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Improved scintillation luminescence and thermal stability of $In_2Si_2O_7$ ceramic phosphor

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ABSTRACT

$In_2Si_2O_7$ is a known indium-based scintillator with fast ultraviolet photoluminescence. Unfortunately the emission only can be detected below 200 K. the poor thermal stability limits its application at room temperature. In this work, the luminescence improvement of $In_2Si_2O_7$ was realized by F^--ions doping in the lattices. The ceramic phosphors were via typical solid-state reaction method. The pure crystalline phase with thortveirite-type structure was confirmed by X-ray diffraction (XRD) Rietveld refinements. The photoluminescence (PL) emission and excitation spectra together with the luminescence thermal stability were tested. The fluorescence decay curves CIE emission Stokes shifts were measured. The ceramic samples could present blue luminescence with maximum wavelength at about 340 nm under the excitation of UV light or high energy X-ray irradiation. The pure sample only presents luminescence below 200 K, however, the F-doping can be greatly enhance the luminescence thermal stability. The F-doped $In_2Si_2O_7$ could present emission signals with fast decay lifetime of 850 ns at room temperature. The luminescence transitions from the In^{3+}-O^{2-} charge transfer (CT) were discussed on the structure properties.

1. Introduction

The preparation, structure and luminescence properties of inorganic scintillators have been investigated for a long time in pure or rare earth ions doped oxides [1–7]. For example, it has been confirmed that indium oxides with a large amount of ^{115}In could be used as scintillators to detect low energy solar neutrinos according to Raghavan's nuclear reaction [8,9]. The luminescence of Indium oxides is related to the electronic transition in In^{3+} ions with $4d^{10}$ configuration [10,11]. The indium-rich oxides $In_2X_2O_7$ (X=C, Si, Ge, Sn) have been widely reported due to the high scintillation output [12]. Among these scintillation materials, $In_2Si_2O_7$ has been confirmed to be one of the best candidates as radiation detectors because of its advantages of high light output, low afterglow, and fast scintillation decay lifetime and good attenuation power [8].

$In_2Si_2O_7$ has a thortveirite-type crystal structure with monoclinic space group C2/m. The framework is built up of InO_6 octahedra and pyrosilicate group Si_2O_7 sheets. There are InO_6 chains alternating parallel to Si_2O_7 sheets [8]. $In_2Si_2O_7$ presents UV emission with the maximum wavelength at 355 nm because of its high energy level of the emitting states. The scintillation was detected using α-particles (6.09 MeV and 8.785 MeV) from 300 to 4 K [12]. Gaewdang et al. have reported that the decay curve of the emission in $In_2Si_2O_7$ consists of a non-exponential initial component and an exponential part characterized by a decay constant *of* 6 μs at 4.4 K [8]. At low temperature $In_2Si_2O_7$ could present efficient scintillation comparable to $Bi_4Ge_3O_{12}$ (BGO) [9], a well-known scintillation material. Unfortunately the luminescence of $In_2Si_2O_7$ suffers a huge thermal quenching, which completely quench above 200 K [8]. This means it is not promising for any practical application at room temperature.

The present work is devoted to improve the luminescence and enhance the thermal stability of $In_2Si_2O_7$. The dominated strategy is to dope F^- ions in the $In_2Si_2O_7$ lattices by solid-state reaction ceramic preparation. Pure and F-doped $In_2Si_2O_7$ ceramics were prepared by traditional solid-state reaction synthesis. The PL and XEL spectra, luminescence decay curves etc were tested. The luminescence improvement from the In^{3+}-O^{2-} transitions was

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realized and the luminescence enhancement was discussed on the structure properties.

2. Experimental

$In_2Si_2O_7$ ceramics were synthesized through the solid-state reaction. The raw reactants are In_2O_3 (99.99%), SiO_2 (99.9%), and LiF (99.9%). At first, the stoichiometric raw chemicals of In_2O_3 and SiO_2 were carefully ground, and then heated at 850 °C for 4 h using an electric furnace in air atmosphere. Secondly, the mixtures were thoroughly ground and then heated in a crucible at 1400 °C for 8 h to obtain the $In_2Si_2O_7$ precursor powders. The XRD patterns were used to confirm $In_2Si_2O_7$ pure crystal phase. To prepare the F-doped $In_2Si_2O_7$ ceramics, the precursor powders were thoroughly mixed with 5.0 mol % LiF, and then the powders were pressed in pellets under an iso-static pressure of 50 kPa. 8 wt% polyvinylalcohol (PVA) solutions were prepared by dissolving PVA in the water at 80 °C under strong stirring. The powder-to-binder ratio was 95/5 (w/w). Then the pellets were sintered at 1100 °C for 5 h to produce dense ceramics with the relative density of 94.5%. Finally the ceramic pellets with (diameter 15 mm) were prepared.

The X-ray diffraction (XRD) measurement was competed on Rigaku D/Max diffractometer (40 kV, 30 mA) quipped with Cu Kα radiation of $\lambda = 1.5405$ Å. The photoluminescence (PL) emission and excitation spectra were recorded by a spectrometer (Perkin-Elmer LS-50B) equipped with Monk-Gillieson type monochromators. The emission decay curves were measured under 266 nm from the forth harmonics of YAG:Nd pulsed laser. The data was recorded by the digital storage oscilloscope (500 MHz, Tektronics TDS754A) at 10 to 300 K. To detect the scintillation properties, the X-ray excited luminescence (XEL) spectra were tested by the homemade X-ray excited spectrometer (Fluormain) [13–15]. A movableF-30 X-ray tube (W anticathode target) was used as the X-ray source which operated under the condition of (80 kV, 4 mA) at RT. The luminescence spectra were obtained by 44 W plate grating monochromator and Hamamatsu R928-28 photomutiplier.

