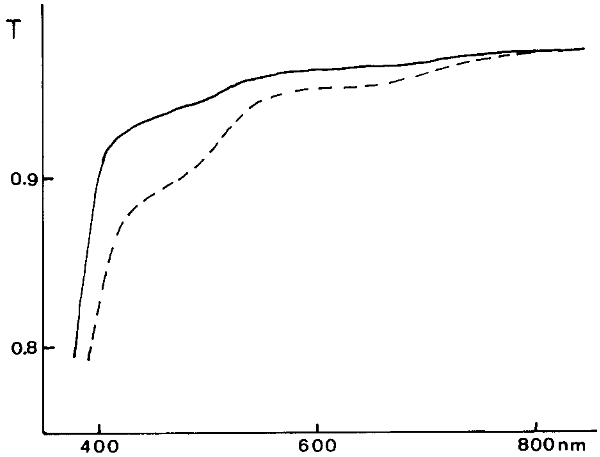

Fig. 1. Transmission spectra of flux-grown $KTiOPO_4$ with (full curve) and without (broken curve) cerium in the flux. After data in ref. 3. *T* is the transmission in reciprocal centimetres.

A comparison with the literature shows that the presence of Ti^{3+} explains the visible part of the absorption spectrum. The absorption band in the 400–500 nm region can be ascribed to the $^2T_2 \rightarrow {}^2E$ transition on the Ti^{3+} ion [7]. In Al_2O_3:Ti^{3+} this transition occurs with a maximum at 500 nm [7] and in $YAlO_3$:Ti^{3+} with maxima at 434 and 492 nm [8]. The broad absorption band at $\lambda < 800$ nm can be assigned to Ti^{3+}–Ti^{4+} intervalence charge transfer. This has been reviewed

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by us elsewhere [9]. It is a matter of taste whether one calls this an intervalence charge transfer or a donor-to-conduction-band transition [10].

The presence of Ti^{3+} has to be ascribed to a small oxygen deficiency of the $KTiOPO_4$ crystals according to

$$2Ti_{Ti}^{x}+O_{O}^{x} \rightleftharpoons 2Ti_{Ti}'+V_{O}^{\cdot\cdot}+\tfrac{1}{2}O_2(g) \qquad (1)$$

where the Kröger–Vink notation has been used [11]. In this way it can be understood why annealing in oxygen increases the optical transmission in the visible region.

A discussion of the role of cerium in $KTiOPO_4$ requires knowledge about its valency in this host lattice. According to ref. 3, the cerium-doped crystals were grown in air. This points to the presence of Ce^{4+}. Since Ce^{3+} as well as Ce^{4+} [12] is expected to absorb in the UV spectral region, the present transmission spectra do not contain information on the cerium valency, since this spectral range is covered by the strong titanate absorption. In view of the size of the Ce^{4+} ion ($r > 1$ Å, [13]), we assume it to be mainly present at the K^+ sites.

The presence of Ce^{4+} on K^+ sites ($Ce_K^{\cdot\cdot\cdot}$) requires charge compensation by potassium vacancies:

$$CeO_2 \longrightarrow Ce_K^{\cdot\cdot\cdot}+2O_O^{x}+3V_K' \qquad (2)$$

Equation (1) implies that the electrons which become available upon oxygen loss are trapped by the Ti^{4+} ions, converting them into Ti^{3+}. No doubt the Ce^{4+} ion is a very suitable electron trap, so that the titanium traps will be emptied in favour of the cerium traps. This can be presented as

$$2Ce_K^{\cdot\cdot\cdot}+O_O^{x} \longrightarrow 2Ce_K^{\cdot\cdot}+V_O^{\cdot\cdot}+\tfrac{1}{2}O_2(g) \qquad (3)$$

In this way the Ti^{3+} absorption decreases whereas the cerium absorption is covered by the host lattice.

This role of cerium shows an analogy to its role in some X-ray computed tomography phosphors [6]. In this type of luminescent material it is imperative that the afterglow of the X-ray-excited luminescence is suppressed [5]. One of the solutions proposed is the addition of cerium. For example, the afterglow of $Gd_3Ga_5O_{12}$:Cr^{3+} is suppressed by the presence of Ce^{4+}. The afterglow has been ascribed to electron trapping by oxygen vacancies and the suppression of the afterglow has been ascribed to the strong electron-trapping character of Ce^{4+}. A similar phenomenon occurs in Gd_2O_2S:Pr^{3+}, where the presence of cerium also reduces the afterglow. Here also Ce^{4+} is assumed to act as an efficient electron trap. Small amounts of cerium can therefore have an important influence on material properties.

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