The Luminescence Properties of Cr-doped Aluminates

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Background

In recent years, compounds doped with transition metal ions are more and more focused because of a wide range of application both in solid state lasers and non-linear optic devices. Particularly, Cr^{3+} is widely used as a dopant in solid state crystals. This cheap activator yields deep red to NIR radiation, bright luminescence and broad optical absorption bands. Materials doped with Cr^{3+} show a broad band luminescence at room temperature and their spectra are easy to interpret on the basis of the Tanabe-Sugano diagram. Aluminate materials are selected as host materials for the Cr-substitution because of the identical electrical charges of both ions. Hence, no charge compensation is required. Moreover, these ions have a similar ionic radius, viz. 67,5 pm for Al^{3+} and 75,5 pm for Cr^{3+}.

Optical Properties

Table 1. The Racah parameters (B, C), nephelauxetic ratio (β), crystal field splitting energy (10Dq) of Cr-doped aluminates.

Cr-phosphor	B [cm^{-1}]	C [cm^{-1}]	ß = B/B$_0$	C/C$_0$	β'	10 Dq [cm^{-1}]
$GdAl_3(BO_3)_4$	705	2792	0,71	0,768	1,045	16667
$YAl_3(BO_3)_4$	696	2828	0,70	0,778	1,046	16750
$BaMgAl_{10}O_{17}$	668	2858	0,67	0,786	1,034	17730
$LaMgAl_{11}O_{19}$	643	2922	0,65	0,803	1,031	17699
$SrAl_{12}O_{19}$	636	2979	0,64	0,820	1,039	17065
$Sr_4Al_{14}O_{25}$	623	2995	0,63	0,823	1,034	17825
$CaAl_2O_4$	611	3034	0,61	0,834	1,036	18050
$SrAl_2O_4$	601	3070	0,60	0,844	1,038	17857

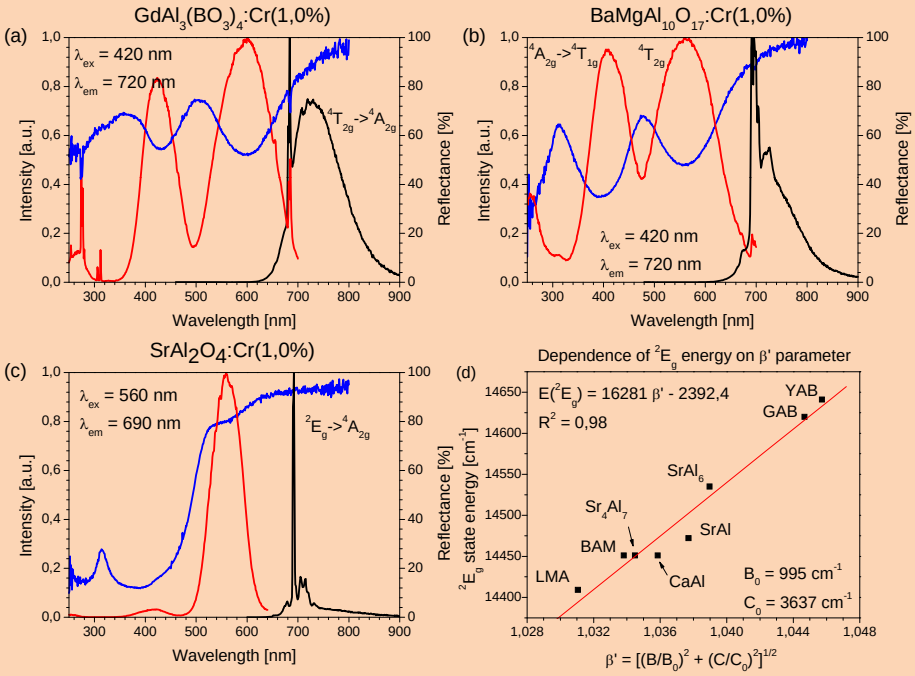

Fig.1. Reflection (blue line), excitation (red line) and emission spectra (black line) of selected Cr-doped aluminates: a) $GdAl_3(BO_3)_4$ (b) $BaMgAl_{10}O_{17}$ (c) $SrAl_2O_4$. Additionally, plot (d) reveals the dependence of ^2E_g energy on the β' parameter.

In order to investigate a possibility to use Cr^{3+} as a covalent sensor – eight types of aluminate host materials were synthesized by conventional solid state reaction (Table 1). Crystal structures were examined by X-ray diffraction patterns. Then, samples were characterized by measuring of the excitation, emission and reflection spectra. The spectroscopic parameters were derived on the basis of experimental data and by using some equations [1].

Among synthesized phosphors both a strong ($SrAl_2O_4$:Cr) and intermediate ($BaMgAl_{10}O_{17}$:Cr, $GdAl_3(BO_3)_4$) crystal field materials are presented (Fig.1). As can be observed in Table 1, the derived magnitudes of Crystal Field Strength, B Racah parameters and β-covalency varies with the nature of the host materials. The incorporation of Cr^{3+} into aluminates causes a decreasing of these parameters as a consequence of the *nephelauxetic effect*.

The role played by covalence effects in the considered systems can be analyzed from another point of view, by using the non-dimensional quantity β' investigated by M. Brik [2]. It turns out that the dependence of the energy of ^2E_g state on the new β' parameter exhibits linear correlation.
In the herein discussed Cr-phosphors a monotonic increase of ^2E_g transition energies with increasing β' can be observed. This is obviously related to the calculated Racah parameters.

Conclusions

Determination of Crystal Field Energy and Racah parameters allows to deduce the kind of emission band and to derive the covalent character of bonds of the activator ion in the respective crystalline environment. It turns out that B and C Racah parameters determine the position of the ^2E_g level. A high covalency causes a strong nephelauxetic effect and $^2E_g \rightarrow {}^4A_{2g}$ emission is red shifted. On the other hand a high ionicity causes a strong nephelauxetic effect and $^2E_g \rightarrow {}^4A_{2g}$ emission is blue shifted. Therefore, Cr^{3+} ion can serve as a good and stable probe, which helps to distinguish between covalent and ionic compounds.

References

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[2] G. Wang et al., *Novel laser gain media based on Cr^{3+} doped mixed borates $RX_3(BO_3)_4$*, Appl. Phys. Lett. 67(26), 1995, 3906-3908.

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