3. Results

3.1. Phase formation

$In_2Si_2O_7$ is closely related to thortveirite-type with the nonnoclinic space group of C2/m and Z=2 [8]. O^{2-} and F^- ions have the same electronic configuration with the close size (1.44 and 1.36 for O^{2-} and F^-, respectively). So it is reasonable that the F^- ions would occupy the O lattice position when F^- ions were doped in $In_2Si_2O_7$ lattices. However, the substitution of the O^{2-} sites by the F^- ions inevitably results in a positive charge $(F_O^-)^\bullet$. Generally, the charge balance could probably be achieved by the possible mechanisms. Firstly, the created defects combine with the In vacancies forming the complexes of $[3(F_O^-)^\bullet\text{ -}V_{Sr}'']$. Such a mechanism is popular in the compounds with heterovalent substitutions such as Eu^{3+}-doped apatite $Ca_5(PO_4)_3F$ [16]. Secondly, the positive charge could be compensated by interstitial oxygen O_i'' ions in the possible of $[2(F_O^-)^\bullet\text{ -}O_i'']$. This has been reported in some oxides with heterovalent substitutions such as Eu^{3+}-doped scheelite $PbWO_4$ [17]. Usually, in the oxide components, the reaction energy to create the O_i'' is higher than that of cation vacancy [18]. Certainly this is only a suggested mechanism with further experimental proof.

The F^- ions should exert influences on the structure and luminescence mechanism. To test that the structure has somewhat distortion from the thortveitite model, the structural Rietveld refinements of pure and F-doped $In_2Si_2O_7$ were performed by GSAS program. The thortveitite-structure was applied as an initial model for the refinement [19].

Fig. 1 presents the structural refinements for pure and F-doped $In_2Si_2O_7$ with the experimental, calculated, and different results. The final structural parameters for pure and F-doped $In_2Si_2O_7$ are shown in Table 1. Two samples have the pure phase formation without the remaining In_2O_3. No other impurity phases were detected, and all the XRD peaks were indexed to a single phase thortveirite with space group C2/m (12). The structural data suggest that the F^- ions could be doped in the lattices. As listed in Table 1 the cell volume for F-doped $In_2Si_2O_7$ is smaller than that of the pure sample. This is consistent with the smaller size of F^- than O^{2-} ions.

The refined atomic coordinates and occupancies in pure and F-doped structure are listed in Table 2. The structure of $In_2Si_2O_7$ (Fig. 2a) is drawn by Diamond Crystal and Molecular Structure Visualization software according to the atomic coordinate's in the refinements. The monoclinic framework of $In_2Si_2O_7$ is constructed by InO_6 octahedra and isolated Si_2O_7 group sheets. InO_6 octahedra form alternating parallel sheets [8]. The Si atom from the opposite side is in a reverse situation. Two SiO_4 tetrahedral connect by sharing with one corner forming an isolated Si_2O_7 group. The edge-shared InO_6 octahedral are in a hexagonal arrangement in ab-planes and the isolated Si_2O_7 groups consist of the corner-shared SiO_4 tetrahedral with a linear Si-O-Si bridge [8].

In a unit cell, the In^{3+} ions coordinated to six oxygens. The

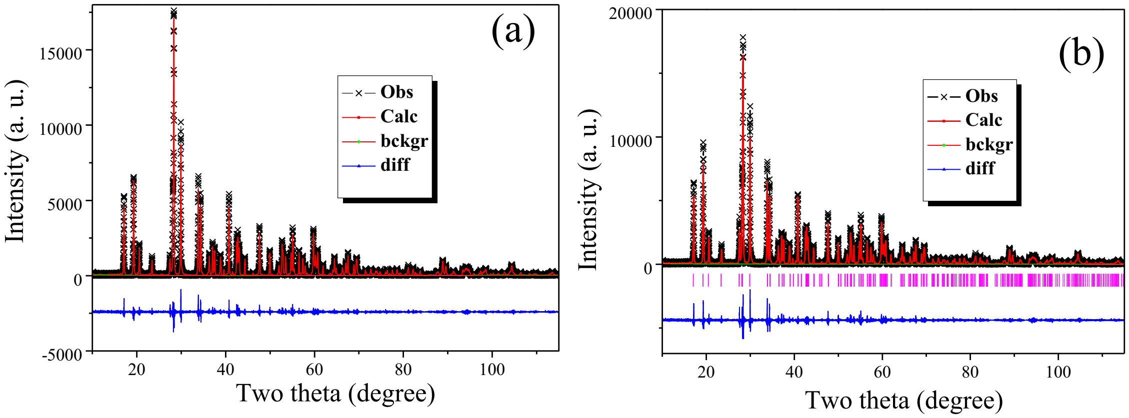

Fig. 1. the experimental (crossed) and calculated (red solid) XRDpattern of pure (a) and F-doped (b) $In_2Si_2O_7$ ceramics. The bottom of the figures displays the profile difference. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)