**Compositional Control of Divalent Cations Mobility**

**in Ca3(VO­4)2 -type Ferroelectric/Optical Nonlinear Materials**

**S.Yu. Stefanovich and B.I. Lazoryak**

Chemistry Department, Lomonosov Moscow State University

Leninskie Gory 1, Moscow, Russia

Sergey Stefanovich: *stefan@tech.chem.msu.ru*

Oxide ferroelectrics often contain single-valent cations such as lithium, sodium, or potassium responsible for ionic-conductive or ion-exchange properties at moderate temperatures. Along with adjustable domain structure these properties open additional technical possibilities for engineering of integrated optics devices. Divalent cation conductivity is still unknown to co-exist with ferroelectricity.

Vanadates Са9M(VO4)7 (М = REE, Y or Bi) structurally related to high-temperature ferroelectric Ca3(VO­4)2 [1] possess ferroelectric-ionic conductor phase transitions at 1000-1200 К [2]. They are shown to have high optical nonlinearities [3], and are also able to generate laser radiation when М = Nd, Tm, Er, Yb [4]. Their large-size Czochralski-grown crystals [5] are now widely investigated as promising nonlinear and laser materials. At around ferroelectric phase transitions the Са9M(VO4)7 demonstrate Са2+-ionic conductivity usually equal 10-2 - 10‑1 Ohm-1cm-1, which is comparable with К+-ionic conductivity near ferroelectric phase transitions in KTiOPO4.

Examined in this work structural and dielectric characteristics, differential thermal analysis, and second harmonic generation (SHG) evidence that Ca10.5-xPbx(VO4)7 solid solution (0 ≤ x ≤ 4.5) belongs to whitlockite-type ferroelectrics. SHG activity strongly increases with x up to its maximum at x = 4.5, where it has a record value among all studied before Ca3(XO4)2‑related compounds (X=P,V). Ferroelectric Curie temperatures of Ca3(VO4)2 drops from its known value Tc = 1368 K (x = 0) to 770 K (x = 4.5). Two-order increased Ca2+- ion conductivity of Са10.5-xPbx(VO4)7 in vicinity of 1000 K at x = 4‑4.5 in combination with their ferroelectric and optical nonlinear properties extends applicability of high-temperature ion-exchange technologies to new promising materials.

Influence of guest atoms on ferroelectric, optical nonlinear and ion-conductive properties of Ca3(VO­4)2 - derived vanadates are studied in details for a group of compositions Ca8-x-yMePbxBi2/3y(VO4)7, where Me = Mg, Zn, Cd. It is found, that lead substitution for calcium is as a major factor controlling ferroelectricity, ionic-conductivity and non-linear optical activity (NOA) in Ca3(VO4)2-based materials. Concentration of bismuth is on the second place in augmenting of NOA in the whitlockites. Atoms of other tested elements (Me = Mg, Zn, Cd) have little influence on NOA and ferroelectric properties. However, located inside the conductivity channels in the crystals these atoms are blocking Ca2+ mobility. As the result, two- to three-orders ionic conductivity reduction characterizes the Ca8-x-yMePbxBi2/3y(VO4)7 in comparison with ionic conductivity of pure Ca3(VO4)2 in technically important middle-temperature range 700-1000 K.

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# References

1. Glass A.M., Abrahams S.C., Ballman A.A., Loiacono G. Ferroelectrics **17**, 579 (1977)

2. Lazoryak B.I., Belik A.A., Stefanovich S.Yu. *et. al*. Dokl. Phys. Chem.. **384,** 144 (2002)

3. Sleight A.W. Huang J. US Patent 5.202.891. 1993

4. Chen X., Zhuang N.F., Hu H.L., Zhuang F.J., Chen J.Z. Appl.Phys., **B88,** 449 (2007)

5. Dobrotvorskaya, M.V. , Gorobets Y.N., Kosmyna M.B. *et. al*. Crystallogr. Rep. **57,**  959 (2012)