

## BRIEF COMMUNICATIONS

### Luminescence Properties of $\text{KMnCl}_3:\text{Eu}^{3+}$

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The luminescence properties of  $\text{Eu}^{3+}$ -doped  $\alpha$ - and  $\beta$ - $\text{KMnCl}_3$  crystals were investigated. It was found that the luminescence spectra at low temperature are dependent on cooling rate. © 1989 Academic Press, Inc.

#### Introduction

$\text{KMnCl}_3$  is known to crystallize in the orthorhombic perovskite structure ( $\alpha$ -phase) (1). The space group is  $P_{nma}$  and  $Z = 4$ . The unit cell parameters are  $a = 7.08$ ,  $b = 9.97$ ,  $c = 6.98$  Å. The X-ray diffraction data reported by Horowitz *et al.* (1) have shown that this perovskite structure is not stable but transforms into another orthorhombic, nonperovskite  $\text{KCdCl}_3$ -type structure ( $\beta$ -phase) with the space group  $P_{nma}$  and  $Z = 4$ . The unit cell parameters of that structure are  $a = 8.769$ ,  $b = 3.883$ ,  $c = 14.42$  Å.

In this paper we report the luminescence properties of  $\text{Eu}^{3+}$ -doped  $\alpha$ - and  $\beta$ -phase  $\text{KMnCl}_3$  crystals. We found that the luminescence spectra of  $\beta$ -phase were dependent on the cooling rate of the crystal.

#### Experimental

$\text{Eu}^{3+}$ -doped  $\alpha$ - $\text{KMnCl}_3$  were prepared by melting a stoichiometric mixture of KCl

(Johnson Matthey Chemicals Limited, Spectrapure),  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (POCH, Gliwice, pure for anal.), and 1 mole% of anhydrous  $\text{EuCl}_3$  (Pierce, 99.5%) in a dried HCl and Ar stream. Before melting the mixture of substrates was heated in three stages at 110, 200, and 300°C. The temperature was raised to the next stage when no traces of water were observed at the reaction ampoule. The sample was crystallized by the Bridgman technique, and then checked by powder X-ray diffraction at room temperature before the luminescence measurements. The europium concentration 2.42 wt% was determined by atomic absorption. The crystal was stored in an evacuated ( $10^{-6}$  Pa) and sealed glass ampoule for 5 years. After this time the X-ray diffraction and luminescence study was repeated. The luminescence spectra were recorded with a grating monochromator GDM 1000 (C. Zeiss Jena) equipped with a cooled photomultiplier. An argon laser ILA 120 (C.

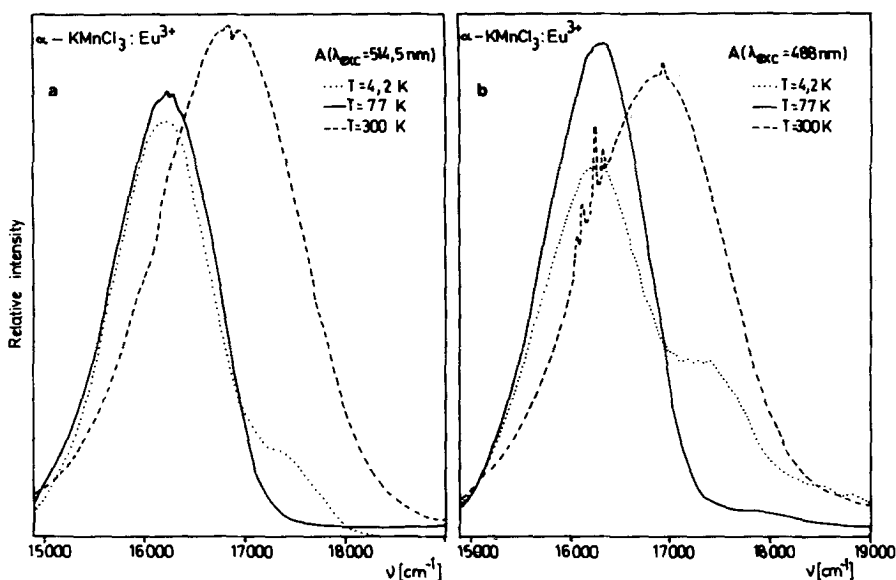


FIG. 1. Luminescence spectrum of  $\alpha\text{-KMnCl}_3:\text{Eu}^{3+}$ : (a) for  $\lambda_{\text{exc}} = 514 \text{ nm}$ , (b) for  $\lambda_{\text{exc}} = 488 \text{ nm}$ .

Zeiss Jena) was used as an excitation source.

## Results

The X-ray diffraction powder pattern of  $\text{Eu}^{3+}$ -doped  $\alpha\text{-KMnCl}_3$  after aging was identified as being the same as the data for the nonperovskite  $\text{KCdCl}_3$  structure ( $\beta\text{-KMnCl}_3$ ), also two weak reflexes corresponding to the  $\alpha\text{-KMnCl}_3$  structure were observed.

The luminescence spectra of  $\text{Eu}^{3+}$ -doped  $\alpha\text{-KMnCl}_3$  measured in a stationary cryostat (denoted by A) are presented in Figs 1a and 1b. The emission was observed from both  $\text{Mn}^{2+}$  and  $\text{Eu}^{3+}$  ions. The  $\text{Mn}^{2+} {}^4T_1 \rightarrow {}^6A_1$  luminescence at RT appears as broadband at  $\sim 16,900 \text{ cm}^{-1}$ . The luminescence spectrum at 4.2 K exhibits broadband with two well-resolved peaks at  $\sim 16,200$  and  $\sim 17,300 \text{ cm}^{-1}$ . The first is dominant. At LN temperature the  $17,300\text{-cm}^{-1}$  peak disappears. The single sharp lines at  $\sim 16,900 \text{ cm}^{-1}$  represent the  $\text{Eu}^{3+} {}^5D_0 \rightarrow {}^7F_1$  transition, and the group of lines to the higher wavelengths was assigned to  ${}^5D_0 \rightarrow {}^7F_2$  transition. It is important to note that at low

temperature no  $\text{Eu}^{3+}$  fluorescence was observed. Also no  $\text{Eu}^{3+}$  fluorescence was observed using an excitation wavelength of 514.5 nm. Instead of europium emission we observed the characteristic reabsorption of the  ${}^7F_1 \rightarrow {}^5D_0$  transition resulting from the Mn-Eu interaction.

The luminescence spectra of  $\text{Eu}^{3+}$ -doped  $\beta\text{-KMnCl}_3$  at 4.2 and 77 K are shown in Fig. 2. We found that the spectra exhibited the significant differences in dependence on the cooling rate on the sample. The samples were cooled in the stationary cryostat (denoted by A) or in the continuous-flow cryostat (denoted by B). The difference between these cryostats is in the different cooling rate of the sample to low temperatures.

The spectra at 4.2 K measured in a stationary cryostat (rapid cooling) shows a maximum of  $\text{Mn}^{2+}$  luminescence at around  $17,300 \text{ cm}^{-1}$ . This maximum is identical to the second weaker intensity luminescence band observed for the  $\alpha$ -phase at 4.2 K. The spectrum measured in the continuous-flow cryostat (slow cooling) exhibits the maximum at  $\sim 16,900 \text{ cm}^{-1}$ .

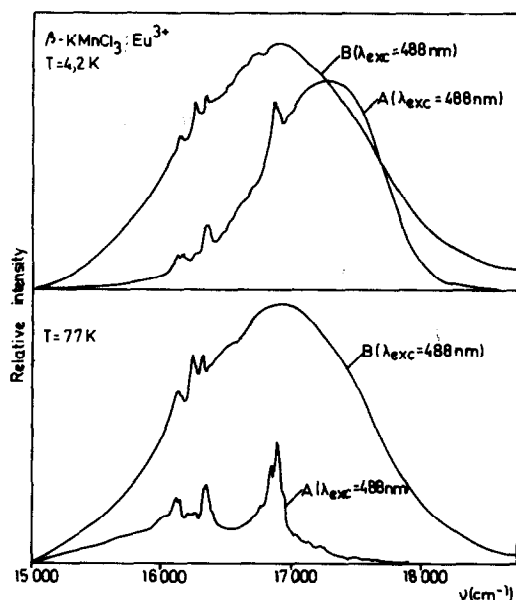


FIG. 2. Luminescence spectrum of  $\beta$ - $\text{KMnCl}_3:\text{Eu}^{3+}$ : (curve A) at stationary cryostat, (curve B) at continuous-flow cryostat.

With increasing temperature up to 77 K  $\text{Mn}^{2+}$  luminescence measured in the stationary cryostat was quenched. Only a very weak band at around  $16,200\text{ cm}^{-1}$  dominated by  $\text{Eu}^{3+}$  fluorescence lines was observed. The position of  $\text{Mn}^{2+}$  band was identical to that for  $\alpha$ -phase. The spectrum in the continuous-flow cryostat was similar to that measured at the same cooling rate.

The  $\text{Eu}^{3+}$  fluorescence of  $\text{Eu}^{3+}$ -doped  $\beta$ - $\text{KMnCl}_3$  was observed at 4.2 and 77 K at both cooling rates.  $\text{Eu}^{3+}$  exhibits several intense sharp multiples. The transitions from the  $^5D_0$  to the  $^7F_2$ ,  $^7F_1$ ,  $^7F_0$  states are observed around  $17,300$ ,  $16,900$ , and  $16,200\text{ cm}^{-1}$ , respectively. This fine structure in the europium emission is the result of both electronic splitting and vibronic effect and will not be investigated in the present study.

### Conclusions

In this paper we have presented the results of luminescence measurements of

$\text{Eu}^{3+}$ -doped  $\text{KMnCl}_3$  crystal, manifesting polytypism. We have found that the  $\text{Mn}^{2+}$  luminescence band centered around  $16,200\text{ cm}^{-1}$  is characteristic for orthorhombic perovskite  $\alpha$ -phase, whereas the band around  $17,300\text{ cm}^{-1}$  is characteristic for orthorhombic nonperovskite  $\beta$ -phase. The  $\text{Mn}^{2+}$  luminescence of the  $\beta$ -phase was rapidly temperature quenched and not observed at 77 K and above. The luminescence of  $\alpha$ -phase shifts from  $\sim 16,200\text{ cm}^{-1}$  at LH and LN temperatures to  $\sim 16,900\text{ cm}^{-1}$  at RT. The changes in position of emission band were observed in photo-excited crystals of halide salts of divalent manganese and can be rationalized in terms of exciton migration by a thermally activated hopping process (2-4).

The luminescence properties of  $\text{Eu}^{3+}$ -doped  $\beta$ - $\text{KMnCl}_3$  crystal were dependent on cooling rate at 4.2 and 77 K, namely the spectra of  $\text{Mn}^{2+}$  recorded in a stationary cryostat (rapid cooling) shifts to the blue at about  $400\text{ cm}^{-1}$  in comparison to the spectra measured in a continuous-flow cryostat (slow cooling). This phenomena was reversible at LN temperature. Additionally, the  $\text{Mn}^{2+}$  luminescence efficiency was very low in comparison to  $\text{Eu}^{3+}$  fluorescence intensity when the sample was slowly refrigerated. The mechanism of that phenomena is unknown at present and we are continuing the investigation of its nature.

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